Hydrolysis of 1-Acyl-2-Thiohydantoins & Related Compounds
THE HYDROLYSIS OF 1-ACYL-2-THIOHYDANTOINS & RELATED COMPOUNDS

by

WAYNE IRVING CONGDON
To Judy and Michelle
THE HYDROLYSIS OF 1-ACYL-2-TTHIOHYDANTOINS & RELATED COMPOUNDS

by

Wayne Irving Congdon, B.Sc. (Chemistry) (Rutgers Univ.)

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Department of Chemistry
McGill University
Montreal, Canada

July 1970
ABSTRACT

The protonation behavior and rate of hydrolysis of l-acyl-2-thiohydantoins (1) and N-acylthioureas (2) in 4-99% sulfuric acid and the rate of hydrolysis of (1) in aqueous alkali have been determined. (2) consecutively diprotonates in this acid region whereas (1) is only partly diprotonated in 99% acid. The reaction rate reaches a maximum near 70% and a minimum near 90% acid for (1) and a maximum near 43% and a minimum near 72% acid for (2). By a study of various empirical parameters and steric effects the rate profile was interpreted in terms of a bimolecular (A-2) mechanism in dilute acid converting near the minimum to a unimolecular (A-1) process. In alkaline solution (1) was shown by empirical parameters and steric effects to hydrolyze by an unusual mechanism involving hydroxide attack on the anion and then intramolecular proton transfer and intermediate break up. Secondary isotope effects versus temperature were studied in dilute and concentrated sulfuric acid and in aqueous alkali for (1).
RESUME

La vitesse de l'hydrolyse de l'acyl-1-thiohydantoin-2 (1) et de N-acylethiourée (2), et leur position de protonation dans l'acide de 4-99% de concentration ont été déterminées. On a trouvé que (2) s'attache consécutivement à deux protons dans cette zone de concentration, tandis que (1) ne le fait que partiellement dans une concentration de 99% d'acide. La vitesse de la réaction de (1) atteint un maximum près de 70% et un minimum à 90% environ, tandis que celle de (2) atteint un maximum à 43% et un minimum à 72% environ. Les résultats peuvent s'expliquer au moyen de paramètres divers et des effets stériques par un mécanisme bimoléculaire A-2 en solution d'acide diluée et un mécanisme unimoléculaire A-1 en solution d'acide très concentrée. En milieu alcalin (1) s'hydrolise d'une façon particulière avec l'ion hydroxide s'attaquant à l'anion, suivi par l'intramoléculaire transfer du proton et par la désintégration de l'intermédiaire. La relation des effets d'isotopes secondaire versus température dans les solutions diluées et concentrées d'acide sulfurique, et dans le milieux aqueux alcalins a été étudiée.
ACKNOWLEDGEMENTS

The writer would like to acknowledge his debt to Dr. J. T. Edward for his guidance during the experimental work and his patient help and encouragement during the preparation of this thesis.

The writer would also like to take this opportunity to express his appreciation to the following:

to McGill University for a demonstratorship 1967-68,
to the National Research Council of Canada for a scholarship 1968-70,
to Drs. P. G. Farrell, J. M. Fresco, and G. Welch for their helpful criticisms and discussions,
to James Tong for his laboratory assistance during the summer of 1969,
to the writer's colleagues in Dr. Edward's laboratory for their help and cooperation,
and to the writer's wife for drawing the Figures in this thesis.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Abstract</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Discussion</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>References</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Part I. The mono- and di-protonation of N-acylthioureas in aqueous sulfuric acid.</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Abstract</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Discussion</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>References</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Part II. Kinetic studies of the hydrolysis of N-acylthioureas in sulfuric acid.</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Abstract</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Discussion</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Part III. The hydrolysis of 1-acyl-2-thiohydantoins in sulfuric acid.</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Abstract</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Discussion</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>--------------------------------------------------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Hydration Parameters</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>Entropies of Activation</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td>Hammett $\sigma$ and $\sigma+$ Relations</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>G-5 Substituent Effects</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>N-3 Substituents</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Experimental</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>References</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
| Part IV. Mechanism of the alkaline hydrolysis of 1-acyl-2-thio-
  hydantoin.                                                |      |
| Abstract                                                     | 103  |
| Discussion                                                   | 105  |
| Experimental                                                | 122  |
| References                                                  | 127  |
| Part V. Secondary isotope effects in the hydrolysis of 1-
  acetyl-5,5-dimethyl-2-thiohydantoin.                       |      |
| Abstract                                                     | 130  |
| Discussion                                                   | 132  |
| Experimental                                                | 141  |
| References                                                  | 144  |
| Summary and Claims to Original Research                      | 145  |
| Appendix                                                    |      |
| A-1. Bimolecular Rate Expression                             | 150  |
| A-2. Unimolecular Rate Expression                            | 151  |
| B. U.V. Spectra of Selected Reactions                       | 152  |
| C. Data                                                      | 164  |
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part I</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.</td>
<td>Absorption spectra of N-acylthioureas</td>
<td>20</td>
</tr>
<tr>
<td>II.</td>
<td>$pK_{BH}^+$ values of substituted N-acylthioureas</td>
<td>24</td>
</tr>
<tr>
<td>III.</td>
<td>$pK_{BH2}^{++}$ values of substituted N-acylthioureas</td>
<td>24</td>
</tr>
<tr>
<td>IV.</td>
<td>Melting points, analyses, and wavelengths used for measurements of ionization of N-acylthioureas</td>
<td>27</td>
</tr>
<tr>
<td><strong>Part II</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.</td>
<td>The experimental and calculated rate of hydrolysis of N-acylthiourea in sulfuric acid at 49.3°C</td>
<td>34</td>
</tr>
<tr>
<td>II.</td>
<td>Temperature dependence of the rate of sulfuric acid catalyzed hydrolysis of N-acylthioureas</td>
<td>46</td>
</tr>
<tr>
<td>III.</td>
<td>Pseudo-first-order rate constants ($k_\psi$) in seconds$^{-1}$ for the hydrolysis of substituted N-benzoylthioureas in sulfuric acid</td>
<td>48</td>
</tr>
<tr>
<td><strong>Part III</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I.</td>
<td>Experimental and calculated rates of hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin in sulfuric acid at 25.3°C</td>
<td>68</td>
</tr>
<tr>
<td>II.</td>
<td>Temperature dependence of the rate of sulfuric acid catalyzed hydrolysis of 1-acyl-2-thiohydantoins</td>
<td>86</td>
</tr>
<tr>
<td>III.</td>
<td>Rates of hydrolysis of substituted 1-benzoyl-2-thiohydantoins in three different concentrations of sulfuric acid at 25.3°C</td>
<td>88</td>
</tr>
</tbody>
</table>
Table

IV-A. The pseudo-first-order rate constants \((10^4 k_c \text{ sec}^{-1})\)
for substituted 1-benzoyl-2-thiohydantoins (substituent shown) in the region of the rate maximum \ldots 95

IV-B. The pseudo-first-order rate constants \((10^4 k_c \text{ sec}^{-1})\)
for 1-acyl-2-thiohydantoins in the region of the rate maximum \ldots 96

V. Analytical data for previously unreported 1-acyl-2-thiohydantoins \ldots 97

VI. Physical properties of 1-acyl-2-thiohydantoins \ldots 98

Part IV

I. Comparison of base-catalyzed hydrolysis rates of
different amide linkages in aqueous solutions \ldots 107

II. \(pK_a\) values of 1-acyl-2-thiohydantoins \ldots 107

III. The effect of pH, buffer concentration and ionic strength on the rate of base catalyzed hydrolysis of 1-acetyl-\(\delta,\delta\)-dimethyl-2-thiohydantoin \ldots \ldots 109

IV. Pseudo-first-order rate constants in seconds\(^{-1}\) for the hydrolysis of substituted 1-benzoyl-2-thiohydantoins in alkaline phosphate buffer at 25.3°C \ldots 113

V. The effect of C-5 substituents on the hydrolysis rates of 1-benzoyl-2-thiohydantoin \ldots 117

VI. Temperature dependence of the rate of alkaline hydrolysis of 1-acyl-2-thiohydantoins \ldots 121

VII. Comparison of hydrolysis rates of benzoyl to acetyl carboxylic acid derivatives \ldots 124
Table

VIII. Physical properties of C-5 substituted 1-acyl-2-thio-
hydantoin s .................................................. 125

Part V

I. The effect of temperature on the pseudo-first-order rates
of hydrolysis of 1-acetyl(\text{d}_3)5,5-dimethyl-2-thiohydantoin
and 1-acetyl-5,5-dimethyl-2-thiohydantoin .................. 133

Appendix C

I. Comparison of $\bar{3}G$ and the average error for randomly
chosen rates .................................................... 167

Appendix C Part I

I. N-acetyithiourea ........................................ 168
II. N-benzoylthiourea ..................................... 169
III. N-\text{m}-fluorobenzoylthiourea ....................... 170
IV. N-\text{m}-chlorobenzoylthiourea ....................... 171
V. N-\text{p}-methoxybenzoylthiourea ....................... 172
VI. N-\text{p}-methylbenzoylthiourea ....................... 173
VII. N-\text{m}-methylbenzoylthiourea ....................... 174
VIII. N-\text{o}-methylbenzoylthiourea ...................... 175
IX. N-\text{p}-nitrobenzoylthiourea ......................... 176
X. N-\text{p}-chlorobenzoylthiourea ......................... 176

Appendix C Part II

I. N-acetyithiourea ........................................ 177
II. N-\text{p}-methoxybenzoylthiourea ....................... 190
III. N-\text{g}-methylbenzoylthiourea ....................... 191
IV. N-\text{p}-methylbenzoylthiourea ....................... 191
Table

V. N-m-methylbenzoylthiourea ........................................ 192
VI. N-benzoylthiourea .................................................. 193
VII. N-p-chlorobenzoylthiourea ...................................... 196
VIII. N-p-chlorobenzoylthiourea ..................................... 196
IX. N-m-fluorobenzoylthiourea ....................................... 197

Appendix C Part III

I. 1-benzoyl-2-thiohydantoin .......................... 198
    1-m-trifluoromethylbenzoyl-2-thiohydantoin ...
    1-p-iodobenzoyl-2-thiohydantoin ............ 198

Appendix C Part III-A

I. 1-p-methoxybenzoyl-2-thiohydantoin ................. 199
II. 1-p-(tert)butylbenzoyl-2-thiohydantoin ............ 205
III. 1-p-methylbenzoyl-2-thiohydantoin ............... 206
IV. 1-m-methylbenzoyl-2-thiohydantoin ............... 207
V. 1-benzoyl-2-thiohydantoin ............................. 208
VI. 1-p-fluorobenzoyl-2-thiohydantoin ................ 215
VII. 1-m-methoxybenzoyl-2-thiohydantoin ............... 216
VIII. 1-p-chlorobenzoyl-2-thiohydantoin ............... 217
IX. 1-p-bromobenzoyl-2-thiohydantoin ................ 220
X. 1-p-iodobenzoyl-2-thiohydantoin ................... 221
XI. 1-m-chlorobenzoyl-2-thiohydantoin ................ 222
XII. 1-m-bromobenzoyl-2-thiohydantoin ................. 223
XIII. 1-m-trifluoromethylbenzoyl-2-thiohydantoin .... 224
XIV. 1-p-nitrobenzoyl-2-thiohydantoin ................ 227
XV. 1-acetyl-5,5-dimethyl-2-thiohydantoin ............ 228
XVI. 1-acetyl(d3)5,5-dimethyl-2-thiohydantoin ....... 240
Table

XVII. 1-acetyl-2-thiohydantoin ........................................... 246
XVIII. 1-benzoyl-3-phenyl-2-thiohydantoin ................................. 252
XIX. 1-benzoyl-5-methyl-2-thiohydantoin ................................ 257
XX. 1-benzoyl-5-isopropyl-2-thiohydantoin ............................... 259
XXI. 1-benzoyl-5-(sec)butyl-2-thiohydantoin ............................. 261

Appendix C Part IV

I. 1-acetyl-5,5-dimethyl-2-thiohydantoin .................................. 263
II. 1-acetyl-2-thiohydantoin .................................................. 274
III. 1-benzoyl-2-thiohydantoin ................................................ 277
IV. 1-p-methylbenzoyl-2-thiohydantoin
    1-m-methylbenzoyl-2-thiohydantoin
    1-m-methoxybenzoyl-2-thiohydantoin
    1-p-fluorobenzoyl-2-thiohydantoin
    1-p-chlorobenzoyl-2-thiohydantoin
    1-p-iodobenzoyl-2-thiohydantoin
    1-p-bromobenzoyl-2-thiohydantoin
    1-m-chlorobenzoyl-2-thiohydantoin
    1-m-bromobenzoyl-2-thiohydantoin
    1-m-trifluoromethylbenzoyl-2-thiohydantoin .......................... 280
V. 1-acetyl(d$_3$)-5,5-dimethyl-2-thiohydantoin ........................... 283
VI. 1-benzoyl-2-thiohydantoin
    1-benzoyl-5-phenyl-2-thiohydantoin
    1-benzoyl-5-isobutyl-2-thiohydantoin
    1-acetyl-5,5-dimethyl-2-thiohydantoin
    1-acetyl-5-methyl-2-thiohydantoin
    1-benzoyl-5,5-dimethyl-2-thiohydantoin .............................. 286
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Part I</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>A: u.v. spectra of N-methylthiourea in sulfuric acid</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>B: u.v. spectra of N-benzoylthiourea in sulfuric acid</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Variation of ionization ratio of N-benzoylthiourea in 35-60% sulfuric acid with acidity function</td>
<td>13</td>
</tr>
<tr>
<td>3.</td>
<td>Dependence of pK's of m- and p- substituted N-benzoylthioureas on σ</td>
<td>16</td>
</tr>
<tr>
<td>4.</td>
<td>A: u.v. spectra of p-toluamide in sulfuric acid</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>B: u.v. spectra of N-p-toluoylthiourea in sulfuric acid</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Variation of ionization ratio of N-benzoylthiourea in 65-96% sulfuric acid with acidity function</td>
<td>22</td>
</tr>
<tr>
<td><strong>Part II</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Rate-acidity dependence for the hydrolysis of N-acetylthio-</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>ureas in aqueous sulfuric acid at 49.3°C</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Log $k_w + H_A - \log \left{ K_{BH^-} / (h_0 ^{-1} + K_{BH^-}) \right}$ versus $-\log a_{H_2O}$</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>for N-acetylthiourea</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Log $k_w + H_o - \log \left{ K_{BH^-} / (K_{BH^-} + h_o ^{-1}) \right}$ versus $-(H_o + \log[H^+])$</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>for N-acetylthiourea</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>A: log $k_w$ versus $\sigma$ for substituted N-benzoylthioureas in</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>28.3% sulfuric acid at 85.0°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B: log $k_w$ versus $\sigma^+$ for substituted N-benzoylthioureas in</td>
<td></td>
</tr>
<tr>
<td></td>
<td>96.9% sulfuric acid at 58.6°C</td>
<td></td>
</tr>
<tr>
<td><strong>Part III</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>The u.v. spectra of 1-o-iodobenzoyl-2-thiohydantoin in sulfuric acid</td>
<td>63</td>
</tr>
</tbody>
</table>
Figure

2. A plot of \( \log I (= [SH^+]/[S]) \) versus \(-H_o\) for 1-benzoyl-2-thiohydantoin; 1-\(\text{m}\)-trifluoromethylbenzoyl-2-thiohydantoin; 1-\(\text{g}\)-iodobenzoyl-2-thiohydantoin .............................................. 66

3. Plot of \( \log k_p \) versus percent sulfuric acid for 1-acetyl-5,5-dimethyl-2-thiohydantoin and 1-acetyl-2-thiohydantoin. 69

4. Plot of \( \log k_p \) at 25.3°C versus concentration of sulfuric acid for 1-benzoyl-3-phenyl-2-thiohydantoin; 1-benzoyl-2-thiohydantoin; 1-benzoyl-5-methyl-2-thiohydantoin; 1-benzoyl 5-(\text{sec})butyl-2-thiohydantoin; and 1-benzoyl-5-isopropyl-2-thiohydantoin ................................................................. 72

5. Plot of \( \log k_p \) at 25.3°C versus concentration of sulfuric acid for 1-benzoyl-2-thiohydantoin; 1-\(\text{p}\)-chlorobenzoyl-2-thiohydantoin; 1-\(\text{p}\)-methoxybenzoyl-2-thiohydantoin; and 1-\(\text{m}\)-trifluoromethylbenzoyl-2-thiohydantoin .............................. 74

6. Plot of \( \log k_p + H_A - \log \left[ K_{SH^+}/(K_{SH^+} + h_a) \right] \) versus \(-\log a_{H_2O}\) for 1-acetyl-5,5-dimethyl-2-thiohydantoin in sulfuric acid at 25.3°C .............................................................................. 78

7. Rate-activity dependence for the hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin in aqueous sulfuric acid at 25.3°C .............................. 80

8. Plot of \( \left\{ \log k_p + H_0 - \log \left[ K_{SH^+}/(K_{SH^+} + h_o) \right] \right\} \) versus \( H_0 + \log \left[ H^+ \right] \) for 1-acetyl-5,5-dimethyl-2-thiohydantoin ..... 84

9. Plot of \( \log k_p \) versus

A: \( \sigma \) for substituted 1-benzoyl-2-thiohydantoins in 58.0% sulfuric acid at 25.3°C

B: \( \sigma^* \) for substituted 1-benzoyl-2-thiohydantoins in 93.8% sulfuric acid at 25.3°C ....................................................... 89
Figure page

10. Plot of log $k_w$ versus $\phi$ for substituted 1-benzoyl-2-thio-
hydantoins in 84.6% sulfuric acid at 25.3°C ............. 91

Part IV

1. Plot of $k_b$ versus $\sqrt{\phi} / (1 + \sqrt{\phi})$ for 1-acetyl-5,5-dimethyl-2-
thiohydantoin, at 25.4°C ........... 110

2. Plot of log $k_w$ versus $\phi$ for substituted 1-benzoyl-2-thio-
hydantoins in an aqueous phosphate buffer pH = 10.75, ionic
strength = 0.42, at 25.3°C ......... 114

3. Plot of log $k_w$ versus $1/TOK \times 10^3$ for: 1-acetyl-5,5-dimethyl-
2-thiohydantoin; 1-benzoyl-2-thiohydantoin; 1-acetyl-2-thio-
hydantoin ................ 119

Part V

1. Plot of $k_{CH_3} / k_{CD_3}$ versus $T^0C$ for the acid catalyzed A-1
hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin ........ 134

2. Plot of $k_{CH_3} / k_{CD_3}$ versus $T^0C$ for: 1-acetyl-5,5-dimethyl-2-
2-thiohydantoin in aqueous alkaline buffer pH = 11.95, ionic
strength = 0.55; ethyl acetate in an alkaline buffer .... 136

3. Plot of $k_{CH_3} / k_{CD_3}$ versus $T^0C$ for the A-2 acid catalyzed
hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin in
39.6% sulfuric acid .............. 138

4. Plot of log $k_w$ versus $1/TOK \times 10^3$ for 1-acetyl($d_3$)5,5-di-
methyl-2-thiohydantoin in: 39.6% sulfuric acid; 96.3%
sulfuric acid; aqueous basic buffer pH = 11.95, ionic
strength = 0.55 .............. 142
Appendix B

1-A. The u.v. spectra showing the reaction of 0.0001M/L N-acetylthiourea in 25.2% sulfuric acid at 40.0°C ...

1-B. The u.v. spectra showing the reaction of 0.00012M/L N-acetylthiourea in 96.4% sulfuric acid at 25.3°C ...

2. The u.v. spectra showing the reaction of 0.00007M/L N-fluorobenzoylthiourea in 95.0% sulfuric acid at 65.8°C..

3. The u.v. spectra showing the reaction of 0.0001M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in 54.9% sulfuric acid at 25.3°C ...

4. The u.v. spectra showing the reaction of 0.0001M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in 96.4% sulfuric acid at 25.3°C ...

5. The u.v. spectra showing the reaction of 0.00009M/L 1-p-chlorobenzoyl-2-thiohydantoin in 93.8% sulfuric acid at 25.3°C ...

6. The u.v. spectra showing the reaction of 0.00008M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in aqueous phosphate buffer pH = 11.95, ionic strength = 0.55 at 25.3°C ...

xlv
GENERAL INTRODUCTION
Following Johnson's method (1) of synthesizing 1-acyl-2-thiohydantoins, Schlack and Kumpf (2) developed a stepwise method for peptide degradation shown in Scheme 1.

\[ \text{SCHEME 1} \]

This method was successful because the 1-acyl group was susceptible to hydrolysis under very mild alkaline conditions which would not affect the peptide linkages farther along the chain, and the 2-thiohydantoins formed usually had easily identifiable physical properties (3,4). Baptist and Bull (5) hydrolyzed the N-acyl linkage by addition of 20% hydrochloric acid directly to the acetic anhydride mixture and heating for one hour at 100°C; these conditions are probably drastic enough to result in the hydrolysis of peptide linkages as well.

The overall yield of 2-thiohydantoin by this procedure is often low. Recently, Cromwell and Stark (6) have modified it to obtain better yields. To get around the insolvability of proteins and peptides, they were first dissolved in hexafluoroacetone trihydrate and water, and then acetic anhydride and ammonium thiocyanate were added. The condensation mixture remained homogeneous in every case, and the reaction was completed after 20 hours at 50°C. The solvent was evaporated and the residue was dissolved in 12N hydrochloric acid at room temperature for 30 minutes. The solution was then evaporated and the resulting 2-thiohydantoin was
purified and identified. This second step avoids the hydrolysis and oxidation of the 2-thiohydantoin which take place under basic conditions (3). Overall yields were about 80%, and no degradation of the peptide chain was observed under the conditions of hydrolysis.

The acid-catalyzed hydrolysis was used initially by Johnson and coworkers (7) to remove the 1-acyl group from 1-acyl-2-thiohydantoins. Nielsen (3) briefly studied the mechanism of this hydrolysis, noting that since 2-thiohydantoins are stable in acid the rates could be easily followed by ultraviolet spectroscopy. His results showed an apparent correlation of the logarithm of the pseudo-first-order rate constant with both log $[H^+]$ and $H_0$ in 0.1 to 2.5 N hydrochloric acid, but the relationships broke down in 5 N hydrochloric acid. He also showed that with 1 N hydrogen chloride in glacial acetic acid hydrolysis occurred at about twice the rate that it did in aqueous 1 N hydrochloric acid, and at 100°C in 80/20 acetic acid/water hydrolysis also occurred. The mechanistic conclusions from these results were uncertain. Liu (8), in a somewhat more systematic study, measured the rates for six substituted 1-acyl-2-thiohydantoins at 25°C in 6% to 66% sulfuric acid. The rates were found to correlate with $H_0$ and not with log $[H^+]$ although the slopes were in the vicinity of 0.4-0.43 instead of unity, indicating that the Hammett-Zucker treatment was invalid (9). Treatment of the data according to the Bunnett $w$ correlation (10) gave $w$ values in the region 2-3.6, apparently indicative of a bimolecular process with water as a nucleophile. Comparison of his data for 1-acetyl, 1-acetyl-5-methyl and 1-acetyl-5,5-dimethyl led to the conclusion that C-5 substituents did not hinder the reaction sterically. A three point Hammett sigma-rho
plot in 15.4% sulfuric acid at 25°C gave $k' > 0$ for the hydrolysis of substituted 1-benzoyl-2-thiohydantoins, and led to the conclusion that the reactive species was an O-protonated species rather than an S-protonated species. This work is reexamined in Part III of this thesis, and Liu's value shown to be seriously in error.

Base-catalyzed hydrolysis of 1-acyl-2-thiohydantoin was used originally by Schlack and Kumpf (2) to remove the 2-thiohydantoin moiety from the peptide linkages, employing 1N sodium hydroxide. Waley and Watson (11) found that hydrolysis could be effected even by 0.01N sodium hydroxide. Neilsen, in attempting to use the ultraviolet spectrophotometric method developed by Kjaer and Eriksen (12) to observe the kinetics of this reaction, found that the increase in absorption at 260 nm due to 2-thiohydantoin formation could not be used for kinetic studies because further hydrolysis of the 2-thiohydantoin to a thio-ureidoacid took place under the alkaline conditions (3). He was able to ascertain that the pseudo-first-order rate constant for the hydrolysis of 1-acyl-2-thiohydantoins was dependent on the alkali concentration and apparently independent of C-$\gamma$ substituent, although he could not obtain meaningful numbers. He also made the interesting observation of nucleophilic catalysis by hydrazine at a pH of 8, giving acethydrazide and benzhydrazide as isolable products. Liu (8) studied the hydrolysis by hydroxide ion, and showed that the rate could be followed by the decrease in absorbance at about 300 nm, since in alkali 2-thiohydantoins do not have appreciable absorbance at this wavelength whereas the acylated starting material does. His results show a crude linear correlation between $\log k'_p$ (the pseudo-first-order rate constant) and pH in the
region 9.5-13 and a three point Hammett rho-sigma plot giving $\rho = 1.12$. He also showed that C-5 methyl groups retard the hydrolysis rate greatly. His experimental data show considerable scatter and he does not specify buffer ionic strength, buffer constituents or details of his kinetic method, including data work up. Part IV of this thesis was undertaken to look more systematically and in greater detail into this reaction, in an attempt to determine why this negatively charged amide should react $10^4$ times more readily with hydroxide than do normal amides.

The goal of this thesis has been to obtain as complete a mechanistic picture as is reasonably possible for the acid- and base-catalyzed hydrolysis of 1-acyl-2-thiohydantoins and for the acid catalyzed hydrolysis of N-acylthioureas which can be regarded as the model compounds. To do this it was necessary to study both kinetics and protonation equilibria for each system.

The results in Parts I-IV essentially fulfill this goal and show these systems to be truly novel. Part V uses the mechanistic results from Parts I-IV to interpret the secondary isotope effects for hydrolysis in alkali and in dilute and concentrated sulfuric acid.
References


PART I

The mono- and di-protonation of

N-acylthioureas in aqueous sulfuric acid
ABSTRACT

The basicities of N-acetylthiourea, N-benzoylthiourea, and eight substituted N-benzoylthioureas have been determined by a spectrophotometric method in sulfuric acid media. Thiocarbonyl protonation takes place in 35-60% sulfuric acid, and follows the $h_o''$ value of the solution; the Hammett rho value for the protonation of $m$- and $p$-substituted N-benzoylthioureas is $-0.42$. A second protonation, on the amide oxygen, takes place in 65-96% sulfuric acid, and follows the $h_A$ value of the solution; for this protonation rho is $-0.86$.

RESUME

On a déterminé les basicités de N-acetylthioure, N-benzoylthioure, et huit N-benzoylthioures substitués dans l'acide sulfurique aqueuse par une méthode spectrophotométrique. Dans l'acide sulfurique 35-60% l'atome de soufre s'attache au proton, et cette protonation est déterminée par la valeur $h_o''$ de l'acide; la constante de Hammett rho de la protonation de N-benzoylthioures $m$- et $p$- substituées est de $-0.42$. Dans l'acide sulfurique 65-96% l'atome d'oxygène s'attache à un deuxième proton, et la protonation est déterminée par la valeur $h_A$ de l'acide; rho pour la deuxième protonation est de $-0.86$. 
The protonation of amides (A) to their conjugate acids (AH+) in aqueous sulfuric acid takes place on the carbonyl oxygen (1), and the ionization ratio (I = [AH+] / [A]) is found to depend on the acidity of the solution as measured by the H_A acidity function (2):

\[ \log ( [AH^+] / [A] ) = pK_{AH^+} - H_A \]

where \( K_{AH^+} \) is the thermodynamic dissociation constant of the conjugate acid. The conjugate acid of benzamide has a \( pK_{AH^+} \) of \(-1.74\), so that the amide is half protonated in 35.2% sulfuric acid (2). On the other hand, the protonation of N-substituted thioureas (B) occurs (3) on the thiocarbonyl sulfur atom (1,4) and follows \( H_O''' \) (3,5):

\[ \log ( [BH^+] / [B] ) = pK_{BH^+} - H_O''' \]

N-Methylthiourea has a \( pK_{BH^+} \) of \(-1.75\), and is half ionized in 22.6% sulfuric acid (3). Thus it is almost identical in basicity to benzamide, although it is half-protonated in less concentrated acid because its protonation depends on a different acidity function.

In N-benzoylthiourea (1) both amide and thiourea function may be expected to have reduced basicities, and it becomes of interest to consider the question: will protonation take place first on the thiourea sulfur or on the benzoyl oxygen? We show below that in this molecule

---

1Protonation on nitrogen may be assumed to take place to a negligible extent for reasons discussed in reference 1: the experimental work described in the present paper can be interpreted without the necessity of invoking any appreciable N-protonation.
both oxygen and sulfur sites have reduced but approximately equal basicities, but because their protonation is governed by different acidity functions ($H_A$ and $H_0'''$), sulfur is protonated first to give the conjugate acid (2).

\[
\begin{align*}
\text{O} & \quad \text{S} \\
\text{C} & \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{H} \quad \text{S} \\
\text{O} & \quad \text{N} \quad \text{C} \quad \text{H} \quad \text{S} \\
\text{O} & \quad \text{N} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

Evidence from which we conclude that the first protonation, occurring in 35 to 60% sulfuric acid, takes place on the thiourea thiocarbonyl rather than on the amide carbonyl consists of three experimental findings. First, the changes in the ultraviolet absorption are qualitatively very similar to those observed when N-methylthiourea is protonated in sulfuric acid, and different from those observed when the benzamide oxygen is protonated. This comparison is shown in Figure 1. In both compounds the strong absorption at longer wavelength, most probably due to a $\pi \rightarrow \pi^*$ transition (6), undergoes a blue shift as the acid strength is increased, and good isosbestic points for the families of spectral curves are observed. This spectral behavior is general for all N-acylthioureas as it is for most thioureas (3,4), and indicates a simple equilibrium involving $B$ and $BH^+$. Second, the ionization ratios, determined by the conventional spectrophotometric method (7), are found to follow $H_0'''$ (equation 2) and not $H_A$ (equation 1). This is shown for N-benzoilthiourea in Figure 2, where the slope of the straight-line obtained by plot-
Figure 1. A: Ultraviolet spectra of N-methylthiourea (ref. 3) in a. 0.0%; b. 15.9%; c. 21.3%; d. 27.1%; e. 66.4% sulfuric acid.
B: Ultraviolet spectra of N-benzoylthiourea in a. 0.0%; b. 47.0%; c. 52.7%; d. 62.4% sulfuric acid.
Figure 2. Variation of ionization ratio (I) of N-benzoylethiourea in 35-60% sulfuric acid with acidity function (Ο, Hₐ: Δ, H₀⁻⁻).
ting log ([BH\(^+\)]/[B\(^-\)]) versus \(H_0^{-}\) lies close to unity, as required by equation 2; a similar plot against \(H_A\) has a slope of 2.2. The slopes, and the \(pK_{BH^+}\) values obtained by application of equation 2 to the spectral data for N-benzoylthiourea and six \(m\)- and \(p\)-substituted N-benzoylthioureas, are given in Table II. A plot of these \(pK_{BH^+}\) values versus \(\sigma\) yields the straight line shown in Figure 3, the slope (Hammett \(\rho\) value) of which equals -0.42 (correlation coefficient 0.961). This \(\rho\) value is the third finding which indicates thiocarbonyl protonation. The Hammett \(\rho\) value for protonation of \(m\)- and \(p\)-substituted benzamides is -0.92 (2), and the value for protonation on the oxygen of \(\perp\) would be expected to lie close to this value. The \(\rho\) value for the protonation of the thiocarbonyl would be expected to be considerably less, and has about the value expected (cf., \(\rho\) of -0.212 for the ionization of \(\perp\) -phenylpropionic acids (8), in which the protonated atom is separated by three atoms from the substituted benzene ring.).

Only minor changes in the ultraviolet spectra of N-benzoylthioureas in sulfuric acid are observed as the acid concentration is increased from 60 to 68%, but at higher acid concentrations a second protonation is indicated by systematic changes in the spectra. This is shown in Figure 4, in which the spectral changes of N-\(p\)-toluamide and N-\(p\)-toluoylthiourea are compared. The similarity in spectral changes gives the first reason for believing protonation now to be taking place on the amide oxygen. For all of the other N-benzoylthioureas, the spectral changes on protonation, reported in Table I, also were fairly similar to those occurring on protonation of the corresponding benzamides, where data on the latter were available.
Figure 3. Dependence of pK's of m- and p-substituted N-benzoylthioureas on σ: △, pK_{BH}^+; ○, pK_{BH2}^{++}. 
Figure 4. A: Ultraviolet spectra of p-toluamide (ref. 12) in
a. 0.0%; b. 20.5%; c. 32.8%; d. 42.3%; e. 57.2% sulfuric acid.
B: Ultraviolet spectra of N-p-toluoylthiourea in a. 60.0%; b. 73.4%
c. 80.0%; d. 85.7%; e. 96.1% sulfuric acid.
<table>
<thead>
<tr>
<th>Acyl group</th>
<th>$\lambda_B$ (nm)</th>
<th>$\varepsilon_B$</th>
<th>$\lambda_{BH^+}$ (nm)</th>
<th>$\varepsilon_{BH^+}$</th>
<th>$\lambda_{BH^{++}}$ (nm)</th>
<th>$\varepsilon_{BH^{++}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl</td>
<td>265</td>
<td>12,700</td>
<td>225</td>
<td>10,400</td>
<td>232</td>
<td>9,200</td>
</tr>
<tr>
<td>Benzoyl</td>
<td>275</td>
<td>13,000</td>
<td>252</td>
<td>16,200</td>
<td>267</td>
<td>13,200</td>
</tr>
<tr>
<td>p-Methoxybenzoyl</td>
<td>285</td>
<td>23,600</td>
<td>300</td>
<td>17,200</td>
<td>298</td>
<td>14,100</td>
</tr>
<tr>
<td>m-Chlorobenzoyl</td>
<td>278</td>
<td>11,500</td>
<td>252</td>
<td>18,000</td>
<td>258</td>
<td>16,800</td>
</tr>
<tr>
<td>p-Chlorobenzoyl</td>
<td>275</td>
<td>15,600</td>
<td>266</td>
<td>17,600</td>
<td>284</td>
<td>16,100</td>
</tr>
<tr>
<td>m-Fluorobenzoyl</td>
<td>278</td>
<td>12,400</td>
<td>248</td>
<td>18,000</td>
<td>254</td>
<td>15,100</td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>275</td>
<td>16,900</td>
<td>271</td>
<td>15,000</td>
<td>291</td>
<td>15,500</td>
</tr>
<tr>
<td>m-Methylbenzoyl</td>
<td>274</td>
<td>11,800</td>
<td>258</td>
<td>11,900</td>
<td>277</td>
<td>13,500</td>
</tr>
<tr>
<td>o-Methylbenzoyl</td>
<td>274</td>
<td>14,100</td>
<td>233</td>
<td>13,100</td>
<td>264</td>
<td>8,800</td>
</tr>
<tr>
<td>p-Nitrobenzoyl</td>
<td>266</td>
<td>17,900</td>
<td>264</td>
<td>18,400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
A second reason for believing protonation now to be taking place on the amide oxygen comes from the fact that the change in log ([BH⁺]/[B]), obtained by the usual spectral analysis (2,7), follows $H_A^2$ and not $H_0'''$, as shown by the example in Figure 5. A third reason comes from the fact that the pK$_{BH2}^{++}$ values of $\textit{m}$- and $\textit{p}$-substituted N-benzoylthioureas, obtained by application of equation 1 to the spectral data, indicate $\rho = -0.86$ (see Figure 3; correlation coefficient: 0.964), in reasonable agreement with $\rho$ of -0.92 for the protonation of benzamides (2).

The basicities listed in Table III indicate that diprotonation of all of the N-benzoylthioureas should be almost complete in 100% sulfuric acid; this was confirmed for N-$\textit{p}$-chlorobenzoylthiourea by cryoscopic measurements. A comparison of the protonation constants listed in Table III with those listed in Table II shows that the oxygen and sulfur

---

2Because of its positive charge, the protonation of $\textit{Z}$ would be expected to follow an as-yet undetermined acidity function $H_A^+$, and not $H_A$. However, the parallelism of $H_0$ and $H_+$ in strongly acid solutions (9) makes it probable that $H_A$ and $H_A^+$ will also be parallel in strongly acid solutions. This parallelism will not extend all the way down through increasingly dilute acids to the standard state, dilute aqueous solution, so that the absolute value of $H_A^+$ is likely to be about 0.3 units higher than that of $H_A$ in 100% sulfurous acid (10), and the pK$_{BH2}^{++}$ values in Table III consequently are likely to be systematically in error by this amount.

3R.J. Gillespie, in some unpublished experiments, found a mean $\nu$ value of 2.9 and a mean $\tau$ value (from conductivity measurements) of 1.7, both indicating fairly complete diprotonation.
Figure 5. Variation of ionization ratio (I) of N-benzoylthiourea in 65-96% sulfuric acid with acidity function (O, $H_A$; Δ, $H_o$).
### TABLE II

*pK*<sub>BH⁺</sub> values of substituted N-acyl thioureas

<table>
<thead>
<tr>
<th>Acyl group</th>
<th>-pK&lt;sub&gt;BH⁺&lt;/sub&gt;</th>
<th>Slope&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl</td>
<td>4.64±0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.09</td>
</tr>
<tr>
<td>p-Methoxybenzoyl</td>
<td>4.37±0.06</td>
<td>1.03</td>
</tr>
<tr>
<td>m-Chlorobenzoyl</td>
<td>4.73±0.06</td>
<td>1.09</td>
</tr>
<tr>
<td>Benzoyl</td>
<td>4.55±0.02</td>
<td>1.03</td>
</tr>
<tr>
<td>m-Fluorobenzoyl</td>
<td>4.61±0.04</td>
<td>1.10</td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>4.50±0.18</td>
<td>0.97</td>
</tr>
<tr>
<td>m-Methylbenzoyl</td>
<td>4.13±0.20</td>
<td>1.05</td>
</tr>
<tr>
<td>o-Methylbenzoyl</td>
<td>4.65±0.05</td>
<td>1.12</td>
</tr>
<tr>
<td>p-Nitrobenzoyl</td>
<td>4.83±0.06</td>
<td>1.17</td>
</tr>
</tbody>
</table>

<sup>a</sup>Slope of log ([BH⁺]/[B]) versus -H<sub>0</sub>.<sup>b</sup>Extrapolation back to zero time necessary.

### TABLE III

*pK*<sub>BH₂⁺⁺</sub> values of substituted N-acyl thioureas

<table>
<thead>
<tr>
<th>Acyl group</th>
<th>-pK&lt;sub&gt;BH₂⁺⁺&lt;/sub&gt;</th>
<th>Slope&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl</td>
<td>4.61±0.12&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.02</td>
</tr>
<tr>
<td>p-Methoxybenzoyl</td>
<td>4.37±0.05&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.13</td>
</tr>
<tr>
<td>m-Chlorobenzoyl</td>
<td>4.96±0.06</td>
<td>1.04&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>p-Chlorobenzoyl</td>
<td>4.93±0.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Benzoyl</td>
<td>4.68±0.06</td>
<td>1.07</td>
</tr>
<tr>
<td>m-Fluorobenzoyl</td>
<td>4.86±0.07</td>
<td>1.00</td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>4.55±0.05</td>
<td>1.00</td>
</tr>
<tr>
<td>m-Methylbenzoyl</td>
<td>4.67±0.08</td>
<td>1.05</td>
</tr>
<tr>
<td>o-Methylbenzoyl</td>
<td>4.67±0.04</td>
<td>1.08</td>
</tr>
</tbody>
</table>

<sup>a</sup>Slope of log ([BH₂⁺⁺]/[BH⁺]) versus H<sub>A</sub>.<sup>b</sup>The change in optical density on protonation was small.
atoms of \( N \)-benzoylthiourea and other \( N \)-acythioureas have about equal basicities, but in spite of this fact protonation on oxygen requires much stronger acid than does protonation on sulfur. This results from the fact that \( H_A \) (which governs protonation on oxygen) increases with acid concentration much more slowly than \( H'_O \) (which governs protonation on sulfur). The fallacious but convenient method of comparing basicities by noting the concentration of sulfuric acid required for half-protonation would have indicated sulfur to be a much more basic center than oxygen. The importance of determining the acidity functions for different classes of compounds is evident.
Experimental Section

General. Fisher reagent grade sulfuric acid and Fisher spectro-grade methanol were used throughout. Sulfuric acid solutions were standardized by titration with B.D.H. standard 0.1N NaOH solution to phenolphthalein end point. Melting points were taken on a hot stage microscope and are uncorrected. Analyses for new compounds were done by A. Bernhardt, Mikroanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany.

Materials. N-Acylthioureas were synthesized in high yields (60-80%) by the method of Douglas and Dains (11). All compounds were recrystallized from ethanol or ethanol-water. Table IV lists melting points and analyses for new compounds. Several are known compounds and are referenced accordingly.

Basicity Measurements. Stock solutions (4-5 x 10^{-3}M) of the N-acylthiourea in methanol were made up and 0.5ml. of this solution was placed in a 25 ml volumetric flask. For solutions up to and including 62% w/w sulfuric acid the flask was diluted to the mark with the appropriate acid. For solutions above 62% the methanol was removed under vacuum and then acid added to the mark. For these solutions up to ten minutes of shaking was required to assure complete dissolution. Shining a light through the solutions revealed no particles in any solution, so that complete solution was assumed. For the first pK, ultraviolet measurements were conducted at 25.0±0.1°C in 1-cm fused silica cells in a Unicam SP-800 spectrophotometer; for the second pK the measurements were conducted at 33.0±1.0°C. The spectral data in Table I were all recorded at 25.0±0.1°C. The wavelengths of absorbance readings from which pK values were determined are listed in Table IV. The pK values and slopes
TABLE IV

Melting points, analyses, and wavelengths used for measurements of ionization of N-acylthioureas

<table>
<thead>
<tr>
<th>Acyl group</th>
<th>Uncorr. M.P. °C</th>
<th>Calcd. Analysis</th>
<th>Found Analysis</th>
<th>λ pK_{BH}+ Measurement nm</th>
<th>λ pK_{BH2}+2 Measurement nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetyl</td>
<td>170-171^a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoyle</td>
<td>178-179^b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Methoxybenzoyl</td>
<td>212-213^c</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-Chlorobenzoyl</td>
<td>190-192</td>
<td>4.8 3.3 13.0</td>
<td>4.5 3.6 12.8</td>
<td>285</td>
<td></td>
</tr>
<tr>
<td>p-Chlorobenzoyl</td>
<td>218-219</td>
<td>4.8 3.3 13.0</td>
<td>4.8 3.3 12.9</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>p-Fluorobenzoyl</td>
<td>192-193</td>
<td>4.8 3.5 14.1</td>
<td>4.8 3.7 14.3</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>226-228</td>
<td>5.7 5.1 14.4</td>
<td>5.8 4.9 14.6</td>
<td>230</td>
<td></td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>163-164</td>
<td>5.7 5.1 14.4</td>
<td>5.7 5.1 14.6</td>
<td>280</td>
<td></td>
</tr>
<tr>
<td>p-Methylbenzoyl</td>
<td>193-194</td>
<td>5.7 5.1 14.4</td>
<td>5.9 5.3 14.6</td>
<td>275</td>
<td></td>
</tr>
<tr>
<td>p-Nitrobenzoyl</td>
<td>214-216</td>
<td>4.2 3.1 18.7</td>
<td>4.3 3.4</td>
<td>295</td>
<td></td>
</tr>
</tbody>
</table>

recorded in Tables II and III were determined from a least squares computer program for log I versus $E_x$. The absorbance of N-acylthiourea in about 62% sulfuric acid was taken to be that of the monoprotonated form 2. The spectral changes occurring when acid concentration was further increased were due to further protonation plus a strong medium effect, similar to the changes already observed to accompany the protonation of amides (2), and the spectral data were treated in the manner already described for the latter (2) to obtain the data recorded in Tables II and III.
References


PART II

Kinetic studies of the hydrolysis of

N-acylthioureas in sulfuric acid
ABSTRACT

N-acylthioureas are slowly hydrolyzed in sulfuric acid to the corresponding carboxylic acid and thiourea. The pseudo-first-order rate constant increases with sulfuric acid concentration to a maximum in about 43% acid, then decreases to a minimum in about 72% acid, and then increases again. This behavior is accounted for in terms of a change-over in mechanism from a bimolecular mechanism (A-2), involving water as a nucleophile in the rate determining step, in 0-70% acid, to a unimolecular mechanism (A-1) in 70-100% acid. The change in mechanism is experimentally demonstrated by a change in Arrhenius parameters, Hammett rho values, and various empirical correlations. A reasonable analytical expression for the entire rate profile over 0-100% acid is derived, and is used to show that an N,S-diprotonated species is the most probable intermediate in the A-1 hydrolysis, and an O-monoprotonated species the most probable intermediate in the A-2 hydrolysis.

RESUME

N-Acyle thiourées s'hydrolysent lentement dans l'acide sulfurique pour donner l'acide carboxylique et la thiourée: La constante de vitesse (pseudo 1er ordre) augmente avec la concentration d'acide atteignant un maximum à la concentration de 43%, environ, puis diminue jusqu'à un minimum à 72% d'acide pour augmenter de nouveau. Ce comportement peut s'expliquer par un changement de mécanisme d'un mécanisme bimoléculaire (A-2) avec l'eau comme nucleophile entre 0-70% d'acide, à un mécanisme unimoléculaire A-1 entre 70-100% d'acide. Ce changement de vitesse est
démontré par un changement de paramètre d'Arrhénius des valeurs rho de Hammett, et d'autre correlations empiriques. On a trouvé une expression analytique pour la vitesse de réaction globale qui montre que la molécule diprotone aux atomes N et S est l'intermédiaire dans le mécanisme A-1, et que la molécule protonée à l'atome O est l'intermédiaire dans le mécanisme A-2.
The N-acylthiourea grouping is of interest because of its occurrence in thiopurines and thiopyrimidines, which are minor constituents of transfer-ribonucleic acid (1-4). We have shown recently (5) that simple N-acylthioureas undergo successive mono- and diprotonation in aqueous sulfuric acid as the acid concentration is increased to 100%. For example, over the concentration range 36% to 60% acid N-acetylthiourea is protonated on sulfur ($pK_{BH^+} = -4.64$), the extent of protonation being governed by the $H_0^\text{***}$ value of the medium; and over the concentration range 65% to 95% it is protonated on the amide oxygen ($pK_{BH_2^{++}} = -1.61$), the extent of diprotonation being governed by the $H_A$ value of the medium. Subsequent to mono- or diprotonation there is a slow hydrolysis to acetic acid and thiourea (6). The mechanism of the hydrolysis of this and other N-acylthioureas has never been studied. In the present paper we report our studies on the kinetics of the hydrolysis of N-acetylthiourea, N-benzoylthiourea, and seven substituted N-benzoylthioureas. The kinetic data are best explained by assuming that, in addition to spectroscopically-observable S-protonation and S,O-diprotonation, there is also a small amount of O-protonation and S,N-diprotonation.

Because the ultraviolet absorption spectra of N-acylthioureas differ considerably from that of thiourea (7), their hydrolysis may be followed conveniently by ultraviolet spectroscopy. In the large excess of acid used, the reactions all show simple first-order kinetics. The pseudo-first-order rate constants ($k_\mu$) for the hydrolysis of N-acetylthiourea in 4-99% sulfuric acid at 49.3°C are given in Table I, and displayed graphically in Figure 1. The rate increases with acid concentration up to a maximum in about 46% acid, decreases to a minimum in about 72% acid,
TABLE I

The experimental and calculated rate of hydrolysis of N-acetyltiourea in sulfuric acid at 49.3°C

<table>
<thead>
<tr>
<th>Wt. percent sulfuric acid</th>
<th>Experimental(^a) ( k \nu \times 10^4 ) (sec(^{-1}))</th>
<th>Calculated(^a) ( k \nu \times 10^4 ) (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>0.54±0.01</td>
<td>1.30</td>
</tr>
<tr>
<td>15.9</td>
<td>2.74±0.03</td>
<td>3.32</td>
</tr>
<tr>
<td>25.2</td>
<td>4.94±0.06</td>
<td>7.20</td>
</tr>
<tr>
<td>34.7</td>
<td>7.95±0.09</td>
<td>9.25</td>
</tr>
<tr>
<td>39.6</td>
<td>9.10±0.14</td>
<td>10.60</td>
</tr>
<tr>
<td>43.7</td>
<td>9.18±0.12</td>
<td>10.80</td>
</tr>
<tr>
<td>47.2</td>
<td>8.18±0.12</td>
<td>8.60</td>
</tr>
<tr>
<td>50.4</td>
<td>6.52±0.18</td>
<td>5.74</td>
</tr>
<tr>
<td>53.5</td>
<td>4.73±0.03</td>
<td>1.89</td>
</tr>
<tr>
<td>57.9</td>
<td>1.31±0.01</td>
<td>0.38</td>
</tr>
<tr>
<td>62.4</td>
<td>0.29±0.006</td>
<td>0.14</td>
</tr>
<tr>
<td>70.0</td>
<td>0.36±0.01</td>
<td>0.29</td>
</tr>
<tr>
<td>84.9</td>
<td>0.29±0.01</td>
<td>0.40</td>
</tr>
<tr>
<td>88.4</td>
<td>0.14±0.02</td>
<td>1.00</td>
</tr>
<tr>
<td>92.2</td>
<td>1.09±0.06</td>
<td>1.58</td>
</tr>
<tr>
<td>94.4</td>
<td>1.43±0.02</td>
<td>2.12</td>
</tr>
<tr>
<td>96.4</td>
<td>2.23±0.06</td>
<td>1.05</td>
</tr>
<tr>
<td>98.9</td>
<td>3.33±0.09</td>
<td>1.05</td>
</tr>
</tbody>
</table>

\(^a\)pseudo-first-order rate constants. \(^b\)HA unmeasured in this region.
Figure 1. Rate-acidity dependence for the hydrolysis of N-acetylthiourea in aqueous sulfuric acid at 49.3°C. Points: experimental $k_p$ (in sec$^{-1}$). The theoretical curve derived from equation 11: ———
The theoretical curve derived from equation 6: ————.
and then increases again rapidly in the higher concentrations of acid. The rate-concentration profile closely resembles those of esters of secondary alcohols studied by Yates and McClelland (8), and analogy with these cases would suggest that hydrolysis occurs by two distinct mechanisms:

i. In acid concentrations up to 72%, by an A-2 mechanism, in which one or more molecules of water add to the protonated N-acetylthiourea in the rate-determining step;

ii. In acid concentrations above 72%, by an A-1 mechanism, in which the rate-determining step involves the rupture of one bond of di-protonated N-acetylthiourea without the intervention of water molecules.

This dichotomy of mechanism is supported by various lines of evidence reported below; furthermore, it will be shown that the most satisfactory variant of the possible A-2 mechanisms is that given in Scheme 1.

\[
\begin{align*}
&\text{Scheme 1} \\
&\begin{array}{c}
\begin{array}{c}
\text{R-C-NH-C-NH} \\
\text{O} \\
\text{S}
\end{array}
\end{array}
\end{align*}
\]
One line of evidence comes from the modification of the Bunnett hydration parameter treatment (9) introduced by Yates and his coworkers (10). In applying this treatment in the present instance, we must take account of the fact that increasing acid concentration not only leads to protonation of N-acetyltiourea (A<sub>i</sub> R = Me) to give the reactive intermediate A<sub>H</sub><sup>+</sup>, the amount formed being dependent on the protonation constant K<sub>AH</sub><sup>+</sup> and (we may assume) the H<sub>A</sub> (≡ -log h<sub>A</sub>) value (11) of the acid solution, but it also (and more extensively) leads to protonation to give the unreactive species B<sub>H</sub><sup>+</sup>, the amount formed being dependent on the protonation constant K<sub>BH</sub><sup>+</sup> and the H<sub>'</sub><sup>''</sup> (≡ -log h<sub>'</sub><sup>''</sup>) value (11) of the solution. The evidence already cited (5) indicates that in 36-60% acid the formation of B<sub>H</sub><sup>+</sup> is not attended by the formation of appreciable amounts of A<sub>H</sub><sup>+</sup>, and consequently application of the Bronsted equation to the situation outlined in Scheme 1 yields:

\[
\text{Rate of reaction} = k_1 \left([A] + [B_H^+]\right) = k_1 K_{AH} [A] h_A a_{H_2O}^{+} f_{AH}^{+} / K_{AH}^{+} f_{+}
\]

where \( k_1 \) is the rate-constant for the slow reaction: A<sub>H</sub><sup>+</sup> + rH<sub>2</sub>O → I;

\( a_{H_2O} \) is the activity of water; the \( f \)'s are activity coefficients; and

---

Protonated benzamide has a pK<sub>AH</sub><sup>+</sup> of -1.74 (10). The attachment of the electron attracting -CS-NH<sub>2</sub> group to A<sub>H</sub><sup>+</sup> would be expected to reduce pK<sub>AH</sub><sup>+</sup> to about -4.0 (12), in which case half-ionization would occur in 73% sulfuric acid (10,11). By contrast, half-protonation to give B<sub>H</sub><sup>+</sup> occurs in 50% acid. The corresponding pK<sub>AH</sub><sup>+</sup> value for acetamide (10,13) is less certain, but the spectroscopic evidence for N-acetyltiourea (5), indicates that the formation of B<sub>H</sub><sup>+</sup> is not attended by formation of appreciable quantities of A<sub>H</sub><sup>+</sup>. 

---
the other symbols can be understood by reference to Scheme 1. Equation 1 may be rearranged to:

\[ k_p = \left\{ \frac{k_1K_i h_A a_{H_2O} f_{AH^+}}{f_i K_{AH^+}} \right\} \left\{ \frac{[A]/[A] + [BH^+]}{} \right\} \]

from which may be derived:

\[ \log k_p + H_A - \log \left\{ \frac{K_{BH^+}/(h_o^'} + K_{BH^+})}{(k_1K_i f_{AH^+})/(K_{AH^+}f_i)} \right\} = r\log a_{H_2O} + \log \left\{ \frac{(k_1K_i f_{AH^+})/(K_{AH^+}f_i)}{} \right\} \]

In Figure 2 is shown a plot of \( \log k_p + H_A - \log \left\{ K_{BH^+}/(h_o^'} + K_{BH^+}) \right\} \) against \( \log a_{H_2O} \). From 30% to 65% sulfuric acid the points lie close to a straight line of slope \( r = 1.5 \) and intercept \( \log \left\{ (k_1K_i f_{AH^+})/(K_{AH^+}f_i) \right\} \) equal to -0.6. This can be interpreted as indicating that about two water molecules react with the protonated amide group of N-acetylthiourea to give the intermediate I. Similar treatments have indicated that over the range 0-70% sulfuric acid, 2.1 molecules of water react with protonated ester molecules in the slow step of hydrolyses (8), and that over the range 0-55% acid 2.6 molecules of water react in the slow step with protonated amide molecules (10). The curvature of a line drawn through the experimental points of Figure 2 can be interpreted as indicating that \( r \) decreases as the water activity of the acid solution decreases (13), or that the ratio \( (f_{AH^+}/f_i) \) is not completely invariant with acid concentration, or both. However, considering the Bunnett-Yates

\footnote{Water activities measured at 25°C were used in this plot (26), although the rates were measured at 49.3°C.}
Figure 2. \( \log k_\mu + H_A - \log \left( \frac{K_{BH^+}}{(h_{o}^{''''} + K_{BH^+})} \right) \) versus \(-\log a_{H_2O}\) for N-acetylthioureas.
\[ \log a_{H_2O} = \log \left( \frac{K_{H_2}^\circ + K_{H_4}^\circ}{K_{H_2}^\circ} \right) - a_{H^+} + \phi K \log a_{H^+} \]
plot as purely an empirical criterion of reaction mechanism, the experimental curve of Figure 2 indicates an A-2 mechanism of hydrolysis up to 72% sulfuric acid, and then an abrupt change (shown by the change of slope to -0.78) to an A-1 mechanism.

Bunnett and Olsen (15) have found that plots of \((\log k_{w} + H_0)\) against \((H_0 + \log[H^+])\) (rather than against \(\log a_{H_2O}\), as in the original Bunnett treatment (9)) are more generally linear, and that the slopes \(\bar{a}\) are useful empirical criteria of reaction type. For example, \(\bar{a}\) for A-2 hydrolyses of amides is generally about +0.6, while for A-1 hydrolyses it is lower and may be negative. The Bunnett-Olsen plot of the results for N-acetylthiourea, shown in Figure 3, has satisfactory linearity over the region 0-65% sulfuric acid; \(\bar{a}\) (1.01) is large, but not unprecedented (15), for A-2 hydrolyses. Again, the indication of a change in mechanism when the acid concentration exceeds 72% is unmistakeable as \(\bar{a}\) (-0.37) changes sign.

Another line of evidence indicating a change from an A-2 to an A-1 mechanism comes from measurements of the entropy of activation \((\Delta S^\|$). It has been found that acid-catalyzed ester and amide hydrolyses proceeding by an A-1 mechanism have \(\Delta S^\$\) of 0 to +10 e.u., while those proceeding by an A-2 mechanism have \(\Delta S^\$\) of -15 to -30 e.u. (16-19,21). Plots of \(\log k_{w}\) versus \(1/T_{OK}\) for N-acetylthiourea in 25.2%, 57.9% and 96.9% sulfuric acid are linear, and indicate \(\Delta S^\$\) values of -26, -21 and -11 e.u. respectively in these concentrations of acid (Table II). The entropy of activation in the first two acid concentrations, which are on each side of the concentration for maximal rate (Figure 1), indicate an A-2 mechanism with essentially no competing A-1 component. The large
Figure 3. \( \log k' + H_0 - \log \left\{ \frac{K_{BH^+}}{K_{BH^+} + h_0''} \right\} \text{ versus } -(H_0 + \log[H^+]) \) for N-acetyliourea.
\[
\left\{ \frac{K_H}{K_H^K} \right\}^{\log \frac{[H^+]}{[H_2O]} + \log K_H} - \left[ 1 - \frac{H_2O}{[H^+] + K_H} \right]^{\log [H^+]} - 2.0
\]

slope = -0.37

slope = 1.01
change in $\Delta S^+$ in 96.9% sulfuric acid is consistent with a change to an A-1 mechanism; the value is more negative than expected, but this aberration is explained below.

The $\Delta S^+$ for the hydrolysis of N-benzoylthiourea (Table II) in 39.6% acid also is indicative of an A-2 mechanism for this concentration.

A third line of evidence for a change from an A-2 to an A-1 mechanism comes from the Hammett rho values for the hydrolysis of m- and p-substituted N-benzoylthioureas. The rates of A-1 hydrolyses of p-substituted methyl-mesitoates, substituted benzamides and benzyol chlorides follow $\sigma^+$, and have $\rho$ values of near -3, because of the large effect of electron releasing groups in stabilizing the intermediate acylium ion \(^{(20)}\). On the other hand, the rates of A-2 hydrolyses follow $\sigma$, and have $\rho_{\sigma}$ close to zero, because of the compensating effects of electron-releasing groups on the preequilibrium protonation (which they encourage) and on the subsequent rate-determining attack of water (which they discourage) \(^{(23)}\). For example, the small $\rho_{\sigma}$ (0.12) for the hydrolysis of substituted benzamides is made up of two components almost equal but opposite in sign: $\rho_1$ for the protonation step (-0.92: ref. 10) and $\rho_2$ for the attack of water on the protonated benzamide (+1.05: ref. 20 and references therein).

$$\rho_{\sigma} = \rho_1 + \rho_2$$

In attempting to estimate $\rho_{\sigma}$ for the hydrolysis of N-benzoylthioureas

\(^1\)The rate of hydrolysis of the p-methoxy compound in 96.9% sulfuric acid falls below that predicted by the $\rho_{\sigma}$ relationship. This deviation may be explained by hydrogen bonding of methoxyl with sulfuric acid with consequent increase in $\sigma^+$. Using the correction suggested by Yates and Stewart \(^{(22)}\) of +0.16, giving $\sigma^+ = -0.618$, log $k_p$ of N-p-methoxybenzoylthiourea fits nicely on the straight line of Figure 4.
TABLE II

Temperature dependence of the rate of sulfuric acid catalyzed hydrolysis of N-acylthioureas

<table>
<thead>
<tr>
<th>Compound and % sulfuric acid</th>
<th>Temp. °C</th>
<th>$k_r \times 10^4$ (sec$^{-1}$)$^a$</th>
<th>log A (sec$^{-1}$)</th>
<th>$\Delta S^\dagger$ (e.u.)</th>
<th>$E_a$ (KCal/Mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-acetyltiourea</td>
<td>40.0</td>
<td>2.21±0.09</td>
<td>7.57±0.2</td>
<td>-26 ± 2</td>
<td>16 ± 2</td>
</tr>
<tr>
<td></td>
<td>49.3</td>
<td>4.94±0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.6</td>
<td>20.80±1.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>73.6</td>
<td>26.19±0.70</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-acetyltiourea</td>
<td>40.0</td>
<td>0.52±0.01</td>
<td>8.64±0.27</td>
<td>-21 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td></td>
<td>49.3</td>
<td>1.31±0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>68.6</td>
<td>7.06±0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-acetyltiourea</td>
<td>58.6</td>
<td>5.41±0.07</td>
<td>10.80±0.07</td>
<td>-11 ± 1</td>
<td>21 ± 1</td>
</tr>
<tr>
<td></td>
<td>68.9</td>
<td>11.20±0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.1</td>
<td>40.10±1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-benzoyltiourea</td>
<td>49.1</td>
<td>0.39±0.03</td>
<td>9.60±0.33</td>
<td>-17 ± 2</td>
<td>21 ± 2</td>
</tr>
<tr>
<td></td>
<td>68.6</td>
<td>2.25±0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>79.9</td>
<td>6.60±0.63</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Pseudo-first-order rate constants.
according to Scheme 1, we must take account of a third effect: that of an
electron-releasing group in encouraging the diversion of $\text{A}$ into the pool
of inactive cation $\text{BH}^+$ ($\gamma_3 = -0.42$: ref. 5). If it is assumed that $\gamma_1$,
for the step: $\text{A} + \text{H}^+ = \text{AH}^+$; and $\gamma_2$, for the step: $\text{AH}^+ + \text{H}_2\text{O} \rightarrow \text{products};$
have the same values as the corresponding $\gamma_1$ and $\gamma_2$ for the hydrolysis of
substituted benzamides, then $\gamma_\omega$, given by

$$\gamma_\omega = \gamma_1 + \gamma_2 - \gamma_3$$

is calculated as +0.56, extremely close to the experimental $\gamma_\omega$ of
+0.54 found from plots of log $k_\psi$ against $\sigma$ for six substituted
N-benzoylthioureas in 28.3% sulfuric acid (Table III and Figure 4).
This result supports the A-2 mechanism of Scheme 1, but is also compatible
with other possible A-2 mechanisms, such as that involving $\text{BH}^+$ rather
than $\text{AH}^+$ as an intermediate:

\[ \begin{align*}
\text{O} & \quad \text{N} \quad \text{N} \\
\text{C} & \quad \text{C} \quad \text{S} \\
\text{R} & \quad \text{C} \quad \text{N} \quad \text{C} \quad \text{S} \quad \text{H}
\end{align*} \]
\[ \text{K}_{\text{BH}^+} \quad \xrightarrow{\text{H}^+} \quad \text{K}_3 \]
\[ \text{R-C-OH} + \text{NH}_2-C-NH_2 \]

\text{SCHEME 2}
TABLE III

Pseudo-first-order rate constants (k_p) in seconds⁻¹ for the hydrolysis of substituted N-benzoylthioureas in sulfuric acid

<table>
<thead>
<tr>
<th>Substituent</th>
<th>28.3% H₂SO₄&lt;sup&gt;a&lt;/sup&gt; 10⁴k_p (sec⁻¹)</th>
<th>96.9% H₂SO₄&lt;sup&gt;b&lt;/sup&gt; 10⁴k_p (sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxy</td>
<td>2.63±0.09</td>
<td>79.70±4.80</td>
</tr>
<tr>
<td>p-methyl</td>
<td>2.89±0.24</td>
<td>25.30±1.30</td>
</tr>
<tr>
<td>o-methyl</td>
<td>-</td>
<td>47.50±2.40</td>
</tr>
<tr>
<td>m-methyl</td>
<td>-</td>
<td>14.80±1.30</td>
</tr>
<tr>
<td>p-hydrogen</td>
<td>4.02±0.30</td>
<td>11.10±0.30</td>
</tr>
<tr>
<td>p-chloro</td>
<td>4.83±0.30</td>
<td>4.75±0.02</td>
</tr>
<tr>
<td>m-fluoro</td>
<td>6.31±0.60</td>
<td>-</td>
</tr>
<tr>
<td>m-chloro</td>
<td>5.15±0.24</td>
<td>2.03±0.04</td>
</tr>
</tbody>
</table>

<sup>a</sup>Measurements made at 85.0°C.  <sup>b</sup>Measurements made at 58.6°C.
Figure 4. A: log $k_\mu$ versus $\sigma$ for substituted N-benzoylthioureas in 28.3% sulfuric acid at 85.0°C ($\Delta$). B: log $k_\mu$ versus $\sigma^+$ for substituted N-benzoylthioureas in 96.9% sulfuric acid at 58.6°C ($\circ$).
Such a mechanism would require $\alpha \approx 1.0$ for the step: $BH^+ + H_2O \rightarrow \text{products}$ — a reasonable value (cf. $\alpha$ for $Al^+ + H_2O \rightarrow \text{products}$). However, this mechanism is less successful than that of Scheme 1\(^5\) in accounting for the rate concentration profile of the reaction. The theoretical curve of equation 2, based on Scheme 1, fits the experimental points considerably better in the dilute region where the rate is proportional to the acidity function chosen than does the curve based on equation 6, which is derived by application of the Bronsted equation to the kinetic situation depicted in Scheme 2:

\[ k_\psi = \left(\frac{k_3 f_{BH^+}}{f_t}\right) \left\{\frac{h_0'''/(h_0'' + K_{BH^+})}{a_{H_2O}^r} \right\} \]

Bunnett-Yates plots of $(\log k_\psi + \log \left\{\frac{h_0'''/(h_0'' + K_{BH^+})}{a_{H_2O}^r} \right\})$ against $\log a_{H_2O}$ give a value of 4.5 for $\psi$, which has been used in calculating the theoretical curve based on equation 6 shown in Figure 1; the use of lower values of $\psi$ increases further the divergence of the theoretical curve from the experimental points.

The change from an A-2 to an A-1 mechanism when hydrolysis is carried out in 96.9% sulfuric acid is shown by the fact that $\log k_\psi$ now follows $\sigma^+$ rather than $\sigma$, and that $\omega$ has changed from $+0.54$ to $-1.60$ — about the value expected for an A-1 reaction although it is somewhat more positive (20). A more detailed analysis indicates, as a plausible mechanism for the hydrolysis in concentrated acid, that shown

\[ A \text{ third possible A-2 mechanism would involve attack of water on the N-protonated intermediate, R-CO-NH}_2^+ - CS - NH_2. \] It would seem impossible at the moment to distinguish between this possibility and that of Scheme 1 (cf. analogous case of acid hydrolysis of amides (24)).
in Scheme 3. In such a case

\[ \Delta S^\circ = \Delta S + \Delta S - \Delta S \]

Since \( \Delta S = -0.86 \) (5), this would indicate that \( \Delta S + \Delta S = -2.46 \), about the same value as \( \Delta S \) for the A-1 hydrolysis of benzanilides (20), which also proceeds by N-protonation followed by cleavage to give the acylium ion. The mechanism of Scheme 3 would also explain the low \( \Delta S^\dagger (-11 \text{ e.u.}) \) observed for hydrolysis of N-acetylthiourea in 96.9% sulfuric acid, mentioned above. In this concentration of acid diprotonation to \( \text{BH}_2^{2+} \) is essentially complete, and so the overall reaction is:

\[ [8] \quad \text{BH}_2^{2+} \rightarrow \text{BH}^+ \rightarrow \text{CH}_2^{2+} \rightarrow \text{M}^+ \rightarrow \text{products}. \]

The value of \( \Delta S^\dagger \) of 0 to +10 e.u. observed for A-1 acid-catalyzed ester hydrolysies (16) would suggest a \( \Delta S^\dagger \) value of 0 to +10 e.u. for the steps \( \text{BH}^+ \rightarrow \text{products} \); however, in the present reaction we must take account of the additional stage \( \text{BH}_2^{2+} \rightarrow \text{BH}^+ \). It is difficult to estimate with confidence \( \Delta S^\circ \) for this stage because of lack of information
... on ionization processes in sulfuric acid, but if the solvation changes are similar to those accompanying ionization processes in water, a $\Delta S^0$ of $-10$ to $-20$ e.u. would be reasonable (16). The addition of the $\Delta S^0$ and $\Delta S^\ddagger$ terms would then lead to the overall $\Delta S^\ddagger$ of $-11$ e.u. observed.

In 70-100% sulfuric acid, the stoichiometric concentration of N-acetylthiourea is made up almost completely of BH$^+$ and BH$_2^{\ddagger\ddagger}$ in varying proportions, and so application of the Bronsted equation to the kinetic situation of Scheme 3 leads to:

$$\text{Rate} = k_2 \left( [BH^+] + [BH_2^{\ddagger\ddagger}] \right)$$

where $k_2$ is the rate constant for the reaction: $\overrightarrow{CH_2^{\ddagger\ddagger}}$→ products.

It is known that $[BH_2^{\ddagger\ddagger}]/[BH^+] = h_0/K_{BH_2^{\ddagger\ddagger}}$ (5), and if it is assumed that $[CH_2^{\ddagger\ddagger}]/[BH^+] = h_0/K_{CH_2^{\ddagger\ddagger}}$, it can be shown that equation 9 leads to

$$k_2 p = k_2 K_{BH_2^{\ddagger\ddagger}} h_0 f_{CH_2^{\ddagger\ddagger}} \left/ \left( K_{CH_2^{\ddagger\ddagger}} f_{CH_2^{\ddagger\ddagger}} + h_0 \right) \right. \left/ f_{CH_2^{\ddagger\ddagger}} \right.$$  

$$= \left\{ \left( k_2 K_{BH_2^{\ddagger\ddagger}} h_0 f_{CH_2^{\ddagger\ddagger}} \right) \left/ \left( K_{CH_2^{\ddagger\ddagger}} f_{CH_2^{\ddagger\ddagger}} \right) \right. \right\} \left/ \left( K_{BH_2^{\ddagger\ddagger}} + h_0 \right) \right.$$  

A plot of log $k_2 p$ versus $-[H_0] - \log \left( K_{BH_2^{\ddagger\ddagger}} + h_A \right)$ gives a straight line of unit slope over the range 84.9-96.4% sulfuric acid, as required by equation 10 if the activity coefficient ratio $f_{CH_2^{\ddagger\ddagger}}/f_\ddagger$ is invariant.

---

6It might be expected that the protonation of BH$^+$ to give $\overrightarrow{CH_2^{\ddagger\ddagger}}$ would be governed by an acidity function applying to secondary amines; however, in 80-100% sulfuric acid the slopes of $H_0$ and $H_0^{\ddagger\ddagger}$ against percent acid are roughly parallel, and so it seems likely that the ionization of $\overrightarrow{CH_2^{\ddagger\ddagger}}$ will follow $H_0$ fairly closely.
with acid concentration. The intercept gives 
\[
\log \left\{ \frac{k_2 K_{BH_2++} f_{CH_2++}}{K_{CH_2++}} \right\} = -2.47
\]
equal to \( \log f \). Combining equations 2 and 10 gives

\[
k_\nu = \left\{ \frac{(k_1 K_A h_A a_{H_2O} f_{A^+})}{(f_{A^+} K_A)} \right\} \left\{ \frac{K_{BH_2++}}{(h_{o'''} + K_{BH_2++})} \right\}
+ \left\{ \frac{(k_2 K_{BH_2++} f_{CH_2++})}{(K_{CH_2++} f_{A^+})} \right\} \left\{ \frac{h_A}{(h_A + K_{BH_2++})} \right\}
\]

and this equation covers fairly well the variation of rate with acid concentration from 0% to 100% sulfuric acid (Table I and Figure 1).

Finally it should be noted that \( N-o \)-methylbenzoylthiourethane would be expected to show a very different rate-concentration profile from that displayed in Figure 1. In 28.3% acid, the rate was too slow to be measureable, as might be expected for an A-2 mechanism subject to steric hindrance; on the other hand, in 96.9% acid the rate was 90% greater than that of the \( p \)-methyl isomer, as would be expected for an A-1 mechanism subject to steric acceleration. For \( o \)-toluoyl-\( p \)-nitroanilide Duffy and Leisten (21) found a much greater (28-fold) enhancement of rate over that of the \( p \)-methyl isomer in the A-1 acid catalyzed region.

**Experimental**

The physical properties of all compounds used in this study were previously reported (5). Most rate measurements were made on the Unicam SP-800 recording U.V. Spectrophotometer with 6, 20 and 60 minute single wavelength time scans (or by using a scale expander and slave recorder) using a 1 cm fused silica cell with Teflon stopper in a controlled temperature (\( \pm 0.1^\circ \text{C} \)) cell block. For very slow rates the reaction was carried out in a 50 ml flask immersed in a constant-temperature bath. Aliquots (3 ml) were removed periodically, quenched by cooling, and measured for ultraviolet absorbance.
In dilute solution rates could be conveniently followed by absorbance measurements at about 280 nm for most compounds, but in concentrated acid the wavelength for maximal absorbance change was highly dependent upon the type of acyl substituent; in general measurements were taken near 230 nm and/or near 300 nm. $k_W$ was shown to be invariant with substrate concentration in the observed range of 0.002 to 0.00005 M/L and $k_W$ measured for product formation was shown to equal $k_W$ for substrate disappearance. Products were shown to be stable under the reaction conditions, since after 7-10 half-lives in every case the isosbestic points were still sharply defined. Rates were followed for at least two half-lives, and infinity values were taken after 6-10 half lives. The final spectrum in all cases was identical with the spectrum of thiourea and the carboxylic acid in the appropriate concentration of sulfuric acid. Frequently for the slower reactions the Guggenheim method (25) was used to obtain the rate. All calculations were done by an IBM-360 computer and a least squares program for log $(A_t - A_\infty)$ versus time was used throughout. In nearly every case correlation coefficients of better than 0.998 for eight points were obtained.

For very fast reactions, for which a sampling technique was not possible, 3 ml of acid were placed in a stoppered cell, which was left to reach thermal equilibrium in the cell block for a minimum of 10 minutes, 8-10$\mu$l of methanolic stock solution was then injected into the solution, which was shaken and placed back into the thermostated cell block; spectra were recorded after a three to ten minute re-equilibration. For the kinetics carried out in the thermostated
50 ml flask, 50 ml of acid was placed in the flask and left for a minimum of 15 minutes to reach thermal equilibrium. A 10 μl sample of stock solution of N-acylthiourea was then injected by use of a Hamilton syringe with a Chaney adaptor, the solution was well shaken, and after one-half hour back in the bath, the initial aliquot was taken.
References

19. D. P. Weeks, A. Grodski, and R. Fanucci. J. Amer. Chem. Soc. 90, 11588 (1968);


PART III

The hydrolysis of 1-acyl-2-thiohydantoins in sulfuric acid
ABSTRACT

The rates of hydrolysis of 22 1-acyl-2-thiohydantoins in aqueous sulfuric acid to give 2-thiohydantoin and the appropriate carboxylic acid have been determined. In 0 to about 90% sulfuric acid hydrolysis takes place by an A-2 mechanism, and the rate reaches a maximum in about 70% acid. In acid above about 90% hydrolysis takes place by an A-1 mechanism, and the rate increases monotonically. Evidence for the two mechanisms comes from Yates parameters; from entropies of activation; from $\Delta G$ and $\Delta G^+$ relations; and from steric effects.

RESUME

On a déterminé les vitesses de l'hydrolyse de vingt deux acyle-1 thiohydantoines-2 dans l'acide sulfurique, fournissant le thiohydantoin-2 et une acide carboxylique. Dans la zone de concentration de 0-90% d'acide sulfurique la réaction se passe par un mécanisme A-2, et la vitesse de la reaction atteint un maximum dans une concentration de 70% acide environ. Entre 90-100% concentration d'acide la réaction suit une mechanism A-1 et la vitesse de la réaction s'augmente continuellement avec la concentration d'acide. La dualité des mécanismes est supportée par: les parameters $r$ de Yates et $\phi$ de Bunnett et Olsen; les entropies d'activation; les relations $\Delta G$ ou $\Delta G^+$; et les effects stériques.
1-Acyl-2-thiohydantoins (Scheme 1) are hydrolyzed in aqueous acid exclusively to the corresponding carboxylic acid and 2-thiohydantoin (See review in ref. 1); a report to the contrary was found incorrect (2). The mechanism of this hydrolysis is of interest because of its use in certain modifications (3) of Schlack and Kumpf's procedure (4) for identifying the C-terminal amino acid residue of peptides. In the present paper we show that hydrolysis in aqueous sulfuric acid may take place by an A-2 or an A-1 mechanism, depending on the concentration of acid; the mechanism of the reaction proves to be very similar to that of the acid catalyzed hydrolysis of N-acylthioureas (5).

As a first step it was necessary to study the protonation of 1-acyl-2-thiohydantoins in sulfuric acid. It is already known that 2-thiohydantoin itself undergoes mono- and then partial diprotonation as the concentration of sulfuric acid varies from 0 to 100%. Over the range 0 to 80% sulfuric acid the spectral changes indicate protonation to be taking place on the thiocarbonyl sulfur ($pK_{BH^+} = -4.83$), the extent of protonation depending on the $H_0$ value of the solution;2 and in acid concentrations above 90% the spectral changes indicate a second protonation on the carbonyl oxygen.3 The compound is about half converted into the diprotonated form in 100% acid.4 We have found that 1-acyl-2-thiohydantoins to differ in this respect from thioureas and N-acylthioureas (6), the protonation of which follows $h_0''''$ and not $h_0$.5

2G. Derdall, in unpublished researches, has found 2-thiohydantoins to differ in this respect from thioureas and N-acylthioureas (6), the protonation of which follows $h_0''''$ and not $h_0$.

3W. I. Congdon, unpublished researches.

4R. J. Gillespie, in unpublished cryoscopic and conductometric studies, found a mean $\mu$ value of 2.5 and a mean $\sigma$ of 1.4 for 2-thiohydantoin in 100% sulfuric acid.
thiohydantoins show very similar changes in their ultraviolet spectra when they are dissolved in varying concentrations of acid. However, a quantitative determination of the extent of their protonation was made difficult by their rapid hydrolysis. Eventually, it was found that 1-0-iodobenzoyl-2-thiohydantoin was sufficiently stable in different concentrations of acid at 25.3°C to give the spectra shown in Figure 1. The character of the spectral changes indicated protonation to be taking place on the sulfur atom (6) to give the cation BH⁺ (see Scheme 1).
Figure 1. The ultraviolet absorption spectra of 1-α-iodobenzoyl-2-thiocydantoin in A. 0.0%; B. 74.9%; C. 78.1%; D. 96.3% sulfuric acid.
Analysis of the spectral changes by conventional methods (7,8) showed that the ionization ratio \([\frac{[BH^+]}{[B]}]\) was proportional to \(h_o\) (Figure 2), and that the \(pK_{BH^+}\) was -6.8.

By lowering the temperature of the solutions to 9.4°C, and by extrapolating absorbance readings back to the time of mixing, it was possible to measure the ultraviolet absorbance of 1-benzoyl-2-thiohydantoin and of 1-m-trifluoromethylbenzoyl-2-thiohydantoin in different concentrations of acid. Again, the ionization ratio was found to follow \(h_o\) (Figure 2), and the \(pK_{BH^+}\) values of -6.6 and -6.7, respectively, were obtained. The similarity of these values indicates that the basicity at the sulfur atom is little affected by substitution in the benzene ring, but a more precise analysis (e.g. a ~ analysis) is probably not warranted in view of the limited accuracy of the \(pK_{BH^+}\) values.

In acid concentrations above about 94% spectral changes similar to those accompanying the diprotonation of N-acylthioureas (6) were observed suggesting the formation of the cations \(\overline{BH_2H^+}\) and \(\overline{B'H_2H^+}\) (Scheme 1); however, no systematic study of these changes was made because hydrolysis of the 1-acyl-2-thiohydantoins was too rapid.

The hydrolysis, followed by ultraviolet absorbance changes, was found to follow first-order kinetics in the large excess of acid used. The pseudo-first-order rate constants \((k_p)\) for the hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin in 6-99% sulfuric acid are given in Table I. The rate constants increased with acid concentration up to a maximum in about 70% acid, then decreased to a minimum in about 92% acid, and then increased again, as shown in Figure 3. Also shown in this figure is the rate profile for 1-acetyl-2-thiohydantoin, which is fairly similar to
Figure 2. A plot of log I (=[SH+]/[S]) versus -H_0 for 1-benzoyl-2-thiohydantoin (slope = 1.02, pK_{BH^+} = -6.6; □); 1-m-trifluoromethyl-benzoyl-2-thiohydantoin (slope = 1.03, pK_{BH^+} = -6.7; Δ); 1-o-iodo-benzoyl-2-thiohydantoin (slope = 0.95, pK_{BH^+} = -6.8; ⊙).
<table>
<thead>
<tr>
<th>% sulfuric acid</th>
<th>Exptl. (10^4k_r) (sec(^{-1}))</th>
<th>Calcd. A-2 (10^4k_r) (sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>1.6*</td>
<td>**</td>
</tr>
<tr>
<td>24.2</td>
<td>7.5*</td>
<td>5.0</td>
</tr>
<tr>
<td>39.6</td>
<td>26.0±0.05</td>
<td>23.0</td>
</tr>
<tr>
<td>53.5</td>
<td>78.5±0.50</td>
<td>78.0</td>
</tr>
<tr>
<td>58.0</td>
<td>127.5±1.60</td>
<td>120.0</td>
</tr>
<tr>
<td>62.4</td>
<td>178.0±1.10</td>
<td>170.0</td>
</tr>
<tr>
<td>66.1</td>
<td>231.0±5.70</td>
<td>214.0</td>
</tr>
<tr>
<td>68.0</td>
<td>253.5±0.50</td>
<td>220.0</td>
</tr>
<tr>
<td>70.1</td>
<td>290.0±4.40</td>
<td>240.0</td>
</tr>
<tr>
<td>72.7</td>
<td>254.0±5.70</td>
<td>220.0</td>
</tr>
<tr>
<td>74.9</td>
<td>238.0±3.50</td>
<td>180.0</td>
</tr>
<tr>
<td>77.5</td>
<td>175.0±4.50</td>
<td>120.0</td>
</tr>
<tr>
<td>80.0</td>
<td>199.6±1.80</td>
<td>60.0</td>
</tr>
<tr>
<td>84.2</td>
<td>13.6±0.40</td>
<td>14.0</td>
</tr>
<tr>
<td>88.4</td>
<td>4.4±0.10</td>
<td>4.4</td>
</tr>
<tr>
<td>91.2</td>
<td>3.0±0.12</td>
<td>1.5</td>
</tr>
<tr>
<td>94.4</td>
<td>3.5±0.16</td>
<td>0.4</td>
</tr>
<tr>
<td>96.3</td>
<td>5.9±0.20</td>
<td>0.2</td>
</tr>
<tr>
<td>97.1</td>
<td>7.6±0.12</td>
<td>**</td>
</tr>
<tr>
<td>97.9</td>
<td>12.2±0.36</td>
<td>**</td>
</tr>
<tr>
<td>98.9</td>
<td>22.6±0.48</td>
<td>**</td>
</tr>
</tbody>
</table>

**\(H_A\) is unmeasured for this acid concentration.
Figure 3. Plot of log $k_\text{p}$ versus percent sulfuric acid for 1-acetyl-5,5-dimethyl-2-thiohydantoin (○) and 1-acetyl-2-thiohydantoin (△).
that of the 5,5-dimethyl derivative over most of the range of acid concentrations, but has a rate minimum in about 98% acid. Other 1-acyl-2-thiohydantoins showed somewhat similar rate-concentration profiles, as shown in Figures 4 and 5, with maximum rates in about 70% acid. However, the positions of the minima varied considerably, and none could be observed for the hydrolysis of 1-m-trifluoromethylbenzoyl-2-thiohydantoin (see Figure 5).

From analogy with similar rate profiles already reported (5, 9), these results suggest an A-2 mechanism for hydrolysis in approximately 0-90% acid, followed by an A-1 mechanism for hydrolysis of most (but not all: e.g. not of 1-m-trifluoromethylbenzoyl-2-thiohydantoin) of the 1-acyl-2-thiohydantoins in higher concentrations of acid. This dualism of mechanism would explain most of the qualitative features of the rate profiles, if it is assumed that the A-2 hydrolysis takes place by the mechanism outlined in Scheme 2, and the A-1 hydrolysis by the mechanism outlined in Scheme 1.
Figure 4. A plot of log $k_p$ at 25.3°C versus concentration of sulfuric acid for 1-benzoyl-3-phenyl-2-thiohydantoin (◊); 1-benzoyl-2-thiohydantoin (▼); 1-benzoyl-5-methyl-2-thiohydantoin (□); 1-benzoyl-5-(sec)butyl-2-thiohydantoin (◇); and 1-benzoyl-5-isopropyl-2-thiohydantoin (△).
Figure 5. A plot of log $k_\psi$ at 25.3°C versus concentration of sulfuric acid for 1-benzoyl-2-thiohydantoin ($\nabla$); 1-$p$-cholorobenzoyl-2-thiohydantoin ($\Delta$); 1-$p$-methoxybenzoyl-2-thiohydantoin ($\Theta$); and 1-$m$-trifluoromethylbenzoyl-2-thiohydantoin ($\square$).
Geminal dimethyl substitution at the 5-position should not affect appreciably the basicity of the various centers, but should slow down the A-2 reaction (by steric hindrance in the step: $\text{AH}^+ + r\text{H}_2\text{O} \rightarrow \text{intermediate}$), and should accelerate the A-1 reaction (by steric acceleration of the N-acyl fission). This would account for the change in the position of the minimum in the rate profile on going from 1-acetyl-2-thiohydantoin to 1-acetyl-5,5-dimethyl-2-thiohydantoin (Figure 3). The general effect of 5-substitution in decreasing the rate of the A-2 reaction is illustrated in Figure 4. Electron-withdrawing substituents on the benzene ring of substituted 1-benzoyl-2-thiohydantoins should, from analogy with the behavior of substituted benzamides (10), shift the maximum of the rate profile to higher acidities, and this effect is shown to a very slight extent (Figure 5); much more dramatic is the effect in inhibiting the A-1 reaction (see Figure 5) by destabilizing the acylium ion. The stability of 1-iodobenzoyl-2-thiohydantoin arises from both the steric effect of the large iodine atom in slowing the A-2 reaction, and its electronic effect in slowing the A-1 reaction.

The duality of mechanism is supported by various quantitative analyses of the kinetic data. This evidence is as follows:

1. **Hydration Parameters**

Yates and his coworkers (11) have modified the original Bunnett hydration parameter treatment (12) to take account of the correct acidity function to apply to the protonation of the substrate being hydrolyzed. In the present case it is most reasonable to assume that the extent of protonation of $\text{B}$ to give the reactive intermediate $\text{AH}^+$ (Scheme 2) is governed by the acidity function $H_A$ (13), and that $[\text{AH}^+] \ll [\text{BH}^+]$ (cf.
ref. 5). In such a case, the mechanism of Scheme 2 necessitates the following rate expression:

$$k_r = \left\{ \frac{K_{AH+}}{(K_{BH+} + h_o)} \right\} \left\{ \frac{K_{BH+}}{(K_{BH+} + h_o)} \right\}$$

where $k_r$ is the rate constant for the reaction: $AH^+ + H_2O \rightarrow$ products; $a_{H_2O}$ is the activity of water; the $f_i$'s are activity coefficients; and the other symbols can be understood by reference to Scheme 2. A plot against log $a_{H_2O}$ of (log $k_r^* + H_A^* - \log \left\{ \frac{K_{BH+}}{(K_{BH+} + h_o)} \right\}$) for 1-acetyl-5,5-dimethyl-2-thiohydantoin, assuming $pK_{BH+} = -6.4$, gives a fairly good straight line between 24.2 and 88.1% sulfuric acid (correlation coefficient 0.9977) (see Figure 6), as required by equation 1 if $(f_{AH+/f_A})$ is invariant with acid concentration. The $r$ value of 0.61 given by the slope of this line is considerably lower than usual for amide hydrolyses (11); however, $r$ values are found to become lower for hydrolyses in more concentrated acids (5). In any case, the change in slope above 84.2% acid is clearly indicative of a change from an A-2 to an A-1 mechanism (9). The intercept shown in Figure 6 gives

$$\log \left( \frac{k_r f_{AH+/f_A}}{K_{AH+}} \right) = -4.45$$

(14) if we make the usual assumption that the activity coefficient ratio is invariant with acid concentration. Use of this value, and $r = 0.61$, gives the theoretical curve for the rates of hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin shown in Figure 7. The agreement with the experimental points is reasonably good in view of the various assumptions, and offers strong support for the A-2 mechanism outlined in Scheme 2. An alternative mechanism would

61-benzoyl-2-thiohydantoin has a $pK_{BH+}$ of -6.6; substitution of methyl groups at the 5-position should affect the basicity very little (14), but substitution of the phenyl by a methyl group would be expected to strengthen the basicity slightly. The results of the calculations are not greatly affected by small variations in the precise $pK_{BH+}$ assumed.
Figure 6. A plot of \( \log k_w + H_A - \log \left( \frac{K_{SH^+}}{K_{SH^+} + h_0} \right) \) versus \(-\log a_{H_2O}\) for 1-acetyl-5,5-dimethyl-2-thiohydantoin in sulfuric acid at 25.3°C.
Figure 7. Rate-acidity dependence for the hydrolysis of \(1\)-acetyl-5,5-dimethyl-2-thiohydantoin in aqueous sulfuric acid at 25.3°C. Points: experimental \(k_w\) (in seconds\(^{-1}\)). The theoretical curve derived from equation 1 \(-\). The theoretical curve derived from equation 2 \(-\).
be that of Scheme 3, which would lead to the following rate equation:

\[ k_v = \left( k_1 \frac{a_{H_2O} f_{BH^+}}{f_1} \right) \left( h_0 / (K_{BH^+} + h_0) \right) \]

Analysis of the kinetic data by this equation yields \( r = 1.65 \) and \( \log (k_1 f_{BH^+}/f_1) = -1.0 \), but the fit with the experimental results is much poorer, as shown in Figure 7.

Bunnett and Olsen (15) have produced an equation, based on a modification of the original hydration hypothesis (12), which has proved highly successful in predicting the variation of the rates of acid-catalyzed reactions with acid concentration. Applied to the kinetic situation of Scheme 2, this equation becomes

\[ \log k_v + H_0 - \log \left( \frac{k_{SH^+}}{(K_{SH^+} + h_0)} \right) = \bar{E}(H_0 + \log [H^+] ) + \text{const.} \]
A plot of \((\log k_v + H_o - \log \left\{ \frac{K_{BH^+}}{(K_{BH^+} + H_o)} \right\})\) against \((H_o + \log [H^+])\) (assuming \([H^+] = [H_2SO_4] (16)\)) gives a curve of gratifying linearity up to 88% sulfuric acid, having a slope \(\bar{s} = 0.81\), normal for an amide hydrolysis by an A-2 mechanism. Again, the change to a slope of \(\bar{s} = -0.98\) in acid concentrations above 88% is indicative of a change to an A-1 mechanism. See Figure 8.

It is not possible to deduce a kinetic expression for the A-1 hydrolysis based on Scheme 1, because the required \(h_A\) values of strong sulfuric acid solutions are not available. However, it is obvious that the rate will increase more slowly with acid concentration than does the \(h_A\) value of the solution, because the latter is governing not only the formation of the useful intermediate \(\text{BH}_{2^{-}}^{++}\), but the formation of the pool of useless dication \(\text{BH}_{2}^{++}\).

2. **Entropies of activation**

Plots of \(\log k_v\) against \(1/T\) for 1-acetyl, 1-benzoyl and 1-acetyl-5,5-dimethyl-2-thiohydantoin gave straight lines from which entropies of activation \((\Delta S^\ddagger)\) were calculated. For hydrolyses in 39.6% and 84.9% sulfuric acid these had about the values (near -20 e.u.) expected for an A-2 reaction (17); the marked increase in \(\Delta S^\ddagger\) for hydrolyses in more concentrated acids was indicative of a change to an A-1 mechanism. In 96.4% sulfuric acid hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin would be expected to take place nearly completely by the A-1 mechanism (see Table II and Figures 3 and 7), and \(\Delta S^\ddagger\) was -2 e.u., while hydrolysis of 1-acetyl-2-thiohydantoin would be expected, from inspection of Figure 3 to be about 70% A-2 and 30% A-1, and \(\Delta S^\ddagger\) was -5 e.u. Lack of information on the extent and position of diprotonation prevents a
Figure 8. A plot of \( \log k_w + H_0 - \log \left[ \frac{K_{SH^+}}{K_{SH^+} + h_0} \right] \) versus \( H_0 + \log [H^+] \) for 1-acetyl-5,5-dimethyl-2-thiohydantoin.
### TABLE II

Temperature dependence of the rate of sulfuric acid catalyzed hydrolysis of 1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>Compound and % sulfuric acid</th>
<th>Temp. °C</th>
<th>$10^6 k_a$ (sec$^{-1}$)</th>
<th>$\log A$ (sec$^{-1}$)</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
<th>$E_a$ (KCal/Mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-acetyl-2-thiohydantoin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.6% sulfuric acid</td>
<td>25.3</td>
<td>19.3±1.50</td>
<td>9.4±0.2</td>
<td>-18±2</td>
<td>17±2</td>
</tr>
<tr>
<td></td>
<td>35.9</td>
<td>48.3±0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin</td>
<td>11.0</td>
<td>7.2±0.03</td>
<td>8.3±0.1</td>
<td>-22±1</td>
<td>14±1</td>
</tr>
<tr>
<td>39.6% sulfuric acid</td>
<td>25.3</td>
<td>26.0±0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>54.7±0.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-2-thiohydantoin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>84.9% sulfuric acid</td>
<td>25.3</td>
<td>12.0±0.2</td>
<td>9.9±0.2</td>
<td>-15±2</td>
<td>18±2</td>
</tr>
<tr>
<td></td>
<td>35.9</td>
<td>28.5±0.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-2-thiohydantoin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>96.4% sulfuric acid</td>
<td>25.3</td>
<td>2.1±0.07</td>
<td>12.0±0.2</td>
<td>-5±2</td>
<td>22±2</td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>6.7±0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin</td>
<td>10.8</td>
<td>1.1±0.04</td>
<td>12.8±0.2</td>
<td>-2±2</td>
<td>22±2</td>
</tr>
<tr>
<td>96.4% sulfuric acid</td>
<td>35.5</td>
<td>21.2±0.60</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>49.6</td>
<td>124.0±4.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-benzoyl-2-thiohydantoin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.6% sulfuric acid</td>
<td>25.3</td>
<td>6.9±0.10</td>
<td>8.6±0.2</td>
<td>-21±2</td>
<td>16±2</td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>16.8±0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45.6</td>
<td>37.1±0.72</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Pseudo-first-order rate constants. $^b$Value obtained by extrapolation from the rate profile.
further interpretation of these values.

3. Hammett $\rho$ and $\sigma^+$ relations

The rate profile for 1-benzoyl-2-thiohydantoin (Figure 5) suggests an A-2 mechanism of hydrolysis in 0-90% acid and an A-1 mechanism in 90-100% acid. The rate constants ($k_\gamma$) for the hydrolysis of thirteen substituted 1-benzoyl-2-thiohydantoins in 58.0% sulfuric acid, of ten substituted 1-benzoyl compounds in 84.6% sulfuric acid and of ten substituted 1-benzoyl compounds in 93.8% acid are given in Table III and Figures 9 and 10.

An A-2 mechanism would be expected to result in log $k_\gamma$ varying as $\rho$ rather than $\sigma^+$; and this indeed is found for hydrolyses in 58.0% sulfuric acid, as shown in Figure 9. The $\rho$ given by the slope of the line is -0.41. A small value of $\rho$ would be expected from the mechanism of Scheme 2 because of the compensating effects of substituents on the various pre-equilibria as well as on the rate-determining step; an exact estimate of the separate $\rho$ values is difficult in the present case.\footnote{Models indicate that for the conformation of B shown in Scheme 1, the benzene ring cannot be coplanar with the carbonyl group (in such cases the carbonyl group is generally coplanar with trigonal nitrogen in preference to phenyl (18)). This would result in $\rho$ values different from those of analogous substituted phenyl compounds in which the benzene ring approached coplanarity with the carbonyl group.}

The mechanism of Scheme 3 might be expected to lead, however, to a larger $\rho$ value than -0.41: $\rho_1$ for the step $B \rightleftharpoons BH^+$ should approach zero, but $\rho_2$ for the step $BH^+ + \text{H}_2\text{O} \rightarrow \text{products}$ would be expected to be about +1 (19), so that the overall $\rho_{\gamma}$ ($= \rho_1 + \rho_2$) should be about 1.

An A-1 mechanism would be expected to result in log $k_\gamma$ varying as $\sigma^+$ rather than $\sigma$: this is observed for hydrolysis in 93.8% acid.
TABLE III
Rates of hydrolysis of substituted 1-benzoyl-2-thiohydantoins in three different concentrations of sulfuric acid at 25.3°C

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$10^5 k_p$ (sec$^{-1}$)$^a$ 58.0% $\text{H}_2\text{SO}_4$</th>
<th>$10^5 k_p$ (sec$^{-1}$)$^a$ 84.6% $\text{H}_2\text{SO}_4$</th>
<th>$10^5 k_p$ (sec$^{-1}$)$^a$ 93.8% $\text{H}_2\text{SO}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxy</td>
<td>37.20±0.20</td>
<td>55.00$^b$</td>
<td>171.20±1.50$^c$</td>
</tr>
<tr>
<td>p-(tert)butyl</td>
<td>50.60±0.15</td>
<td>-</td>
<td>33.00±0.65</td>
</tr>
<tr>
<td>p-methyl</td>
<td>49.80±0.17</td>
<td>23.30±1.20</td>
<td>32.70±0.45</td>
</tr>
<tr>
<td>m-methyl</td>
<td>52.00±0.35</td>
<td>9.00±0.36</td>
<td>11.85±0.01</td>
</tr>
<tr>
<td>hydrogen</td>
<td>49.80±0.50</td>
<td>6.04±0.21</td>
<td>7.40±0.30</td>
</tr>
<tr>
<td>p-fluoro</td>
<td>35.10±0.10</td>
<td>4.43±0.18</td>
<td>5.32±0.06</td>
</tr>
<tr>
<td>m-methoxy</td>
<td>42.10±0.80</td>
<td>-</td>
<td>1.14±0.24$^c$</td>
</tr>
<tr>
<td>p-chloro</td>
<td>35.50±0.30</td>
<td>4.26±0.09</td>
<td>2.87±0.03</td>
</tr>
<tr>
<td>p-bromo</td>
<td>35.60±1.05</td>
<td>3.76±0.15</td>
<td>2.54±0.07</td>
</tr>
<tr>
<td>p-iodo</td>
<td>36.50±0.60</td>
<td>4.00±0.24</td>
<td>-</td>
</tr>
<tr>
<td>m-chloro</td>
<td>32.60±0.14</td>
<td>4.10±0.08</td>
<td>1.06±0.15</td>
</tr>
<tr>
<td>m-bromo</td>
<td>31.60±0.10</td>
<td>3.70±0.24</td>
<td>-</td>
</tr>
<tr>
<td>m-trifluoromethyl</td>
<td>26.00±0.05</td>
<td>-</td>
<td>0.44±0.03</td>
</tr>
<tr>
<td>p-nitro</td>
<td>21.53±0.08</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Pseudo-first-order rate constants. $^b$Value obtained by extrapolation from the rate profile. $^c$The sigma value used was that suggested by Stewart and Yates (20) for hydrogen bonded methoxyl groups in concentrated sulfuric acid.
Figure 9. A plot of log $k_\psi$ versus $A$: A for substituted 1-benzoyl-2-thiohydantoin in 58.0% sulfuric acid at 25.3°C (cc: 0.950; sd: 0.04) ($\Delta$). B: $G^*$ for substituted 1-benzoyl-2-thiohydantoin in 93.8% sulfuric acid at 25.3°C (cc: 0.992; sd: 0.11) (☉).
Figure 10. A plot of $\log k$ versus $\sigma$ for substituted 1-benzoyl-2-thiohydantoins in 84.6% sulfuric acid at 25.3°C.
(Figure 9). The value of \( \rho \) (-2.51) thus obtained has about the magnitude observed for other A-1 reactions yielding acylium ions (21).

In 84.6% sulfuric acid the plot of \( \log k_\nu \) versus \( \sigma \) changes slope at \( \sigma = 0.0 \) (Figure 10). This is consonant with a mechanism dependent on the nature of the substituents in the benzoyl group: electron-releasing groups promote reaction by an A-1 mechanism (hence the steep slope of the line on the left-hand side of Figure 10); electron-withdrawing groups ensure that the A-2 mechanism still predominates at the acid concentration (hence the small slope of the line on the right hand side of Figure 10). This evidence can also be construed in support of the mechanism of Scheme 2 rather than that of Scheme 3.

4. C-5 Substituent Effects

As shown in Figure 4, substituents at the 5-position reduce the height but do not greatly alter the position of the rate maximum in plots of \( \log k_\nu \) versus acid concentration. From Figure 3 it is apparent, however, that they do alter the position and depth of the minimum. The effect of C-5 substituents on the height of the maximum is interpretable in terms of steric hindrance to hydrated water attack on the protonated substrate as might be expected for an A-2 mechanism. Comparison of the entropy and enthalpy values for 1-acetyl and 1-acetyl-5,5-dimethyl-2-thiohydantoin in 39.6% acid (Table II) (bearing in mind the error discussion in reference 17) leads to the following relative values: \( T\Delta S^\ddagger = 1.5 \) KCal; \( \Delta H^\ddagger = 1.6 \) KCal. The results are similar to those for formation and hydrolysis of semicarbazones (22) of substituted ketones. This decrease in \( \Delta S^\ddagger \) is in agreement with the modified qualitative Hammett-Price rule for a reaction in a highly polar solvent having a highly polar transition state (23), in that the more highly complex molecule (with substituents adjacent to the reaction...
center) has a lower activation entropy.

5. **N-3 Substituents**

As seen in Figure 4, replacement of hydrogen by a phenyl group at the N-3 position increases the height of the maximum but does not effect the position in a plot of \( \log k_2 \) versus percent acid. Also it may be noted that it decreases the minimum rate but not the position of the minimum. The phenyl group as noted earlier is more electron withdrawing than hydrogen (\( pK_{BH^+} = -4.83 \) for 2-thiohydantoin and -5.18 for 3-phenyl-2-thiohydantoin), so that one might expect a higher maximum for the A-2 mechanism, since the 3-phenyl-2-thiohydantoin would be a better leaving group. The result in concentrated acid is thought to be rather important.

\[ \phi = 2.3 \text{ for } \text{m- and p- anilide substituted mesityl anilide hydrolysis in 96.2\% sulfuric acid at 25.0^oC (2h)} \]. In view of this result, if one were to assume a similar mechanism, one might expect that the 3-phenyl isomer would enhance the rate rather than decrease it. The fact that the minimum rate and those in the A-1 region are about 30\% slower than those for the unsubstituted isomer may be interpreted as support for a mechanism involving \( \text{BH}_2^{++} \). In this acid region only the C-4 carbonyl basicity would be appreciably affected by N-3 substitution. (Table IV)

**Experimental**

1-Acyl-2-thiohydantoins were synthesized according to Johnson and Nicolet (25), and were recrystallized from methanol or ethanol. 1-benzoyl-3-phenyl-2-thiohydantoin (2) was a gift of J. K. Liu. Melting points were determined on a hot stage microscope and are uncorrected. Tables V and VI list physical properties of each compound. Analyses were done by A. Bernhardt of West Germany. Experimental methods for ionization
TABLE IV-A

The pseudo-first-order rate constants ($10^4 k_\text{y} \text{ sec}^{-1}$) for substituted 1-benzoyl-2-thiohydantoin (substituent shown) in the region of the rate maximum

<table>
<thead>
<tr>
<th>Sulfuric acid (%)</th>
<th>1-benzoyl-</th>
<th>1-p-methoxybenzoyl-</th>
<th>1-benzoyl-3-phenyl-</th>
<th>1-p-chlorobenzoyl-</th>
<th>1-m-trifluoromethylbenzoyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.6</td>
<td>6.92±0.09</td>
<td>-</td>
<td>6.61±0.14</td>
<td>5.34±0.15</td>
<td>4.44±0.05</td>
</tr>
<tr>
<td>46.2</td>
<td>18.30±0.21</td>
<td>11.53±0.36</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>50.1</td>
<td>21.4±0.10</td>
<td>17.66±0.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>53.5</td>
<td>26.50±0.55</td>
<td>18.30±0.21</td>
<td>-</td>
<td>-</td>
<td>14.00±0.18</td>
</tr>
<tr>
<td>58.0</td>
<td>49.80±0.50</td>
<td>26.50±0.55</td>
<td>18.30±0.21</td>
<td>106.90±1.10</td>
<td>118.20±2.10</td>
</tr>
<tr>
<td>62.4</td>
<td>100.90±2.00</td>
<td>67.80±1.05</td>
<td>50.90±1.70</td>
<td>66.50±1.05</td>
<td>76.70±1.65</td>
</tr>
<tr>
<td>66.1</td>
<td>158.00±4.80</td>
<td>103.90±2.80</td>
<td>168.20±1.80</td>
<td>106.90±1.10</td>
<td>118.20±2.10</td>
</tr>
<tr>
<td>68.0</td>
<td>180.80±9.50</td>
<td>127.20±2.25</td>
<td>210.60±3.30</td>
<td>126.00±1.50</td>
<td>-</td>
</tr>
<tr>
<td>70.1</td>
<td>205.70±4.00</td>
<td>131.70±3.90</td>
<td>250.20±8.10</td>
<td>151.00±2.80</td>
<td>118.20±2.10</td>
</tr>
<tr>
<td>72.7</td>
<td>195.10±7.90</td>
<td>127.10±4.70</td>
<td>157.30±4.00</td>
<td>111.50±3.18</td>
<td>-</td>
</tr>
<tr>
<td>74.9</td>
<td>139.20±4.80</td>
<td>103.80±5.80</td>
<td>159.00±4.50</td>
<td>136.10±1.20</td>
<td>136.30±1.00</td>
</tr>
<tr>
<td>77.5</td>
<td>70.30±3.30</td>
<td>83.35±0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>78.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>79.8</td>
<td>-</td>
<td>-</td>
<td>75.30±1.70</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80.9</td>
<td>14.90±0.75</td>
<td>-</td>
<td>18.70±0.54</td>
<td>14.80±0.33</td>
<td>22.90±1.45</td>
</tr>
<tr>
<td>82.4</td>
<td>-</td>
<td>61.60±1.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>83.1</td>
<td>-</td>
<td>-</td>
<td>9.05±0.14</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>84.6</td>
<td>6.01±0.21</td>
<td>-</td>
<td>5.80±0.25</td>
<td>4.28±0.08</td>
<td>-</td>
</tr>
<tr>
<td>86.4</td>
<td>-</td>
<td>18.50±2.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>88.4</td>
<td>-</td>
<td>-</td>
<td>4.13±0.11</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>89.4</td>
<td>-</td>
<td>-</td>
<td>5.66±0.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>91.2</td>
<td>-</td>
<td>-</td>
<td>5.63±0.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>92.1</td>
<td>5.69±0.12</td>
<td>105.30±2.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>93.8</td>
<td>7.10±0.50</td>
<td>171.20±1.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>94.4</td>
<td>-</td>
<td>-</td>
<td>5.16±0.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>94.9</td>
<td>-</td>
<td>-</td>
<td>5.05±0.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>96.4</td>
<td>9.10±0.27</td>
<td>32.10±0.30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97.1</td>
<td>-</td>
<td>-</td>
<td>7.02±0.16</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97.9</td>
<td>17.90±0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE IV-B

The pseudo-first-order rate constants \(10^4k_f\ sec^{-1}\) for 1-acyl-2-thiohydantoins in the region of the rate maximum

<table>
<thead>
<tr>
<th>Sulfuric acid (%)</th>
<th>1-acetyl 5-methyl-</th>
<th>1-benzoyl-5-methyl-</th>
<th>1-benzoyl-5-isopropyl-</th>
<th>1-benzoyl-5-(sec)butyl-</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.6%</td>
<td>19.30±1.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>58.0</td>
<td>380.00±11.7</td>
<td>35.50±0.63</td>
<td>19.60±0.40</td>
<td>17.90±0.40</td>
</tr>
<tr>
<td>62.1</td>
<td>170.00±18.0</td>
<td>71.80±0.90</td>
<td>29.30±0.42</td>
<td>21.80±0.36</td>
</tr>
<tr>
<td>66.1</td>
<td>187.00±39.00</td>
<td>81.90±1.83</td>
<td>33.60±0.66</td>
<td>35.50±0.60</td>
</tr>
<tr>
<td>68.0</td>
<td>163.00±33.6</td>
<td>93.10±3.24</td>
<td>37.90±1.20</td>
<td>40.80±0.90</td>
</tr>
<tr>
<td>70.1</td>
<td>111.00±15.0</td>
<td>81.10±2.70</td>
<td>36.60±1.15</td>
<td>37.30±0.66</td>
</tr>
<tr>
<td>72.7</td>
<td>325.00±5.70</td>
<td>70.20±2.30</td>
<td>29.30±0.78</td>
<td>32.10±1.32</td>
</tr>
<tr>
<td>74.9</td>
<td>102.00±2.55</td>
<td>19.10±1.00</td>
<td>10.30±0.48</td>
<td>-</td>
</tr>
<tr>
<td>78.1</td>
<td>31.60±0.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80.9</td>
<td>8.71±0.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>86.1</td>
<td>5.78±0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>88.1</td>
<td>1.90±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>92.2</td>
<td>3.55±0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>93.8</td>
<td>3.05±0.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>94.9</td>
<td>2.11±0.09</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>96.4</td>
<td>2.09±0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>97.9</td>
<td>1.89±0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>98.9</td>
<td>2.3±0.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>99.1</td>
<td>4.69±0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>96.1</td>
<td>-</td>
<td>5.08±0.18</td>
<td>8.91±0.27</td>
<td>10.30±0.23</td>
</tr>
</tbody>
</table>
### TABLE V

Analytical data for previously unreported 1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>L-substituent</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1-m-anisoyl</td>
<td>52.8</td>
<td>4.0</td>
</tr>
<tr>
<td>1-p-toluoyl</td>
<td>56.4</td>
<td>4.3</td>
</tr>
<tr>
<td>1-m-toluoyl</td>
<td>56.4</td>
<td>4.3</td>
</tr>
<tr>
<td>1-p-(tert)butyl-benzoyl</td>
<td>60.9</td>
<td>10.2</td>
</tr>
<tr>
<td>1-p-fluorobenzoyl</td>
<td>50.4</td>
<td>2.9</td>
</tr>
<tr>
<td>1-p-chlorobenzoyl</td>
<td>47.1</td>
<td>2.8</td>
</tr>
<tr>
<td>1-m-chlorobenzoyl</td>
<td>47.1</td>
<td>2.8</td>
</tr>
<tr>
<td>1-p-bromobenzoyl</td>
<td>40.2</td>
<td>2.3</td>
</tr>
<tr>
<td>1-m-bromobenzoyl</td>
<td>40.2</td>
<td>2.3</td>
</tr>
<tr>
<td>1-p-iodobenzoyl</td>
<td>34.7</td>
<td>2.0</td>
</tr>
<tr>
<td>1-m-iodobenzoyl</td>
<td>34.7</td>
<td>2.0</td>
</tr>
<tr>
<td>1-m-trifluoromethyl-benzoyl</td>
<td>45.8</td>
<td>2.4</td>
</tr>
<tr>
<td>1-p-nitrobenzoyl*</td>
<td>45.3</td>
<td>2.6</td>
</tr>
<tr>
<td>1-benzoyl-5-(sec)butyl</td>
<td>61.0</td>
<td>5.8</td>
</tr>
<tr>
<td>1-benzoyl-5-isopropyl</td>
<td>59.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

### TABLE VI

Physical properties of 1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Melting Point (°C)</th>
<th>Type I U. V. absorption peaks</th>
<th>Type II U. V. absorption peaks</th>
<th>Type III U. V. absorption peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(nm) ε</td>
<td>(nm) ε</td>
<td>(nm) ε</td>
</tr>
<tr>
<td>1-p-anisoyl</td>
<td>169-170</td>
<td>368 390</td>
<td>281 18200</td>
<td>237 21000</td>
</tr>
<tr>
<td>1-m-anisoyl</td>
<td>176-178</td>
<td>370 190</td>
<td>375 12800</td>
<td>241 71000</td>
</tr>
<tr>
<td>1-p-tolouyl</td>
<td>153-155</td>
<td>372 180</td>
<td>275 11500</td>
<td>241 20600</td>
</tr>
<tr>
<td>1-m-toluoyl</td>
<td>162-164</td>
<td>370 145</td>
<td>281 10300</td>
<td>241 21300</td>
</tr>
<tr>
<td>1-p-(tert)butyl benzoyl</td>
<td>165-168</td>
<td>370 190</td>
<td>278 11800</td>
<td>241 20800</td>
</tr>
<tr>
<td>1-benzoyl</td>
<td>159-161</td>
<td>372 110</td>
<td>283 11100</td>
<td>242 12100</td>
</tr>
<tr>
<td>1-p-fluorobenzoyl</td>
<td>196-198</td>
<td>374 110</td>
<td>279 11200</td>
<td>241 22700</td>
</tr>
<tr>
<td>1-p-chlorobenzoyl</td>
<td>204-206</td>
<td>374 301</td>
<td>277 11200</td>
<td>241 22700</td>
</tr>
<tr>
<td>1-m-chlorobenzoyl</td>
<td>197-198</td>
<td>375 130</td>
<td>286 11000</td>
<td>241 32600</td>
</tr>
<tr>
<td>1-p-bromobenzoyl</td>
<td>194-195</td>
<td>375 200</td>
<td>276 15900</td>
<td>241 22900</td>
</tr>
<tr>
<td>1-m-bromobenzoyl</td>
<td>203-205</td>
<td>378 130</td>
<td>284 11100</td>
<td>240 22600</td>
</tr>
<tr>
<td>1-p-iodobenzoyl</td>
<td>212-214</td>
<td>375 60</td>
<td>285 11800</td>
<td>241 23300</td>
</tr>
<tr>
<td>1-m-iodobenzoyl</td>
<td>207-209</td>
<td>370 305</td>
<td>275 16200</td>
<td>239 21200</td>
</tr>
<tr>
<td>1-m-trifluoromethyl benzoyl</td>
<td>194-196</td>
<td>374 125</td>
<td>287 10100</td>
<td>241 23500</td>
</tr>
<tr>
<td>1-p-nitrobenzoyl</td>
<td>230-231</td>
<td>370 291</td>
<td>285 11100</td>
<td>243 21200</td>
</tr>
<tr>
<td>1-acetyl</td>
<td>176-177</td>
<td>365 34</td>
<td>277 18200</td>
<td>233 16000</td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl</td>
<td>186-187</td>
<td>366 30</td>
<td>279 19000</td>
<td>233 16000</td>
</tr>
<tr>
<td>1-benzoyl-5-methyl</td>
<td>161-163</td>
<td>370 180</td>
<td>280 9800</td>
<td>241 24800</td>
</tr>
<tr>
<td>1-benzoyl-5-isopropyl</td>
<td>179-180</td>
<td>373 180</td>
<td>283 9200</td>
<td>241 23200</td>
</tr>
<tr>
<td>1-benzoyl-5-(sec)butyl</td>
<td>167-169</td>
<td>369 200</td>
<td>280 8700</td>
<td>242 18000</td>
</tr>
<tr>
<td>1-benzoyl-3-phenyl</td>
<td>132-133</td>
<td>375 120</td>
<td>285 9200</td>
<td>241 18300</td>
</tr>
</tbody>
</table>

---

98

---

measurements and kinetic measurements have been previously described, including the method of data work up (26). Duplicate kinetic runs agreed to within 4%, and correlation coefficients for eight points were in general greater than 0.998.
References


5. W. I. CONGDON and J. T. EDWARD. Part II.


26. See experimental sections of References 5 and 6.
PART IV

Mechanism of the alkaline hydrolysis of l-acyl-2-thiohydantoins
**Abstract**

l-Acyl-2-thiohydantoins are very rapidly hydrolyzed in dilute base to the corresponding carboxylic acid and 2-thiohydantoin. These compounds ionize in alkaline solution (pK~7), and the hydrolysis in solutions more alkaline that pH>11 has been shown to involve attack of an hydroxide ion on the conjugate base of the l-acyl-2-thiohydantoin. The reaction is very much faster than the normal alkaline hydrolysis of amides, and a cyclic proton-transfer mechanism involving the thiocarbonyl group has been invoked to explain the results. This mechanism accords with the entropy of activation, which is more positive than usual for base-catalyzed amide hydrolyses. l-Benzoyl-2-thiohydantoin hydrolyzes more rapidly than l-acetyl-2-thiohydantoin, possibly because the ground state of the former molecule is destabilized by having the phenyl ring twisted out of the plane of the rest of the molecule.
RESUME

Acy1-l-thiohydantoin-2 s'hydrolyse rapidement en milieu basique dilué aux acides carboxylique et thiohydantoin-2. Ce composés s'ionisent en milieu alcalin (pK ~ 7). En milieu très alcalin (pH > 11) l'hydrolyse se fait par l'attaque de l'ion hydroxide à la base conjuguée de l'acyl-l-thiohydantoin-2. La réaction qui est beaucoup plus vite que celle des amides ordinaires, peut s'expliquer par un mécanisme de proton transfercyclization du groupe thiocarbonyl. Ce mécanism est en accord avec l'entropie de l'activation. Le benzoyl-l-thiohydantoin-2 s'hydrolise plus vite que l'acetyl-l-thiohydantoin-2, peut-être parce que le premier est déstabilisé par le groupe phenyl qui se trouve en dehors du plan de la molécule.
The study of the deacylation of 1-acyl-2-thiohydantoins (1) by acid or alkali (2) is of interest in connection with the procedure of Schlack and Kumpf (2) for the stepwise degradation of peptides or proteins. This procedure received only desultory attention for many years (3), but lately has been the focus of renewed interest (4). It consists of converting

\[ \text{Scheme 1} \]

\[ \begin{align*}
&\text{1} \\
&\text{2} \\
&\text{3} \\
&\text{4} \\
&\text{5} \\
&\text{6} \\
&\text{7}
\end{align*} \]
the C-terminal amino acid of a polypeptide or protein into a 2-thiohydantoin derivative, attached to the remainder of the peptide chain by a 1-acyl linkage, as in \( \text{1} \) (\( R = \text{polypeptide} \)). This 1-acyl linkage can then be selectively cleaved by acid or alkali under unusually mild conditions (1). Thus, as shown in Table I, 1-acetyl-5,5-dimethyl-2-thiohydantoin (\( R = R' = \text{Me} \)) is cleaved about 16,800 times more rapidly than acetanilide under similar conditions of mild alkalinity, and 1-benzoyl-2-thiohydantoin (\( R = \text{Ph}, R' = \text{H} \)) about 120,000 times more rapidly than benzamide. In the present paper we show that the extraordinary facility of this reaction is most probably explained by a cyclic proton-transfer mechanism which is possible for 1-acyl-2-thiohydantoins but not for more typical amides or anilides.

1-Acyl-2-thiohydantoins ionize as weak acids (\( \text{1} \rightarrow \text{2} + \text{H}^+ \)), and have \( pK_a \) values of 6.5-7.0 (Table II). Consequently, in the solutions more alkaline than pH of 9, in which they begin to be hydrolysed at appreciable rates they must be more than 99% in the ionized form \( \text{2} \). Even in such circumstances, hydrolysis could proceed mainly through the unionized form \( \text{1} \) if its rate of hydrolysis were more than about \( 10^3 \) times greater than that of the ionized form \( \text{2} \). This has been found true for the alkaline ring-opening of 2-thiohydantoins (6) to thioureido-acids (7), (and for the alkaline hydrolysis of N-acylthioureas- unpublished research) which involves chiefly attack of hydroxide ion on the unionized (6), rather than on the more abundant ionized form (5), so that the rate of the reaction is zeroth-order with respect to hydroxide ion (7). However, in this case the negative charge of \( \text{5} \) is delocalized over the amide carbonyl group to be attacked. The negative charge of \( \text{2} \) is not delocalized over.
### TABLE I
Comparison of base-catalyzed hydrolysis rates of different amide linkages in aqueous solutions

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction Conditions</th>
<th>Rates*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide (5)</td>
<td>0.239N NaOH, θ = 1.0, 24.8°C</td>
<td>$k_\psi = 0.018 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>1-Acetyl-5,5-dimethyl-2-thiohydantoin</td>
<td>0.2N NaOH, θ = 1.0, 25.4°C</td>
<td>$k_\psi = 302.0 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>Benzamide (6)</td>
<td>0.1N NaOH, θ = 0.1, 40.7°C</td>
<td>$k_b = 0.4 \times 10^{-4}$ 1/M-sec</td>
</tr>
<tr>
<td>1-Benzoyl-2-thiohydantoin</td>
<td>pH = 10.95, θ = 1.0, 40.7°C**</td>
<td>$k_b = 4.9$ 1/M-sec</td>
</tr>
</tbody>
</table>

*$k_\psi$ = pseudo first-order rate constant; $k_b$ = second-order rate constant or $k'_f$.[OH$^-$.]

**Value obtained by interpolation from Arrhenius plot.

### TABLE II
pK$_a$ values of 1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>Compound</th>
<th>pK$_a$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Acetyl-2-thiohydantoin**</td>
<td>7.03</td>
</tr>
<tr>
<td>1-Acetyl-5-methyl-2-thiohydantoin***</td>
<td>6.95</td>
</tr>
<tr>
<td>1-Acetyl-5,5-dimethyl-2-thiohydantoin****</td>
<td>6.93</td>
</tr>
<tr>
<td>1-Benzoyl-2-thiohydantoin**</td>
<td>6.50</td>
</tr>
<tr>
<td>1-p-Anisoyl-2-thiohydantoin***</td>
<td>6.65</td>
</tr>
<tr>
<td>1-p-Nitrobenzoyl-2-thiohydantoin**</td>
<td>6.45</td>
</tr>
</tbody>
</table>

*All measurements were determined spectrophotometrically.

**Unpublished work by I.C.Wang.

***Unpublished work by J.K.Liu.

****Unpublished work by I.Lantos.
the l-acyl carbonyl group which is attacked in alkaline hydrolysis, and so might be expected to reduce its reactivity by a factor of about $10^2$ (cf. ref. 8) or less. In such a case the greater reactivity of 1 would not be expected to compensate for the greater abundance of 2. This expectation is realized: the rate of hydrolysis of various l-acyl-2-thio-
hydantoins increases in a linear manner with hydroxide ion concentration (at constant ionic strength), as shown by the invariance of the second order rate constants in Table III. Consequently, hydrolysis must proceed mainly by attack of hydroxide ion on the anion 2, as illustrated in Scheme 1.

This mechanism is supported by observations of the effect of ionic strength on the rate of the reaction. For a reaction between two charged ions the observed rate will be affected by the ionic strength of the medium. The necessary expression, derived from Debye-Huckel theory applied to the rate expression (9), is the following:

$$
\log k_b = \log k_o + 1.02 Z_a Z_b \sqrt{\mu}/(1 + \sqrt{\mu})
$$

where $k_b = k_{\omega}/[OH^-]$ the second order rate constant, $k_o$ the second order rate constant at zero ionic strength, and $\mu$ the ionic strength. In the present instance the ionic charges $Z_a = Z_b = -1$, so that $k_b$ increases with ionic strength. The plot of log $k_b$ for the hydrolysis of l-acetyl-5,5-dimethyl-2-thiohydantoin versus $\sqrt{\mu}/(1 + \sqrt{\mu})$ gives a curve similar to that obtained for the base-catalyzed hydrolysis of a series of dicarboxylic acid half esters EtO-CO-(CH$_2$)$_n$-CO$_2^-$ ($n = 0$ to 4) (10), with the slope approaching unity as $\mu \rightarrow 0$: this is shown in Figure 1.

To get an idea of the magnitude of the salt effect on the rate at
TABLE III

The effect of pH, buffer concentration and ionic strength on the rate of base catalyzed hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Buffer Composition</th>
<th>pH</th>
<th>Ionic Strength</th>
<th>kν x 10^4 (sec^-1)^a</th>
<th>k_b (Liters/M-sec)^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03M K_2HPO_4, 0.01M K_3PO_4</td>
<td>10.95^b</td>
<td>1.0000</td>
<td>1.57±0.05</td>
<td>0.176</td>
</tr>
<tr>
<td>0.0025N NaOH</td>
<td>11.40^c</td>
<td>0.0025</td>
<td>2.04±0.01</td>
<td></td>
</tr>
<tr>
<td>0.005M K_2HPO_4, 0.005M K_3PO_4</td>
<td>11.47^b</td>
<td>1.0000</td>
<td>5.13±0.08</td>
<td>0.174</td>
</tr>
<tr>
<td>0.01M K_2HPO_4, 0.01M K_3PO_4</td>
<td>11.55^b</td>
<td>1.0000</td>
<td>6.25±0.05</td>
<td>0.172</td>
</tr>
<tr>
<td>0.01N NaOH</td>
<td>11.88^b</td>
<td>0.0100</td>
<td>12.10±0.15</td>
<td>0.159</td>
</tr>
<tr>
<td>0.01N NaOH</td>
<td>12.00^c</td>
<td>0.0100</td>
<td>8.94±0.23</td>
<td></td>
</tr>
<tr>
<td>0.0175N NaOH</td>
<td>12.25^c</td>
<td>1.0000</td>
<td>10.41±0.01</td>
<td></td>
</tr>
<tr>
<td>0.025N NaOH</td>
<td>12.40^c</td>
<td>1.0000</td>
<td>11.23±0.23</td>
<td></td>
</tr>
<tr>
<td>0.063N NaOH</td>
<td>12.80^c</td>
<td>1.0000</td>
<td>12.00±0.20</td>
<td></td>
</tr>
<tr>
<td>0.1N NaOH</td>
<td>13.00^c</td>
<td>0.5000</td>
<td>12.00±0.20</td>
<td></td>
</tr>
<tr>
<td>0.2N NaOH</td>
<td>13.30^c</td>
<td>1.0000</td>
<td>25.60±0.15</td>
<td>0.114</td>
</tr>
<tr>
<td>0.5N NaOH</td>
<td>13.70^c</td>
<td>1.0000</td>
<td>41.40±0.20</td>
<td>0.165</td>
</tr>
<tr>
<td>0.8N NaOH</td>
<td>13.90^c</td>
<td>1.0000</td>
<td>102.40±0.15</td>
<td>0.162</td>
</tr>
<tr>
<td>1.0N NaOH</td>
<td>14.00^c</td>
<td>1.0000</td>
<td>136.50±0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>118.00±0.70</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>302.00±0.05</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>764.00±11.00</td>
<td>0.152</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1340.00±13.00</td>
<td>0.169</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1740.00±30.00</td>
<td>0.174</td>
</tr>
</tbody>
</table>

^aPseudo first-order rate constants at 25.4°C. ^bPH measured in quintuplicate (±0.04 pH units) with a Radiometer 202-C glass electrode versus a saturated KCl electrode on a Radiometer TTT-1 recording pH meter. ^cNo correction is applied for the decrease in pH with added neutral KCl and the pH of these solutions is calculated from the amount of NaOH added. ^dThe mean k_b = 0.16±0.01 (±6.1%) for the hydrolysis at an ionic strength of one.
Figure 1. A plot of $k_b$ (the second order rate constant in liters mole$^{-1}$ second$^{-1}$) versus $\sqrt{\mu} / (1 + \sqrt{\mu})$ for 1-acetyl-5,5-dimethyl-2-thiohydantoin at 25.4°C.
\[
\log K_\psi + p\text{OH}
\]

\[
\frac{\sqrt{\mu}}{1 + \sqrt{\mu}}
\]

slope = 1.00
25.4°C, the second order rate constant at zero ionic strength ($k_0 = 0.072$ L·M⁻¹ sec⁻¹) (obtained by extrapolation in Figure 1) may be compared with the value ($k_0 = 0.16$ L·M⁻¹ sec⁻¹) at $\kappa = 1$, the ionic strength used for the study of the effect of pH on $k_\psi$. Evidently the effect of ionic strength is large enough so that it cannot be neglected.

The addition of the hydroxide to the amide group to form the tetrahedral adduct 3 (Scheme 1) is analogous to the presently accepted mechanism of amide hydrolysis (11). To show that this reaction is in fact analogous, a Hammett $\rho\sigma$ plot was made with a series of substituted 1-benzoyl-2-thiohydantoins (Table IV and Figure 2). The points for log $k_\psi$ plotted against $\sigma$ lie on a straight line of slope $\rho = 1.18$ (correlation coefficient 0.990). The $\rho$ is very close to that found (1.055; ref. 12) for the hydrolysis of substituted benzamides. This offers support for the postulation of 3 as an intermediate: a postulation further supported by a detailed consideration of its stereochemistry. If indeed the hydroxyl group is in the plane of the 2-thiohydantoin ring, as might be expected (from a study of models) to lead to the strongest possible hydrogen bond between the partially-negative
TABLE IV

Pseudo-first-order rate constants in seconds\(^{-1}\) for the hydrolysis of substituted 1-benzoyl-2-thiohydantoins in alkaline phosphate buffer at 25.3\(^{\circ}\)C

<table>
<thead>
<tr>
<th>Substituent</th>
<th>(10^4k_w) (sec(^{-1}))(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-p-methoxybenzoyl</td>
<td>5.12±0.15</td>
</tr>
<tr>
<td>1-p-methylbenzoyl</td>
<td>6.17±0.16</td>
</tr>
<tr>
<td>1-m-methylbenzoyl</td>
<td>7.61±0.23</td>
</tr>
<tr>
<td>1-benzoyl</td>
<td>9.31±0.18</td>
</tr>
<tr>
<td>1-p-fluorobenzoyl</td>
<td>13.30±0.30</td>
</tr>
<tr>
<td>1-m-methoxybenzoyl</td>
<td>11.90±0.30</td>
</tr>
<tr>
<td>1-p-chlorobenzoyl</td>
<td>19.10±0.20</td>
</tr>
<tr>
<td>1-p-bromobenzoyl</td>
<td>21.90±0.28</td>
</tr>
<tr>
<td>1-p-iodobenzoyl</td>
<td>20.80±0.30</td>
</tr>
<tr>
<td>1-m-chlorobenzoyl</td>
<td>25.90±0.45</td>
</tr>
<tr>
<td>1-m-bromobenzoyl</td>
<td>27.10±0.32</td>
</tr>
<tr>
<td>1-m-trifluoromethylbenzoyl</td>
<td>32.90±0.41</td>
</tr>
</tbody>
</table>

\(^a\)pH = 10.75 and \(\mu = 0.42\).
Figure 2. A plot of $\log k_\psi$ versus $\sigma$ for substituted 1-benzoyl-2-thiohydantoin (cc: 0.9902; sd: 0.05) in an aqueous phosphate buffer pH = 10.75, ionic strength = 0.12, at 25.3°C.
sulfur and the hydroxyl group, then the transformation $\ce{2 <=> 3}$ results in the eclipsing of the $\text{R}^\prime$ groups at the 5-position by the $\text{R}$ and $\text{O}^\text{- (solvated)}$ groups of the tetrahedral intermediate. This would explain the large effect of bulky groups at the 5-position in slowing the hydrolysis, as shown in Table V.

The steric requirements for the acid and base catalyzed bimolecular hydrolysis are thought to be essentially the same (13). Substituents in base catalyzed hydrolyses, unlike acid catalyzed hydrolyses where polar effects cancel, are generally thought to exert both a steric and a polar effect on the reaction. However, if one were to assume that the mechanism for the basic hydrolysis of acetanilide is similar to that for the hydrolysis of $\ce{1}$, then any substituent in the 2-thiohydantoin ring should exert only steric effects, since $\varphi = 0.1$ for substituted acetanilides (5).

However, a comparison of C-5 substituent effects in both dilute acid and in dilute base shows (Table V) that substituents are more rate retarding in the base-catalyzed reaction than in the acid-catalyzed reaction. This indicates that their effect is not steric alone, since in that event the results would agree. A reasonable explanation of this difference would involve a polar factor as well. Although C-5 substituents do not greatly affect the basicity of the thiocarbonyl (14) they would be expected to effect the N-1 nitrogen to a larger extent since it is adjacent. If the above explanation is true and the N-1 basicity affects the rate then this is support for the mechanism in Scheme 1 since for this, unlike the mechanism for acetanilide, no amide amine protonation is necessary for hydrolysis to occur.

To investigate this mechanism further and to decide what factors
TABLE V

The effect of C-5 substituents on the hydrolysis rates of 1-benzoyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>C-5 Substituent</th>
<th>$10^4 k_v^a$</th>
<th>$10^4 k_v^b$</th>
<th>Relative Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsubstituted</td>
<td>31.4±0.40</td>
<td>49.8±0.50</td>
<td>1.00</td>
</tr>
<tr>
<td>5-methyl</td>
<td>12.7±0.21</td>
<td>35.5±0.60</td>
<td>0.41</td>
</tr>
<tr>
<td>5-phenyl</td>
<td>10.2±0.66</td>
<td>22.8±0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>5-isopropyl</td>
<td>4.7±0.18</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>5-isobutyl</td>
<td>6.6±0.15</td>
<td>18.4±0.54</td>
<td>0.21</td>
</tr>
<tr>
<td>5-(sec)butyl</td>
<td>4.6±0.16</td>
<td>17.9±0.40</td>
<td>0.15</td>
</tr>
<tr>
<td>5,5-dimethyl</td>
<td>2.3±0.06</td>
<td>29.4±1.32</td>
<td>0.08</td>
</tr>
</tbody>
</table>

$^a$Pseudo first-order rate constants measured at 25.3°C in a phosphate buffer at an ionic strength of 0.15 and a pH = 11.2.

$^b$Pseudo first-order rate constants measured at 25.3°C in 56.0% sulfuric acid.
make this system reactive in spite of its negative charge, the Arrhenius parameters were measured. Plots of log \((k_w/[\text{OH}^-])\) versus \(1/\text{T}^0\)C (shown in Figure 3 and Table VI) are straight lines (although no correction was made for the four percent change in the Debye-Huckel coefficient over the temperature range), the slopes of which give activation energy \((E_a/2.3R)\) in KCal/M and the intercept, the log of the frequency factor, \(\log A_{\text{total}}\), in liters/mol-sec. This must however be modified for the effect of ionic strength at one temperature to obtain meaningful entropy values (strictly speaking one should plot \(\log k_0\) versus \(1/\text{T}^0\)C to obtain the frequency factor without the complication of ionic strength but in this study this type of treatment led to large uncertainty in the \(k_0\) values so that the other treatment was preferred).

A useful comparison can be made of these values with the values for the base-catalyzed hydrolysis of benzamide (6). From the basic Arrhenius equation one can derive for the amide hydrolysis (15) the following:

\[
\log A_{\text{total}} = \log \left(\frac{A_1 A_2}{A_3}\right)
\]

For benzamide, \(\log A_1 = 8.25\) and \(\log \left(\frac{A_2}{A_3}\right) = 2.82\) L/M-sec. This leads to a value for \(\log A_{\text{total}} = 5.43\) L/M-sec and \(E_a(\text{overall}) = 14.8\) KCal/M.

For 1-benzoyl-2-thiohydantoin, as shown in Table VI \(\log A_{\text{total}} = 10.4\) L/M-sec and \(E_a(\text{overall}) = 16.3\) KCal/mol. The activation entropy calculated from the frequency factor leads to a value of \(-36\) L-cal/M^2-deg for benzamide and, as shown in Table VI, \(-13\) L-cal/M^2-deg for 1-benzoyl-2-thiohydantoin. From these differences it is apparent that the high reactivity of 1 when compared with normal amides is due to a large increase in the activation entropy. This seems unusual since it is known that the reaction of
Figure 3. A plot of log $k_\psi$ versus $1/T_0K \times 10^3$ for: 1-acetyl-5,5-dimethyl-2-thiohydantoin ($\bigcirc$); 1-benzoyl-2-thiohydantoin (□); 1-acetyl-2-thiohydantoin ($\Delta$).
The graph shows a plot of $\log K_\Psi$ against $\frac{1}{T^oK} \times 10^3$. The data points are represented by different symbols and are connected by lines, indicating a trend as $T^oK$ increases.
TABLE VI

Temperature dependence of the rate of alkaline hydrolysis of 1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>Compound and buffer solution</th>
<th>Temp. °C</th>
<th>(10^4k_a ) (sec(^{-1}))</th>
<th>( \log A_b ) (L/M-sec)</th>
<th>( \Delta S^f ) (e.u.)</th>
<th>( E_a ) (KC(\text{aL/M})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-acetyl-2-thiohydantoin</td>
<td>20.0</td>
<td>3.98±0.13</td>
<td>10.9±0.2</td>
<td>-11±2</td>
<td>18±2</td>
</tr>
<tr>
<td>pH = 10.95; ( \kappa ) = 1.0; 0.03M K(_2)HPO(_4), 0.01M K(_3)PO(_4)</td>
<td>25.4</td>
<td>6.97±0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.4</td>
<td>11.5±0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>18.20±0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>41.5</td>
<td>30.80±1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-benzoyl-2-thiohydantoin</td>
<td>20.0</td>
<td>8.83±0.06</td>
<td>10.5±0.2</td>
<td>-13±2</td>
<td>16±2</td>
</tr>
<tr>
<td>pH = 10.95; ( \kappa ) = 1.0; 0.03M K(_2)HPO(_4), 0.01M K(_3)PO(_4)</td>
<td>25.4</td>
<td>16.40±0.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30.4</td>
<td>25.60±0.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35.6</td>
<td>39.10±1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>41.5</td>
<td>65.80±0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin</td>
<td>11.0</td>
<td>3.65±0.02</td>
<td>10.1±0.2</td>
<td>-14±2</td>
<td>15±2</td>
</tr>
<tr>
<td>pH = 11.95; ( \kappa ) = 0.55; 0.1M Na(_2)HPO(_4), 0.075M NaOH</td>
<td>25.3</td>
<td>12.90±0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>39.6</td>
<td>95.80±0.93</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>58.1</td>
<td>177.00±2.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) Pseudo first-order rate constants. \( b \) Based on \( k_y/\left[\text{OH}^{-}\right] \) in liters/mol-sec.

\( c \) The standard state for \( \Delta S^f \) utilizing second order rates is 1 mole per liter and \( \Delta n^f \) in the Arrhenius equation is assumed small since this is a bimolecular reaction in solution (23).

\( b, c \) These values have been corrected for the effect of ionic strength at one temperature (25.3°C).
like-charged particles reduces the entropy of activation by about 10 e.u. and hence the frequency factor by about a factor of 100 (16). One can, however, rationalize this result in the following way. If one assumes that the value of log $A_1$ for the addition of hydroxide to benzamide is the usual value for uncharged amide addition the value for 1 should be closer to 6.2. A mechanism of intermediate break up as shown in Scheme 1 would have a high probability and lead to large values for $A_3$ and decrease in values for $A_2$. A value of log $A_3/A_2 = 4.2$ would not be unlikely in this case. The increase in entropy arises from this intramolecular decomposition since no proton transfer agent is needed to protonate the amide amine. This is vaguely analogous to the hydrolysis mechanism for acetyl imidazole (17). This intramolecular transfer is apparently effective enough so that there is no phosphate or hydroxide second order catalysis (see Table III) as there is in the case of anilides (11), and essentially accounts for the rapid hydrolysis rates.

The comparison of benzamide with 1-benzoyl-2-thiohydantoin is in one respect unfair. A Courtalds model of 1 reveals that the 1-benzoyl group can assume only one position, assuming that the amide carbonyl is in the plane of the 2-thiohydantoin ring to allow normal amide pi overlap, and that is with the carbonyl group having the conformation shown in 1. In such a case the phenyl group is flanked by the bulky sulfur atom and rotated about 90° out of the plane of the carbonyl group. (The alternative conformation, which preserves the necessary planarity of the carbonyl-N linkage (18), would have the carbonyl and thiocarbonyl groups parallel, and would be strongly disfavoured by dipolar effects. Twisting the phenyl group out of the amide plane of the carbonyl does not allow ground
state resonance interaction between the carbonyl and the phenyl ring, so that only phenyl polar effects may be expected. In a case such as this, one would expect (19) in the base-catalyzed hydrolysis the benzoyl derivative to react at a faster rate than the corresponding acetyl derivative since the Hammett rho value is positive and the phenyl is more electron withdrawing ($\sigma^*=0.60$) than the methyl group ($\sigma^*=0.0$). As shown in Table VII this is indeed true. This kinetic proof is, however, subject to activity effects (see Tables VI and VII) since the ratio of rates for 1B/1A apparently depends to some extent upon ionic strength, being more positive at higher ionic strengths.

**Experimental Section**

All compounds were made and purified according to the procedure of Johnson and Nicolet (20). Most were known compounds and the physical properties of each are listed in Table VIII, excluding those reported in Part III (21). Buffer solutions were made using Fisher reagent grade KCl, $K_2HPO_4$, $K_3PO_4$ and distilled water. pH values were measured at 25°C using a TTT-1 automatic titrator and a Radiometer 202-C electrode versus a saturated KCl electrode. pH values were found to remain constant during the reaction. For buffer solutions above pH of 12, standard B. D. H. 1 N NaOH was used with KCl to prepare solutions. pH values for these solutions were calculated from the amount of base added.

For the kinetic runs 3 mls of buffer were pipetted into a 1 cm stoppered U.V. cell which was then equilibrated for a minimum of 10 minutes in the thermostated cell compartment. 10$\mu$L of methanolic stock solution was then injected, using a Hamilton syringe with Chaney adaptor, the cell vigorously shaken and then the spectrum at constant wavelength was recorded. All kinetic measurements were carried out with
TABLE VII

Comparison of hydrolysis rates of benzoyl to acetyl carboxylic acid derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Base a $k_b/k_a$</th>
<th>Base $\log (k_b/k_a)$</th>
<th>Acid a $k_b/k_a$</th>
<th>Acid $\log (k_b/k_a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-benzoyl-2-thiohydantoin</td>
<td></td>
<td>31.4±0.4 b</td>
<td></td>
<td>47.8±0.4 b</td>
</tr>
<tr>
<td>1-acetyl-2-thiohydantoin</td>
<td></td>
<td>21.4±0.4</td>
<td></td>
<td>202.0±0.4</td>
</tr>
<tr>
<td>1-benzoyl-5-methyl-2-thiohydantoin</td>
<td></td>
<td>12.7±0.2 b</td>
<td></td>
<td>35.5±0.6 b</td>
</tr>
<tr>
<td>1-acetyl-5-methyl-2-thiohydantoin</td>
<td></td>
<td>12.0±0.5</td>
<td></td>
<td>171.0±1.5</td>
</tr>
<tr>
<td>1-benzoyl-5,5-dimethyl-2-thiohydantoin</td>
<td></td>
<td>2.38±0.06 b</td>
<td></td>
<td>29.1±1.32 b</td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin</td>
<td></td>
<td>2.10±0.10</td>
<td></td>
<td>127.5±4.60</td>
</tr>
<tr>
<td>N-benzoylthiourea</td>
<td></td>
<td>3.69±0.30 c</td>
<td></td>
<td>0.39±0.01 e</td>
</tr>
<tr>
<td>N-acetylthiourea</td>
<td></td>
<td>3.69±0.30 c</td>
<td></td>
<td>0.39±0.01 e</td>
</tr>
<tr>
<td>Ethyl benzoate</td>
<td></td>
<td>-1.06 d</td>
<td></td>
<td>-2.55 d</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td></td>
<td>-</td>
<td></td>
<td>-2.55 d</td>
</tr>
</tbody>
</table>

aPseudo first-order rate constants. bRate measured in aqueous phosphate buffer at an ionic strength of 0.15, pH = 11.2. cRate measured in aqueous 1N NaOH at 25.3°C. dValues taken from ref. 13, pgs 589 and 604. eRates measured in 39.6% sulfuric acid at 49.1°C. fRates measured in 58.0% sulfuric acid at 25.3°C.
TABLE VIII

Physical properties of C-5 substituted
1-acyl-2-thiohydantoins

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Type I</th>
<th>Ultraviolet Spectra</th>
<th>Type III</th>
<th>M.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>nm</td>
<td>ε</td>
<td>nm</td>
<td>ε</td>
</tr>
<tr>
<td>1-benzoyl-5-phenyl</td>
<td>372</td>
<td>130</td>
<td>282</td>
<td>9600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-benzoyl-5-isobutyl</td>
<td>365</td>
<td>220</td>
<td>273</td>
<td>11600</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-benzoyl-5,5-dimethyl</td>
<td>366</td>
<td>160</td>
<td>275</td>
<td>12000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-acetyl-5-methyl</td>
<td>366</td>
<td>28</td>
<td>277</td>
<td>18800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

aA. KJAER. Acta Chem. Scand. 7, 889-899 (1953), quotes M.P. 200-201°C.
cT. B. JOHNSON. J. Biol. Chem. 111, 97 (1933) quotes M.P. 166°C.
dSee Reference 3 for an explanation of band characterization. Ethanol was used as solvent.
eAnalysis: Calc; C: 58.1%; H: 4.8%; N: 11.3%
Found; C: 57.8%; H: 4.0%; N: 11.0%.
a Unicam S P 800 recording U.V. spectrophotometer with scale expander and
slave recorder attachments. Measurements were always made in the region
300-330 nm because the unstable 2-thiohydantoin has no appreciable
absorption in this region. Results were obtained by a linear least
squares program using log \((A_\text{t} - A_\infty)\) versus time. \(A_\infty\) was taken after
7-10 half-lives, and for several slow reactions Guggenheim's method
was used (22). Correlation coefficients for individual runs were generally
greater than 0.999 for 8 points and separate runs were found to be
reproducible to within 3-4\%.
References


23. Reference 9, p. 90.
PART V

Secondary isotope effects in the hydrolysis of
1-acetyl-5,5-dimethyl-2-thiohydantoin
ABSTRACT

The secondary isotope effect versus temperature has been observed for the A-1 and A-2 acid catalyzed and A-2 base catalyzed hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin. $k_{CH_3}/k_{CD_3}$ was shown to increase for the A-1 hydrolysis from 1.05 at 58.1°C to 1.31 at 10.8°C. For the A-2 acid and base catalyzed reactions $k_{CH_3}/k_{CD_3}$ versus temperature passed through a minimum (an inverse isotope effect) of about 0.9 at about 30°C. The unimolecular results were those expected in analogy to SN-1 reactions but the bimolecular results could not be explained at present.

RESUME

On a observé l'effet isotope secondaire versus temperature des hydrolyses de l'acetyl-l-dimethyl-5,5-thiohydantoin-2 via A₁ et A₂ en milieu acide et l'hydrolyse via A₂ en milieu alcalin. $k_{CH_3}/k_{CD_3}$ augmente de 1.05 à 58.1°C à 1.31 à 10.8°C pour l'hydrolyse via mécanisme A-1. Pour le hydrolyses via le mécanisme A-2 en milieu acide et basique $k_{CH_3}/k_{CD_3}$ versus température passe par un minimum de 0.90 a 30°C. Les résultats provenant des réactions unimoléculaire sont en accord avec ceux obtenus dans les reactions SN-1 mais les
résultats provenant des reactions via A-2 ne se prêtent pas encore à une interpretation.
The hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin has been shown to proceed by attack of hydroxide ion on the anion of the 2-thiohydantoin in alkaline solution; by an A-2 mechanism in 0-90% sulfuric acid; and by an A-1 mechanism, involving fission to an acylium ion, in 90-100% sulfuric acid. The solid support for these different mechanisms offered by a great variety of evidence makes the molecule a reasonable one for investigation of secondary deuterium isotope effects. Accordingly, we have investigated the effect on the rates of the various reactions of substituting deuterium for protium in the 1-acetyl group. The results are given in Table I, and shown graphically in Figures 1, 2, and 3.

In a recent study of secondary deuterium isotope effects in the hydrolysis of acyl compounds, Bender (1) compared the secondary isotope effects in the spontaneous hydrolysis of acetyl chloride in acetone-water mixtures at -22°C (apparently hydrolysing by an A-1 mechanism) with the basic hydrolysis of ethyl acetate at 25°C (a well-known A-2 mechanism). Halevi (2), recognizing the danger of drawing mechanistic conclusions from secondary isotope effects at two different temperatures, studied the basic hydrolysis of ethyl acetate over a fairly large temperature range. His results and those of Bender are shown graphically along with the results of this study in Figures 1-3. The observed minimum in Figure 2 was explained (2) in terms of solvation differences between CD₃ and CH₃ and a recent review (3) suggests that these results possibly arise from a change in hydrolysis mechanism.

If one regards the formation of an acylium ion as a process similar to an SN-1 reaction, as fully discussed by reference 1, one would expect a secondary isotope effect in the same direction and, depending upon the
### TABLE I

The effect of temperature on the pseudo-first-order rates of hydrolysis of 1-acetyl (d₃)-5,5-dimethyl-2-thiohydantoin and 1-acetyl-5,5-dimethyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Temperature °C</th>
<th>$k_w$ [^a] for 1-CH(_3)</th>
<th>no. of runs</th>
<th>$k_w$ [^a] for 1-CD(_3)</th>
<th>no. of runs</th>
<th>$k_{CH_3}/k_{CD_3}$</th>
<th>Ave. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.3% sulfuric acid</td>
<td>10.8</td>
<td>1.15±0.04</td>
<td>2</td>
<td>0.88±0.03</td>
<td>2</td>
<td>1.31</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>3.11±0.04</td>
<td>2</td>
<td>2.57±0.01</td>
<td>2</td>
<td>1.22</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>24.20±0.60</td>
<td>3</td>
<td>21.30±0.60</td>
<td>3</td>
<td>1.14</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>49.6</td>
<td>124.00±12.00</td>
<td>3</td>
<td>114.00±2.40</td>
<td>3</td>
<td>1.08</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>58.1</td>
<td>266.00±12.00</td>
<td>3</td>
<td>253.00±7.30</td>
<td>3</td>
<td>1.05</td>
<td>0.08</td>
</tr>
<tr>
<td>39.6% sulfuric acid</td>
<td>11.0</td>
<td>7.15±0.03</td>
<td>3</td>
<td>7.52±0.12</td>
<td>3</td>
<td>0.95</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>26.00±0.04</td>
<td>2</td>
<td>28.10±0.19</td>
<td>2</td>
<td>0.93</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>54.70±0.13</td>
<td>3</td>
<td>56.70±0.86</td>
<td>3</td>
<td>0.96</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>49.6</td>
<td>190.00±12.22</td>
<td>5</td>
<td>190.00±11.54</td>
<td>2</td>
<td>1.00</td>
<td>0.06</td>
</tr>
<tr>
<td>pH = 11.95, $\mu$ = 0.55</td>
<td>11.0</td>
<td>3.65±0.02</td>
<td>2</td>
<td>3.64±0.13</td>
<td>3</td>
<td>1.00</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>25.3</td>
<td>12.90±0.04</td>
<td>3</td>
<td>13.20±0.02</td>
<td>2</td>
<td>0.97</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>49.6</td>
<td>96.80±0.93</td>
<td>3</td>
<td>98.30±0.83</td>
<td>3</td>
<td>0.97</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>58.1</td>
<td>177.00±12.10</td>
<td>3</td>
<td>177.00±1.30</td>
<td>3</td>
<td>1.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\[^a\]Pseudo first-order rate constants in 10^4 seconds\(^{-1}\).
Figure 1. A plot of $k_{CH_2}/k_{CD_3}$ versus $T^\circ C$ for the acid catalyzed A-1 hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin ($\phi$).

$\phi$ represents the value obtained by Bender and Feng (1) for the A-1 hydrolysis of acetyl chloride in 10% aqueous acetone.
Figure 2. A plot of $k_{CH_3}/k_{CD_3}$ versus $T^0$ for: 1-acetyl-5,5-dimethyl-2-thiohydantoin in an aqueous alkaline buffer pH = 11.95, ionic strength = 0.55 ($\mathcal{O}$); ethyl acetate in an alkaline buffer ($\mathcal{O}$) (2).
The graph shows the ratio $k_{CH_3}/k_{CD_3}$ as a function of temperature ($T^\circ C$). The data points are connected with curves, and error bars are indicated at selected temperatures.
Figure 3. A plot of $k_{CH_3}/k_{CD_3}$ versus $T^{0}$C for the A-2 acid catalyzed hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin in 39.6% $H_2SO_4$. 
solvent and the temperature, of similar magnitudes to those found for 
SN-1 solvolyses. As shown in Part III (4), in concentrated sulfuric 
acid the hydrolysis mechanism for 1-acetyl-5,5-dimethyl-2-thiohydantoin 
involves acylium ion formation in the rate controlling step. In such 
a case, where there is a positive charge developing in the transition 
state, one would expect that the rate of reaction would be greater for 
the protium compound than for the deuterium compound. This may be 
explained either in terms of hyperconjugation (CH\textsubscript{3} allows greater 
hyperconjugative stabilization of positive charge (3,5) or in terms of 
steric differences between the CD\textsubscript{3} and the CH\textsubscript{3} group (6). Reference to 
Figure 1 and Table I shows that the expected isotope effect is observed, 
and that the effect, as expected, increases with decreasing temperature. 
Bender's value at -22\textdegree C fits in well with our values at higher temperatures.

Halevi's results (2) for alkaline hydrolysis of methyl acetate at 
different temperatures (Figure 2) show a minimum (an inverse isotope 
effect) in the region 25-35\textdegree C. Using an argument based on ground state 
stabilization by hyperconjugation, Bender (1) predicted an inverse 
isotope effect in the base catalyzed reaction. The reason for the mini­ 
mum, however, is unclear. Halevi's explanation (2) invoking vaguely 
defined solvent effects (ice-like water structure, hydrogen-bonding etc.) 
are not likely to apply to the 39.6% sulfuric acid used for the hydrolysis 
of 1-acetyl-5,5-dimethyl-2-thiohydantoin, which shows the same effect 
with temperature (Figure 3). This is especially surprising in view of 
the fact that one would predict, from considerations of hyperconjugation, 
little or no effect.

Thornton (3) suggests that the minimum observed by Halevi may be due
to a change in mechanism but, at least in the present investigation, this is not a possibility since the Arrhenius equation is well followed over the temperature range studied (Figure 4).

No good explanation, based on sound principles, can be proposed at this time to explain the bimolecular results. However, apparently this extraordinary temperature dependence also occurs for isotope exchange reactions as was shown in recent calculations (7) for a large number of reactions over the temperature range 0-2000°K. For these results also no explanation was propounded.

The results of this experiment, although lacking explanation, show that the effect of CD₃/CH₃ versus temperature for an acyl hydrolysis differs greatly for unimolecular and bimolecular processes. To show the generality of these results more examples are needed but it is felt that this type of comparison may represent a practical physical-organic tool for mechanistic studies just as proposed in reference 1.

Experimental Section

d₆ acetic anhydride and d₄ acetic acid were purchased from Stohler Isotope of Canada and used in the general procedure (8) for the preparation of 1-acyl-2-thiohydantoins. 1-acetyl-5,5-dimethyl-2-thiohydantoin was characterized by M.P. (uncorr.) 186-187°C (Reference 9 quotes 186-187°C.) and by N.M.R. 3H-singlet at 7.33t and 6H-singlet 8.5t. 1-acetyl(d₃)-5,5-dimethyl-2-thiohydantoin was also characterized by M.P. (uncorr.) 186-188°C (from absolute alcohol) and by N.M.R. 6H-singlet at 8.5t. The U.V. spectra in aqueous solution for both compounds was the same as reported in Part III(4) and for every hydrolysis good isosbestic points were obtained. The general hydrolytic procedures were the same as described in Parts II and IV (10,11), as was the method of data work up.
Figure 4. A plot of log $k_p$ versus $1/T^oK \times 10^3$ for 1-acetyl(d3)5,5-dimethyl-2-thiohydantoin in: 39.6% $\text{H}_2\text{SO}_4$ (Δ); 96.3% $\text{H}_2\text{SO}_4$ (○); aqueous basic buffer pH = 11.95, ionic strength = 0.55 (□).
References

4. W. I. CONGDON and J. T. EDWARD. Part III.
10. W. I. CONGDON and J. T. EDWARD. Part II.
11. W. I. CONGDON and J. T. EDWARD. Part IV.
SUMMARY AND CLAIMS TO ORIGINAL RESEARCH

Part I

The protonation of N-acetylthiourea, N-benzoylthiourea and eight substituted N-benzoylthioureas are determined in aqueous sulfuric acid by the spectrophotometric method of Hammett. Mono protonation is shown to occur on the thiocarbonyl near 50% and then diprotonation on the amide carbonyl near 82% sulfuric acid. The position of protonation is determined by U.V. spectral characteristic comparisons with model compounds and correlations of ionization ratios with $H_0'''$ for thiourea protonation and $H_A \rightleftharpoons H_A^+$ for the amide carbonyl protonation. The Hammett rho-sigma correlations for substituted N-benzoylthioureas give $\rho_1 = -0.42 \pm 0.05$ and $\rho_2 = -0.86 \pm 0.09$ for the first and second protonations respectively. Diprotonation for N-p-chlorobenzoylthiourea in 100% sulfuric acid is confirmed by cryoscopic measurements ($\gamma = 2.9$) and conductivity measurements ($\gamma = 1.7$).

Part II

N-Acylthioureas are slowly hydrolyzed in sulfuric acid solution to the corresponding carboxylic acid and thiourea. The value of rho for the pseudo-first-order rate constant $k_\psi$ in 28.3% sulfuric acid for the hydrolysis of substituted N-benzoylthioureas is $+0.54 \pm 0.06$; in 96.9% sulfuric acid $-1.60 \pm 0.09$. Plots of log $k_\psi$ versus $1/T_0K$ give entropy of activation values of $-26 \pm 2$ e.u. (25.2% sulfuric acid), $-21 \pm 2$ e.u. (57.9% sulfuric acid) and $-11 \pm 1$ e.u. (96.9% sulfuric acid), for N-acetyltiourea. A plot of log $k_\psi$ versus percent sulfuric acid for N-acetyltiourea shows first a maximum and then a minimum. These data are analyzed according to the Bunnett-Olsen $\delta$ treatment and the Yates $\tau$ treatment, which
indicate a bimolecular process in dilute solution, with water as a nucleophile, changing to a unimolecular acylium ion-forming mechanism in concentrated acid. An empirical equation is derived which gives fair agreement with the observed rates over the entire range of acid concentrations.

Part III

The protonation of l-benzoyl-, l-m-trifluoromethylbenzoyl-, and l-o-iodobenzoyl-2-thiohydantoin in aqueous sulfuric acid, determined spectroscopically, is found to follow $H_0$: $pK_{BH^+}$ values of -6.6, -6.7, and -6.8 are obtained. The nature of the changes in the ultraviolet spectra accompanying protonation show that protonation takes place on the thiocarbonyl sulfur, as has already been found in previous studies of 2-thiohydantoins. In more concentrated acid 2-thiohydantoin is diprotonated on the l-carbonyl oxygen, as shown by U.V. and cryoscopic measurements, and U.V. indicates a possible secondary protonation for l-acyl-2-thiohydantoins. The overall Hammett rho value for the pseudo-first-order rates of hydrolysis of substituted 1-benzoyl-2-thiohydantoins in 58% sulfuric acid is $-0.4 \pm 0.04$, and in 93.8% sulfuric acid is $-2.5 \pm 0.11$. In 84.6% sulfuric acid the rho plot shows a break. These and the preceding facts indicate a change in mechanism of hydrolysis with acid concentration. This is also indicated by the activation entropy for l-acetyl-2-thiohydantoin which in 39.6% sulfuric acid is $-18 \pm 2$ e.u., in 84.9% is $-15 \pm 2$ e.u., and in 96.4% is $-5 \pm 2$ e.u. Plots of log $k$ versus percent sulfuric acid from 6-99% sulfuric acid for l-benzoyl, l-acetyl, and l-p-methoxybenzoyl-2-thiohydantoin and l-acetyl-5,5-dimethyl-2-thiohydantoin show first a maximum and then a minimum, just as in the
case of N-acetylthiourea; however, the maxima and minima are now found at much higher acid concentrations. Plots for several substituted 1-benzoyl derivatives show that the position and height of the maximum is only slightly dependent upon the nature of the benzoyl substituent. C-5 substituents are shown to depress the height of the maximum due to steric hindrance to water attack and to decrease the depth and position of the minimum by steric acceleration. N-3 phenyl group is shown to increase the height of the maximum slightly, due to its electron withdrawing ability and to increase the depth of the minimum, possibly by decreasing the basicity of the 4-carbonyl group, thereby decreasing the rate of the A-1 reaction. Treatment of the rate data for 1-acetyl-5,5-dimethyl-2-thiohydantoin according to the Bunnett-Olsen and Yates equations indicate a change from an A-2 to an A-1 mechanism of hydrolysis as the acid concentration is increased beyond 90%. An empirical equation is derived which gives fair agreement with the observed rates in the bimolecular region, and tends to favor a reactive O-protonated species rather than the more abundant S-protonated species.

Part IV

The bimolecular rate constant $k_b$ for the hydrolysis of 1-acetyl-5,5-dimethyl-2-thiohydantoin at pH 10.95-14.0, an ionic strength of 1.0 and at 25.4°C is found to be $0.16 \pm 0.01$ Liters/Mol-sec (twelve points). Phosphate buffers do not catalyze the reaction and a plot of log $k_b$ versus $\sqrt{\mu}/(1 + \sqrt{\mu})$ tends in dilute solution toward a slope of unity ($k_o = 0.072$ Liters/Mol-sec). A plot of log $k_\psi$ versus $1/T_0K$ at pH = 10.95, $\mu = 1.0$, for 1-acetyl- and 1-benzoyl-2-thiohydantoin; at pH = 11.95, $\mu = 0.55$, for 1-acetyl-5,5-dimethyl-2-thiohydantoin are linear and indicate entropy
of activation values $11 \pm 2$ e.u., $-13 \pm 2$ e.u. and $-14 \pm 2$ e.u. respectively. These values are corrected for ionic strength at one temperature only and are based on second order rates.

Rho for the hydrolysis of substituted 1-benzoyl-2-thiohydantoins is found to equal $1.18 \pm 0.05$. C-5 substituents retard the rate, both by steric hindrance and by inductive effects. Comparison of the hydrolysis rates for 1-acyl-2-thiohydantoins with those for acetonilide and benzamide under similar conditions show that 1-acyl-2-thiohydantoins are $10^4$-$10^5$ times more reactive. A mechanism involving hydroxide attack on the ionized 1-acyl-2-thiohydantoin substrate, intramolecular proton exchange, and adduct break-up is proposed to explain the above results.

**Part V**

1-Acetyl($d_3$)-5,5-dimethyl-2-thiohydantoin is synthesized and used to observe secondary isotope effects in the acid-catalyzed A-1 and A-2 hydrolyses, and in the A-2 base-catalyzed hydrolysis. A plot of $k_{CH_3}/k_{CD_3}$ versus $T^\circ C$ shows a minimum near $30^\circ C$ for the acid A-2 and the basic A-2 reactions. For the acid catalyzed A-1 reaction the curve shows a uniform increase in $k_{CH_3}/k_{CD_3}$ on going from $58.1^\circ C(1.05)$ to $10.8^\circ C(1.31)$. Plots of log $k$ versus $1/T^\circ K$ give straight lines and tend to exclude a change in mechanism. The A-1 results are interpretable in terms of greater hyperconjugative stabilization of the acylium ion by CH$_3$ as compared with CD$_3$. The results of the bimolecular case are similar to those reported for ester hydrolysis. No reasonable explanation is apparent.
APPENDIX A-1

Calculation of the bimolecular rate expression used in PARTS II and III

Refer to Part II, Scheme 1 for an explanation of the notation used below.

\[1\] \[\text{rate} = k_1[M] \]

\[2\] \[K_+ = [M]a_{H^2O}a_{AH^+} \]

\[3\] \[\text{rate} = k_1K_+a_{H^2O}a_{AH^+}/f_+ \]

\[4\] \[K_{AH^+} = h_A[A]/[AH^+] \]

\[5\] \[\text{rate} = k_1K_+a_{H^2O}h_A[A]a_{AH^+}/f_+K_{AH^+} \]

\[6\] \[\text{rate} = k_\psi(\text{Total substrate concentration}) \]

\[7\] \[\text{rate} = k_\psi([A] + [BH^+]) \]

\[8\] \[k_\psi = k_1K_+a_{AH^+}a_{H^2O}h_A[A]/K_{AH^+}f_+(h_A[A] + [BH^+]) \]

\[9\] \[K_{BH^+} = [A]h_o''''/[BH^+] \]

\[10\] \[k_\psi = k_1K_+f_{AH^+}a_{H^2O}h_AK_{BH^+}/K_{AH^+}f_+(h_o'''' + K_{BH^+}) \]

\[11\] \[\log k_\psi + h_A - \log \left\{K_{BH^+}/(K_{BH^+} + h_o''''\right\} = \log(k_1K_+f_{AH^+}/K_{AH^+}f_+) + r\log a_{H^2O} \]
Calculation of the unimolecular rate expression used in PART II

Refer to Part II, Scheme 3 for an explanation of the notation used below.

\[ \text{rate} = k_r [M^+] \]

\[ K_r = a_{CH_2^{++}} / a_M \]

\[ k_2 = k_r / K_r \]

\[ \text{rate} = k_2 [CH_2^{++}] f_{CH_2^{++}} / f_\psi \]

\[ \text{rate} = k_2 [BH^+] \left( \frac{[BH^{++}]}{[BH_2^{++}]} \right) \]

\[ k_\psi = k_2 [BH^{++}] f_{BH_2^{++}} / f_\psi \left( [BH^+] + [BH_2^{++}] \right) \]

\[ K_{BH_2^{++}} = a_B [BH^+] / [BH_2^{++}] \]

\[ K_{CH_2^{++}} = a_o [BH^+] / [CH_2^{++}] \]

\[ k_\psi = k_2 K_{BH_2^{++}} h_o f_{CH_2^{++}} / K_{CH_2^{++}} (K_{BH_2^{++}} + a_B) f_\psi \]

\[ k_\psi = \left( k_2 K_{BH_2^{++}} f_{CH_2^{++}} / K_{CH_2^{++}} f_\psi \right) \left( h_o / (K_{BH_2^{++}} + a_B) \right) \]
APPENDIX B

Figure 1-A
The U.V. spectra showing the reaction of 0.0001M/L N-acetylthiourea in 25.2% H₂SO₄ at 40.0°C. a. 0 seconds (660 seconds after mixing); b. 1560 seconds; c. 5040 seconds; d. 72000 seconds.

Figure 1-B
The U.V. spectra showing the reaction of 0.00012M/L N-acetylthiourea in 96.4% H₂SO₄ at 25.3°C. a. 0 seconds (600 seconds after mixing); b. 11050 seconds; c. 32380 seconds; d. 80000 seconds; e. five days.
APPENDIX B

Figure 2

The U.V. spectra showing the reaction of 0.00007M/L N-μ-fluorobenzoylthiourea in 95.0% H₂SO₄ at 65.8°C. a. 0 (500 seconds after mixing); b. 1600 seconds; c. 5900 seconds; d. 32280 seconds.
APPENDIX B

Figure 3

The U.V. spectra showing the reaction of 0.0001M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in 54.9% H₂SO₄ at 25.3°C. a. 0 seconds (30 seconds after mixing); b. 90 seconds; c. 200 seconds; d. 1200 seconds.
APPENDIX B

Figure 4

The U.V. spectra showing the reaction of 0.0001M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in 96.4% H₂SO₄ at 25.3°C. a. 0 seconds (200 seconds after mixing); b. 450 seconds; c. 1735 seconds; d. 8570 seconds.
APPENDIX B

Figure 5

The U.V. spectra showing the reaction of 0.00009M/L 1-p-chlorobenzoyl-2-thiohydantoin in 93.8% H₂SO₄ at 25.3°C. a. 0 (200 seconds after mixing); b. 2003 seconds; c. 2003 seconds; d. 14530 seconds.
APPENDIX B

Figure 6

The U.V. spectra showing the reaction of 0.00008M/L 1-acetyl-5,5-dimethyl-2-thiohydantoin in aqueous phosphate buffer pH = 11.95, ionic strength = 0.55, at 25.3°C. a. 0 seconds (100 seconds after mixing); b. 300 seconds; c. 900 seconds; d. 5400 seconds.
APPENDIX C

The following pages contain the raw data, derived rates (generally not rounded off in order to avoid cumulative round off error in the mean value), and statistical parameters for the kinetic and thermodynamic experiments described in the main body of the thesis. The data are usually presented in separate tables for each compound studied roughly in the order that the results appear in the text. A detailed index is included in the List of Tables.

The following notation is used in the tables that follow:

\( A_{1}, A_{2} \): the value of the optical density at the specified wave length.

\( \# \): the set of optical density measurements used to calculate \( \log I \).

\( \log I : \log \left\{ \frac{(O.D. - O.D.)}{(O.D. - O.D. +)} \right\} \).

Slope: the slope of a plot of \( \log I \) versus \( H_{X} \).

Time: elapsed time in seconds (unless otherwise noted) not necessarily from the time of mixing.

\( dA \): the absolute value in O.D. units of the difference between the O.D. at the time stated and the O.D. at the time stated plus \( t(G) \) or the optical density reading at the time stated. To obtain the difference in the second case, \( A_{i} \) the O.D. value at infinite time \( t \), must be subtracted. The O.D. values for the second case often do not represent the true O.D. reading of the substrate concentration in the solution because the back off attachment has been used freely and without notice to obtain the best possible O.D. change.

\( C \): the concentration of the mineral acid used in the run, determined by titration with standard alkali.
pH: the value of $-\log (H^+)$ determined by the quantity of standard alkali added.

m: the pH of the buffer solution determined by measurement using a standardized Radiometer 202-c electrode versus a saturated KCl electrode coupled with a TTT-1 recording pH meter. The measurements were done in quintuplicate giving an average error of $\pm 0.04$ pH units.

B: buffer constituents of Fisher reagent grade chemicals.

I: ionic strength $= \frac{1}{2} \sum M Z^2$ where $M$ is the concentration of ionic species in moles per liter and $Z$ is the ionic charge.

S: the concentration of the title compound at the beginning of the run.

T: temperature of the run controlled to $\pm 0.1^\circ C$ or better during the run. The temperature in the cell compartment was measured by drilling a hole in the cell compartment and inserting a thermometer into a cell.

L: wavelength at which the reaction was followed. The recorded value is good only to about $\pm 5$ nm since the rates are independent of wavelength (see Part III, Table VI in this Appendix), but the actual wavelength during a run was locked in one position.

t: time at which the 'infinite time' reading of the optical density was taken, when the reaction was assumed to be at equilibrium (seven to ten half-lives).

t(G): time interval between the two sets of optical density readings used to determine the rate constant by the Guggenheim method.

Ai: the optical density reading at infinite time.

t_d: the half-life of the reaction in seconds unless otherwise noted.

r: optical density values times 5.
r1: optical density values times 10.

r2: optical density values times 2.

cc: correlation coefficient for the integrated first-order rate equation; 0.999 for 84% of all runs included; 0.997 or better for 96% of all runs included. The lowest correlation coefficient used was 0.9902 (93.8% sulfuric acid, Part III, Table XI in this Appendix) and was duplicated giving cc: 0.9991 and rate value varying by about 3%.

rate: pseudo-first-order rate constant calculated by the method of least-squares from the integrated first-order rate equation.

sd: standard deviation for the rate constant, pK or slope value expressed in the same units as the numerical value to which it applies. For the pK measurements in which there are five to eleven log \( \frac{1}{2} \) values, to assure 99.9% confidence limits for the pK value, the error is approximated by six times the standard deviation. For example, for a pK\(_{BH^+}\) with the following results:

\[
pK_{BH^+} = -4.64
\]
\[
\text{sd} = 0.02
\]

the true pK\(_{BH^+}\) within 99.9% confidence limits would be:

\[
pK_{BH^+} = -4.64 \pm 0.12.
\]

For the kinetic results for runs with eight or more points (98% of the runs included) the probable error for 99% confidence limits is approximated by three times the standard deviation. For better than 70% of the runs the error quoted is the average error for duplicate up to quintuplicate runs. When the average error is compared with three times the standard deviation in most cases 3-sigma is more conservative. This point is made in Table I which contains randomly picked examples from the data.
# TABLE I

Comparison of $3\sigma$ and the average error for randomly chosen rates

<table>
<thead>
<tr>
<th>Compound and reaction conditions</th>
<th>No. of runs</th>
<th>Mean rate in $10^4$ sec$^{-1}$</th>
<th>Average Error No. %</th>
<th>Mean value of $3\sigma$ No. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-acetyltiourea $96.9% H_2SO_4$, $58.6^\circ C$</td>
<td>2</td>
<td>$5.44$</td>
<td>0.07 1.3</td>
<td>0.10 1.8</td>
</tr>
<tr>
<td>1-benzoyl-2-thiohydantoin, $93.8% H_2SO_4$, $25.3^\circ C$</td>
<td>3</td>
<td>$7.63$</td>
<td>0.36 4.7</td>
<td>0.22 2.9</td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin $53.5% H_2SO_4$, $25.3^\circ C$</td>
<td>2</td>
<td>$78.5$</td>
<td>0.35 0.5</td>
<td>1.85 2.4</td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin, $96.3% H_2SO_4$, $58.1^\circ C$</td>
<td>3</td>
<td>$1740.$</td>
<td>40. 2.3</td>
<td>28.1 1.6</td>
</tr>
<tr>
<td>1-acetyl-2-thiohydantoin, pH $= 14$, $1N$ NaOH, $25.4^\circ C$</td>
<td>2</td>
<td>$266.$</td>
<td>12. 4.5</td>
<td>20. 7.5</td>
</tr>
<tr>
<td>1-acetyl-2-thiohydantoin, pH $= 10.95$, 20.1$^\circ C$, $\mu = 1.0$</td>
<td>3</td>
<td>$3.97$</td>
<td>0.12 3.0</td>
<td>0.2 5.0</td>
</tr>
<tr>
<td>1-benzoyl-2-thiohydantoin, $58.0% H_2SO_4$, $25.3^\circ C$</td>
<td>2</td>
<td>$49.8$</td>
<td>0.5 1.0</td>
<td>0.95 1.9</td>
</tr>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin $pH = 11.95$, $49.6^\circ C$, $\mu = 0.55$</td>
<td>3</td>
<td>$95.8$</td>
<td>0.4 0.12</td>
<td>1.8 1.9</td>
</tr>
</tbody>
</table>
**PART I**

**TABLE I**

<table>
<thead>
<tr>
<th>N-acetyli thiourea</th>
<th>% Sulfuric Acid</th>
<th>(265) nm</th>
<th>(270) nm</th>
<th>(\log I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-1*</td>
<td>A-2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>00.0 (B)</td>
<td>1.153</td>
<td>1.102</td>
<td>-1.343</td>
<td></td>
</tr>
<tr>
<td>39.6</td>
<td>1.104</td>
<td>1.037</td>
<td>-0.424</td>
<td></td>
</tr>
<tr>
<td>47.2</td>
<td>.844</td>
<td>.800</td>
<td>-0.047</td>
<td></td>
</tr>
<tr>
<td>50.4</td>
<td>.620</td>
<td>.582</td>
<td>0.245</td>
<td></td>
</tr>
<tr>
<td>53.5</td>
<td>.435</td>
<td>.400</td>
<td>0.226</td>
<td></td>
</tr>
<tr>
<td>58.0</td>
<td>.121</td>
<td>.106</td>
<td>1.032</td>
<td></td>
</tr>
<tr>
<td>64.0 (BH⁺)</td>
<td>.026</td>
<td>.022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(pK_{BH⁺} = -4.64\) (on the \(H_o^{‴}\) acidity scale.)

sd: 0.02
Slope: 1.09
sd: 0.02
cr: 0.9992

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>(240) nm</th>
<th>(245) nm</th>
<th>(\log I)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A-1</td>
<td>A-2*</td>
<td></td>
</tr>
<tr>
<td>62.5</td>
<td>.486</td>
<td>.281</td>
<td></td>
</tr>
<tr>
<td>65.3 (BH⁺)</td>
<td>.474</td>
<td>.275</td>
<td></td>
</tr>
<tr>
<td>68.1</td>
<td>.486</td>
<td>.286</td>
<td></td>
</tr>
<tr>
<td>73.4</td>
<td>.508</td>
<td>.311</td>
<td>-0.562</td>
</tr>
<tr>
<td>77.2</td>
<td>.528</td>
<td>.336</td>
<td>-0.294</td>
</tr>
<tr>
<td>80.0</td>
<td>.542</td>
<td>.360</td>
<td>-0.053</td>
</tr>
<tr>
<td>83.9</td>
<td>.562</td>
<td>.396</td>
<td>0.301</td>
</tr>
<tr>
<td>85.7</td>
<td>.578</td>
<td>.414</td>
<td>0.520</td>
</tr>
<tr>
<td>88.5</td>
<td>.597</td>
<td>.430</td>
<td></td>
</tr>
<tr>
<td>91.2 (BH₂⁺)</td>
<td>.618</td>
<td>.456</td>
<td></td>
</tr>
<tr>
<td>96.1</td>
<td>.640</td>
<td>.468</td>
<td></td>
</tr>
</tbody>
</table>

\(pK_{BH₂⁺} = -4.61\) (on the \(H_A\) acidity scale.)

sd: 0.02
Slope: 1.02
sd: 0.05
cr: 0.9949
### TABLE II

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>280 nm</th>
<th>275 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 (B)</td>
<td>.935</td>
<td>.977</td>
<td></td>
</tr>
<tr>
<td>36.0</td>
<td>.889</td>
<td>.936</td>
<td></td>
</tr>
<tr>
<td>45.0</td>
<td>.818</td>
<td>.875</td>
<td>-0.578</td>
</tr>
<tr>
<td>47.0</td>
<td>.745</td>
<td>.805</td>
<td>-0.319</td>
</tr>
<tr>
<td>48.6</td>
<td>.690</td>
<td>.755</td>
<td>-0.188</td>
</tr>
<tr>
<td>51.1</td>
<td>.604</td>
<td>.880</td>
<td>0.104</td>
</tr>
<tr>
<td>52.7</td>
<td>.543</td>
<td>.680</td>
<td>0.297</td>
</tr>
<tr>
<td>55.0</td>
<td>.471</td>
<td>.568</td>
<td>0.566</td>
</tr>
<tr>
<td>58.0</td>
<td>.367</td>
<td>.504</td>
<td>1.117</td>
</tr>
<tr>
<td>60.0</td>
<td>.357</td>
<td>.478</td>
<td></td>
</tr>
<tr>
<td>62.4 (BH⁺)</td>
<td>.345</td>
<td>.468</td>
<td></td>
</tr>
</tbody>
</table>

\[ pK_{BH⁺} = -4.55 \] (on the \( H_0^{11} \) acidity scale)

sd: .004
Slope: 1.03
sd: .01
c: .9995

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>250 nm</th>
<th>280 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.2</td>
<td>1.710</td>
<td>.598</td>
<td></td>
</tr>
<tr>
<td>65.3 (BH⁺)</td>
<td>1.710</td>
<td>.617</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>1.622</td>
<td>.666</td>
<td>-1.003</td>
</tr>
<tr>
<td>75.9</td>
<td>1.554</td>
<td>.760</td>
<td>-0.494</td>
</tr>
<tr>
<td>80.0</td>
<td>1.478</td>
<td>.858</td>
<td>-0.097</td>
</tr>
<tr>
<td>81.5</td>
<td>1.431</td>
<td>.904</td>
<td>0.051</td>
</tr>
<tr>
<td>84.2</td>
<td>1.368</td>
<td>.975</td>
<td>0.290</td>
</tr>
<tr>
<td>88.4</td>
<td>1.300</td>
<td>1.076</td>
<td>0.743</td>
</tr>
<tr>
<td>92.2 (BH₂⁺²)</td>
<td>1.246</td>
<td>1.159</td>
<td></td>
</tr>
<tr>
<td>96.4</td>
<td>1.210</td>
<td>1.228</td>
<td></td>
</tr>
</tbody>
</table>

\[ pK_{BH₂⁺²} = -4.68 \] (on the \( H_A \) acidity scale)

sd: .01
Slope: 1.07
sd: .02
c: .9991
TABLE III

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>280 nm</th>
<th>285 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0 (B)</td>
<td>1.293</td>
<td>1.182</td>
<td></td>
</tr>
<tr>
<td>35.6</td>
<td>1.242</td>
<td>1.143</td>
<td></td>
</tr>
<tr>
<td>47.2</td>
<td>1.042</td>
<td>.955</td>
<td>-0.446</td>
</tr>
<tr>
<td>49.0</td>
<td>.929</td>
<td>.853</td>
<td>-0.208</td>
</tr>
<tr>
<td>51.2</td>
<td>.797</td>
<td>.732</td>
<td>0.037</td>
</tr>
<tr>
<td>53.2</td>
<td>.671</td>
<td>.617</td>
<td>0.275</td>
</tr>
<tr>
<td>55.6</td>
<td>.520</td>
<td>.480</td>
<td>0.635</td>
</tr>
<tr>
<td>58.8</td>
<td>.401</td>
<td>.364</td>
<td>1.172</td>
</tr>
<tr>
<td>65.8 (BH+)</td>
<td>.341</td>
<td>.300</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH+} = -4.64 (on the H_0'''' acidity scale.)

sd: .006
Slope: 1.10
sd: .01
cc: .9996

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>275 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.3</td>
<td>.366</td>
<td></td>
</tr>
<tr>
<td>70.2 (BH+)</td>
<td>.374</td>
<td></td>
</tr>
<tr>
<td>75.9</td>
<td>.421</td>
<td>-0.628</td>
</tr>
<tr>
<td>80.0</td>
<td>.466</td>
<td>-0.271</td>
</tr>
<tr>
<td>81.5</td>
<td>.480</td>
<td>-0.147</td>
</tr>
<tr>
<td>83.9</td>
<td>.513</td>
<td>0.078</td>
</tr>
<tr>
<td>85.7</td>
<td>.540</td>
<td>0.213</td>
</tr>
<tr>
<td>89.4</td>
<td>.582</td>
<td>0.578</td>
</tr>
<tr>
<td>92.2</td>
<td>.630</td>
<td></td>
</tr>
<tr>
<td>93.4 (BH_2+2)</td>
<td>.670</td>
<td></td>
</tr>
<tr>
<td>96.1</td>
<td>.670</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH_2+2} = -4.88 (on the H_A acidity scale.)

sd: .011
Slope: 1.000
sd: .02
cc: .9989
### TABLE IV

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>285 nm</th>
<th>280 nm</th>
<th>log ι</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0 (B)</td>
<td>0.530</td>
<td>0.555</td>
<td>-1.292</td>
</tr>
<tr>
<td>41.5</td>
<td>0.514</td>
<td>0.548</td>
<td>-0.836</td>
</tr>
<tr>
<td>44.1</td>
<td>0.508</td>
<td>0.542</td>
<td>-0.569</td>
</tr>
<tr>
<td>47.0</td>
<td>0.488</td>
<td>0.511</td>
<td>-0.210</td>
</tr>
<tr>
<td>49.6</td>
<td>0.472</td>
<td>0.490</td>
<td>-0.210</td>
</tr>
<tr>
<td>52.9</td>
<td>0.399</td>
<td>0.425</td>
<td>0.138</td>
</tr>
<tr>
<td>53.9</td>
<td>0.386</td>
<td>0.408</td>
<td>0.213</td>
</tr>
<tr>
<td>56.4</td>
<td>0.300</td>
<td>0.320</td>
<td>0.619</td>
</tr>
<tr>
<td>58.6</td>
<td>0.258</td>
<td>0.280</td>
<td>1.068</td>
</tr>
<tr>
<td>60.0 (BH⁺)</td>
<td>0.209</td>
<td>0.235</td>
<td></td>
</tr>
<tr>
<td>66.0 (BH²⁺)</td>
<td>0.200</td>
<td>0.235</td>
<td></td>
</tr>
</tbody>
</table>

**pK_{BH⁺} = -4.73** (on the H₀⁺⁺ acidity scale.)

sd: .01

Slope: 1.09

sd: .016

cc: .9991

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>280 nm</th>
<th>275 nm</th>
<th>log ι</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.3</td>
<td>0.626</td>
<td>0.645</td>
<td></td>
</tr>
<tr>
<td>70.2 (BH⁺)</td>
<td>0.616</td>
<td>0.636</td>
<td>-0.747</td>
</tr>
<tr>
<td>75.9</td>
<td>0.546</td>
<td>0.560</td>
<td>-0.387</td>
</tr>
<tr>
<td>80.0</td>
<td>0.415</td>
<td>0.428</td>
<td>0.007</td>
</tr>
<tr>
<td>84.2</td>
<td>0.309</td>
<td>0.320</td>
<td>0.404</td>
</tr>
<tr>
<td>88.4</td>
<td>0.204</td>
<td>1.036</td>
<td>0.905</td>
</tr>
<tr>
<td>92.2</td>
<td>0.176</td>
<td>1.120</td>
<td></td>
</tr>
<tr>
<td>94.4 (BH²⁺)</td>
<td>0.128</td>
<td>1.174</td>
<td></td>
</tr>
<tr>
<td>96.1</td>
<td>0.148</td>
<td>1.190</td>
<td></td>
</tr>
</tbody>
</table>

**pK_{BH²⁺} = -4.96** (on the H₂⁺⁺ acidity scale.)

sd: .01

Slope: 1.04

sd: .02

cc: .9987
<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>280 nm A-1</th>
<th>285 nm A-2</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0</td>
<td>1.188</td>
<td>1.200</td>
<td></td>
</tr>
<tr>
<td>30.2 (B)</td>
<td>1.153</td>
<td>1.175</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>1.127</td>
<td>1.150</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>1.084</td>
<td>1.107</td>
<td>-0.794</td>
</tr>
<tr>
<td>6.0</td>
<td>1.026</td>
<td>1.077</td>
<td>-0.468</td>
</tr>
<tr>
<td>6.0</td>
<td>.959</td>
<td>1.019</td>
<td>-0.180</td>
</tr>
<tr>
<td>6.6</td>
<td>.905</td>
<td>.973</td>
<td>-0.006</td>
</tr>
<tr>
<td>8.1</td>
<td>.814</td>
<td>.898</td>
<td>0.324</td>
</tr>
<tr>
<td>8.5</td>
<td>.768</td>
<td>.865</td>
<td>0.526</td>
</tr>
<tr>
<td>10.0</td>
<td>.721</td>
<td>.805</td>
<td>0.804</td>
</tr>
<tr>
<td>15.0</td>
<td>.653</td>
<td>.754</td>
<td></td>
</tr>
</tbody>
</table>

$pK_{BH^+} = -4.37$ (on the $H_0^{+}$ acidity scale.)

Slope: 1.03
sd: .02
cc: .9979

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>300 nm A-1</th>
<th>340 nm A-2*</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.3</td>
<td>.733</td>
<td>.014</td>
<td></td>
</tr>
<tr>
<td>60.0</td>
<td>.756</td>
<td>.026</td>
<td></td>
</tr>
<tr>
<td>52.5 (BH+)</td>
<td>.711</td>
<td>.030</td>
<td></td>
</tr>
<tr>
<td>65.3</td>
<td>.727</td>
<td>.037</td>
<td></td>
</tr>
<tr>
<td>68.1</td>
<td>.722</td>
<td>.045</td>
<td>-0.836</td>
</tr>
<tr>
<td>70.2</td>
<td>.705</td>
<td>.052</td>
<td>-0.639</td>
</tr>
<tr>
<td>73.4</td>
<td>.683</td>
<td>.067</td>
<td>-0.340</td>
</tr>
<tr>
<td>77.2</td>
<td>.666</td>
<td>.088</td>
<td>-0.014</td>
</tr>
<tr>
<td>80.0</td>
<td>.635</td>
<td>.107</td>
<td>0.274</td>
</tr>
<tr>
<td>83.9</td>
<td>.629</td>
<td>.126</td>
<td>0.644</td>
</tr>
<tr>
<td>85.7</td>
<td>.627</td>
<td>.134</td>
<td>0.872</td>
</tr>
<tr>
<td>88.5 (BH$_2^{+2}$)</td>
<td>.626</td>
<td>.148</td>
<td></td>
</tr>
<tr>
<td>91.2</td>
<td>.625</td>
<td>.155</td>
<td></td>
</tr>
<tr>
<td>94.3</td>
<td>.619</td>
<td>.161</td>
<td></td>
</tr>
</tbody>
</table>

$pK_{BH_2^{+2}} = -4.34$ (on the $H_A$ acidity scale.)

Slope: 1.13
sd: .02
cc: .9991
### Table VI

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>230 nm</th>
<th>255 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.9 (B)</td>
<td>.523</td>
<td>1.019</td>
<td>-1.331</td>
</tr>
<tr>
<td>35.6</td>
<td>.540</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.9</td>
<td>.552</td>
<td></td>
<td></td>
</tr>
<tr>
<td>44.6</td>
<td>.595</td>
<td>.992</td>
<td>-0.633</td>
</tr>
<tr>
<td>46.3</td>
<td>.623</td>
<td></td>
<td>-0.414</td>
</tr>
<tr>
<td>47.2</td>
<td>.636</td>
<td></td>
<td>-0.375</td>
</tr>
<tr>
<td>49.0</td>
<td>.679</td>
<td>.950</td>
<td>-0.159</td>
</tr>
<tr>
<td>51.1</td>
<td>.726</td>
<td>.913</td>
<td>0.057</td>
</tr>
<tr>
<td>51.8</td>
<td>.763</td>
<td></td>
<td>0.231</td>
</tr>
<tr>
<td>52.9</td>
<td>.792</td>
<td></td>
<td>0.381</td>
</tr>
<tr>
<td>53.9</td>
<td>.821</td>
<td></td>
<td>0.555</td>
</tr>
<tr>
<td>54.8</td>
<td>.840</td>
<td>.830</td>
<td>0.695</td>
</tr>
<tr>
<td>58.8</td>
<td>.884</td>
<td>.796</td>
<td></td>
</tr>
<tr>
<td>62.4 (BH+)</td>
<td>.904</td>
<td>.762</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{pK}_{\text{BH}^+} = -4.50 \text{ (on the H}_0 \text{ acidity scale.)} \]

sd: .03  
Slope: 0.970  
sd: .05  
cc: .9872

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>265 nm</th>
<th>300 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.3</td>
<td>1.377</td>
<td>.983</td>
<td></td>
</tr>
<tr>
<td>60.0</td>
<td>1.335</td>
<td>.510</td>
<td></td>
</tr>
<tr>
<td>65.3 (BH+)</td>
<td>1.295</td>
<td>.580</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>1.218</td>
<td>.668</td>
<td></td>
</tr>
<tr>
<td>73.4</td>
<td>1.168</td>
<td>.737</td>
<td>-0.820</td>
</tr>
<tr>
<td>75.9</td>
<td>1.124</td>
<td>.801</td>
<td>-0.514</td>
</tr>
<tr>
<td>77.7</td>
<td>1.086</td>
<td>.850</td>
<td>-0.307</td>
</tr>
<tr>
<td>80.0</td>
<td>1.052</td>
<td>.936</td>
<td>-0.170</td>
</tr>
<tr>
<td>83.9</td>
<td>.928</td>
<td>1.050</td>
<td>0.056</td>
</tr>
<tr>
<td>85.7</td>
<td>.888</td>
<td>1.112</td>
<td>0.351</td>
</tr>
<tr>
<td>89.4</td>
<td>.796</td>
<td>1.178</td>
<td>0.587</td>
</tr>
<tr>
<td>92.2 (BH(_2)+)</td>
<td>.784</td>
<td>1.250</td>
<td>0.920</td>
</tr>
<tr>
<td>94.3</td>
<td>.750</td>
<td>1.281</td>
<td></td>
</tr>
<tr>
<td>96.1</td>
<td>.745</td>
<td>1.313</td>
<td></td>
</tr>
</tbody>
</table>

\[ \text{pK}_{\text{BH}_2^+} = -4.55 \text{ (on the H}_a \text{ acidity scale.)} \]

sd: .009  
Slope: 1.00  
sd: .02  
cc: .9989
### TABLE VII

N-\text{-}m\text{-}methylbenzoylthiourea

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>280 nm A-1</th>
<th>285 nm A-2</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.9 (B)</td>
<td>1.342</td>
<td>1.202</td>
<td></td>
</tr>
<tr>
<td>35.5</td>
<td>1.306</td>
<td>1.170</td>
<td></td>
</tr>
<tr>
<td>38.9</td>
<td>1.284</td>
<td>1.145</td>
<td>-1.052</td>
</tr>
<tr>
<td>41.6</td>
<td>1.197</td>
<td>1.055</td>
<td>-0.592</td>
</tr>
<tr>
<td>47.2</td>
<td>1.097</td>
<td>0.960</td>
<td>-0.279</td>
</tr>
<tr>
<td>49.0</td>
<td>1.015</td>
<td>0.877</td>
<td>-0.070</td>
</tr>
<tr>
<td>51.1</td>
<td>0.901</td>
<td>0.768</td>
<td>0.213</td>
</tr>
<tr>
<td>52.9</td>
<td>0.772</td>
<td>0.615</td>
<td>0.507</td>
</tr>
<tr>
<td>58.8</td>
<td>0.633</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>63.2 (BH+)</td>
<td>0.631</td>
<td>0.486</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH^+} = -4.43 (on the H_o''' acidity scale.)

sd: 0.4
Slope: 1.06
sd: 0.08
cc: 0.9832

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>255 nm A-1</th>
<th>285 nm A-2</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>57.3</td>
<td>1.586</td>
<td>.660</td>
<td></td>
</tr>
<tr>
<td>60.0</td>
<td>1.563</td>
<td>.612</td>
<td></td>
</tr>
<tr>
<td>65.3 (BH+)</td>
<td>1.476</td>
<td>.670</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>1.446</td>
<td>.761</td>
<td>-0.599</td>
</tr>
<tr>
<td>73.4</td>
<td>1.382</td>
<td>.816</td>
<td>-0.384</td>
</tr>
<tr>
<td>75.9</td>
<td>1.302</td>
<td>.919</td>
<td>-0.064</td>
</tr>
<tr>
<td>80.0</td>
<td>1.214</td>
<td>.957</td>
<td>0.046</td>
</tr>
<tr>
<td>81.5</td>
<td>1.165</td>
<td>1.056</td>
<td>0.331</td>
</tr>
<tr>
<td>83.9</td>
<td>1.094</td>
<td>1.044</td>
<td>0.502</td>
</tr>
<tr>
<td>85.7</td>
<td>1.057</td>
<td>1.162</td>
<td>0.815</td>
</tr>
<tr>
<td>88.4</td>
<td>1.038</td>
<td>1.250</td>
<td></td>
</tr>
<tr>
<td>92.2 (BH_2^+2)</td>
<td>1.030</td>
<td>1.325</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH_2^+2} = -4.62 (on the H_A acidity scale.)

sd: 0.013
Slope: 1.05
sd: 0.03
cc: 0.9970
TABLE VIII

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>275 nm</th>
<th>280 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0 (B)</td>
<td>1.652</td>
<td>1.557</td>
<td></td>
</tr>
<tr>
<td>49.7</td>
<td>1.566</td>
<td>1.467</td>
<td>-0.752</td>
</tr>
<tr>
<td>48.6</td>
<td>1.494</td>
<td>1.384</td>
<td>-0.463</td>
</tr>
<tr>
<td>47.2</td>
<td>1.383</td>
<td>1.282</td>
<td>-0.252</td>
</tr>
<tr>
<td>49.0</td>
<td>1.275</td>
<td>1.180</td>
<td>-0.023</td>
</tr>
<tr>
<td>51.1</td>
<td>1.141</td>
<td>1.040</td>
<td>0.1149</td>
</tr>
<tr>
<td>52.1</td>
<td>1.038</td>
<td>.937</td>
<td>0.310</td>
</tr>
<tr>
<td>52.2</td>
<td>.947</td>
<td>.854</td>
<td>0.519</td>
</tr>
<tr>
<td>55.0</td>
<td>.846</td>
<td>.755</td>
<td></td>
</tr>
<tr>
<td>55.6</td>
<td>.772</td>
<td>.685</td>
<td></td>
</tr>
<tr>
<td>58.8</td>
<td>.634</td>
<td>.544</td>
<td></td>
</tr>
<tr>
<td>65.8 (BH+)</td>
<td>.602</td>
<td>.497</td>
<td></td>
</tr>
</tbody>
</table>

\( p_{KBH^+} = -4.65 \) (on the H_o'''' acidity scale.)

sd: .009

Slope: 1.12

sd: .029

cc: .9976

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>255 nm</th>
<th>280 nm</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>62.5</td>
<td>.825</td>
<td>.322</td>
<td></td>
</tr>
<tr>
<td>65.3 (BH+)</td>
<td>.820</td>
<td>.328</td>
<td></td>
</tr>
<tr>
<td>70.2</td>
<td>.804</td>
<td>.348</td>
<td>-0.983</td>
</tr>
<tr>
<td>73.4</td>
<td>.788</td>
<td>.364</td>
<td>-0.688</td>
</tr>
<tr>
<td>75.9</td>
<td>.780</td>
<td>.384</td>
<td>-0.445</td>
</tr>
<tr>
<td>77.2</td>
<td>.757</td>
<td>.396</td>
<td>-0.326</td>
</tr>
<tr>
<td>80.0</td>
<td>.741</td>
<td>.422</td>
<td>-0.097</td>
</tr>
<tr>
<td>82.0</td>
<td>.727</td>
<td>.444</td>
<td>0.082</td>
</tr>
<tr>
<td>83.9</td>
<td>.708</td>
<td>.463</td>
<td>0.215</td>
</tr>
<tr>
<td>85.7</td>
<td>.697</td>
<td>.487</td>
<td>0.477</td>
</tr>
<tr>
<td>88.5</td>
<td>.683</td>
<td>.508</td>
<td></td>
</tr>
<tr>
<td>90.0</td>
<td>.672</td>
<td>.518</td>
<td></td>
</tr>
<tr>
<td>91.4</td>
<td>.660</td>
<td>.521</td>
<td></td>
</tr>
<tr>
<td>94.3 (BH_2^+)</td>
<td>.652</td>
<td>.540</td>
<td></td>
</tr>
<tr>
<td>96.4</td>
<td>.642</td>
<td>.550</td>
<td></td>
</tr>
</tbody>
</table>

\( p_{KBH_2^+} = -4.67 \) (on the H_A acidity scale.)

sd: .007

Slope: 1.07

sd: .02

cc: .9990
TABLE IX

N-p-nitrobenzylthiourea

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>295 nm A-1*</th>
<th>300 nm A-2</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>00.0 (B)</td>
<td>1.110</td>
<td>.950</td>
<td></td>
</tr>
<tr>
<td>43.0</td>
<td>1.083</td>
<td>.924</td>
<td></td>
</tr>
<tr>
<td>46.6</td>
<td>1.029</td>
<td>.876</td>
<td></td>
</tr>
<tr>
<td>48.2</td>
<td>.998</td>
<td>.846</td>
<td></td>
</tr>
<tr>
<td>51.7</td>
<td>.878</td>
<td>.737</td>
<td></td>
</tr>
<tr>
<td>53.0</td>
<td>.808</td>
<td>.673</td>
<td></td>
</tr>
<tr>
<td>54.9</td>
<td>.726</td>
<td>.595</td>
<td></td>
</tr>
<tr>
<td>56.9</td>
<td>.657</td>
<td>.528</td>
<td></td>
</tr>
<tr>
<td>58.0</td>
<td>.628</td>
<td>.497</td>
<td></td>
</tr>
<tr>
<td>60.5</td>
<td>.590</td>
<td>.461</td>
<td></td>
</tr>
<tr>
<td>62.4 (BH+)</td>
<td>.560</td>
<td>.440</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH+} = -4.83 (on the H_0 acidity scale.)

sd: .01
Slope: 1.17
sd: .02
cc: .9985

TABLE X

N-p-chlorobenzylthiourea

<table>
<thead>
<tr>
<th>% Sulfuric Acid</th>
<th>265 nm A-1</th>
<th>295 nm A-2*</th>
<th>log I</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.0</td>
<td>1.766</td>
<td>.598</td>
<td></td>
</tr>
<tr>
<td>65.3</td>
<td>1.717</td>
<td>.630</td>
<td></td>
</tr>
<tr>
<td>70.2 (BH+)</td>
<td>1.661</td>
<td>.707</td>
<td></td>
</tr>
<tr>
<td>75.9</td>
<td>1.598</td>
<td>.823</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>1.535</td>
<td>.927</td>
<td></td>
</tr>
<tr>
<td>83.9</td>
<td>1.430</td>
<td>1.042</td>
<td></td>
</tr>
<tr>
<td>85.7</td>
<td>1.397</td>
<td>1.124</td>
<td></td>
</tr>
<tr>
<td>88.4</td>
<td>1.315</td>
<td>1.206</td>
<td></td>
</tr>
<tr>
<td>92.2</td>
<td>1.257</td>
<td>1.308</td>
<td></td>
</tr>
<tr>
<td>96.1 (BH_2+2)</td>
<td>1.186</td>
<td>1.390</td>
<td></td>
</tr>
<tr>
<td>98.3</td>
<td>1.090</td>
<td>1.524</td>
<td></td>
</tr>
</tbody>
</table>

pK_{BH_2+2} = -4.93 (on the H_A acidity scale.)

sd: .009
Slope: 1.000
sd: .02
cc: .9988
# PART II

## TABLE I

<table>
<thead>
<tr>
<th>N-acetylthiourea</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 4.08%         | 0    | 0.775 |
| S: 0.0020 M/L    | 2400 | 0.681 |
| T: 49.3°C        | 4800 | 0.599 |
| L: 300 nm        | 7200 | 0.525 |
| t(G): 43200 sec  | 9600 | 0.463 |
| cc: 0.9999       | 12000| 0.409 |
| rate: 0.54 x 10^{-4} sec^{-1} | 14400| 0.356 |
| sd: 0.001        | 16800| 0.311 |
| t_{1/2}: 12810 sec |     |      |

<p>| C: 15.9%         | 0    | 0.625 |
| S: 0.0020 M/L    | 600  | 0.530 |
| T: 49.3°C        | 1200 | 0.453 |
| L: 300 nm        | 1800 | 0.383 |
| t(G): 3600 sec   | 2400 | 0.328 |
| cc: 0.9999       | 3000 | 0.277 |
| rate: 2.74 x 10^{-4} sec^{-1} | 3600 | 0.233 |
| sd: 0.01         | 4200 | 0.197 |
| t_{1/2}: 2525 sec |     |      |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>660</td>
<td>1.223</td>
</tr>
<tr>
<td>1620</td>
<td>0.996</td>
</tr>
<tr>
<td>2220</td>
<td>0.894</td>
</tr>
<tr>
<td>3060</td>
<td>0.765</td>
</tr>
<tr>
<td>5700</td>
<td>0.489</td>
</tr>
<tr>
<td>7020</td>
<td>0.400</td>
</tr>
<tr>
<td>9000</td>
<td>0.283</td>
</tr>
<tr>
<td>9900</td>
<td>0.251</td>
</tr>
</tbody>
</table>

C: 25.2\%
S: 0.0001 M/L
T: 40.0°C
L: 270 nm
t: 72000 sec; A1: 0.110
cc: 0.9993
rate: 2.21 × 10⁻⁴ sec⁻¹
sd: 0.03
t₁/₂: 3140 sec

C: 25.2\%
S: 0.0002 M/L
T: 73.6°C
L: 270 nm
t(0): 500 sec
cc: 0.9997
rate: 26.4 × 10⁻⁴ sec⁻¹
sd: 0.23
t₁/₂: 260 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.794</td>
</tr>
<tr>
<td>100</td>
<td>.660</td>
</tr>
<tr>
<td>200</td>
<td>.530</td>
</tr>
<tr>
<td>300</td>
<td>.441</td>
</tr>
<tr>
<td>400</td>
<td>.358</td>
</tr>
<tr>
<td>500</td>
<td>.299</td>
</tr>
<tr>
<td>600</td>
<td>.215</td>
</tr>
<tr>
<td>700</td>
<td>.200</td>
</tr>
</tbody>
</table>

C: 25.2%
S: .0001M/L
T: 68.6°C
t(0): 1400 sec
c0: .9999
rate: \(19.7 \times 10^{-4}\) sec\(^{-1}\)
sd: .1
t\(_2\): 352 sec

---

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.700</td>
</tr>
<tr>
<td>100</td>
<td>.565</td>
</tr>
<tr>
<td>200</td>
<td>.470</td>
</tr>
<tr>
<td>300</td>
<td>.370</td>
</tr>
<tr>
<td>400</td>
<td>.300</td>
</tr>
<tr>
<td>500</td>
<td>.250</td>
</tr>
<tr>
<td>600</td>
<td>.192</td>
</tr>
<tr>
<td>700</td>
<td>.145</td>
</tr>
</tbody>
</table>

C: 25.2%
S: .0001M/L
T: 68.6°C
t(0): 1000 sec
c0: .9984
rate: \(22.0 \times 10^{-4}\) sec\(^{-1}\)
sd: .4
t\(_2\): 315 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>( \text{dA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.604</td>
</tr>
<tr>
<td>300</td>
<td>0.525</td>
</tr>
<tr>
<td>600</td>
<td>0.454</td>
</tr>
<tr>
<td>900</td>
<td>0.392</td>
</tr>
<tr>
<td>1200</td>
<td>0.339</td>
</tr>
<tr>
<td>1500</td>
<td>0.289</td>
</tr>
<tr>
<td>1800</td>
<td>0.250</td>
</tr>
<tr>
<td>2100</td>
<td>0.215</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>( \text{dA} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.733</td>
</tr>
<tr>
<td>300</td>
<td>0.587</td>
</tr>
<tr>
<td>600</td>
<td>0.463</td>
</tr>
<tr>
<td>900</td>
<td>0.363</td>
</tr>
<tr>
<td>1200</td>
<td>0.286</td>
</tr>
<tr>
<td>1500</td>
<td>0.227</td>
</tr>
<tr>
<td>1800</td>
<td>0.178</td>
</tr>
<tr>
<td>2100</td>
<td>0.138</td>
</tr>
</tbody>
</table>

**Conditions:**
- **C:** 25.2%  
- **S:** 0.0020 M/L  
- **T:** 49.3°C  
- **L:** 300 mm  
- **t(G):** 2800 sec  
- cc: 0.9999  
- rate: 4.94 \( \times 10^{-4} \) sec\(^{-1} \)  
- sd: 0.02  
- \( t_{\frac{1}{2}} \): 1100 sec

---

**Conditions:**
- **C:** 34.7%  
- **S:** 0.0020 M/L  
- **T:** 49.3°C  
- **L:** 300 mm  
- **t(G):** 1000 sec  
- cc: 0.9999  
- rate: 7.95 \( \times 10^{-4} \) sec\(^{-1} \)  
- sd: 0.03  
- \( t_{\frac{1}{2}} \): 870 sec
<table>
<thead>
<tr>
<th></th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 39.6%</td>
<td>0</td>
<td>.606</td>
</tr>
<tr>
<td>S: .0020 M/L</td>
<td>150</td>
<td>.536</td>
</tr>
<tr>
<td>T: 49.3°C</td>
<td>300</td>
<td>.467</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>450</td>
<td>.408</td>
</tr>
<tr>
<td>t(0): 2100 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc: .9999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate: 9.10 x 10^-4 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t_1/2: 760 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 43.7%</td>
<td>0</td>
<td>.659</td>
</tr>
<tr>
<td>S: .0020 M/L</td>
<td>150</td>
<td>.580</td>
</tr>
<tr>
<td>T: 49.3°C</td>
<td>300</td>
<td>.506</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>450</td>
<td>.441</td>
</tr>
<tr>
<td>t(0): 1800 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc: .9999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate: 9.18 x 10^-4 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t_1/2: 755 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 47.2%</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>150</td>
<td>.594</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.521</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.463</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>.363</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.275</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>.245</td>
<td></td>
</tr>
</tbody>
</table>

T: 49.3°C
L: 300 nm

\( t(0) \): 1500 sec
cc: .9999
rate: \( 8.48 \times 10^{-4} \) sec\(^{-1} \)
sd: .04
\( t_{\frac{1}{2}} \): 815 sec

<table>
<thead>
<tr>
<th>C: 50.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>.637</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.588</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>.534</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.483</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>.437</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.397</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>.357</td>
<td></td>
</tr>
</tbody>
</table>

T: 49.3°C
L: 295 nm

\( t(0) \): 2400 sec
cc: .9996
rate: \( 6.52 \times 10^{-4} \) sec\(^{-1} \)
sd: .06
\( t_{\frac{1}{2}} \): 1060 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>ΔA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.678</td>
</tr>
<tr>
<td>300</td>
<td>.587</td>
</tr>
<tr>
<td>600</td>
<td>.511</td>
</tr>
<tr>
<td>900</td>
<td>.443</td>
</tr>
<tr>
<td>1200</td>
<td>.385</td>
</tr>
<tr>
<td>1500</td>
<td>.332</td>
</tr>
<tr>
<td>1800</td>
<td>.290</td>
</tr>
<tr>
<td>2100</td>
<td>.250</td>
</tr>
</tbody>
</table>

C: 53.5%
S: .0015 M/L
T: 49.3°C
L: 295 nm
t(0): 2100 sec
cC: .9999
rate: 4.74 x 10⁻⁴ sec⁻¹
sd: .01
t₁/₂: 1460 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>ΔA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.617</td>
</tr>
<tr>
<td>1200</td>
<td>.527</td>
</tr>
<tr>
<td>2400</td>
<td>.466</td>
</tr>
<tr>
<td>3600</td>
<td>.384</td>
</tr>
<tr>
<td>4800</td>
<td>.328</td>
</tr>
<tr>
<td>6000</td>
<td>.280</td>
</tr>
<tr>
<td>7200</td>
<td>.240</td>
</tr>
<tr>
<td>8400</td>
<td>.204</td>
</tr>
</tbody>
</table>

C: 57.9%
S: .0015 M/L
T: 49.3°C
L: 285 nm
t(0): 10000 sec
cC: .9999
rate: 1.31 x 10⁻⁴ sec⁻¹
sd: .004
t₁/₂: 5280 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.100</td>
<td></td>
</tr>
<tr>
<td>0.864</td>
<td></td>
</tr>
<tr>
<td>0.744</td>
<td></td>
</tr>
<tr>
<td>0.702</td>
<td></td>
</tr>
<tr>
<td>0.643</td>
<td></td>
</tr>
</tbody>
</table>

C: 57.9%
S: 0.0001M/L
T: 40.0°C
L: 235 nm
t: 200000 sec; Ai: .166
cc: .9930
r: .52 x 10^-4 sec^-1
sd: .03
t_1/2: 13400 sec

c: 57.9%
S: 0.00012M/L
T: 68.6°C
L: 235 nm
t(G): 1500 sec
cc: .9997
rate: 7.06 x 10^-4 sec^-1
sd: .06
t_1/2: 980 sec
<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 62.4</td>
<td>.570</td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>.532</td>
</tr>
<tr>
<td>S: 0.0015M/L</td>
<td>.495</td>
</tr>
<tr>
<td>4800</td>
<td></td>
</tr>
<tr>
<td>7200</td>
<td>.461</td>
</tr>
<tr>
<td>T: 49.5°C</td>
<td>.430</td>
</tr>
<tr>
<td>9600</td>
<td></td>
</tr>
<tr>
<td>12000</td>
<td>.399</td>
</tr>
<tr>
<td>L: 268 nm</td>
<td>.376</td>
</tr>
<tr>
<td>16800</td>
<td></td>
</tr>
<tr>
<td>t(0): 40000 sec</td>
<td>.348</td>
</tr>
<tr>
<td>cc: .9998</td>
<td></td>
</tr>
<tr>
<td>rate: .29 x 10^{-4} sec^{-1}</td>
<td></td>
</tr>
<tr>
<td>sd: .002</td>
<td></td>
</tr>
<tr>
<td>t_{1/2}: 23700 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (Minutes)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 70.0%</td>
<td>.493</td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>.483</td>
</tr>
<tr>
<td>S: 0.00005M/L</td>
<td>.409</td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>.326</td>
</tr>
<tr>
<td>L: 230 nm</td>
<td>.262</td>
</tr>
<tr>
<td>3920</td>
<td></td>
</tr>
<tr>
<td>t: **; Ai: .09</td>
<td></td>
</tr>
<tr>
<td>cc: .9998</td>
<td></td>
</tr>
<tr>
<td>rate: .036 x 10^{-4} sec^{-1}</td>
<td></td>
</tr>
<tr>
<td>sd: .0035</td>
<td></td>
</tr>
<tr>
<td>t_{1/2}: 194,000 sec</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>$\text{dA}$</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>0</td>
<td>186</td>
</tr>
<tr>
<td>2400</td>
<td>4.31</td>
</tr>
<tr>
<td>4800</td>
<td>3.97</td>
</tr>
<tr>
<td>7200</td>
<td>3.62</td>
</tr>
<tr>
<td>9600</td>
<td>3.26</td>
</tr>
<tr>
<td>12000</td>
<td>2.93</td>
</tr>
<tr>
<td>16800</td>
<td>2.60</td>
</tr>
<tr>
<td>22800</td>
<td>2.35</td>
</tr>
</tbody>
</table>

**Reaction 1**

- $C$: 84.9% 0.165 2400 0.431 $S$: 0.0015M/L
- $T$: 49.3°C
- $L$: 264 mm
- $t(G)$: 30600 sec
- $cc$: 0.9994
- $rate$: $0.29 \times 10^{-4}$ sec$^{-1}$
- $sd$: 0.004
- $t_{1/2}$: 23500 sec

**Reaction 2**

- $C$: 88.4% 0.359 2400 0.324 $S$: 0.0023M/L
- $T$: 49.3°C
- $L$: 266 mm
- $t(G)$: 10000 sec
- $cc$: 0.9990
- $rate$: $0.44 \times 10^{-4}$ sec$^{-1}$
- $sd$: 0.007
- $t_{1/2}$: 15640 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>C: 92.2%</th>
<th>S: 0.0020 M/L</th>
<th>T: 49.3 °C</th>
<th>L: 267 nm</th>
<th>t(0): 3000 sec</th>
<th>cc: 0.9982</th>
<th>rate: 1.09 x 10^{-4} sec^{-1}</th>
<th>sd: 0.02</th>
<th>$t_{1/2}$: 6360 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.425</td>
<td>0.342</td>
<td>0.00201 I/L</td>
<td>0.271</td>
<td>0.214</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>0.342</td>
<td>0.271</td>
<td>0.214</td>
<td>0.166</td>
<td>0.123</td>
<td>0.091</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4800</td>
<td>0.342</td>
<td>0.271</td>
<td>0.214</td>
<td>0.166</td>
<td>0.123</td>
<td>0.091</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7200</td>
<td>0.271</td>
<td>0.214</td>
<td>0.166</td>
<td>0.123</td>
<td>0.091</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9600</td>
<td>0.214</td>
<td>0.166</td>
<td>0.123</td>
<td>0.091</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12000</td>
<td>0.166</td>
<td>0.123</td>
<td>0.091</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14400</td>
<td>0.123</td>
<td>0.091</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16800</td>
<td>0.091</td>
<td>0.069</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>C: 94.4%</th>
<th>S: 0.0004 M/L</th>
<th>T: 49.3 °C</th>
<th>L: 252 nm</th>
<th>t: 54000 sec; $A_t$: 0.124</th>
<th>cc: 0.9999</th>
<th>rate: 1.43 x 10^{-4} sec^{-1}</th>
<th>sd: 0.005</th>
<th>$t_{1/2}$: 4860 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.824</td>
<td>0.713</td>
<td>0.621</td>
<td>0.539</td>
<td>0.476</td>
<td>0.374</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.713</td>
<td>0.621</td>
<td>0.539</td>
<td>0.476</td>
<td>0.374</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>0.621</td>
<td>0.539</td>
<td>0.476</td>
<td>0.374</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>0.539</td>
<td>0.476</td>
<td>0.374</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4800</td>
<td>0.476</td>
<td>0.374</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>0.374</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7200</td>
<td>0.336</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8400</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.497</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.427</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.374</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.326</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>.286</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>.252</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3600</td>
<td>.221</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4200</td>
<td>.193</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C: 96.1%  
S: .0004μM/L  
T: 49.3°C  
L: 256 nm  
t(G): 3600 sec  
cc: .9998  
rate: 2.23 x 10^{-4} sec^{-1}  
sd: .02  
t\(\frac{1}{2}\): 3110 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.472</td>
</tr>
<tr>
<td>300</td>
<td>.427</td>
</tr>
<tr>
<td>600</td>
<td>.390</td>
</tr>
<tr>
<td>900</td>
<td>.351</td>
</tr>
<tr>
<td>1200</td>
<td>.317</td>
</tr>
<tr>
<td>1500</td>
<td>.287</td>
</tr>
<tr>
<td>1800</td>
<td>.257</td>
</tr>
<tr>
<td>2100</td>
<td>.237</td>
</tr>
</tbody>
</table>

C: 98.9%  
S: .0004μM/L  
T: 49.3°C  
L: 247 nm  
t(G): 3300 sec  
cc: .9997  
rate: 3.33 x 10^{-4} sec^{-1}  
sd: .03  
t\(\frac{1}{2}\): 2085 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.667</td>
</tr>
<tr>
<td>50</td>
<td>0.555</td>
</tr>
<tr>
<td>100</td>
<td>0.458</td>
</tr>
<tr>
<td>150</td>
<td>0.380</td>
</tr>
<tr>
<td>200</td>
<td>0.309</td>
</tr>
<tr>
<td>250</td>
<td>0.262</td>
</tr>
<tr>
<td>300</td>
<td>0.211</td>
</tr>
<tr>
<td>350</td>
<td>0.169</td>
</tr>
</tbody>
</table>

| C: 96.9% | 0 | 0.603 |
| S: .0001M/L | 50 | 0.620 |
| T: 80.4°C | 100 | 0.529 |
| L: 250 nm | 150 | 0.398 |
| t(o): 210 sec | 200 | 0.326 |
| cc: .9998 | 250 | 0.270 |
| rate: 38.88 x 10^{-4} sec^{-1} | 300 | 0.217 |
| sd: .42 | 350 | 0.176 |
| t\(\frac{1}{2}\): 178 sec | |

| C: 96.9% | 0 | 0.692 |
| S: .0001M/L | 96 | 0.602 |
| T: 68.9°C | 192 | 0.529 |
| L: 250 nm | 288 | 0.466 |
| t(o): 960 sec | 384 | 0.405 |
| cc: .9998 | 480 | 0.352 |
| rate: 14.15 x 10^{-4} sec^{-1} | 576 | 0.306 |
| sd: .26 | 672 | 0.267 |
| t\(\frac{1}{2}\): 168 sec | |

| C: 96.9% | 0 | 0.691 |
| S: .0001M/L | 96 | 0.612 |
| T: 68.9°C | 192 | 0.535 |
| L: 250 nm | 288 | 0.468 |
| t(o): 790 sec | 384 | 0.406 |
| cc: .9997 | 480 | 0.356 |
| rate: 14.25 x 10^{-4} sec^{-1} | 576 | 0.304 |
| sd: .12 | 672 | 0.268 |
| t\(\frac{1}{2}\): 490 sec | |

<p>| C: 96.9% | 0(Min) | 0.617 |
| S: .0001M/L | 4 | 0.513 |
| T: 58.6°C | 8 | 0.478 |
| L: 250 nm | 12 | 0.421 |
| t(o): 900 sec | 16 | 0.369 |
| cc: .9998 | 20 | 0.320 |
| rate: 5.51 x 10^{-4} sec^{-1} | 24 | 0.280 |
| sd: .03 | 28 | 0.245 |
| t(\frac{1}{2}): 1257 sec | |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(Min)</td>
<td>.635</td>
</tr>
<tr>
<td>6</td>
<td>.551</td>
</tr>
<tr>
<td>8</td>
<td>.480</td>
</tr>
<tr>
<td>12</td>
<td>.124</td>
</tr>
<tr>
<td>16</td>
<td>.376</td>
</tr>
<tr>
<td>20</td>
<td>.330</td>
</tr>
<tr>
<td>24</td>
<td>.289</td>
</tr>
<tr>
<td>28</td>
<td>.256</td>
</tr>
</tbody>
</table>

**TABLE II**

### N-p-methoxybenzoylthiourea

<table>
<thead>
<tr>
<th>C: 96.9%</th>
<th>0.536rl</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00005M/L</td>
<td>.183</td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td>.331</td>
</tr>
<tr>
<td>L: 250 nm</td>
<td>.377</td>
</tr>
<tr>
<td>t(G): 1200 sec</td>
<td>.350</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>.262</td>
</tr>
<tr>
<td>rate: 5.37 x 10^-4 sec^-1</td>
<td>.208</td>
</tr>
<tr>
<td>t[½]: 1290 sec</td>
<td>.158</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.9%</th>
<th>.432rl</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00005M/L</td>
<td>.373</td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td>.334</td>
</tr>
<tr>
<td>L: 330 nm</td>
<td>.291</td>
</tr>
<tr>
<td>t(G): 120 sec</td>
<td>.265</td>
</tr>
<tr>
<td>cc: .9988</td>
<td>.212</td>
</tr>
<tr>
<td>rate: 82.32 x 10^-4 sec^-1</td>
<td>.179</td>
</tr>
<tr>
<td>t[½]: 84 sec</td>
<td>.144</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.9%</th>
<th>.272rl</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00005M/L</td>
<td>.228</td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td>.212</td>
</tr>
<tr>
<td>L: 223 nm</td>
<td>.190</td>
</tr>
<tr>
<td>t(G): 300 sec</td>
<td>.171</td>
</tr>
<tr>
<td>cc: .9975</td>
<td>.124</td>
</tr>
<tr>
<td>rate: 84.22 x 10^-4 sec^-1</td>
<td>.096</td>
</tr>
<tr>
<td>t[½]: 82 sec</td>
<td>.079</td>
</tr>
</tbody>
</table>
\begin{table}[h]
\centering
\begin{tabular}{llll}
& Time & & \\
& 100 & & 1.392 \\
& 790 & & 1.191 \\
& 1485 & & 1.015 \\
& 2275 & & 0.837 \\
& 3370 & & 0.690 \\
& 3720 & & 0.627 \\
& 4830 & & 0.500 \\
& 6235 & & 0.382 \\
& 8885 & & 0.241 \\
\end{tabular}
\caption{N-o-methylbenzoylthiourea}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{llll}
& C: 28.3\% & & \\
& S: .0001M/L & & \\
& T: 85.0\degree C & & \\
& L: 290 mm & & \\
& t: 11000 sec; Ai: .133 & & \\
& cc: .9995 & & \\
& rate: 2.63 \times 10^{-4} sec^{-1} & & \\
& sd: .03 & & \\
& t_{1/2}: 2640 sec & & \\
\end{tabular}
\caption{N-o-methylbenzoylthiourea}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{llll}
& C: 96.9\% & & \\
& S: .00006M/L & & \\
& T: 58.6\degree C & & \\
& L: 210 mm & & \\
& t: 1570 sec; Ai: .267 & & \\
& cc: .9998 & & \\
& rate: 49.90 \times 10^{-4} sec^{-1} & & \\
& sd: .33 & & \\
& t_{1/2}: 139 sec & & \\
\end{tabular}
\caption{N-p-methylbenzoylthiourea}
\end{table}
<table>
<thead>
<tr>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>68</td>
<td>.378\textsuperscript{r}</td>
</tr>
<tr>
<td>96</td>
<td>.315</td>
</tr>
<tr>
<td>192</td>
<td>.305</td>
</tr>
<tr>
<td>240</td>
<td>.267</td>
</tr>
<tr>
<td>288</td>
<td>.239</td>
</tr>
<tr>
<td>336</td>
<td>.207</td>
</tr>
<tr>
<td>384</td>
<td>.178</td>
</tr>
<tr>
<td>480</td>
<td>.157</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>.954</td>
</tr>
<tr>
<td>2000</td>
<td>.851</td>
</tr>
<tr>
<td>2500</td>
<td>.755</td>
</tr>
<tr>
<td>3000</td>
<td>.663</td>
</tr>
<tr>
<td>3500</td>
<td>.572</td>
</tr>
<tr>
<td>4000</td>
<td>.491</td>
</tr>
<tr>
<td>4500</td>
<td>.412</td>
</tr>
<tr>
<td>5000</td>
<td>.347</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.749\textsuperscript{rl}</td>
</tr>
<tr>
<td>96</td>
<td>.664</td>
</tr>
<tr>
<td>192</td>
<td>.604</td>
</tr>
<tr>
<td>288</td>
<td>.528</td>
</tr>
<tr>
<td>384</td>
<td>.464</td>
</tr>
<tr>
<td>480</td>
<td>.411</td>
</tr>
<tr>
<td>576</td>
<td>.350</td>
</tr>
<tr>
<td>672</td>
<td>.299</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.253\textsuperscript{r}</td>
</tr>
<tr>
<td>96</td>
<td>.212</td>
</tr>
<tr>
<td>192</td>
<td>.212</td>
</tr>
<tr>
<td>288</td>
<td>.195</td>
</tr>
<tr>
<td>384</td>
<td>.173</td>
</tr>
<tr>
<td>480</td>
<td>.150</td>
</tr>
<tr>
<td>576</td>
<td>.110</td>
</tr>
<tr>
<td>672</td>
<td>.098</td>
</tr>
</tbody>
</table>

**TABLE V**

<table>
<thead>
<tr>
<th>N-m-methylbenzoylthiourea</th>
<th>C: 96.9%</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00005M/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L: 240 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t(G): 960 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc: .9975</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate: 13.53 x 10^{-4} sec^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t_{1/2}: 512 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>N-m-methylbenzoylthiourea</th>
<th>C: 96.9%</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00005M/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L: 235 mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t(G): 1200 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc: .9985</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate: 16.12 x 10^{-4} sec^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t_{1/2}: 430 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-benacetylthiourea</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>----------------------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>C: 28.3%</td>
<td>0</td>
<td>1.378</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>688</td>
<td>1.083</td>
</tr>
<tr>
<td>T: 85.0°C</td>
<td>1h00</td>
<td>.830</td>
</tr>
<tr>
<td>L: 275 mm</td>
<td>2130</td>
<td>.660</td>
</tr>
<tr>
<td>t: 12750 sec; A1: .160</td>
<td>3270</td>
<td>.461</td>
</tr>
<tr>
<td>s0: .9972</td>
<td>4605</td>
<td>.334</td>
</tr>
<tr>
<td>rate: 4.02 x 10⁻⁴ sec⁻¹</td>
<td>6055</td>
<td>.249</td>
</tr>
<tr>
<td>sdr: .10</td>
<td>8170</td>
<td>.211</td>
</tr>
</tbody>
</table>

| C: 95.0%             | 0    | .668   |
| S: .00008 M/L        | 760  | .566   |
| T: 65.8°C            | 1026 | .546   |
| L: 280 mm            | 1710 | .509   |
| t: 9100 sec; A1: .370 | 2650 | .481   |
| s0: .9920            | 3000 | .470   |
| rate: 3.92 x 10⁻⁴ sec⁻¹ | 3850 | .433   |
| sdr: .18             | 5100 | .405   |

| t²: 1730 sec         |      |      |

<p>| t²: 1760 sec         |      |      |</p>
<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$\Delta A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.040</td>
</tr>
<tr>
<td>1200</td>
<td>0.940</td>
</tr>
<tr>
<td>1800</td>
<td>0.910</td>
</tr>
<tr>
<td>2400</td>
<td>0.840</td>
</tr>
<tr>
<td>3000</td>
<td>0.760</td>
</tr>
<tr>
<td>3600</td>
<td>0.700</td>
</tr>
<tr>
<td>4800</td>
<td>0.740</td>
</tr>
</tbody>
</table>

C: 39.6\%  
S: 0.00008 M/L  
T: 49.1°C  
L: 275 nm  
$t(0)$: 12000 sec  
cc: 0.9983  
rates: $3.9 \times 10^{-4}$ sec$^{-1}$  
sd: 0.01  
$t_\frac{1}{2}$: 17580 sec

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$\Delta A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.030</td>
</tr>
<tr>
<td>600</td>
<td>0.850</td>
</tr>
<tr>
<td>1200</td>
<td>0.770</td>
</tr>
<tr>
<td>1800</td>
<td>0.670</td>
</tr>
<tr>
<td>2400</td>
<td>0.570</td>
</tr>
<tr>
<td>3000</td>
<td>0.512</td>
</tr>
<tr>
<td>3600</td>
<td>0.451</td>
</tr>
<tr>
<td>4200</td>
<td>0.390</td>
</tr>
</tbody>
</table>

C: 39.6\%  
S: 0.00008 M/L  
T: 68.6°C  
L: 275 nm  
t(0): 5000 sec  
cc: 0.9985  
rates: $2.25 \times 10^{-4}$ sec$^{-1}$  
sd: 0.04  
$t_\frac{1}{2}$: 3075 sec
<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.446</td>
</tr>
<tr>
<td>600</td>
<td>1.137</td>
</tr>
<tr>
<td>1080</td>
<td>0.928</td>
</tr>
<tr>
<td>1620</td>
<td>0.756</td>
</tr>
<tr>
<td>2100</td>
<td>0.642</td>
</tr>
<tr>
<td>2760</td>
<td>0.531</td>
</tr>
<tr>
<td>3600</td>
<td>0.424</td>
</tr>
<tr>
<td>4500</td>
<td>0.356</td>
</tr>
<tr>
<td>6050</td>
<td>0.563</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.63</td>
</tr>
<tr>
<td>96</td>
<td>0.606</td>
</tr>
<tr>
<td>192</td>
<td>0.587</td>
</tr>
<tr>
<td>288</td>
<td>0.568</td>
</tr>
<tr>
<td>384</td>
<td>0.552</td>
</tr>
<tr>
<td>576</td>
<td>0.527</td>
</tr>
<tr>
<td>768</td>
<td>0.506</td>
</tr>
<tr>
<td>960</td>
<td>0.488</td>
</tr>
<tr>
<td>1050</td>
<td>0.452</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.227</td>
</tr>
<tr>
<td>96</td>
<td>0.206</td>
</tr>
<tr>
<td>192</td>
<td>0.184</td>
</tr>
<tr>
<td>288</td>
<td>0.163</td>
</tr>
<tr>
<td>384</td>
<td>0.145</td>
</tr>
<tr>
<td>576</td>
<td>0.115</td>
</tr>
<tr>
<td>768</td>
<td>0.095</td>
</tr>
<tr>
<td>960</td>
<td>0.077</td>
</tr>
<tr>
<td>1050</td>
<td>0.058</td>
</tr>
</tbody>
</table>

**Results: C: 39.6% S: 0.0001M/L T: 79.9°C L: 275 nm t: 8000 sec; A: .300 cc: .9960 rate: 6.60 x 10^{-4} sec^{-1} sd: .21 t_{1/2}: 1050**

**Results: C: 96.9% S: 0.00006M/L T: 58.6°C L: 240 mm t: 320 sec; A: .412 cc: .9998 rate: 10.88 x 10^{-4} sec^{-1} sd: .085 t_{1/2}: 637 sec**

**Results: C: 96.9% S: 0.00006M/L T: 58.6°C L: 240 mm t(G): 1250 sec cc: .9995 rate: 10.57 x 10^{-4} sec^{-1} sd: .13 t_{1/2}: 608 sec**
TABLE VII

<table>
<thead>
<tr>
<th>N-p-chlorobenzoylthiourea</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 96.9%</td>
<td>0(min)</td>
<td>.510r</td>
</tr>
<tr>
<td>S: .00005M/L</td>
<td></td>
<td>.665</td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td>4</td>
<td>.414</td>
</tr>
<tr>
<td>L: 230 nm</td>
<td>8</td>
<td>.371</td>
</tr>
<tr>
<td>t(0): 4.50 min</td>
<td>16</td>
<td>.331</td>
</tr>
<tr>
<td>cc: .9995</td>
<td>20</td>
<td>.292</td>
</tr>
<tr>
<td>rate: 4.768 x 10^-4 sec^-1</td>
<td>24</td>
<td>.260</td>
</tr>
<tr>
<td>sd: .05</td>
<td>28</td>
<td>.231</td>
</tr>
<tr>
<td>t_1/2: 24 min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 96.9%                  | 0(min)| .520r  |
| S: .00005M/L              |       | .479   |
| T: 58.6°C                 | 4     | .384   |
| L: 230 nm                 | 8     | .345   |
| t(0): 56 min             | 16    | .269   |
| cc: .9981                 | 20    | .238   |
| rate: 4.738 x 10^-4 sec^-1| 24    |        |
| sd: .10                  | 28    |        |
| t_1/2: 24 min            |       |        |

| C: 28.3%                  | 0     | 1.098  |
| S: .0001M/L               | 705   | .840   |
| T: 85.0°C                 | 1375  | .660   |
| L: 275 nm                 | 2170  | .500   |
| t: 8510 sec; Ai: .1h6     | 3165  | .370   |
| cc: .9985                 | 4370  | .276   |
| rate: 4.83 x 10^-4 sec^-1 | 5845  | .200   |
| sd: .10                  |       |        |
| t_1/2: 1h30 sec          |       |        |

TABLE VIII

<table>
<thead>
<tr>
<th>N-m-chlorobenzoylthiourea</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 96.9%</td>
<td>0 (min)</td>
<td>.362r</td>
</tr>
<tr>
<td>S: .00005M/L</td>
<td></td>
<td>.329</td>
</tr>
<tr>
<td>T: 58.6°C</td>
<td>8</td>
<td>.296</td>
</tr>
<tr>
<td>L: 240 nm</td>
<td>16</td>
<td>.267</td>
</tr>
<tr>
<td>t(0): 114.4 min</td>
<td>32</td>
<td>.217</td>
</tr>
<tr>
<td>cc: .9994</td>
<td>40</td>
<td>.227</td>
</tr>
<tr>
<td>rate: 1.993 x 10^-4 sec^-1</td>
<td>48</td>
<td>.206</td>
</tr>
<tr>
<td>sd: .018</td>
<td>56</td>
<td>.185</td>
</tr>
<tr>
<td>t_1/2: 58 min</td>
<td>64</td>
<td>.171</td>
</tr>
<tr>
<td></td>
<td>72</td>
<td>.157</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>.114</td>
</tr>
<tr>
<td></td>
<td>88</td>
<td>.127</td>
</tr>
<tr>
<td></td>
<td>96</td>
<td>.113</td>
</tr>
<tr>
<td></td>
<td>104</td>
<td>.102</td>
</tr>
<tr>
<td>C (%)</td>
<td>S (mM/L)</td>
<td>T (°C)</td>
</tr>
<tr>
<td>-------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>96.9</td>
<td>0.0005</td>
<td>58.6</td>
</tr>
<tr>
<td>28.3</td>
<td>0.001</td>
<td>85.0</td>
</tr>
<tr>
<td>95.0</td>
<td>0.0008</td>
<td>65.8</td>
</tr>
</tbody>
</table>

TABLE IX

N-m-fluorobenzoylthiourea

<table>
<thead>
<tr>
<th>C (%)</th>
<th>S (mM/L)</th>
<th>T (°C)</th>
<th>L (nm)</th>
<th>t (sec)</th>
<th>Ai</th>
<th>cc</th>
<th>rate (sec^{-1})</th>
<th>sd</th>
<th>t\frac{1}{2} (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.3</td>
<td>0.0013</td>
<td>85.0</td>
<td>280</td>
<td>12000</td>
<td>.910</td>
<td>.9959</td>
<td>6.31 x 10^{-4}</td>
<td>.20</td>
<td>9015</td>
</tr>
<tr>
<td>95.0</td>
<td>0.0008</td>
<td>65.8</td>
<td>230</td>
<td>32300</td>
<td>.809</td>
<td>.9993</td>
<td>1.71 x 10^{-4}</td>
<td>.02</td>
<td>h055</td>
</tr>
</tbody>
</table>
### PART III

**Table I**

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Sulfuric Acid</th>
<th>285 nm</th>
<th>( A-1^* )</th>
<th>log ( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1-benzoyl-2-thiophydantoin</strong></td>
<td>71.0</td>
<td>1.022</td>
<td>-0.783</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72.7</td>
<td>0.957</td>
<td>-1.17</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.0</td>
<td>0.895</td>
<td>-1.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.9</td>
<td>0.870</td>
<td>-1.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.0</td>
<td>0.835</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78.1</td>
<td>0.740</td>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>0.690</td>
<td>0.700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>81.8</td>
<td>0.655</td>
<td>0.985</td>
<td></td>
</tr>
<tr>
<td></td>
<td>85.5 (BH(^+))</td>
<td>0.610</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>00.0 (B)</td>
<td>1.090</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( pK_{BH^+} = -6.64; \) sd: .02; Slope(versus \( H_0 \)) = 1.02; sd: .025; cc: .9978

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Sulfuric Acid</th>
<th>285 nm</th>
<th>( A-1^* )</th>
<th>log ( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1-m-trifluoromethylbenzoyl-2-thiophydantoin</strong></td>
<td>70.0</td>
<td>1.020</td>
<td>-0.914</td>
<td></td>
</tr>
<tr>
<td></td>
<td>72.7</td>
<td>0.931</td>
<td>-1.296</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.9</td>
<td>0.846</td>
<td>-2.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>76.0</td>
<td>0.830</td>
<td>-1.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>77.5</td>
<td>0.649</td>
<td>0.295</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78.1</td>
<td>0.595</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>0.551</td>
<td>0.674</td>
<td></td>
</tr>
<tr>
<td></td>
<td>86.4 (BH(^+))</td>
<td>0.424</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>65.0 (B)</td>
<td>1.093</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( pK_{BH^+} = -6.68; \) sd: .02; Slope(versus \( H_0 \)) = 1.03; sd: .03; cc: .9968

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Sulfuric Acid</th>
<th>285 nm</th>
<th>( A-1^* )</th>
<th>log ( I )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1-o-iodobenzoyl-2-thiophydantoin</strong></td>
<td>72.7</td>
<td>1.092</td>
<td>-0.500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.9</td>
<td>1.020</td>
<td>-0.319</td>
<td></td>
</tr>
<tr>
<td></td>
<td>78.1</td>
<td>0.720</td>
<td>0.173</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80.9</td>
<td>0.669</td>
<td>0.718</td>
<td></td>
</tr>
<tr>
<td></td>
<td>84.9</td>
<td>0.360</td>
<td>1.231</td>
<td></td>
</tr>
<tr>
<td></td>
<td>94.4 (BH(^+))</td>
<td>0.302</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>00.0 (B)</td>
<td>1.342</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( pK_{BH^+} = -6.82; \) sd: .03; Slope(versus \( H_0 \)) = .95; sd: .04; cc: .9944
### TABLE I

<table>
<thead>
<tr>
<th>l-p-methoxybenzoyl-2-thiodydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>.950</td>
</tr>
<tr>
<td>S: .001 mM/L</td>
<td>20</td>
<td>.720</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>40</td>
<td>.565</td>
</tr>
<tr>
<td>L: 350 nm</td>
<td>60</td>
<td>.464</td>
</tr>
<tr>
<td>t: 600 sec; Ai: .214</td>
<td>80</td>
<td>.390</td>
</tr>
<tr>
<td>cc: .9991</td>
<td>100</td>
<td>.340</td>
</tr>
<tr>
<td>rate: 170.3 x 10^{-4} sec^{-1}</td>
<td>120</td>
<td>.300</td>
</tr>
<tr>
<td>sD: 1.86</td>
<td>140</td>
<td>.280</td>
</tr>
<tr>
<td>t(_1/2): 40.7 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 93.8%                           | 0    | 1.420|
| S: .001 mM/L                       | 10   | 1.200|
| T: 25.3°C                          | 20   | 1.010|
| L: 350 nm                          | 30   | .860|
| t: 700 sec; Ai: .220               | 40   | .755|
| cc: .9977                          | 50   | .670|
| rate: 169.9 x 10^{-4} sec^{-1}     | 60   | .600|
| sD: 3.66                           | 80   | .500|
| t\(_1/2\): 40.8 sec                | 100  | .420|

| C: 93.8%                           | 0    | 1.175|
| S: .001 mM/L                       | 10   | 1.025|
| T: 25.3°C                          | 20   | .900 |
| L: 350 nm                          | 30   | .790 |
| t: 500 sec; Ai: .260               | 40   | .710 |
| cc: .9999                          | 50   | .610 |
| rate: 173.6 x 10^{-4} sec^{-1}     | 60   | .580 |
| sD: .64                           | 70   | .530 |
| t\(_1/2\): 39.9 sec                | 80   | .486 |

<p>| C: 58.0%                           | 0    | .680 |
| S: .0001M/L                        | 58   | .561 |
| T: 25.3°C                          | 116  | .465 |
| L: 300 mm                          | 174  | .381 |
| t: 2100 sec; Ai: .04               | 232  | .314 |
| cc: .9997                          | 290  | .262 |
| rate: 37.4 x 10^{-4} sec^{-1}      | 318  | .218 |
| sD: .31                           | 406  | .179 |
| t(_1/2): 185 sec                |      |     |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.639</td>
</tr>
<tr>
<td>58</td>
<td>0.524</td>
</tr>
<tr>
<td>116</td>
<td>0.430</td>
</tr>
<tr>
<td>174</td>
<td>0.352</td>
</tr>
<tr>
<td>232</td>
<td>0.287</td>
</tr>
<tr>
<td>290</td>
<td>0.238</td>
</tr>
<tr>
<td>348</td>
<td>0.192</td>
</tr>
<tr>
<td>406</td>
<td>0.157</td>
</tr>
<tr>
<td>t½: 187 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.844</td>
</tr>
<tr>
<td>150</td>
<td>0.658</td>
</tr>
<tr>
<td>300</td>
<td>0.509</td>
</tr>
<tr>
<td>450</td>
<td>0.395</td>
</tr>
<tr>
<td>600</td>
<td>0.306</td>
</tr>
<tr>
<td>750</td>
<td>0.216</td>
</tr>
<tr>
<td>900</td>
<td>0.194</td>
</tr>
<tr>
<td>t½: 378 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.028</td>
</tr>
<tr>
<td>50</td>
<td>0.756</td>
</tr>
<tr>
<td>100</td>
<td>0.559</td>
</tr>
<tr>
<td>150</td>
<td>0.405</td>
</tr>
<tr>
<td>200</td>
<td>0.307</td>
</tr>
<tr>
<td>250</td>
<td>0.233</td>
</tr>
<tr>
<td>300</td>
<td>0.180</td>
</tr>
<tr>
<td>t½: 102 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.600</td>
</tr>
<tr>
<td>20</td>
<td>1.338</td>
</tr>
<tr>
<td>40</td>
<td>1.119</td>
</tr>
<tr>
<td>60</td>
<td>0.958</td>
</tr>
<tr>
<td>80</td>
<td>0.825</td>
</tr>
<tr>
<td>100</td>
<td>0.724</td>
</tr>
<tr>
<td>120</td>
<td>0.640</td>
</tr>
<tr>
<td>t½: 66.7 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.137</td>
</tr>
<tr>
<td>15</td>
<td>1.059</td>
</tr>
<tr>
<td>30</td>
<td>0.957</td>
</tr>
<tr>
<td>45</td>
<td>0.871</td>
</tr>
<tr>
<td>60</td>
<td>0.802</td>
</tr>
<tr>
<td>75</td>
<td>0.713</td>
</tr>
<tr>
<td>90</td>
<td>0.703</td>
</tr>
<tr>
<td>t½: 54.5 sec</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>-----</td>
<td>-----------</td>
</tr>
<tr>
<td>70.1</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>72.7</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>74.9</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>77.5</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>77.5</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>77.5</td>
<td>.0001M/L</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>1.334</td>
</tr>
<tr>
<td>1.096</td>
</tr>
<tr>
<td>.931</td>
</tr>
<tr>
<td>.813</td>
</tr>
<tr>
<td>.727</td>
</tr>
<tr>
<td>.659</td>
</tr>
<tr>
<td>.602</td>
</tr>
<tr>
<td>.562</td>
</tr>
<tr>
<td>1.356</td>
</tr>
<tr>
<td>1.160</td>
</tr>
<tr>
<td>1.017</td>
</tr>
<tr>
<td>.918</td>
</tr>
<tr>
<td>.816</td>
</tr>
<tr>
<td>.791</td>
</tr>
<tr>
<td>.747</td>
</tr>
<tr>
<td>.712</td>
</tr>
<tr>
<td>1.230</td>
</tr>
<tr>
<td>1.059</td>
</tr>
<tr>
<td>.936</td>
</tr>
<tr>
<td>.810</td>
</tr>
<tr>
<td>.771</td>
</tr>
<tr>
<td>.718</td>
</tr>
<tr>
<td>.669</td>
</tr>
<tr>
<td>.628</td>
</tr>
<tr>
<td>1.000</td>
</tr>
<tr>
<td>.870</td>
</tr>
<tr>
<td>.765</td>
</tr>
<tr>
<td>.680</td>
</tr>
<tr>
<td>.605</td>
</tr>
<tr>
<td>.580</td>
</tr>
<tr>
<td>.460</td>
</tr>
<tr>
<td>.380</td>
</tr>
<tr>
<td>.324</td>
</tr>
<tr>
<td>1.048</td>
</tr>
<tr>
<td>.925</td>
</tr>
<tr>
<td>.820</td>
</tr>
<tr>
<td>.725</td>
</tr>
<tr>
<td>.660</td>
</tr>
<tr>
<td>.580</td>
</tr>
<tr>
<td>.510</td>
</tr>
<tr>
<td>.300</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>0%</td>
</tr>
<tr>
<td>25°C</td>
</tr>
<tr>
<td>25°C</td>
</tr>
<tr>
<td>340 nm</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>340 nm</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>340 nm</td>
</tr>
<tr>
<td>C: 86.4%</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>S: .0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 340 nm</td>
</tr>
<tr>
<td>t: 1600 sec; Ai: .070</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 50.6 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td>sd: .12</td>
</tr>
<tr>
<td>t½: 137 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 89.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.890</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.756</td>
</tr>
<tr>
<td>L: 340 nm</td>
<td>30</td>
<td>.620</td>
</tr>
<tr>
<td>t: 1300 sec; Ai: .137</td>
<td>110</td>
<td>.510</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>140</td>
<td>.320</td>
</tr>
<tr>
<td>rate: 67.3 x 10^{-4} sec^{-1}</td>
<td>210</td>
<td>.260</td>
</tr>
<tr>
<td>sd: .57</td>
<td>270</td>
<td></td>
</tr>
<tr>
<td>t½: 103 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 89.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.835</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.770</td>
</tr>
<tr>
<td>L: 340 nm</td>
<td>30</td>
<td>.670</td>
</tr>
<tr>
<td>t: 1200 sec; Ai: .097</td>
<td>90</td>
<td>.595</td>
</tr>
<tr>
<td>cc: .9990</td>
<td>150</td>
<td>.480</td>
</tr>
<tr>
<td>rate: 65.2 x 10^{-4} sec^{-1}</td>
<td>190</td>
<td>.360</td>
</tr>
<tr>
<td>sd: 1.0</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>t½: 106 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 92.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.990</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>20</td>
<td>.850</td>
</tr>
<tr>
<td>L: 340 nm</td>
<td>40</td>
<td>.700</td>
</tr>
<tr>
<td>t: 1200 sec; Ai: .132</td>
<td>80</td>
<td>.570</td>
</tr>
<tr>
<td>cc: .9989</td>
<td>100</td>
<td>.480</td>
</tr>
<tr>
<td>rate: 105.3 x 10^{-4} sec^{-1}</td>
<td>120</td>
<td>.355</td>
</tr>
<tr>
<td>sd: 1.2</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>t½: 65.8 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.730</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>1.305</td>
</tr>
<tr>
<td>L: 340 nm</td>
<td>20</td>
<td>1.026</td>
</tr>
<tr>
<td>t: 700 sec; Ai: .422</td>
<td>40</td>
<td>.850</td>
</tr>
<tr>
<td>cc: .9957</td>
<td>50</td>
<td>.720</td>
</tr>
<tr>
<td>rate: 313.6 x 10^{-4} sec^{-1}</td>
<td>70</td>
<td>.642</td>
</tr>
<tr>
<td>sd: 10.3</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>t½: 22.1 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C: 96.4%
S: 0.0001M/L
T: 25.3°C
L: 310 nm
t: 500 sec; Ai: 0.370
cc: 0.9969
rate: 335.1 x 10⁻⁴ sec⁻¹
sd: 8.3
τ₁/₂: 20.7 sec

pH: 10.75
B: 0.1M Na₂HPO₄, 0.1M NaOH, 0.09M NaCl
I: 0.12
S: 0.0005M/L
T: 25.3°C
L: 310 nm
t(0): 500 sec
cc: 0.9996
rate: 5.12 x 10⁻⁴ sec⁻¹
sd: 0.048
τ₁/₂: 1353 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.200</td>
</tr>
<tr>
<td>29</td>
<td>1.095</td>
</tr>
<tr>
<td>116</td>
<td>.830</td>
</tr>
<tr>
<td>203</td>
<td>.660</td>
</tr>
<tr>
<td>261</td>
<td>.574</td>
</tr>
<tr>
<td>377</td>
<td>.450</td>
</tr>
<tr>
<td>464</td>
<td>.390</td>
</tr>
<tr>
<td>206</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>1.250</td>
</tr>
<tr>
<td>58</td>
<td>1.150</td>
</tr>
<tr>
<td>116</td>
<td>.990</td>
</tr>
<tr>
<td>174</td>
<td>.870</td>
</tr>
<tr>
<td>232</td>
<td>.772</td>
</tr>
<tr>
<td>290</td>
<td>.698</td>
</tr>
<tr>
<td>348</td>
<td>.640</td>
</tr>
<tr>
<td>493</td>
<td>.540</td>
</tr>
<tr>
<td>214</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.734</td>
</tr>
<tr>
<td>58</td>
<td>.600</td>
</tr>
<tr>
<td>116</td>
<td>.502</td>
</tr>
<tr>
<td>174</td>
<td>.430</td>
</tr>
<tr>
<td>232</td>
<td>.373</td>
</tr>
<tr>
<td>290</td>
<td>.332</td>
</tr>
<tr>
<td>348</td>
<td>.301</td>
</tr>
<tr>
<td>406</td>
<td>.280</td>
</tr>
<tr>
<td>0</td>
<td>.741</td>
</tr>
<tr>
<td>58</td>
<td>.602</td>
</tr>
<tr>
<td>116</td>
<td>.501</td>
</tr>
<tr>
<td>174</td>
<td>.421</td>
</tr>
<tr>
<td>232</td>
<td>.362</td>
</tr>
<tr>
<td>290</td>
<td>.318</td>
</tr>
<tr>
<td>348</td>
<td>.286</td>
</tr>
<tr>
<td>406</td>
<td>.261</td>
</tr>
<tr>
<td>1-p-methylbenzoyl-2-thiohydantoin</td>
<td>Time</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
</tr>
<tr>
<td>S: .00006M/L</td>
<td>113</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>208</td>
</tr>
<tr>
<td>L: 276 nm</td>
<td>303</td>
</tr>
<tr>
<td>t: 3000 sec; Ai: 1.090</td>
<td>397</td>
</tr>
<tr>
<td>cc: .9991</td>
<td>492</td>
</tr>
<tr>
<td>rate: 33.1 x 10⁻¹ sec⁻¹</td>
<td>595</td>
</tr>
<tr>
<td>sd: .3</td>
<td></td>
</tr>
<tr>
<td>t½: 208 sec</td>
<td></td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
</tr>
<tr>
<td>S: .00006M/L</td>
<td>29</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>58</td>
</tr>
<tr>
<td>L: 236 nm</td>
<td>87</td>
</tr>
<tr>
<td>t: 2400 sec; Ai: .60</td>
<td>116</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>145</td>
</tr>
<tr>
<td>rate: 32.2 x 10⁻¹ sec⁻¹</td>
<td>203</td>
</tr>
<tr>
<td>sd: .2</td>
<td>261</td>
</tr>
<tr>
<td>t½: 211 sec</td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
</tr>
<tr>
<td>S: .00007M/L</td>
<td>58</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>174</td>
</tr>
<tr>
<td>t: 1500 sec; Ai: .380</td>
<td>232</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>290</td>
</tr>
<tr>
<td>rate: 49.3 x 10⁻¹ sec⁻¹</td>
<td>348</td>
</tr>
<tr>
<td>sd: .2h</td>
<td>406</td>
</tr>
<tr>
<td>t½: 139 sec</td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
</tr>
<tr>
<td>S: .00007M/L</td>
<td>58</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>174</td>
</tr>
<tr>
<td>t: 1500 sec; Ai: .386</td>
<td>232</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>290</td>
</tr>
<tr>
<td>rate: 49.6 x 10⁻¹ sec⁻¹</td>
<td>348</td>
</tr>
<tr>
<td>sd: .4h</td>
<td>406</td>
</tr>
<tr>
<td>t½: 140 sec</td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
</tr>
<tr>
<td>S: .0003M/L</td>
<td>60</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>120</td>
</tr>
<tr>
<td>L: 325 nm</td>
<td>180</td>
</tr>
<tr>
<td>t: 2100 sec; Ai: .761</td>
<td>240</td>
</tr>
<tr>
<td>cc: .9987</td>
<td>300</td>
</tr>
<tr>
<td>rate: 23.3 x 10⁻¹ sec⁻¹</td>
<td>360</td>
</tr>
<tr>
<td>sd: .42</td>
<td>1420</td>
</tr>
<tr>
<td>t½: 297 sec</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE IV

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Time (sec)</th>
<th>Rate (sec(^{-1}))</th>
<th>SD</th>
<th>T₁/₂ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>79.4</td>
<td>0.388</td>
<td>585</td>
</tr>
<tr>
<td>S: 0.0015 M/L</td>
<td>115</td>
<td>662</td>
<td>0.365</td>
<td>584</td>
</tr>
<tr>
<td>L: 340 nm</td>
<td>290</td>
<td>549</td>
<td>0.329</td>
<td></td>
</tr>
<tr>
<td>t(0): 900 sec</td>
<td>580</td>
<td>459</td>
<td>0.279</td>
<td></td>
</tr>
<tr>
<td>cc: 9999</td>
<td>725</td>
<td>388</td>
<td>0.239</td>
<td></td>
</tr>
<tr>
<td>rate: 11.85 x 10(^{-4}) sec(^{-1})</td>
<td>870</td>
<td>329</td>
<td>0.279</td>
<td></td>
</tr>
<tr>
<td>sd: 0.13</td>
<td>1015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 585 sec</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 93.8%      | 0          | 72.3                  | 0.365 | 584        |
| S: 0.0015 M/L | 115        | 607                   | 0.365 | 584        |
| L: 340 nm     | 290        | 514                   | 0.329 |            |
| t(0): 1000 sec| 580        | 433                   | 0.279 |            |
| cc: 9999      | 725        | 365                   | 0.239 |            |
| rate: 11.86 x 10\(^{-4}\) sec\(^{-1}\) | 870 | 309 | 0.255 | |
| sd: 0.06     | 1015       |                       |      |            |
| t₁/₂: 584 sec|            |                       |      |            |

| C: 58.0%      | 0          | 724                  | 0.22  | 133        |
| S: 0.00008 M/L| 58         | 600                   | 0.258 |            |
| L: 330 nm     | 116        | 510                   | 0.258 |            |
| T: 25.3°C     | 174        | 439                   | 0.258 |            |
| t: 1800 sec; A: 24 | 232  | 385                   | 0.258 |            |
| cc: 9999      | 290        | 347                   | 0.258 |            |
| rate: 52.3 x 10\(^{-4}\) sec\(^{-1}\) | 318 | 320 | 0.298 | |
| sd: 0.22     | 406        |                       |      |            |
| t₁/₂: 133 sec|            |                       |      |            |

| C: 58.0%      | 0          | 662                  | 0.258 | 134        |
| S: 0.00008 M/L| 58         | 545                   | 0.258 |            |
| L: 330 nm     | 116        | 458                   | 0.258 |            |
| T: 25.3°C     | 174        | 392                   | 0.258 |            |
| t: 1800 sec; A: 201 | 232  | 341                   | 0.258 |            |
| cc: 9999      | 290        | 303                   | 0.258 |            |
| rate: 51.6 x 10\(^{-4}\) sec\(^{-1}\) | 318 | 320 | 0.258 | |
| sd: 0.25     | 406        |                       |      |            |
| t₁/₂: 134 sec|            |                       |      |            |

<p>| C: 84.6%      | 0          | 441                  | 0.258 | 770        |
| S: 0.0003 M/L | 100        | 401                   | 0.258 |            |
| L: 300 nm     | 200        | 368                   | 0.258 |            |
| T: 25.3°C     | 300        | 338                   | 0.258 |            |
| t(0): 1600 sec| 400        | 301                   | 0.258 |            |
| cc: 9992      | 500        | 283                   | 0.258 |            |
| rate: 9.00 x 10(^{-4}) sec(^{-1}) | 600 | 261 | 0.258 | |
| sd: 12       | 700        |                       |      |            |
| t₁/₂: 770 sec|            |                       |      |            |</p>
<table>
<thead>
<tr>
<th>l-benzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>.600</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .0003M/L</td>
<td>300</td>
<td>.684</td>
</tr>
<tr>
<td>L: 310 nm</td>
<td>600</td>
<td>.392</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>900</td>
<td>.316</td>
</tr>
<tr>
<td>t(G): 1500 sec</td>
<td>1200</td>
<td>.257</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>1500</td>
<td>.210</td>
</tr>
<tr>
<td>rate: 7.10 x 10⁻⁴ sec⁻¹</td>
<td>1800</td>
<td>.165</td>
</tr>
<tr>
<td>sd: .037</td>
<td>2100</td>
<td>.135</td>
</tr>
<tr>
<td>t½: 976 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.186</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>156</td>
<td>1.437</td>
</tr>
<tr>
<td>L: 210 nm</td>
<td>261</td>
<td>1.113</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>360</td>
<td>1.384</td>
</tr>
<tr>
<td>t: 6000 sec; Aï: 1.052</td>
<td>468</td>
<td>1.350</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>569</td>
<td>1.333</td>
</tr>
<tr>
<td>rate: 7.7 x 10⁻⁴ sec⁻¹</td>
<td>673</td>
<td>1.317</td>
</tr>
<tr>
<td>sd: .06</td>
<td>782</td>
<td>1.289</td>
</tr>
<tr>
<td>t½: 895 sec</td>
<td>887</td>
<td>1.274</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>1.050</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>156</td>
<td>1.112</td>
</tr>
<tr>
<td>L: 211 nm</td>
<td>261</td>
<td>1.157</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>360</td>
<td>1.206</td>
</tr>
<tr>
<td>t: 6000 sec; Aï: 1.710</td>
<td>468</td>
<td>1.244</td>
</tr>
<tr>
<td>cc: .9986</td>
<td>569</td>
<td>1.323</td>
</tr>
<tr>
<td>rate: 8.1 x 10⁻⁴ sec⁻¹</td>
<td>673</td>
<td>1.352</td>
</tr>
<tr>
<td>sd: .12</td>
<td>782</td>
<td>1.382</td>
</tr>
<tr>
<td>t½: 855 sec</td>
<td>887</td>
<td>1.382</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>.743</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>58</td>
<td>.629</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.521</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>174</td>
<td>.474</td>
</tr>
<tr>
<td>t: 1500 sec; .269: Aï</td>
<td>232</td>
<td>.329</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.381</td>
</tr>
<tr>
<td>rate: 50.3 x 10⁻⁴ sec⁻¹</td>
<td>3h8</td>
<td>.352</td>
</tr>
<tr>
<td>sd: .3h</td>
<td>406</td>
<td>.331</td>
</tr>
<tr>
<td>t½: 138 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>.663</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>58</td>
<td>.539</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.440</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>174</td>
<td>.365</td>
</tr>
<tr>
<td>t: 1500 sec; .111: Aï</td>
<td>232</td>
<td>.308</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.267</td>
</tr>
<tr>
<td>rate: 49.3 x 10⁻⁴ sec⁻¹</td>
<td>3h8</td>
<td>.238</td>
</tr>
<tr>
<td>sd: .30</td>
<td>406</td>
<td>.211</td>
</tr>
<tr>
<td>t½: 111 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>3.78</td>
</tr>
<tr>
<td>S: 0.0003M/L</td>
<td>300</td>
<td>.313</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.263</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>900</td>
<td>.219</td>
</tr>
<tr>
<td>t(0): 200 sec</td>
<td>1200</td>
<td>1.181</td>
</tr>
<tr>
<td>cc: 99.999</td>
<td>1500</td>
<td>1.156</td>
</tr>
<tr>
<td>rate: 6.04 x 10^-4 sec^-1</td>
<td>1800</td>
<td>1.124</td>
</tr>
<tr>
<td>sd: .067</td>
<td>2100</td>
<td>.107</td>
</tr>
<tr>
<td>t_½: 11168 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 39.6% | 0 | .830 |
| S: 0.0001M/L | 300 | .667 |
| T: 25.3°C | 600 | .539 |
| L: 300 nm | 900 | .441 |
| t(0): 1000 sec | 1200 | .363 |
| cc: 99.999 | 1500 | .292 |
| rate: 6.92 x 10^-4 sec^-1 | 1800 | .238 |
| sd: .03 | 2100 | .192 |
| t_½: 1002 sec |

| C: 39.6% | 0 | .575 |
| S: 0.0001M/L | 120 | .475 |
| T: 35.5°C | 240 | .385 |
| L: 300 nm | 360 | .358 |
| t: 5640 sec; A_1: .100 | 180 | .310 |
| cc: 99.999 | 600 | .272 |
| rate: 16.8 x 10^-4 sec^-1 | 720 | .243 |
| sd: .07 | 840 | .215 |
| t_½: 413 sec |

| C: 39.6% | 0 | 1.197 |
| S: 0.0001M/L | 50 | 1.024 |
| T: 45.6°C | 100 | .876 |
| L: 300 nm | 150 | .743 |
| t: 1800 sec; A_1: .100 | 200 | .630 |
| cc: 99.998 | 250 | .541 |
| rate: 37.1 x 10^-4 sec^-1 | 300 | .466 |
| sd: .24 | 350 | .401 |
| t_½: 187 sec |

<p>| C: 53.5% | 0 | 1.049 |
| S: 0.0001M/L | 58 | .934 |
| T: 25.3°C | 116 | .799 |
| L: 300 nm | 174 | .704 |
| t: 2100 sec; A_1: .142 | 232 | .624 |
| cc: 99.999 | 290 | .556 |
| rate: 27.0 x 10^-4 sec^-1 | 348 | .499 |
| sd: .13 | 493 | .379 |
| t_½: 257 sec |</p>
<table>
<thead>
<tr>
<th>C: 53.5%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.132</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>58</td>
<td>.977</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.850</td>
</tr>
<tr>
<td>t: 2400 sec; A_i: .089</td>
<td>232</td>
<td>.742</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.654</td>
</tr>
<tr>
<td>rate: 25.9 x 10^{-4} sec^{-1}</td>
<td>3h8</td>
<td>.576</td>
</tr>
<tr>
<td>sd: .135</td>
<td>493</td>
<td>.512</td>
</tr>
<tr>
<td>t_1/2: 268 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 62.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.138</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>20</td>
<td>.987</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>40</td>
<td>.831</td>
</tr>
<tr>
<td>t: 700 sec; A_i: .179</td>
<td>80</td>
<td>.709</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>100</td>
<td>.610</td>
</tr>
<tr>
<td>rate: 103. x 10^{-4} sec^{-1}</td>
<td>1h0</td>
<td>.534</td>
</tr>
<tr>
<td>sd: .3h</td>
<td>200</td>
<td>.466</td>
</tr>
<tr>
<td>t_1/2: 67 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 66.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.139</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>20</td>
<td>.952</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>40</td>
<td>.811</td>
</tr>
<tr>
<td>t: 44 sec; A_i: .362</td>
<td>80</td>
<td>.666</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>100</td>
<td>.579</td>
</tr>
<tr>
<td>rate: 157.4 x 10^{-4} sec^{-1}</td>
<td>1h0</td>
<td>.523</td>
</tr>
<tr>
<td>sd: .87</td>
<td>1h0</td>
<td>.482</td>
</tr>
<tr>
<td>t_1/2: 44 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 66.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.138</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>20</td>
<td>.961</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>40</td>
<td>.807</td>
</tr>
<tr>
<td>t: 650 sec; A_i: .329</td>
<td>80</td>
<td>.698</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>100</td>
<td>.601</td>
</tr>
<tr>
<td>rate: 158.7 x 10^{-4} sec^{-1}</td>
<td>1h0</td>
<td>.526</td>
</tr>
<tr>
<td>sd: 1.27</td>
<td>1h0</td>
<td>.411</td>
</tr>
<tr>
<td>t_1/2: 65 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>68.0%</td>
<td>Time</td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>S</td>
<td>.0001M/L</td>
<td>0</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>20</td>
</tr>
<tr>
<td>L</td>
<td>300 nm</td>
<td>60</td>
</tr>
<tr>
<td>t</td>
<td>450 sec; Ai: .322</td>
<td>80</td>
</tr>
<tr>
<td>cc</td>
<td>.9998</td>
<td>100</td>
</tr>
<tr>
<td>rate:</td>
<td>195.0 x 10^-4 sec^-1</td>
<td>120</td>
</tr>
<tr>
<td>sd:</td>
<td>1.3</td>
<td>140</td>
</tr>
<tr>
<td>t_1/2:</td>
<td>35.5 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>68.0%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>.0001M/L</td>
<td>0</td>
<td>1.144</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>20</td>
<td>.879</td>
</tr>
<tr>
<td>L</td>
<td>300 nm</td>
<td>60</td>
<td>.711</td>
</tr>
<tr>
<td>t</td>
<td>700 sec; Ai: .372</td>
<td>80</td>
<td>.599</td>
</tr>
<tr>
<td>cc</td>
<td>.9998</td>
<td>100</td>
<td>.528</td>
</tr>
<tr>
<td>rate:</td>
<td>172.8 x 10^-4 sec^-1</td>
<td>120</td>
<td>.479</td>
</tr>
<tr>
<td>sd:</td>
<td>1.0</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>t_1/2:</td>
<td>40.1 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>68.0%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>.00008M/L</td>
<td>15</td>
<td>1.138</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>30</td>
<td>.883</td>
</tr>
<tr>
<td>L</td>
<td>300 nm</td>
<td>60</td>
<td>.697</td>
</tr>
<tr>
<td>t</td>
<td>450 sec; Ai: .066</td>
<td>60</td>
<td>.552</td>
</tr>
<tr>
<td>cc</td>
<td>.9999</td>
<td>75</td>
<td>.528</td>
</tr>
<tr>
<td>rate:</td>
<td>174.5 x 10^-4 sec^-1</td>
<td>90</td>
<td>.351</td>
</tr>
<tr>
<td>sd:</td>
<td>.54</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>t_1/2:</td>
<td>39.7 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>70.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>.0001M/L</td>
<td>10</td>
<td>1.070</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>40</td>
<td>.816</td>
</tr>
<tr>
<td>L</td>
<td>300 nm</td>
<td>60</td>
<td>.665</td>
</tr>
<tr>
<td>t</td>
<td>700 sec; Ai: .375</td>
<td>80</td>
<td>.566</td>
</tr>
<tr>
<td>cc</td>
<td>.9984</td>
<td>100</td>
<td>.501</td>
</tr>
<tr>
<td>rate:</td>
<td>201.7 x 10^-4 sec^-1</td>
<td>120</td>
<td>.457</td>
</tr>
<tr>
<td>sd:</td>
<td>1.08</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>t_1/2:</td>
<td>31.4 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>70.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>.0001M/L</td>
<td>20</td>
<td>1.045</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>40</td>
<td>.901</td>
</tr>
<tr>
<td>L</td>
<td>300 nm</td>
<td>60</td>
<td>.716</td>
</tr>
<tr>
<td>t</td>
<td>650 sec; Ai: .365</td>
<td>80</td>
<td>.592</td>
</tr>
<tr>
<td>cc</td>
<td>.9995</td>
<td>100</td>
<td>.512</td>
</tr>
<tr>
<td>rate:</td>
<td>209.8 x 10^-4 sec^-1</td>
<td>120</td>
<td>.461</td>
</tr>
<tr>
<td>sd:</td>
<td>2.23</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>t_1/2:</td>
<td>33.0 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.079</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.813</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.688</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.586</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>.516</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.467</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>.434</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h0</td>
<td>.412</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3h1</td>
<td>.371</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.976</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.766</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.611</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.561</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>.509</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.473</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>.442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h0</td>
<td>.433</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.0</td>
<td>.403</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.784</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.640</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.531</td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>.481</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.442</td>
<td></td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>.413</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1h0</td>
<td>.404</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.8</td>
<td>.383</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.881</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>.793</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>.724</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.693</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.674</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>.621</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>.573</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9h</td>
<td>.543</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>.929</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>.840</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>.772</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100</td>
<td>.732</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.665</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>.618</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>.578</td>
<td></td>
<td></td>
</tr>
<tr>
<td>103.6</td>
<td>.548</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>80.9%</td>
<td>0</td>
<td>0.525</td>
<td></td>
</tr>
<tr>
<td>91.2%</td>
<td>0</td>
<td>0.696</td>
<td></td>
</tr>
<tr>
<td>92.1%</td>
<td>0</td>
<td>0.593</td>
<td></td>
</tr>
<tr>
<td>96.3%</td>
<td>0</td>
<td>0.909</td>
<td></td>
</tr>
<tr>
<td>96.3%</td>
<td>0</td>
<td>0.726</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S</th>
<th>0.0002M/L</th>
<th>0.0002M/L</th>
<th>0.0002M/L</th>
<th>0.0003M/L</th>
<th>0.0003M/L</th>
<th>0.0003M/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L</td>
<td>310 nm</td>
<td>310 nm</td>
<td>310 nm</td>
<td>310 nm</td>
<td>310 nm</td>
<td>310 nm</td>
</tr>
<tr>
<td>t(0)</td>
<td>900 sec</td>
<td>300 sec</td>
<td>2100 sec</td>
<td>500 sec</td>
<td>800 sec</td>
<td>800 sec</td>
</tr>
<tr>
<td>cc</td>
<td>0.9989</td>
<td>0.9998</td>
<td>0.9998</td>
<td>0.9998</td>
<td>0.9998</td>
<td>0.9998</td>
</tr>
<tr>
<td>rate</td>
<td>$1.49 \times 10^{-4}$ sec$^{-1}$</td>
<td>$5.63 \times 10^{-4}$ sec$^{-1}$</td>
<td>$5.63 \times 10^{-4}$ sec$^{-1}$</td>
<td>$9.13 \times 10^{-4}$ sec$^{-1}$</td>
<td>$9.13 \times 10^{-4}$ sec$^{-1}$</td>
<td>$9.13 \times 10^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>sd</td>
<td>0.25</td>
<td>0.04</td>
<td>0.11</td>
<td>0.11</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>t$_{1/2}$</td>
<td>465 sec</td>
<td>1232 sec</td>
<td>1218 sec</td>
<td>759 sec</td>
<td>715 sec</td>
<td>715 sec</td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.199</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1.063</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.961</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>.880</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.817</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>.768</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.731</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>.703</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C: 97.9%  
S: .0003M/L  
T: 25.3°C  
L: 310 nm  
t: 1000 sec; Ai: .614  
cc: .9999  
rate: 17.94 x 10^{-4} sec^{-1}  
sd: .07  
t\(_\frac{1}{2}\): 386 sec

C: 98.9%  
S: .0003M/L  
T: 25.3°C  
L: 310 nm  
t: 2600 sec; Ai: .262  
cc: .9997  
rate: 21.66 x 10^{-4} sec^{-1}  
sd: .19  
t\(_\frac{1}{2}\): 320 sec

C: 98.9%  
S: .0003M/L  
T: 25.3°C  
L: 310 nm  
t(0): 600 sec  
cc: .9997  
rate: 22.40 x 10^{-4} sec^{-1}  
sd: .18  
t\(_\frac{1}{2}\): 310 sec
<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-p-fluorobenzoyl-2-thiohydantoin</td>
<td>0.925</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.955</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.925</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.936</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.790</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.732</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
</tbody>
</table>

**Table 6**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.28</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>2.37</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>2.15</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>1.93</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>1.59</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
</tbody>
</table>

**Table 6 continued**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.80</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>3.27</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>1.93</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>1.59</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.90</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
</tbody>
</table>

**Table 6 continued**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.865</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.750</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.661</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.590</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.532</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.442</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
</tbody>
</table>

**Table 6 continued**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.314</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.276</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.216</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.213</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.190</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.143</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
</tbody>
</table>

**Table 6 continued**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.314</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.276</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.216</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.213</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.190</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td></td>
<td>0.143</td>
<td>5.26 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td>C</td>
<td>S</td>
<td>T</td>
</tr>
<tr>
<td>-----------</td>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>93.8%</td>
<td>.0001M/L</td>
<td>25.3°C</td>
</tr>
<tr>
<td>58.0%</td>
<td>.0001M/L</td>
<td>25.3°C</td>
</tr>
<tr>
<td>58.0%</td>
<td>.0001M/L</td>
<td>25.3°C</td>
</tr>
<tr>
<td>l-p-chlorobenzoyl-2-thiohydantoin</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>1.170</td>
</tr>
<tr>
<td>S: .00009M/L</td>
<td>203</td>
<td>1.129</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>118</td>
<td>1.108</td>
</tr>
<tr>
<td>L: 245 nm</td>
<td>649</td>
<td>1.968</td>
</tr>
<tr>
<td>t: 15000 sec; A1: .570</td>
<td>853</td>
<td>1.040</td>
</tr>
<tr>
<td>cc: .9973</td>
<td>1140</td>
<td>1.008</td>
</tr>
<tr>
<td>rate: 2.84 x 10⁻⁴ sec⁻¹</td>
<td>1520</td>
<td>.963</td>
</tr>
<tr>
<td>sd: .05</td>
<td>2247</td>
<td>.886</td>
</tr>
<tr>
<td>t½: 2130 sec</td>
<td>2870</td>
<td>.836</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>104</td>
<td>1.252</td>
</tr>
<tr>
<td>S: .00009M/L</td>
<td>303</td>
<td>1.217</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>530</td>
<td>1.174</td>
</tr>
<tr>
<td>L: 240 nm</td>
<td>753</td>
<td>1.150</td>
</tr>
<tr>
<td>t: 15000 sec; A1: .63</td>
<td>961</td>
<td>1.117</td>
</tr>
<tr>
<td>cc: .9975</td>
<td>1331</td>
<td>1.073</td>
</tr>
<tr>
<td>rate: 2.89 x 10⁻⁴ sec⁻¹</td>
<td>1768</td>
<td>1.016</td>
</tr>
<tr>
<td>sd: .06</td>
<td>2247</td>
<td>.972</td>
</tr>
<tr>
<td>t½: 2390 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.782</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>58</td>
<td>.700</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.631</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>174</td>
<td>.579</td>
</tr>
<tr>
<td>t: 1800 sec; A1: .341</td>
<td>232</td>
<td>.538</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>290</td>
<td>.501</td>
</tr>
<tr>
<td>rate: 35.83 x 10⁻⁴ sec⁻¹</td>
<td>348</td>
<td>.469</td>
</tr>
<tr>
<td>sd: .11</td>
<td>406</td>
<td>.446</td>
</tr>
<tr>
<td>t½: 193 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.840</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>58</td>
<td>.751</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.680</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>174</td>
<td>.621</td>
</tr>
<tr>
<td>t: 2100 sec; A1: .370</td>
<td>232</td>
<td>.573</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.537</td>
</tr>
<tr>
<td>rate: 35.25 x 10⁻⁴ sec⁻¹</td>
<td>348</td>
<td>.504</td>
</tr>
<tr>
<td>sd: .20</td>
<td>406</td>
<td>.480</td>
</tr>
<tr>
<td>t½: 197 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.123</td>
</tr>
<tr>
<td>S: .0003M/L</td>
<td>300</td>
<td>.373</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.324</td>
</tr>
<tr>
<td>L: 315 nm</td>
<td>900</td>
<td>.288</td>
</tr>
<tr>
<td>t(G): 900 sec</td>
<td>1200</td>
<td>.254</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>1500</td>
<td>.222</td>
</tr>
<tr>
<td>rate: 4.28 x 10⁻⁴ sec⁻¹</td>
<td>1800</td>
<td>.197</td>
</tr>
<tr>
<td>sd: .026</td>
<td>2100</td>
<td>.171</td>
</tr>
<tr>
<td>t½: 1619 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 39.6%</td>
<td>Time</td>
<td>da</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.908</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>.768</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>600</td>
<td>.616</td>
</tr>
<tr>
<td>t(0): 1400 sec</td>
<td>900</td>
<td>.54u</td>
</tr>
<tr>
<td>cc: .9996</td>
<td>1200</td>
<td>.466</td>
</tr>
<tr>
<td>rate: 5.34 x 10^{-4} sec^{-1}</td>
<td>1500</td>
<td>.403</td>
</tr>
<tr>
<td>sd: .05</td>
<td>1800</td>
<td>.315</td>
</tr>
<tr>
<td>t½: 1297 sec</td>
<td>2100</td>
<td>.294</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 62.4%</th>
<th></th>
<th>1.384</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td></td>
<td>1.126</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td></td>
<td>.928</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td></td>
<td>.773</td>
</tr>
<tr>
<td>t: 1300 sec; A1: .055</td>
<td></td>
<td>.651</td>
</tr>
<tr>
<td>rate: 66.5 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.54u</td>
</tr>
<tr>
<td>cc: .9999</td>
<td></td>
<td>.452</td>
</tr>
<tr>
<td>sd: .35</td>
<td></td>
<td>.380</td>
</tr>
<tr>
<td>t½: 104 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 66.4%</th>
<th></th>
<th>1.230</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td></td>
<td>.990</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td></td>
<td>.803</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td></td>
<td>.658</td>
</tr>
<tr>
<td>t: 800 sec; A1: .033</td>
<td></td>
<td>.510</td>
</tr>
<tr>
<td>rate: 106.9 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.443</td>
</tr>
<tr>
<td>cc: .9999</td>
<td></td>
<td>.361</td>
</tr>
<tr>
<td>sd: .36</td>
<td></td>
<td>.300</td>
</tr>
<tr>
<td>t½: 61.7 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 68.0%</th>
<th></th>
<th>1.162</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td></td>
<td>.903</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td></td>
<td>.712</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td></td>
<td>.561</td>
</tr>
<tr>
<td>t: 800 sec; A1: .044</td>
<td></td>
<td>.447</td>
</tr>
<tr>
<td>rate: 126.0 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.391</td>
</tr>
<tr>
<td>sd: .498</td>
<td></td>
<td>.233</td>
</tr>
<tr>
<td>t½: 55 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 70.1%</th>
<th></th>
<th>1.144</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td></td>
<td>.855</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td></td>
<td>.656</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td></td>
<td>.503</td>
</tr>
<tr>
<td>t: 1100 sec; A1: .092</td>
<td></td>
<td>.396</td>
</tr>
<tr>
<td>rate: 151.0 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.319</td>
</tr>
<tr>
<td>sd: .94</td>
<td></td>
<td>.261</td>
</tr>
<tr>
<td>t½: 45.9 sec</td>
<td></td>
<td>.219</td>
</tr>
<tr>
<td>C</td>
<td>S</td>
<td>T</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>72.7%</td>
<td></td>
<td>25.3°C</td>
</tr>
<tr>
<td>74.9%</td>
<td>1.309</td>
<td>290 nm</td>
</tr>
<tr>
<td>78.1%</td>
<td></td>
<td>310 nm</td>
</tr>
<tr>
<td>80.9%</td>
<td>25.3°C</td>
<td>315 mm</td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.690</td>
<td></td>
</tr>
<tr>
<td>1105</td>
<td>.670</td>
<td></td>
</tr>
<tr>
<td>1826</td>
<td>.650</td>
<td></td>
</tr>
<tr>
<td>2663</td>
<td>.620</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.580</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.550</td>
<td></td>
</tr>
<tr>
<td>3200 sec</td>
<td>.525</td>
<td></td>
</tr>
<tr>
<td>4580</td>
<td>.515</td>
<td></td>
</tr>
<tr>
<td>5880</td>
<td>.450</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.525</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.500</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.490</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.470</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.420</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.370</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.315</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>.330</td>
<td></td>
</tr>
<tr>
<td>7200</td>
<td>.265</td>
<td></td>
</tr>
<tr>
<td>1458</td>
<td>.220</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>.182</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.182</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.136</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.123</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.096</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.070</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.050</td>
<td></td>
</tr>
<tr>
<td>2800 sec</td>
<td>.030</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE IX**

<table>
<thead>
<tr>
<th>1-p-bromobenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>.690</td>
</tr>
<tr>
<td>S: .00005M/L</td>
<td>143</td>
<td>.670</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>386</td>
<td>.650</td>
</tr>
<tr>
<td>L: 215 mm</td>
<td>721</td>
<td>.620</td>
</tr>
<tr>
<td>t: 16000 sec; A1: .22</td>
<td>1105</td>
<td>.580</td>
</tr>
<tr>
<td>rate: 2.6 x 10^-4 sec^-1</td>
<td>1826</td>
<td>.550</td>
</tr>
<tr>
<td>sd: .1</td>
<td>2663</td>
<td>.525</td>
</tr>
<tr>
<td>t_1/2: 2650 sec</td>
<td></td>
<td>.450</td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>.525</td>
</tr>
<tr>
<td>S: .00005M/L</td>
<td>300</td>
<td>.500</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.490</td>
</tr>
<tr>
<td>L: 215 mm</td>
<td>900</td>
<td>.470</td>
</tr>
<tr>
<td>t: 20000 sec; A1: .270</td>
<td>2100</td>
<td>.420</td>
</tr>
<tr>
<td>rate: 2.47 x 10^-4 sec^-1</td>
<td>5880</td>
<td>.370</td>
</tr>
<tr>
<td>sd: .07</td>
<td>8700</td>
<td>.315</td>
</tr>
<tr>
<td>t_1/2: 2800 sec</td>
<td></td>
<td>.330</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.714</td>
</tr>
<tr>
<td>S: .00007M/L</td>
<td>58</td>
<td>.630</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.560</td>
</tr>
<tr>
<td>L: 288 mm</td>
<td>174</td>
<td>.502</td>
</tr>
<tr>
<td>t: 2100 sec; A1: .252</td>
<td>232</td>
<td>.458</td>
</tr>
<tr>
<td>rate: 36.6 x 10^-4 sec^-1</td>
<td>318</td>
<td>.419</td>
</tr>
<tr>
<td>sd: .47</td>
<td>406</td>
<td>.381</td>
</tr>
<tr>
<td>t_1/2: 189 sec</td>
<td></td>
<td>.356</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.821</td>
</tr>
<tr>
<td>S: .00007M/L</td>
<td>58</td>
<td>.723</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.618</td>
</tr>
<tr>
<td>L: 288 mm</td>
<td>174</td>
<td>.582</td>
</tr>
<tr>
<td>t: 2100 sec; A1: .299</td>
<td>232</td>
<td>.521</td>
</tr>
<tr>
<td>rate: 34.5 x 10^-4 sec^-1</td>
<td>318</td>
<td>.487</td>
</tr>
<tr>
<td>sd: .20</td>
<td>406</td>
<td>.457</td>
</tr>
<tr>
<td>t_1/2: 201 sec</td>
<td></td>
<td>.427</td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.271</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>300</td>
<td>.239</td>
</tr>
<tr>
<td>L: 320 mm</td>
<td>600</td>
<td>.211</td>
</tr>
<tr>
<td>t(0): 600 sec</td>
<td>900</td>
<td>.190</td>
</tr>
<tr>
<td>rate: 3.76 x 10^-4 sec^-1</td>
<td>1200</td>
<td>.168</td>
</tr>
<tr>
<td>sd: .019</td>
<td>1500</td>
<td>.151</td>
</tr>
<tr>
<td>t_1/2: 1844 sec</td>
<td></td>
<td>.136</td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.123</td>
</tr>
<tr>
<td>1-p-iodobenzoyl-2-thiohydantoin</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.643</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>58</td>
<td>.560</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.495</td>
</tr>
<tr>
<td>L: 310 nm</td>
<td>174</td>
<td>.433</td>
</tr>
<tr>
<td>t: 2400 sec; Ai: .191</td>
<td>232</td>
<td>.388</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.319</td>
</tr>
<tr>
<td>rate: 37.1 x 10⁻⁴ sec⁻¹</td>
<td>348</td>
<td>.300</td>
</tr>
<tr>
<td>sd: .27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 187 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.687</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>58</td>
<td>.601</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.537</td>
</tr>
<tr>
<td>L: 310 nm</td>
<td>174</td>
<td>.478</td>
</tr>
<tr>
<td>t: 1800 sec; Ai: .237</td>
<td>232</td>
<td>.431</td>
</tr>
<tr>
<td>cc: .9993</td>
<td>290</td>
<td>.392</td>
</tr>
<tr>
<td>rate: 35.9 x 10⁻⁴ sec⁻¹</td>
<td>348</td>
<td>.360</td>
</tr>
<tr>
<td>sd: .18</td>
<td></td>
<td>.338</td>
</tr>
<tr>
<td>t₁/₂: 193 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.287</td>
</tr>
<tr>
<td>S: .0003 M/L</td>
<td>300</td>
<td>.264</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.236</td>
</tr>
<tr>
<td>L: 310 nm</td>
<td>900</td>
<td>.210</td>
</tr>
<tr>
<td>t(G): 800 sec</td>
<td>1200</td>
<td>.183</td>
</tr>
<tr>
<td>cc: .9985</td>
<td>1500</td>
<td>.159</td>
</tr>
<tr>
<td>rate: 4.0 x 10⁻⁴ sec⁻¹</td>
<td>1800</td>
<td>.183</td>
</tr>
<tr>
<td>sd: .08</td>
<td>2100</td>
<td>.127</td>
</tr>
<tr>
<td>t₁/₂: 1730 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Time</td>
<td>(dA)</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td>1-m-chlorobenzoyl-2-thiohydantoin</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>.440</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>1103</td>
<td>.365</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>2167</td>
<td>.320</td>
</tr>
<tr>
<td>L: 218 nm</td>
<td>3420</td>
<td>.275</td>
</tr>
<tr>
<td>(t(0)): 3000 sec</td>
<td>4765</td>
<td>.225</td>
</tr>
<tr>
<td>cc: .9991</td>
<td>6978</td>
<td>.165</td>
</tr>
<tr>
<td>rate: (1.07 \times 10^{-4}) sec(^{-1})</td>
<td>9092</td>
<td>.115</td>
</tr>
<tr>
<td>sd: .08</td>
<td>11481</td>
<td>.080</td>
</tr>
<tr>
<td>(t_\frac{1}{2}): 6640 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 93.8%</td>
<td>0</td>
<td>.355</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>658</td>
<td>.330</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>1741</td>
<td>.300</td>
</tr>
<tr>
<td>L: 218 nm</td>
<td>2789</td>
<td>.265</td>
</tr>
<tr>
<td>(t(0)): 2500 sec</td>
<td>4165</td>
<td>.215</td>
</tr>
<tr>
<td>cc: .9902</td>
<td>5431</td>
<td>.180</td>
</tr>
<tr>
<td>rate: (1.04 \times 10^{-4}) sec(^{-1})</td>
<td>6261</td>
<td>.110</td>
</tr>
<tr>
<td>sd: .1</td>
<td>8133</td>
<td>.105</td>
</tr>
<tr>
<td>(t_\frac{1}{2}): 6640 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.375</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>58</td>
<td>.731</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.656</td>
</tr>
<tr>
<td>L: 303 nm</td>
<td>174</td>
<td>.593</td>
</tr>
<tr>
<td>(t): 1800 sec; (A1): .283</td>
<td>232</td>
<td>.540</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>290</td>
<td>.498</td>
</tr>
<tr>
<td>rate: (32.76 \times 10^{-4}) sec(^{-1})</td>
<td>348</td>
<td>.460</td>
</tr>
<tr>
<td>sd: .15</td>
<td>406</td>
<td>.427</td>
</tr>
<tr>
<td>(t_\frac{1}{2}): 212 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.876</td>
</tr>
<tr>
<td>S: .0001 M/L</td>
<td>58</td>
<td>.766</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.688</td>
</tr>
<tr>
<td>L: 303 nm</td>
<td>174</td>
<td>.621</td>
</tr>
<tr>
<td>(t): 2100 sec; (A1): .300</td>
<td>232</td>
<td>.566</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>290</td>
<td>.520</td>
</tr>
<tr>
<td>rate: (32.48 \times 10^{-4}) sec(^{-1})</td>
<td>348</td>
<td>.482</td>
</tr>
<tr>
<td>sd: .19</td>
<td>406</td>
<td>.451</td>
</tr>
<tr>
<td>(t_\frac{1}{2}): 213 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.367</td>
</tr>
<tr>
<td>S: .0003 M/L</td>
<td>300</td>
<td>.322</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.282</td>
</tr>
<tr>
<td>L: 295 nm</td>
<td>900</td>
<td>.252</td>
</tr>
<tr>
<td>(t(0)): 1500 sec</td>
<td>1200</td>
<td>.224</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>1500</td>
<td>.197</td>
</tr>
<tr>
<td>rate: (4.10 \times 10^{-4}) sec(^{-1})</td>
<td>1800</td>
<td>.175</td>
</tr>
<tr>
<td>sd: .025</td>
<td>2100</td>
<td>.154</td>
</tr>
<tr>
<td>(t_\frac{1}{2}): 1692 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>l-m-bromobenzoyle-2-thiohydantoin</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>-----------------------------------</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>.976</td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>58</td>
<td>.865</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.778</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>174</td>
<td>.706</td>
</tr>
<tr>
<td>t: 2400 sec; Ai: .358</td>
<td>232</td>
<td>.649</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>348</td>
<td>.599</td>
</tr>
<tr>
<td>rate: 31.73 x 10^-4 sec^-1</td>
<td></td>
<td>.561</td>
</tr>
<tr>
<td>sd: .21</td>
<td>406</td>
<td>.528</td>
</tr>
<tr>
<td>t₁/₂: 218 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>1.051</td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>58</td>
<td>.922</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>116</td>
<td>.821</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>174</td>
<td>.741</td>
</tr>
<tr>
<td>t: 2400 sec; Ai: .340</td>
<td>232</td>
<td>.672</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>348</td>
<td>.618</td>
</tr>
<tr>
<td>rate: 31.52 x 10^-4 sec^-1</td>
<td></td>
<td>.573</td>
</tr>
<tr>
<td>sd: .30</td>
<td>406</td>
<td>.538</td>
</tr>
<tr>
<td>t₁/₂: 220 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 84.6%</td>
<td>0</td>
<td>.264</td>
</tr>
<tr>
<td>S: .0003M/L</td>
<td>300</td>
<td>.238</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.207</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>900</td>
<td>.192</td>
</tr>
<tr>
<td>t: 1000 sec</td>
<td>1200</td>
<td>.164</td>
</tr>
<tr>
<td>cc: .9980</td>
<td>1500</td>
<td>.152</td>
</tr>
<tr>
<td>rate: 3.70 x 10^-4 sec^-1</td>
<td>1800</td>
<td>.138</td>
</tr>
<tr>
<td>sd: .08</td>
<td>2100</td>
<td>.120</td>
</tr>
<tr>
<td>t₁/₂: 1873 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE XIII

1-m-trifluoromethylbenzoyl-2-thiodydantoin

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.790</td>
</tr>
<tr>
<td>1698</td>
<td>.810</td>
</tr>
<tr>
<td>6577</td>
<td>.863</td>
</tr>
<tr>
<td>9397</td>
<td>.880</td>
</tr>
<tr>
<td>21757</td>
<td>.920</td>
</tr>
<tr>
<td>28597</td>
<td>.970</td>
</tr>
<tr>
<td>16170</td>
<td>.990</td>
</tr>
</tbody>
</table>

C: 93.8%
S: .000350M/L
T: 25.3°C
L: 222 mm
t: 86100 sec; Ai: 1.080
cc: .9975
rate: \( 1.14 \times 10^{-4} \) sec\(^{-1} \)
sd: .007
\( t_\frac{1}{2} \): 16170 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.820</td>
</tr>
<tr>
<td>3372</td>
<td>.840</td>
</tr>
<tr>
<td>5167</td>
<td>.870</td>
</tr>
<tr>
<td>12667</td>
<td>.920</td>
</tr>
<tr>
<td>20767</td>
<td>.980</td>
</tr>
<tr>
<td>27187</td>
<td>1.005</td>
</tr>
</tbody>
</table>

C: 93.8%
S: .000051M/L
T: 25.3°C
L: 222 mm
t: 87000 sec; Ai: 1.080
cc: .9961
rate: \( 1.17 \times 10^{-4} \) sec\(^{-1} \)
sd: .01
\( t_\frac{1}{2} \): 11680 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.918</td>
</tr>
<tr>
<td>58</td>
<td>.831</td>
</tr>
<tr>
<td>116</td>
<td>.756</td>
</tr>
<tr>
<td>174</td>
<td>.696</td>
</tr>
<tr>
<td>12667</td>
<td>.612</td>
</tr>
<tr>
<td>20767</td>
<td>.598</td>
</tr>
<tr>
<td>27187</td>
<td>.560</td>
</tr>
<tr>
<td>5167</td>
<td>.526</td>
</tr>
</tbody>
</table>

C: 58.0%
S: .00007M/L
T: 25.3°C
L: 288 nm
t: 2400 sec; Ai: .319
cc: .9999
rate: \( 26.08 \times 10^{-4} \) sec\(^{-1} \)
sd: .11
\( t_\frac{1}{2} \): 266 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.100</td>
</tr>
<tr>
<td>58</td>
<td>.981</td>
</tr>
<tr>
<td>116</td>
<td>.885</td>
</tr>
<tr>
<td>174</td>
<td>.804</td>
</tr>
<tr>
<td>232</td>
<td>.740</td>
</tr>
<tr>
<td>290</td>
<td>.683</td>
</tr>
<tr>
<td>318</td>
<td>.638</td>
</tr>
<tr>
<td>406</td>
<td>.596</td>
</tr>
</tbody>
</table>

C: 58.0%
S: .00007M/L
T: 25.3°C
L: 288 nm
t: 2400 sec; Ai: .329
cc: .9999
rate: \( 25.98 \times 10^{-4} \) sec\(^{-1} \)
sd: .29
\( t_\frac{1}{2} \): 267 sec

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.100</td>
</tr>
<tr>
<td>58</td>
<td>.981</td>
</tr>
<tr>
<td>116</td>
<td>.885</td>
</tr>
<tr>
<td>174</td>
<td>.804</td>
</tr>
<tr>
<td>232</td>
<td>.740</td>
</tr>
<tr>
<td>290</td>
<td>.683</td>
</tr>
<tr>
<td>318</td>
<td>.638</td>
</tr>
<tr>
<td>406</td>
<td>.596</td>
</tr>
</tbody>
</table>

C: 39.6%
S: .00007M/L
T: 25.3°C
L: 288 nm
t(0): 450 sec
cc: .9999
rate: \( 1.14 \times 10^{-4} \) sec\(^{-1} \)
sd: .017
\( t_\frac{1}{2} \): 1563 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.826</td>
</tr>
<tr>
<td>100</td>
<td>.716</td>
</tr>
<tr>
<td>200</td>
<td>.622</td>
</tr>
<tr>
<td>300</td>
<td>.517</td>
</tr>
<tr>
<td>400</td>
<td>.472</td>
</tr>
<tr>
<td>500</td>
<td>.411</td>
</tr>
<tr>
<td>600</td>
<td>.358</td>
</tr>
<tr>
<td>700</td>
<td>.309</td>
</tr>
<tr>
<td>496</td>
<td>.309</td>
</tr>
<tr>
<td>1000</td>
<td>.101</td>
</tr>
<tr>
<td>150</td>
<td>.525</td>
</tr>
<tr>
<td>180</td>
<td>.461</td>
</tr>
<tr>
<td>210</td>
<td>.401</td>
</tr>
<tr>
<td>1750</td>
<td>1.012</td>
</tr>
<tr>
<td>210</td>
<td>1.008</td>
</tr>
<tr>
<td>260</td>
<td>.815</td>
</tr>
<tr>
<td>310</td>
<td>.685</td>
</tr>
<tr>
<td>360</td>
<td>.599</td>
</tr>
<tr>
<td>410</td>
<td>.525</td>
</tr>
<tr>
<td>460</td>
<td>.461</td>
</tr>
<tr>
<td>510</td>
<td>.401</td>
</tr>
<tr>
<td>560</td>
<td>1.296</td>
</tr>
<tr>
<td>610</td>
<td>1.098</td>
</tr>
<tr>
<td>660</td>
<td>.815</td>
</tr>
<tr>
<td>710</td>
<td>.685</td>
</tr>
<tr>
<td>760</td>
<td>.599</td>
</tr>
<tr>
<td>810</td>
<td>.525</td>
</tr>
<tr>
<td>860</td>
<td>.461</td>
</tr>
<tr>
<td>910</td>
<td>.401</td>
</tr>
<tr>
<td>960</td>
<td>1.296</td>
</tr>
<tr>
<td>1010</td>
<td>1.098</td>
</tr>
<tr>
<td>1060</td>
<td>.815</td>
</tr>
<tr>
<td>1110</td>
<td>.685</td>
</tr>
<tr>
<td>1160</td>
<td>.599</td>
</tr>
<tr>
<td>1210</td>
<td>.525</td>
</tr>
<tr>
<td>1260</td>
<td>.461</td>
</tr>
<tr>
<td>1310</td>
<td>.401</td>
</tr>
<tr>
<td>1360</td>
<td>1.296</td>
</tr>
<tr>
<td>1410</td>
<td>1.098</td>
</tr>
</tbody>
</table>

**C**: 53.5%

**S**: .00007M/L

**T**: 25.3°C

**L**: 288 nm

**t(0)**: 350 sec

**cc**: .9999

**rate**: $1.4 \times 10^{-3}$ sec$^{-1}$

**sd**: .056

**$t_{1/2}$**: 496 sec

---

**C**: 62.1%

**S**: .00008M/L

**T**: 25.3°C

**L**: 290 nm

**t**: 1750 sec; **Ai**: .020

**cc**: .9999

**rate**: $4.5 \times 10^{-3}$ sec$^{-1}$

**sd**: .21

**$t_{1/2}$**: 153 sec

---

**C**: 66.1%

**S**: .00008M/L

**T**: 290 nm

**t**: 1200 sec; **Ai**: .031

**cc**: .9998

**rate**: $7.6 \times 10^{-3}$ sec$^{-1}$

**sd**: .55

**$t_{1/2}$**: 90.3 sec

---

**C**: 70.1%

**S**: .00008M/L

**T**: 290 nm

**t**: 900 sec; **Ai**: .022

**cc**: .9998

**rate**: $11.8 \times 10^{-4}$ sec$^{-1}$

**sd**: .66

**$t_{1/2}$**: 58.6 sec

---

**C**: 72.7%

**S**: .0001M/L

**T**: 290 nm

**t**: 900 sec; **Ai**: .052

**cc**: .9998

**rate**: $1.1 \times 10^{-3}$ sec$^{-1}$

**sd**: 1.06

**$t_{1/2}$**: 49 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.938</td>
</tr>
<tr>
<td>20</td>
<td>.716</td>
</tr>
<tr>
<td>40</td>
<td>.549</td>
</tr>
<tr>
<td>60</td>
<td>.419</td>
</tr>
<tr>
<td>80</td>
<td>.321</td>
</tr>
<tr>
<td>100</td>
<td>.247</td>
</tr>
<tr>
<td>120</td>
<td>.191</td>
</tr>
<tr>
<td>140</td>
<td>.145</td>
</tr>
<tr>
<td>160</td>
<td>.105</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.075</td>
</tr>
<tr>
<td>20</td>
<td>.883</td>
</tr>
<tr>
<td>40</td>
<td>.711</td>
</tr>
<tr>
<td>60</td>
<td>.624</td>
</tr>
<tr>
<td>80</td>
<td>.531</td>
</tr>
<tr>
<td>100</td>
<td>.452</td>
</tr>
<tr>
<td>120</td>
<td>.383</td>
</tr>
<tr>
<td>140</td>
<td>.333</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.306</td>
</tr>
<tr>
<td>30</td>
<td>1.041</td>
</tr>
<tr>
<td>60</td>
<td>.860</td>
</tr>
<tr>
<td>90</td>
<td>.725</td>
</tr>
<tr>
<td>120</td>
<td>.611</td>
</tr>
<tr>
<td>150</td>
<td>.521</td>
</tr>
<tr>
<td>180</td>
<td>.440</td>
</tr>
<tr>
<td>210</td>
<td>.373</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.575</td>
</tr>
<tr>
<td>50</td>
<td>.506</td>
</tr>
<tr>
<td>100</td>
<td>.449</td>
</tr>
<tr>
<td>150</td>
<td>.353</td>
</tr>
<tr>
<td>200</td>
<td>.285</td>
</tr>
<tr>
<td>300</td>
<td>.229</td>
</tr>
<tr>
<td>400</td>
<td>.181</td>
</tr>
<tr>
<td>500</td>
<td>.143</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.575</td>
</tr>
<tr>
<td>50</td>
<td>.506</td>
</tr>
<tr>
<td>100</td>
<td>.449</td>
</tr>
<tr>
<td>150</td>
<td>.353</td>
</tr>
<tr>
<td>200</td>
<td>.285</td>
</tr>
<tr>
<td>300</td>
<td>.229</td>
</tr>
<tr>
<td>400</td>
<td>.181</td>
</tr>
<tr>
<td>500</td>
<td>.143</td>
</tr>
</tbody>
</table>

C: 74.9%  
S: .0001 M/L  
T: 25.3°C  
L: 290 nm  
t: 1200 sec; Ai: .008  
cc: .999  
rate: 136.3 x 10⁻⁴ sec⁻¹  
sd: .34  
t₁/₂: 50.9 sec  

C: 77.5%  
S: .0001 M/L  
T: 25.3°C  
L: 290 nm  
t: 1200 sec; Ai: .083  
cc: .999  
rate: 98.1 x 10⁻⁴ sec⁻¹  
sd: .53  
t₁/₂: 70.7 sec  

C: 78.1%  
S: .0001 M/L  
T: 25.3°C  
L: 290 nm  
t: 1400 sec; Ai: .07  
cc: .999  
rate: 65.7 x 10⁻⁴ sec⁻¹  
sd: .80  
t₁/₂: 106 sec  

C: 80.9%  
S: .0001 M/L  
T: 25.3°C  
L: 290 nm  
t(G): 300 sec  
cc: .9998  
rate: 22.9 x 10⁻⁴ sec⁻¹  
sd: .15  
t₁/₂: 302 sec
<table>
<thead>
<tr>
<th>1-p-nitrobenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>1.179</td>
</tr>
<tr>
<td>S: .00006 M/L</td>
<td>116</td>
<td>1.054</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>232</td>
<td>.951</td>
</tr>
<tr>
<td>L: 290 mm</td>
<td>314</td>
<td>.879</td>
</tr>
<tr>
<td>t: 2400 sec; A1: 464</td>
<td></td>
<td>.819</td>
</tr>
<tr>
<td>cc: .9934</td>
<td>580</td>
<td>.775</td>
</tr>
<tr>
<td>rate: 21.6 x 10^{-4} sec^{-1}</td>
<td>638</td>
<td>.756</td>
</tr>
<tr>
<td>sd: 1.0</td>
<td>696</td>
<td>.740</td>
</tr>
<tr>
<td>t½: 319 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| C: 58.0%                        | 0     | 1.084 |
| S: .00006 M/L                   | 58    | 1.008 |
| T: 25.3°C                       | 116   | .945  |
| L: 290 mm                       | 174   | .891  |
| t: 2400 sec; A1: 480            | 232   | .814  |
| cc: .9998                       | 290   | .799  |
| rate: 21.45 x 10^{-4} sec^{-1}  | 314   | .764  |
| sd: .17                         | 406   | .733  |
| t½: 323 sec                     |       |       |</p>
<table>
<thead>
<tr>
<th>TABLE XV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-acetyl-5,5-dimethyl-2-thiohydantoin</td>
</tr>
<tr>
<td>C: 39.6%</td>
</tr>
<tr>
<td>S: .00013M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 290 nm</td>
</tr>
<tr>
<td>t(0): 100 sec</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 26.01 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td>sd: .13</td>
</tr>
<tr>
<td>t_{1/2}: 267 sec</td>
</tr>
</tbody>
</table>

| C: 39.6% | 0 | 1.121 |
| S: .00013M/L | 87 | .927 |
| T: 25.3°C | 145 | .825 |
| L: 290 nm | 203 | .738 |
| t: 2700 sec; Ai: 199 | 290 | .631 |
| cc: .9999 | 493 | .518 |
| rate: 26.09 x 10^{-4} sec^{-1} | 493 | .452 |
| sd: .06 | 580 | .401 |
| t_{1/2}: 266 sec | |

| C: 53.5% | 0 | 1.218 |
| S: .00013M/L | 20 | 1.023 |
| T: 25.3°C | 140 | .864 |
| L: 295 nm | 60 | .735 |
| t(0): 950 sec | 80 | .629 |
| cc: .9997 | 110 | .518 |
| rate: 78.15 x 10^{-4} sec^{-1} | 110 | .396 |
| sd: .63 | 210 | .185 |
| t_{1/2}: 89 sec | |

| C: 53.5% | 0 | 1.472 |
| S: .00013M/L | 20 | 1.245 |
| T: 25.3°C | 140 | 1.044 |
| L: 295 nm | 70 | .823 |
| t(0): 100 sec | 100 | .618 |
| cc: .9998 | 130 | .518 |
| rate: 78.35 x 10^{-4} sec^{-1} | 130 | .12 |
| sd: .59 | 200 | .302 |
| t_{1/2}: 88 sec | |

<p>| C: 58.0% | 0 | 1.764 |
| S: .00013M/L | 20 | 1.396 |
| T: 25.3°C | 140 | 1.115 |
| L: 290 nm | 60 | .911 |
| t: 800 sec; Ai: .269 | 80 | .761 |
| cc: .9996 | 100 | .656 |
| rate: 131.7 x 10^{-4} sec^{-1} | 130 | .536 |
| sd: 1.31 | 160 | .443 |
| t_{1/2}: 53 sec | |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>C: 58.0%</th>
<th>S: .00013M/L</th>
<th>T: 25.3°C</th>
<th>L: 290 mm</th>
<th>t: 800 sec; A1: .211</th>
<th>cc: .9997</th>
<th>rate: 130.2 x 10^{-4} sec^{-1}</th>
<th>sd: 1.20</th>
<th>t_{1/2}: 53 sec</th>
<th>DA: 1.417</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.417</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.258</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.125</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.009</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.908</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.748</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.628</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.510</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>C: 58.0%</th>
<th>S: .00013M/L</th>
<th>T: 25.3°C</th>
<th>L: 290 mm</th>
<th>t: 700 sec; A1: .224</th>
<th>cc: .9998</th>
<th>rate: 120.7 x 10^{-4} sec^{-1}</th>
<th>sd: .74</th>
<th>t_{1/2}: 57 sec</th>
<th>DA: 1.410</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.410</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.037</td>
</tr>
<tr>
<td>58</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.788</td>
</tr>
<tr>
<td>87</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.622</td>
</tr>
<tr>
<td>116</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.506</td>
</tr>
<tr>
<td>145</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.426</td>
</tr>
<tr>
<td>174</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.366</td>
</tr>
<tr>
<td>203</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.325</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>C: 62.4%</th>
<th>S: .00013M/L</th>
<th>T: 25.3°C</th>
<th>L: 290 mm</th>
<th>t: 650 sec; A1: .161</th>
<th>cc: .9999</th>
<th>rate: 176.5 x 10^{-4} sec^{-1}</th>
<th>sd: .58</th>
<th>t_{1/2}: 39 sec</th>
<th>DA: .865</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.865</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.713</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.618</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.499</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.396</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.325</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.277</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.244</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>C: 62.4%</th>
<th>S: .00013M/L</th>
<th>T: 25.3°C</th>
<th>L: 290 mm</th>
<th>t: 500 sec; A1: .163</th>
<th>cc: .9999</th>
<th>rate: 178.7 x 10^{-4} sec^{-1}</th>
<th>sd: .94</th>
<th>t_{1/2}: 39 sec</th>
<th>DA: .839</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.839</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.723</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.637</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.496</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.394</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.325</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.279</td>
</tr>
<tr>
<td>120</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.244</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>C: 66.1%</th>
<th>S: .00013M/L</th>
<th>T: 25.3°C</th>
<th>L: 290 mm</th>
<th>t: 500 sec; A1: .058</th>
<th>cc: .9998</th>
<th>rate: 237 x 10^{-4} sec^{-1}</th>
<th>sd: 1.29</th>
<th>t_{1/2}: 29 sec</th>
<th>DA: .611</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.611</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.522</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.425</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.351</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.296</td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.205</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.154</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>.119</td>
</tr>
<tr>
<td>C: 66.1%</td>
<td>Time</td>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: .00013M/L</td>
<td>0</td>
<td>.864</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.695</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L: 295 nm</td>
<td>20</td>
<td>.561</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| t: 600 sec; A:
| 40 | .372 |
| cc: 9999 | 60 | .260 |
| rate: 225.6 x 10^{-4} sec^{-1} | 80 | .179 |
| sd: .98 | 100 | .135 |
| t\frac{1}{2}: 30.7 sec | | |

<table>
<thead>
<tr>
<th>C: 68.0%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00013M/L</td>
<td>0</td>
<td>.763</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.619</td>
</tr>
<tr>
<td>L: 295 nm</td>
<td>20</td>
<td>.508</td>
</tr>
</tbody>
</table>
| t: 500 sec; A:
| 40 | .426 |
| cc: 9999 | 50 | .360 |
| rate: 253 x 10^{-4} sec^{-1} | 60 | .311 |
| sd: 1.0 | 70 | .276 |
| t\frac{1}{2}: 27.4 sec | | |

<table>
<thead>
<tr>
<th>C: 70.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00013M/L</td>
<td>0</td>
<td>.846</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.639</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>20</td>
<td>.588</td>
</tr>
</tbody>
</table>
| t: 280 sec; A:
| 40 | .370 |
| cc: 9998 | 50 | .294 |
| rate: 294.5 x 10^{-4} sec^{-1} | 60 | .227 |
| sd: 1.89 | 70 | .177 |
| t\frac{1}{2}: 23.5 sec | | |

<table>
<thead>
<tr>
<th>C: 70.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .00013M/L</td>
<td>0</td>
<td>1.298</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.962</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>20</td>
<td>.736</td>
</tr>
</tbody>
</table>
| t: 350 sec; A:
<p>| 40 | .568 |
| cc: 9996 | 50 | .356 |
| rate: 285.8 x 10^{-4} sec^{-1} | 60 | .286 |
| sd: 2.79 | 70 | .237 |
| t\frac{1}{2}: 24.3 sec | | |</p>
<table>
<thead>
<tr>
<th>C</th>
<th>S</th>
<th>T</th>
<th>L</th>
<th>t</th>
<th>Ai</th>
<th>cc</th>
<th>rate</th>
<th>sd</th>
<th>t½</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.7%</td>
<td>.00013 M/L</td>
<td>25.3°C</td>
<td>290</td>
<td>600 sec; Ai: .072</td>
<td>.9998</td>
<td>253.6 x 10⁻⁴ sec⁻¹</td>
<td>1.9</td>
<td>27 sec</td>
<td></td>
</tr>
<tr>
<td>74.9%</td>
<td>.0001 M/L</td>
<td>25.3°C</td>
<td>290</td>
<td>500 sec; Ai: .028</td>
<td>.9999</td>
<td>237.6 x 10⁻⁴ sec⁻¹</td>
<td>1.16</td>
<td>29 sec</td>
<td></td>
</tr>
<tr>
<td>77.5%</td>
<td>.00013 M/L</td>
<td>25.3°C</td>
<td>285</td>
<td>800 sec; Ai: .075</td>
<td>.9997</td>
<td>175 x 10⁻⁴ sec⁻¹</td>
<td>1.5</td>
<td>39.7 sec</td>
<td></td>
</tr>
<tr>
<td>80.0%</td>
<td>.00013 M/L</td>
<td>25.3°C</td>
<td>280</td>
<td>1400 sec</td>
<td>.9998</td>
<td>51.4 x 10⁻⁴ sec⁻¹</td>
<td>.28</td>
<td>135 sec</td>
<td></td>
</tr>
<tr>
<td>80.0%</td>
<td>.00013 M/L</td>
<td>25.3°C</td>
<td>280</td>
<td>1400 sec</td>
<td>.9998</td>
<td>17.6 x 10⁻⁴ sec⁻¹</td>
<td>.40</td>
<td>1145 sec</td>
<td></td>
</tr>
<tr>
<td>C: 81.2%</td>
<td>Time</td>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>84.2%</td>
<td>.859</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.74h</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>.645</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.560</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>.487</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>.428</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.379</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>.331</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>τ₂: 510 sec</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 88.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.719</td>
<td></td>
</tr>
<tr>
<td>240</td>
<td>1.617</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>1.548</td>
<td></td>
</tr>
<tr>
<td>720</td>
<td>1.506</td>
<td></td>
</tr>
<tr>
<td>1020</td>
<td>1.439</td>
<td></td>
</tr>
<tr>
<td>1620</td>
<td>1.318</td>
<td></td>
</tr>
<tr>
<td>2820</td>
<td>1.174</td>
<td></td>
</tr>
<tr>
<td>3780</td>
<td>1.097</td>
<td></td>
</tr>
<tr>
<td>τ₂: 1612 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 91.2%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.028</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.934</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.816</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.774</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.710</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.650</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.596</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>.554</td>
<td></td>
</tr>
<tr>
<td>τ₂: 1545 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 94.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.746</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.669</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.594</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.533</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.478</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.428</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.379</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>.331</td>
<td></td>
</tr>
<tr>
<td>τ₂: 1957 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.764</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.628</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.523</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.372</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.315</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.267</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.215</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.693</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.550</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.356</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.284</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.224</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.176</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.111</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>.532</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.382</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>.271</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.224</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>.184</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.152</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>.126</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.050</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>.828</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.695</td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>.596</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.521</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>.465</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.425</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>.346</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.101</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>.865</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>.681</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>.538</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>.424</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>.316</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>.298</td>
<td></td>
</tr>
</tbody>
</table>
C: 96.3%  
S: .00011 M/L  
T: 49.6°C  
L: 255 mm  
t: 700 sec; Ai: .202  
cc: .9967  
rate: 117.8 x 10^{-4} sec^{-1}  
sd: 3.4  
t_{1/2}: 58.8 sec  

C: 96.3%  
S: .00022 M/L  
T: 49.6°C  
L: 255 mm  
t: 800 sec; Ai: .153  
cc: .9957  
rate: 128.9 x 10^{-4} sec^{-1}  
sd: 4.2  
t_{1/2}: 53.8 sec  

C: 96.3%  
S: .00022 M/L  
T: 35.2°C  
L: 255 mm  
t: 2400 sec; Ai: .386  
cc: .9999  
rate: 23.5 x 10^{-4} sec^{-1}  
sd: .085  
t_{1/2}: 295 sec  

C: 96.3%  
S: .00016 M/L  
T: 35.2°C  
L: 255 mm  
t: 2400 sec; Ai: .279  
cc: .9999  
rate: 24.06 x 10^{-4} sec^{-1}  
sd: .11  
t_{1/2}: 288 sec  

C: 96.3%  
S: .00032 M/L  
T: 35.2°C  
L: 255 mm  
t: 2400 sec; Ai: .600  
cc: .9999  
rate: 25.05 x 10^{-4} sec^{-1}  
sd: .13  
t_{1/2}: 277 sec
<table>
<thead>
<tr>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.706</td>
</tr>
<tr>
<td>15</td>
<td>.573</td>
</tr>
<tr>
<td>24</td>
<td>.502</td>
</tr>
<tr>
<td>30</td>
<td>.463</td>
</tr>
<tr>
<td>45</td>
<td>.364</td>
</tr>
<tr>
<td>60</td>
<td>.299</td>
</tr>
<tr>
<td>75</td>
<td>.250</td>
</tr>
<tr>
<td>90</td>
<td>.224</td>
</tr>
<tr>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>2.505</td>
<td></td>
</tr>
<tr>
<td>1.373</td>
<td></td>
</tr>
<tr>
<td>1.373</td>
<td></td>
</tr>
<tr>
<td>1.373</td>
<td></td>
</tr>
<tr>
<td>1.373</td>
<td></td>
</tr>
<tr>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>32.4</td>
<td></td>
</tr>
<tr>
<td>62.42</td>
<td></td>
</tr>
</tbody>
</table>

<p>| C: 96.3%  |
| S: .00008M/L  |
| T: 58.1°C  |
| L: 255 mm  |
| t: 400 sec; Ai: .162  |
| cc: .9978  |
| rate: $2.88 \times 10^{-3}$ sec$^{-1}$  |
| sd: 5.8  |
| $t_{\frac{1}{2}}$: 27.9 sec  |
| C: 96.3%  |
| S: .00016M/L  |
| T: 58.1°C  |
| L: 255 mm  |
| t: 400 sec; Ai: .305  |
| cc: .9961  |
| rate: $281.9 \times 10^{-5}$ sec$^{-1}$  |
| sd: 8.2  |
| $t_{\frac{1}{2}}$: 24.6 sec  |
| C: 96.3%  |
| S: .00023M/L  |
| T: 58.1°C  |
| L: 255 mm  |
| t: 400 sec; Ai: .419  |
| cc: .9979  |
| rate: $268.8 \times 10^{-5}$ sec$^{-1}$  |
| sd: 6.2  |
| $t_{\frac{1}{2}}$: 25.8 sec  |
| C: 96.3%  |
| S: .0001M/L  |
| T: 10.8°C  |
| L: 272 mm  |
| t: 50000 sec; Ai: .484  |
| cc: .9997  |
| rate: $1.20 \times 10^{-2}$ sec$^{-1}$  |
| sd: 6.2  |
| $t_{\frac{1}{2}}$: 5782 sec  |
| C: 96.3%  |
| S: .00001M/L  |
| T: 10.8°C  |
| L: 270 mm  |
| t: 50000 sec  |
| cc: .9980  |
| rate: $1.11 \times 10^{-4}$ sec$^{-1}$  |
| sd: .025  |
| $t_{\frac{1}{2}}$: 6242 sec  |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.564</td>
</tr>
<tr>
<td>300</td>
<td>.512</td>
</tr>
<tr>
<td>600</td>
<td>.464</td>
</tr>
<tr>
<td>900</td>
<td>.422</td>
</tr>
<tr>
<td>1200</td>
<td>.380</td>
</tr>
<tr>
<td>1500</td>
<td>.321</td>
</tr>
<tr>
<td>1800</td>
<td>.295</td>
</tr>
<tr>
<td>2100</td>
<td>.263</td>
</tr>
<tr>
<td>2228</td>
<td>1.152</td>
</tr>
<tr>
<td>50</td>
<td>.905</td>
</tr>
<tr>
<td>100</td>
<td>.723</td>
</tr>
<tr>
<td>150</td>
<td>.681</td>
</tr>
<tr>
<td>200</td>
<td>.462</td>
</tr>
<tr>
<td>250</td>
<td>.376</td>
</tr>
<tr>
<td>300</td>
<td>.310</td>
</tr>
<tr>
<td>350</td>
<td>.259</td>
</tr>
<tr>
<td>128</td>
<td>1.103</td>
</tr>
<tr>
<td>50</td>
<td>.871</td>
</tr>
<tr>
<td>100</td>
<td>.793</td>
</tr>
<tr>
<td>150</td>
<td>.581</td>
</tr>
<tr>
<td>200</td>
<td>.462</td>
</tr>
<tr>
<td>250</td>
<td>.376</td>
</tr>
<tr>
<td>300</td>
<td>.310</td>
</tr>
<tr>
<td>350</td>
<td>.259</td>
</tr>
<tr>
<td>125</td>
<td>1.089</td>
</tr>
<tr>
<td>50</td>
<td>.864</td>
</tr>
<tr>
<td>100</td>
<td>.688</td>
</tr>
<tr>
<td>150</td>
<td>.555</td>
</tr>
<tr>
<td>200</td>
<td>.462</td>
</tr>
<tr>
<td>250</td>
<td>.376</td>
</tr>
<tr>
<td>300</td>
<td>.310</td>
</tr>
<tr>
<td>350</td>
<td>.259</td>
</tr>
<tr>
<td>127</td>
<td>1.063</td>
</tr>
<tr>
<td>116</td>
<td>.964</td>
</tr>
<tr>
<td>290</td>
<td>.812</td>
</tr>
<tr>
<td>522</td>
<td>.717</td>
</tr>
<tr>
<td>667</td>
<td>.555</td>
</tr>
<tr>
<td>899</td>
<td>.510</td>
</tr>
<tr>
<td>1015</td>
<td>.461</td>
</tr>
<tr>
<td>1160</td>
<td>.422</td>
</tr>
<tr>
<td>Time</td>
<td>da</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>0</td>
<td>.991</td>
</tr>
<tr>
<td>116</td>
<td>.888</td>
</tr>
<tr>
<td>290</td>
<td>.768</td>
</tr>
<tr>
<td>522</td>
<td>.657</td>
</tr>
<tr>
<td>667</td>
<td>.592</td>
</tr>
<tr>
<td>899</td>
<td>.509</td>
</tr>
<tr>
<td>1015</td>
<td>.467</td>
</tr>
<tr>
<td>1160</td>
<td>.423</td>
</tr>
<tr>
<td>0</td>
<td>1.021</td>
</tr>
<tr>
<td>29</td>
<td>.908</td>
</tr>
<tr>
<td>58</td>
<td>.788</td>
</tr>
<tr>
<td>22</td>
<td>.669</td>
</tr>
<tr>
<td>667</td>
<td>.611</td>
</tr>
<tr>
<td>899</td>
<td>.522</td>
</tr>
<tr>
<td>1015</td>
<td>.485</td>
</tr>
<tr>
<td>1160</td>
<td>.437</td>
</tr>
<tr>
<td>0</td>
<td>1.346</td>
</tr>
<tr>
<td>29</td>
<td>.955</td>
</tr>
<tr>
<td>58</td>
<td>.703</td>
</tr>
<tr>
<td>27</td>
<td>.514</td>
</tr>
<tr>
<td>116</td>
<td>.426</td>
</tr>
<tr>
<td>114</td>
<td>.354</td>
</tr>
<tr>
<td>174</td>
<td>.308</td>
</tr>
<tr>
<td>203</td>
<td>.283</td>
</tr>
<tr>
<td>0</td>
<td>1.330</td>
</tr>
<tr>
<td>29</td>
<td>.982</td>
</tr>
<tr>
<td>58</td>
<td>.758</td>
</tr>
<tr>
<td>27</td>
<td>.522</td>
</tr>
<tr>
<td>116</td>
<td>.432</td>
</tr>
<tr>
<td>114</td>
<td>.372</td>
</tr>
<tr>
<td>174</td>
<td>.320</td>
</tr>
<tr>
<td>203</td>
<td>.283</td>
</tr>
<tr>
<td>0</td>
<td>1.816</td>
</tr>
<tr>
<td>29</td>
<td>1.264</td>
</tr>
<tr>
<td>58</td>
<td>.896</td>
</tr>
<tr>
<td>27</td>
<td>.695</td>
</tr>
<tr>
<td>116</td>
<td>.575</td>
</tr>
<tr>
<td>114</td>
<td>.504</td>
</tr>
<tr>
<td>174</td>
<td>.463</td>
</tr>
<tr>
<td>203</td>
<td>.435</td>
</tr>
</tbody>
</table>

\( C: 39.6\% \)

\( S: .0001M/L \)

\( T: 11.0^\circ C \)

\( L: 284 \text{ nm} \)

\( t(0): 1300 \text{ sec} \)

\( cc: .9989 \)

rate: \( 7.20 \times 10^{-1} \text{ sec}^{-1} \)

sd: \( .17 \)

t\(_i\): 963 sec

\( C: 39.6\% \)

\( S: .0001M/L \)

\( T: 11.0^\circ C \)

\( L: 284 \text{ nm} \)

\( t(0): 2000 \text{ sec} \)

\( cc: .9984 \)

sd: \( .14 \)

t\(_i\): 973 sec

rate: \( 7.12 \times 10^{-4} \text{ sec}^{-1} \)

\( C: 39.6\% \)

\( S: .0001M/L \)

\( T: 11.0^\circ C \)

\( L: 284 \text{ nm} \)

\( t: 400 \text{ sec} \)

\( Ai: .241 \)

cc: \( .9995 \)

rate: \( 161.8 \times 10^{-4} \text{ sec}^{-1} \)

sd: \( .93 \)

t\(_i\): 42.8 sec

\( C: 39.6\% \)

\( S: .00015M/L \)

\( T: 49.6^\circ C \)

\( L: 290 \text{ nm} \)

\( t: 700 \text{ sec} \)

\( Ai: .382 \)

cc: \( .9998 \)

rate: \( 159.6 \times 10^{-4} \text{ sec}^{-1} \)

sd: \( .93 \)

t\(_i\): 43.4 sec

\( C: 39.6\% \)

\( S: .00015M/L \)

\( T: 49.6^\circ C \)

\( L: 290 \text{ nm} \)

\( t: 580 \text{ sec} \)

\( Ai: .395 \)

cc: \( .9999 \)

rate: \( 175.8 \times 10^{-4} \text{ sec}^{-1} \)

sd: \( .94 \)

t\(_i\): 39.4 sec
<table>
<thead>
<tr>
<th>C: 39.6%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.00015M/L</td>
<td>0</td>
<td>1.558</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>58</td>
<td>.844</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>87</td>
<td>.685</td>
</tr>
<tr>
<td>t: 580 sec; A1: .440</td>
<td>116</td>
<td>.586</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>145</td>
<td>.529</td>
</tr>
<tr>
<td>rate: 171.8 x 10^{-4} sec^{-1}</td>
<td>174</td>
<td>.475</td>
</tr>
<tr>
<td>sd: 1.104</td>
<td>203</td>
<td>.420</td>
</tr>
<tr>
<td>t½: 4.8 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C: 39.6% | Time | dA |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.00015M/L</td>
<td>0</td>
<td>1.538</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>58</td>
<td>.822</td>
</tr>
<tr>
<td>L: 290 nm</td>
<td>87</td>
<td>.668</td>
</tr>
<tr>
<td>t: 580 sec; A1: .440</td>
<td>116</td>
<td>.576</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>145</td>
<td>.520</td>
</tr>
<tr>
<td>rate: 179.7 x 10^{-4} sec^{-1}</td>
<td>174</td>
<td>.488</td>
</tr>
<tr>
<td>sd: .59</td>
<td>203</td>
<td>.469</td>
</tr>
<tr>
<td>t½: 4.8 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## TABLE XVI

### 1-acetyl(d₃)-5,5-dimethyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.178</td>
</tr>
<tr>
<td>116</td>
<td>1.048</td>
</tr>
<tr>
<td>290</td>
<td>.911</td>
</tr>
<tr>
<td>522</td>
<td>.770</td>
</tr>
<tr>
<td>667</td>
<td>.690</td>
</tr>
<tr>
<td>899</td>
<td>.583</td>
</tr>
<tr>
<td>1015</td>
<td>.538</td>
</tr>
<tr>
<td>1160</td>
<td>.483</td>
</tr>
<tr>
<td>918</td>
<td>.441</td>
</tr>
<tr>
<td>29</td>
<td>1.191</td>
</tr>
<tr>
<td>116</td>
<td>1.116</td>
</tr>
<tr>
<td>290</td>
<td>.986</td>
</tr>
<tr>
<td>522</td>
<td>.850</td>
</tr>
<tr>
<td>667</td>
<td>.782</td>
</tr>
<tr>
<td>899</td>
<td>.683</td>
</tr>
<tr>
<td>1015</td>
<td>.610</td>
</tr>
<tr>
<td>1160</td>
<td>.588</td>
</tr>
<tr>
<td>914</td>
<td>.559</td>
</tr>
<tr>
<td>0</td>
<td>1.132</td>
</tr>
<tr>
<td>116</td>
<td>1.015</td>
</tr>
<tr>
<td>290</td>
<td>.880</td>
</tr>
<tr>
<td>522</td>
<td>.738</td>
</tr>
<tr>
<td>667</td>
<td>.660</td>
</tr>
<tr>
<td>899</td>
<td>.560</td>
</tr>
<tr>
<td>1015</td>
<td>.513</td>
</tr>
<tr>
<td>1160</td>
<td>.459</td>
</tr>
<tr>
<td>904</td>
<td>.410</td>
</tr>
<tr>
<td>0</td>
<td>1.312</td>
</tr>
<tr>
<td>58</td>
<td>1.115</td>
</tr>
<tr>
<td>116</td>
<td>.954</td>
</tr>
<tr>
<td>232</td>
<td>.803</td>
</tr>
<tr>
<td>290</td>
<td>.723</td>
</tr>
<tr>
<td>377</td>
<td>.627</td>
</tr>
<tr>
<td>493</td>
<td>.528</td>
</tr>
<tr>
<td>580</td>
<td>.468</td>
</tr>
<tr>
<td>248</td>
<td>.418</td>
</tr>
<tr>
<td>0</td>
<td>.911</td>
</tr>
<tr>
<td>58</td>
<td>.771</td>
</tr>
<tr>
<td>116</td>
<td>.652</td>
</tr>
<tr>
<td>174</td>
<td>.552</td>
</tr>
<tr>
<td>232</td>
<td>.469</td>
</tr>
<tr>
<td>319</td>
<td>.385</td>
</tr>
<tr>
<td>406</td>
<td>.288</td>
</tr>
<tr>
<td>522</td>
<td>.208</td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>0</td>
<td>1.034</td>
</tr>
<tr>
<td>1800</td>
<td>.788</td>
</tr>
<tr>
<td>58</td>
<td>.617</td>
</tr>
<tr>
<td>232</td>
<td>.491</td>
</tr>
<tr>
<td>1.034</td>
<td>.396</td>
</tr>
<tr>
<td>348</td>
<td>.331</td>
</tr>
<tr>
<td>406</td>
<td>.282</td>
</tr>
<tr>
<td>29.9</td>
<td>.214</td>
</tr>
<tr>
<td>123.6</td>
<td>1.090</td>
</tr>
<tr>
<td>1200</td>
<td>.860</td>
</tr>
<tr>
<td>200</td>
<td>.682</td>
</tr>
<tr>
<td>250</td>
<td>.552</td>
</tr>
<tr>
<td>300</td>
<td>.417</td>
</tr>
<tr>
<td>.998</td>
<td>.394</td>
</tr>
<tr>
<td>350</td>
<td>.305</td>
</tr>
<tr>
<td>119.5</td>
<td>.262</td>
</tr>
<tr>
<td>116</td>
<td>1.085</td>
</tr>
<tr>
<td>145</td>
<td>.850</td>
</tr>
<tr>
<td>174</td>
<td>.682</td>
</tr>
<tr>
<td>203</td>
<td>.554</td>
</tr>
<tr>
<td>123.8</td>
<td>.376</td>
</tr>
<tr>
<td>300</td>
<td>.319</td>
</tr>
<tr>
<td>350</td>
<td>.276</td>
</tr>
<tr>
<td>361</td>
<td>1.072</td>
</tr>
<tr>
<td>145</td>
<td>.691</td>
</tr>
<tr>
<td>174</td>
<td>.575</td>
</tr>
<tr>
<td>203</td>
<td>.555</td>
</tr>
<tr>
<td>46.7</td>
<td>.986</td>
</tr>
<tr>
<td>116</td>
<td>.616</td>
</tr>
<tr>
<td>145</td>
<td>.330</td>
</tr>
<tr>
<td>174</td>
<td>.217</td>
</tr>
<tr>
<td>203</td>
<td>.126</td>
</tr>
<tr>
<td>45.7</td>
<td>.095</td>
</tr>
<tr>
<td>116</td>
<td>.082</td>
</tr>
</tbody>
</table>

**Variables:**
- **C:** Concentration
- **S:** Solution
- **T:** Temperature
- **L:** Length
- **t:** Time
- **Ai:** Initial rate
- **cc:** Constant coefficient
- **rate:** Reaction rate
- **sd:** Standard deviation
- **t1/2:** Half-life
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.228</td>
</tr>
<tr>
<td>15</td>
<td>1.038</td>
</tr>
<tr>
<td>30</td>
<td>.936</td>
</tr>
<tr>
<td>45</td>
<td>.879</td>
</tr>
<tr>
<td>60</td>
<td>.755</td>
</tr>
<tr>
<td>75</td>
<td>.669</td>
</tr>
<tr>
<td>90</td>
<td>.606</td>
</tr>
<tr>
<td></td>
<td>.562</td>
</tr>
<tr>
<td>0</td>
<td>1.482</td>
</tr>
<tr>
<td>15</td>
<td>1.229</td>
</tr>
<tr>
<td>30</td>
<td>1.01</td>
</tr>
<tr>
<td>55</td>
<td>.896</td>
</tr>
<tr>
<td>75</td>
<td>.797</td>
</tr>
<tr>
<td>90</td>
<td>.727</td>
</tr>
<tr>
<td></td>
<td>.681</td>
</tr>
<tr>
<td>0</td>
<td>1.524</td>
</tr>
<tr>
<td>15</td>
<td>1.319</td>
</tr>
<tr>
<td>30</td>
<td>1.217</td>
</tr>
<tr>
<td>55</td>
<td>1.11</td>
</tr>
<tr>
<td>75</td>
<td>1.021</td>
</tr>
<tr>
<td>90</td>
<td>.922</td>
</tr>
<tr>
<td></td>
<td>.862</td>
</tr>
<tr>
<td></td>
<td>.818</td>
</tr>
<tr>
<td>0</td>
<td>1.535</td>
</tr>
<tr>
<td>20</td>
<td>1.370</td>
</tr>
<tr>
<td>40</td>
<td>1.22</td>
</tr>
<tr>
<td>60</td>
<td>1.01</td>
</tr>
<tr>
<td>80</td>
<td>.858</td>
</tr>
<tr>
<td>100</td>
<td>.744</td>
</tr>
<tr>
<td></td>
<td>.663</td>
</tr>
<tr>
<td></td>
<td>.604</td>
</tr>
</tbody>
</table>

**C**: 96.3%

**S**: .00025M/L

**T**: 58.1°C

**L**: 255 nm

**t**: 1400 sec; **Ai**: .475

**cc**: .9987

**rate**: 241.8 x 10^{-4} sec^{-1}

**sd**: 4.4

**t₁**: 28.7 sec

**C**: 96.3%

**S**: .0003M/L

**T**: 58.1°C

**L**: 255 nm

**t**: 1650 sec; **Ai**: .59

**cc**: .9991

**rate**: 254.8 x 10^{-4} sec^{-1}

**sd**: 3.1

**t₁**: 27.2 sec

**C**: 96.3%

**S**: .0003M/L

**T**: 58.1°C

**L**: 255 nm

**t**: 1300 sec; **Ai**: .7h2

**cc**: .9980

**rate**: 261.8 x 10^{-4} sec^{-1}

**sd**: 5.8

**t₁**: 26.5 sec

**C**: 96.3%

**S**: .00026M/L

**T**: 49.6°C

**L**: 255 nm

**t**: 600 sec; **Ai**: .478

**cc**: .9995

**rate**: 121.2 x 10^{-4} sec^{-1}

**sd**: 1.2

**t₁**: 58.8 sec
<table>
<thead>
<tr>
<th>C: 96.3%</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.421</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.298</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.168</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1.016</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.891</td>
<td></td>
</tr>
<tr>
<td>130</td>
<td>0.804</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>0.742</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>0.698</td>
<td></td>
</tr>
<tr>
<td>61.3 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.3%</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.129</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>0.998</td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>0.894</td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>0.811</td>
<td></td>
</tr>
<tr>
<td>664</td>
<td>0.749</td>
<td></td>
</tr>
<tr>
<td>696</td>
<td>0.665</td>
<td></td>
</tr>
<tr>
<td>812</td>
<td>0.639</td>
<td></td>
</tr>
<tr>
<td>313 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.3%</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.152</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>1.041</td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>0.944</td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>0.875</td>
<td></td>
</tr>
<tr>
<td>664</td>
<td>0.817</td>
<td></td>
</tr>
<tr>
<td>696</td>
<td>0.774</td>
<td></td>
</tr>
<tr>
<td>812</td>
<td>0.718</td>
<td></td>
</tr>
<tr>
<td>328 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.3%</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.892</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>0.781</td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>0.701</td>
<td></td>
</tr>
<tr>
<td>316</td>
<td>0.637</td>
<td></td>
</tr>
<tr>
<td>664</td>
<td>0.582</td>
<td></td>
</tr>
<tr>
<td>696</td>
<td>0.511</td>
<td></td>
</tr>
<tr>
<td>812</td>
<td>0.482</td>
<td></td>
</tr>
<tr>
<td>336 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.3%</th>
<th>Time</th>
<th>da</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.546</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.510</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.471</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.432</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.402</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.372</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.351</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.316</td>
<td></td>
</tr>
<tr>
<td>2679 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.524</td>
<td></td>
</tr>
<tr>
<td>2h00</td>
<td>.423</td>
<td></td>
</tr>
<tr>
<td>4h00</td>
<td>.315</td>
<td></td>
</tr>
<tr>
<td>7h20</td>
<td>.283</td>
<td></td>
</tr>
<tr>
<td>9h60</td>
<td>.230</td>
<td></td>
</tr>
<tr>
<td>14h00</td>
<td>.188</td>
<td></td>
</tr>
<tr>
<td>16h80</td>
<td>.154</td>
<td></td>
</tr>
<tr>
<td>17h80</td>
<td>.125</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.266</td>
<td></td>
</tr>
<tr>
<td>1h80</td>
<td>.235</td>
<td></td>
</tr>
<tr>
<td>3h60</td>
<td>.202</td>
<td></td>
</tr>
<tr>
<td>5h40</td>
<td>.171</td>
<td></td>
</tr>
<tr>
<td>7h20</td>
<td>.142</td>
<td></td>
</tr>
<tr>
<td>10h80</td>
<td>.102</td>
<td></td>
</tr>
<tr>
<td>12h60</td>
<td>.087</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.176</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.275</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.106</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.971</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>.808</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>.686</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>.588</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>.514</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.638</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.411</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.216</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.063</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.881</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.717</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.636</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.548</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.379</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.818</td>
</tr>
<tr>
<td>0</td>
<td>.712</td>
</tr>
<tr>
<td>0</td>
<td>.660</td>
</tr>
<tr>
<td>0</td>
<td>.527</td>
</tr>
<tr>
<td>0</td>
<td>.382</td>
</tr>
<tr>
<td>0</td>
<td>.310</td>
</tr>
<tr>
<td>0</td>
<td>.312</td>
</tr>
<tr>
<td>C: 62.1%</td>
<td>Time</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>20</td>
</tr>
<tr>
<td>t: 700 sec; $A_i$: .240</td>
<td>40</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>50</td>
</tr>
<tr>
<td>rate: $188.8 \times 10^{-4} \text{ sec}^{-1}$</td>
<td>60</td>
</tr>
<tr>
<td>sd: .49</td>
<td>80</td>
</tr>
<tr>
<td>$t_{1/2}$: 36.7 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 66.1%</th>
<th>Time</th>
<th>$dA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.799</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.669</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>20</td>
<td>.569</td>
</tr>
<tr>
<td>t: 500 sec; $A_i$: .219</td>
<td>40</td>
<td>.492</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>50</td>
<td>.431</td>
</tr>
<tr>
<td>rate: $248. x 10^{-4} \text{ sec}^{-1}$</td>
<td>60</td>
<td>.381</td>
</tr>
<tr>
<td>sd: 1.87</td>
<td>80</td>
<td>.350</td>
</tr>
<tr>
<td>$t_{1/2}$: 27.9 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 80.0%</th>
<th>Time</th>
<th>$dA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.818</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.704</td>
</tr>
<tr>
<td>L: 280 nm</td>
<td>20</td>
<td>.600</td>
</tr>
<tr>
<td>t: 1200 sec; $A_i$: .388</td>
<td>40</td>
<td>.523</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>50</td>
<td>.460</td>
</tr>
<tr>
<td>rate: $57.0 \times 10^{-4} \text{ sec}^{-1}$</td>
<td>60</td>
<td>.407</td>
</tr>
<tr>
<td>sd: 1.86</td>
<td>80</td>
<td>.368</td>
</tr>
<tr>
<td>$t_{1/2}$: 26.7 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 80.0%</th>
<th>Time</th>
<th>$dA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>.980</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.926</td>
</tr>
<tr>
<td>L: 280 nm</td>
<td>20</td>
<td>.892</td>
</tr>
<tr>
<td>t: 1400 sec; $A_i$: .508</td>
<td>40</td>
<td>.852</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>50</td>
<td>.786</td>
</tr>
<tr>
<td>rate: $53.6 \times 10^{-4} \text{ sec}^{-1}$</td>
<td>60</td>
<td>.729</td>
</tr>
<tr>
<td>sd: .3l</td>
<td>80</td>
<td>.688</td>
</tr>
<tr>
<td>$t_{1/2}$: 129 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 80.0%</th>
<th>Time</th>
<th>$dA$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>0</td>
<td>1.084</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>.926</td>
</tr>
<tr>
<td>L: 280 nm</td>
<td>20</td>
<td>.820</td>
</tr>
<tr>
<td>t: 1400 sec; $A_i$: .388</td>
<td>40</td>
<td>.738</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>50</td>
<td>.664</td>
</tr>
<tr>
<td>rate: $57.0 \times 10^{-4} \text{ sec}^{-1}$</td>
<td>60</td>
<td>.603</td>
</tr>
<tr>
<td>sd: .46</td>
<td>80</td>
<td>.564</td>
</tr>
<tr>
<td>$t_{1/2}$: 122 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TABLE XVII</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td><strong>1-acetyl-2-thiohydantoin</strong></td>
<td><strong>Time</strong></td>
<td><strong>dA</strong></td>
</tr>
<tr>
<td>C: 39.6%</td>
<td>0</td>
<td>.579</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>100</td>
<td>.479</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>200</td>
<td>.397</td>
</tr>
<tr>
<td>L: 282 nm</td>
<td>300</td>
<td>.322</td>
</tr>
<tr>
<td>t(G): 600 sec</td>
<td>400</td>
<td>.245</td>
</tr>
<tr>
<td>cc: .9975</td>
<td>500</td>
<td>.220</td>
</tr>
<tr>
<td>rate: 19.3 x 10⁻⁴ sec⁻¹</td>
<td>600</td>
<td>.185</td>
</tr>
<tr>
<td>sd: .48</td>
<td>700</td>
<td>.151</td>
</tr>
<tr>
<td>t₁/₂: 360 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 39.6% | 0 | 1.164 |
| S: .0001M/L | 50 | .977 |
| T: 35.9°C | 100 | .833 |
| L: 285 nm | 150 | .719 |
| t: 1800 sec; Ai: .302 | 200 | .630 |
| cc: .9999 | 250 | .560 |
| rate: 48.76 x 10⁻⁴ sec⁻¹ | 300 | .501 |
| sd: .17 | 350 | .458 |
| t₁/₂: 142 sec |  |

| C: 84.9% | 0 | 1.084 |
| S: .0001M/L | 30 | .810 |
| T: 45.6°C | 60 | .657 |
| L: 288 nm | 90 | .521 |
| t: 900 sec; Ai: .175 | 120 | .123 |
| cc: .9999 | 150 | .355 |
| rate: 109.7 x 10⁻⁴ sec⁻¹ | 180 | .303 |
| sd: .16 | 210 | .266 |
| t₁/₂: 63 sec |  |

| C: 84.9% | 0 | 1.475 |
| S: .0001M/L | 30 | 1.411 |
| T: 45.6°C | 60 | 1.360 |
| L: 250 nm | 90 | 1.321 |
| t: 700 sec; Ai: 1.137 | 120 | 1.283 |
| cc: .9995 | 150 | 1.257 |
| rate: 70.7 x 10⁻⁴ sec⁻¹ | 180 | 1.234 |
| sd: .79 | 210 | 1.212 |
| t₁/₂: 98 sec |  |

<p>| C: 84.9% | 0 | 1.302 |
| S: .0001M/L | 50 | 1.224 |
| T: 35.9°C | 100 | 1.160 |
| L: 260 nm | 150 | 1.104 |
| t: 2100 sec; Ai: .768 | 200 | 1.031 |
| cc: .9997 | 300 | .989 |
| rate: 28.5 x 10⁻⁴ sec⁻¹ | 400 | .935 |
| sd: .26 | 500 | .896 |
| t₁/₂: 243 sec |  |</p>
<table>
<thead>
<tr>
<th>C: 96.4%</th>
<th>( S: , .0001M/L )</th>
<th>( T: , 25.3^\circ C )</th>
<th>( L: , 260 \text{ nm} )</th>
<th>( t(G): , 2100 \text{ sec} )</th>
<th>( cc: , .9995 )</th>
<th>( \text{rate}: , 2.69 \times 10^{-4} \text{ sec}^{-1} )</th>
<th>( sd: , .021 )</th>
<th>( t\frac{1}{2}: , 3310 \text{ sec} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300</td>
<td>600</td>
<td>900</td>
<td>1200</td>
<td>1500</td>
<td>1800</td>
<td>2100</td>
<td></td>
</tr>
<tr>
<td>C: 96.4%</td>
<td>( S: , .0001M/L )</td>
<td>( T: , 35.5^\circ C )</td>
<td>( L: , 260 \text{ nm} )</td>
<td>( t(G): , 500 \text{ sec} )</td>
<td>( cc: , .9998 )</td>
<td>( \text{rate}: , 6.73 \times 10^{-4} \text{ sec}^{-1} )</td>
<td>( sd: , .012 )</td>
<td>( t\frac{1}{2}: , 1030 \text{ sec} )</td>
</tr>
<tr>
<td>0</td>
<td>240</td>
<td>480</td>
<td>720</td>
<td>960</td>
<td>1200</td>
<td>1440</td>
<td>1680</td>
<td></td>
</tr>
<tr>
<td>C: 96.4%</td>
<td>( S: , .0001M/L )</td>
<td>( T: , 45.6^\circ C )</td>
<td>( L: , 288 \text{ nm} )</td>
<td>( t(G): , 300 \text{ sec} )</td>
<td>( cc: , .9997 )</td>
<td>( \text{rate}: , 19.6 \times 10^{-4} \text{ sec}^{-1} )</td>
<td>( sd: , .16 )</td>
<td>( t\frac{1}{2}: , 354 \text{ sec} )</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
<td>600</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>C: 53.5%</td>
<td>( S: , .0002M/L )</td>
<td>( T: , 25.3^\circ C )</td>
<td>( L: , 288 \text{ nm} )</td>
<td>( t: , 900 \text{ sec} )</td>
<td>( cc: , .9999 )</td>
<td>( \text{rate}: , 92.2 \times 10^{-4} \text{ sec}^{-1} )</td>
<td>( sd: , .49 )</td>
<td>( t\frac{1}{2}: , 75 \text{ sec} )</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>40</td>
<td>60</td>
<td>80</td>
<td>100</td>
<td>120</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>( S: , .0002M/L )</td>
<td>( T: , 25.3^\circ C )</td>
<td>( L: , 288 \text{ nm} )</td>
<td>( t: , 500 \text{ sec} )</td>
<td>( cc: , .9998 )</td>
<td>( \text{rate}: , 202.1 \times 10^{-4} \text{ sec}^{-1} )</td>
<td>( sd: , 1.13 )</td>
<td>( t\frac{1}{2}: , 34.3 \text{ sec} )</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>60</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>62.4%</td>
<td>66.1%</td>
<td>68.0%</td>
<td>70.1%</td>
<td>72.7%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>.0002M/L</td>
<td>.0002M/L</td>
<td>.0002M/L</td>
<td>.0002M/L</td>
<td>.0001M/L</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>288 mm</td>
<td>288 mm</td>
<td>288 mm</td>
<td>288 mm</td>
<td>288 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>400 sec; A1:  .680</td>
<td>300 sec; A1:  .362</td>
<td>300 sec; A1:  .362</td>
<td>300 sec; A1:  .362</td>
<td>300 sec; A1:  .362</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc</td>
<td>.9996</td>
<td>.9994</td>
<td>.9998</td>
<td>.9977</td>
<td>.9994</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate</td>
<td>$380 \times 10^{-4}$ sec$^{-1}$</td>
<td>$470 \times 10^{-6}$ sec$^{-1}$</td>
<td>$487 \times 10^{-6}$ sec$^{-1}$</td>
<td>$463 \times 10^{-4}$ sec$^{-1}$</td>
<td>$463 \times 10^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd</td>
<td>3.86</td>
<td>5.96</td>
<td>2.9</td>
<td>11.2</td>
<td>5.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>18 sec</td>
<td>14.7 sec</td>
<td>14.2 sec</td>
<td>15 sec</td>
<td>16.7 sec</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C</th>
<th>1.304</th>
<th>1.540</th>
<th>1.360</th>
<th>0.755</th>
<th>0.810</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1.104</td>
<td>1.100</td>
<td>0.890</td>
<td>0.518</td>
<td>0.565</td>
</tr>
<tr>
<td>T</td>
<td>0.887</td>
<td>0.818</td>
<td>0.625</td>
<td>0.123</td>
<td>0.101</td>
</tr>
<tr>
<td>L</td>
<td>0.822</td>
<td>0.642</td>
<td>0.555</td>
<td>0.345</td>
<td>0.300</td>
</tr>
<tr>
<td>t</td>
<td>0.779</td>
<td>0.541</td>
<td>0.355</td>
<td>0.274</td>
<td>0.236</td>
</tr>
<tr>
<td>cc</td>
<td>0.747</td>
<td>0.476</td>
<td>0.260</td>
<td>0.159</td>
<td>0.172</td>
</tr>
<tr>
<td>rate</td>
<td>0.724</td>
<td>0.438</td>
<td>0.258</td>
<td>0.153</td>
<td>0.153</td>
</tr>
<tr>
<td>sd</td>
<td>0.709</td>
<td>0.403</td>
<td>0.236</td>
<td>0.153</td>
<td>0.153</td>
</tr>
<tr>
<td>$t_{1/2}$</td>
<td>14.2 sec</td>
<td>14.2 sec</td>
<td>14.2 sec</td>
<td>15 sec</td>
<td>16.7 sec</td>
</tr>
</tbody>
</table>

---

**Notes:**
- All entries are rounded to three decimal places.
- The rate is given in units of sec$^{-1}$.
<table>
<thead>
<tr>
<th>C: 74.9%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001 M/L</td>
<td>0</td>
<td>0.849</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>10</td>
<td>0.619</td>
</tr>
<tr>
<td>L: 288 nm</td>
<td>20</td>
<td>0.448</td>
</tr>
<tr>
<td>t: 500 sec; A1: 0.022</td>
<td>30</td>
<td>0.328</td>
</tr>
<tr>
<td>cc: 0.9998</td>
<td>40</td>
<td>0.242</td>
</tr>
<tr>
<td>rate: 324.8 x 10^{-4} sec^{-1}</td>
<td>50</td>
<td>0.181</td>
</tr>
<tr>
<td>sd: 1.85</td>
<td>60</td>
<td>0.139</td>
</tr>
<tr>
<td>t½: 21.3 sec</td>
<td>70</td>
<td>0.108</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 78.1%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.001 M/L</td>
<td>0</td>
<td>1.150</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>20</td>
<td>0.917</td>
</tr>
<tr>
<td>L: 288 mm</td>
<td>40</td>
<td>0.755</td>
</tr>
<tr>
<td>t: 900 sec; A1: 0.035</td>
<td>60</td>
<td>0.619</td>
</tr>
<tr>
<td>cc: 0.9997</td>
<td>80</td>
<td>0.515</td>
</tr>
<tr>
<td>rate: 102. x 10^{-4} sec^{-1}</td>
<td>100</td>
<td>0.426</td>
</tr>
<tr>
<td>sd: 0.85</td>
<td>120</td>
<td>0.358</td>
</tr>
<tr>
<td>t½: 68 sec</td>
<td>140</td>
<td>0.299</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 80.9%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001 M/L</td>
<td>0</td>
<td>0.812</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>50</td>
<td>0.684</td>
</tr>
<tr>
<td>L: 270 mm</td>
<td>100</td>
<td>0.583</td>
</tr>
<tr>
<td>t(0): 750 sec</td>
<td>200</td>
<td>0.420</td>
</tr>
<tr>
<td>cc: 0.9999</td>
<td>300</td>
<td>0.308</td>
</tr>
<tr>
<td>rate: 31.6 x 10^{-4} sec^{-1}</td>
<td>400</td>
<td>0.228</td>
</tr>
<tr>
<td>sd: 0.15</td>
<td>500</td>
<td>0.167</td>
</tr>
<tr>
<td>t½: 219 sec</td>
<td>600</td>
<td>0.120</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 86.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001 M/L</td>
<td>0</td>
<td>0.773</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>0.601</td>
</tr>
<tr>
<td>L: 270 nm</td>
<td>600</td>
<td>0.467</td>
</tr>
<tr>
<td>t(0): 1400 sec</td>
<td>900</td>
<td>0.362</td>
</tr>
<tr>
<td>cc: 0.9998</td>
<td>1200</td>
<td>0.275</td>
</tr>
<tr>
<td>rate: 8.74 x 10^{-4} sec^{-1}</td>
<td>1500</td>
<td>0.216</td>
</tr>
<tr>
<td>sd: 0.06</td>
<td>1800</td>
<td>0.160</td>
</tr>
<tr>
<td>t½: 793 sec</td>
<td>2100</td>
<td>0.124</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 88.4%</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001 M/L</td>
<td>0</td>
<td>0.744</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>0.626</td>
</tr>
<tr>
<td>L: 270 nm</td>
<td>600</td>
<td>0.525</td>
</tr>
<tr>
<td>t(0): 1200 sec</td>
<td>900</td>
<td>0.439</td>
</tr>
<tr>
<td>cc: 0.9999</td>
<td>1200</td>
<td>0.371</td>
</tr>
<tr>
<td>rate: 5.78 x 10^{-4} sec^{-1}</td>
<td>1500</td>
<td>0.313</td>
</tr>
<tr>
<td>sd: 0.02</td>
<td>1800</td>
<td>0.261</td>
</tr>
<tr>
<td>t½: 1200 sec</td>
<td>2100</td>
<td>0.222</td>
</tr>
<tr>
<td>Time</td>
<td>$dA$</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.807</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.698</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.603</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.521</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.407</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.335</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.297</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.277</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.166</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>1.050</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.949</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.858</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.776</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.701</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.632</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.571</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.784</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.713</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.656</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.603</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.519</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.500</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.456</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.410</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.679</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.627</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.588</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.549</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.508</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.479</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.439</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.406</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.657</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.623</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.586</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>0.555</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.527</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>0.498</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>0.467</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>0.442</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.917</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.860</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.810</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.751</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.705</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.658</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>.572</td>
<td></td>
</tr>
<tr>
<td>2700</td>
<td>.506</td>
<td></td>
</tr>
<tr>
<td>3111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.676</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>.577</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>.506</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>.441</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>.390</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>.333</td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>.286</td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>.251</td>
<td></td>
</tr>
</tbody>
</table>

C: 98.9%
S: .0001M/L
T: 25.3°C
L: 270 nm
t(0): 3300 sec
cc: 9998
rate: 2.23 x 10^-4 sec^-1
sd: .016
t_1/2: 3111 sec

C: 99.1%
S: .0001M/L
T: 25.3°C
L: 270 nm
t(0): 1500 sec
cc: 9998
rate: 4.69 x 10^-4 sec^-1
sd: .016
t_1/2: 1478 sec
<table>
<thead>
<tr>
<th>1-benzoyl-3-phenyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 39.6%</td>
<td>0</td>
<td>.640</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>300</td>
<td>.537</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.445</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>900</td>
<td>.371</td>
</tr>
<tr>
<td>t(G): 700 sec</td>
<td>1200</td>
<td>.301</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>1500</td>
<td>.217</td>
</tr>
<tr>
<td>rate: $6.41 \times 10^{-4}$ sec$^{-1}$</td>
<td>1800</td>
<td>.205</td>
</tr>
<tr>
<td>sd: .045</td>
<td>2100</td>
<td>.168</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 1081 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 46.2%</td>
<td>0</td>
<td>1.005</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>150</td>
<td>.831</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>.695</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>450</td>
<td>.578</td>
</tr>
<tr>
<td>t(G): 900 sec</td>
<td>600</td>
<td>.489</td>
</tr>
<tr>
<td>cc: .9995</td>
<td>750</td>
<td>.411</td>
</tr>
<tr>
<td>rate: $11.53 \times 10^{-4}$ sec$^{-1}$</td>
<td>900</td>
<td>.352</td>
</tr>
<tr>
<td>sd: .12</td>
<td>1050</td>
<td>.299</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 601 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 50.4%</td>
<td>0</td>
<td>1.301</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>150</td>
<td>1.022</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>.818</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>450</td>
<td>.671</td>
</tr>
<tr>
<td>t: 4200 sec; Ai: .172</td>
<td>600</td>
<td>.558</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>750</td>
<td>.471</td>
</tr>
<tr>
<td>rate: $17.68 \times 10^{-4}$ sec$^{-1}$</td>
<td>900</td>
<td>.400</td>
</tr>
<tr>
<td>sd: .093</td>
<td>1050</td>
<td>.345</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 392 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 53.5%</td>
<td>0</td>
<td>1.296</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>100</td>
<td>1.029</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>200</td>
<td>.831</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>300</td>
<td>.679</td>
</tr>
<tr>
<td>t: 3000 sec; Ai: .132</td>
<td>400</td>
<td>.561</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>500</td>
<td>.471</td>
</tr>
<tr>
<td>rate: $24.34 \times 10^{-4}$ sec$^{-1}$</td>
<td>600</td>
<td>.400</td>
</tr>
<tr>
<td>sd: .13</td>
<td>700</td>
<td>.342</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 285 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 58.0%</td>
<td>30</td>
<td>1.222</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>60</td>
<td>1.056</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>90</td>
<td>.915</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>120</td>
<td>.801</td>
</tr>
<tr>
<td>t: 2300 sec; Ai: .130</td>
<td>150</td>
<td>.702</td>
</tr>
<tr>
<td>cc: .9995</td>
<td>180</td>
<td>.626</td>
</tr>
<tr>
<td>rate: $50.89 \times 10^{-4}$ sec$^{-1}$</td>
<td>220</td>
<td>.510</td>
</tr>
<tr>
<td>sd: .56</td>
<td>270</td>
<td>.451</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 136 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 62.1%</td>
<td>66.1%</td>
<td>67.9%</td>
</tr>
<tr>
<td>----------</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>.0001M/L</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>300 mm</td>
<td>300 mm</td>
</tr>
<tr>
<td>t: 1300 sec; A1: .130</td>
<td>500 sec; A1: .067</td>
<td>600 sec; A1: .060</td>
</tr>
<tr>
<td>cc: 9999</td>
<td>9999</td>
<td>9999</td>
</tr>
<tr>
<td>rate: 98.08 x 10^{-4} sec^{-1}</td>
<td>168.2 x 10^{-4} sec^{-1}</td>
<td>210.6 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td>sd: .79</td>
<td>.58</td>
<td>1.10</td>
</tr>
<tr>
<td>t\frac{1}{2}: 71 sec</td>
<td>t\frac{1}{2}: 41 sec</td>
<td>t\frac{1}{2}: 33 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 61.9%</th>
<th>66.1%</th>
<th>67.9%</th>
<th>70.1%</th>
<th>72.7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: .0001M/L</td>
<td>.0001M/L</td>
<td>.0001M/L</td>
<td>.0001M/L</td>
<td>.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>300 mm</td>
<td>300 mm</td>
<td>300 mm</td>
<td>300 mm</td>
</tr>
<tr>
<td>t: 1300 sec; A1: .130</td>
<td>500 sec; A1: .067</td>
<td>600 sec; A1: .060</td>
<td>500 sec; A1: .381</td>
<td>500 sec; A1: .600</td>
</tr>
<tr>
<td>cc: 9999</td>
<td>9999</td>
<td>9999</td>
<td>9999</td>
<td>9999</td>
</tr>
<tr>
<td>rate: 98.08 x 10^{-4} sec^{-1}</td>
<td>168.2 x 10^{-4} sec^{-1}</td>
<td>210.6 x 10^{-4} sec^{-1}</td>
<td>250.2 x 10^{-4} sec^{-1}</td>
<td>277.5 x 10^{-4} sec^{-1}</td>
</tr>
<tr>
<td>sd: .79</td>
<td>.58</td>
<td>1.10</td>
<td>1.10</td>
<td>3.87</td>
</tr>
<tr>
<td>t\frac{1}{2}: 71 sec</td>
<td>t\frac{1}{2}: 41 sec</td>
<td>t\frac{1}{2}: 33 sec</td>
<td>t\frac{1}{2}: 28 sec</td>
<td>t\frac{1}{2}: 25 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.119</td>
</tr>
<tr>
<td>20</td>
<td>.930</td>
</tr>
<tr>
<td>40</td>
<td>.780</td>
</tr>
<tr>
<td>60</td>
<td>.662</td>
</tr>
<tr>
<td>80</td>
<td>.569</td>
</tr>
<tr>
<td>100</td>
<td>.497</td>
</tr>
<tr>
<td>120</td>
<td>.131</td>
</tr>
<tr>
<td>140</td>
<td>.378</td>
</tr>
<tr>
<td>0</td>
<td>1.021</td>
</tr>
<tr>
<td>20</td>
<td>.739</td>
</tr>
<tr>
<td>40</td>
<td>.551</td>
</tr>
<tr>
<td>60</td>
<td>.115</td>
</tr>
<tr>
<td>80</td>
<td>.316</td>
</tr>
<tr>
<td>100</td>
<td>.216</td>
</tr>
<tr>
<td>120</td>
<td>.192</td>
</tr>
<tr>
<td>140</td>
<td>.157</td>
</tr>
<tr>
<td>0</td>
<td>.978</td>
</tr>
<tr>
<td>10</td>
<td>.791</td>
</tr>
<tr>
<td>20</td>
<td>.635</td>
</tr>
<tr>
<td>30</td>
<td>.542</td>
</tr>
<tr>
<td>40</td>
<td>.316</td>
</tr>
<tr>
<td>50</td>
<td>.378</td>
</tr>
<tr>
<td>60</td>
<td>.265</td>
</tr>
<tr>
<td>70</td>
<td>.198</td>
</tr>
<tr>
<td>0</td>
<td>.858</td>
</tr>
<tr>
<td>10</td>
<td>.716</td>
</tr>
<tr>
<td>20</td>
<td>.663</td>
</tr>
<tr>
<td>30</td>
<td>.598</td>
</tr>
<tr>
<td>40</td>
<td>.517</td>
</tr>
<tr>
<td>50</td>
<td>.481</td>
</tr>
<tr>
<td>60</td>
<td>.464</td>
</tr>
<tr>
<td>70</td>
<td>.464</td>
</tr>
<tr>
<td>0</td>
<td>1.469</td>
</tr>
<tr>
<td>10</td>
<td>1.230</td>
</tr>
<tr>
<td>20</td>
<td>1.070</td>
</tr>
<tr>
<td>30</td>
<td>.955</td>
</tr>
<tr>
<td>40</td>
<td>.866</td>
</tr>
<tr>
<td>50</td>
<td>.806</td>
</tr>
<tr>
<td>60</td>
<td>.758</td>
</tr>
<tr>
<td>70</td>
<td>.724</td>
</tr>
<tr>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>74.9%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>80.9%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>83.1%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>84.6%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>88.4%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>93.5%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>96.0%</td>
<td>0.0001M/L</td>
</tr>
<tr>
<td>C: 91.2%</td>
<td>94.9%</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>.0002M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L: 295 nm</td>
<td>290 nm</td>
</tr>
<tr>
<td>t(G): 3000 sec</td>
<td>1500 sec</td>
</tr>
<tr>
<td>cc: .9989</td>
<td>.9995</td>
</tr>
<tr>
<td>rate: 3.92 x 10⁻⁴ sec⁻¹</td>
<td>5.16 x 10⁻⁴ sec⁻¹</td>
</tr>
<tr>
<td>sd: .064</td>
<td>.055</td>
</tr>
<tr>
<td>t½: 1766 sec</td>
<td>1343 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.731</td>
</tr>
<tr>
<td>300</td>
<td>.652</td>
</tr>
<tr>
<td>600</td>
<td>.589</td>
</tr>
<tr>
<td>900</td>
<td>.531</td>
</tr>
<tr>
<td>1200</td>
<td>.470</td>
</tr>
<tr>
<td>1500</td>
<td>.413</td>
</tr>
<tr>
<td>1800</td>
<td>.362</td>
</tr>
<tr>
<td>2100</td>
<td>.321</td>
</tr>
<tr>
<td>0</td>
<td>.674</td>
</tr>
<tr>
<td>300</td>
<td>.580</td>
</tr>
<tr>
<td>600</td>
<td>.499</td>
</tr>
<tr>
<td>900</td>
<td>.429</td>
</tr>
<tr>
<td>1200</td>
<td>.359</td>
</tr>
<tr>
<td>1500</td>
<td>.305</td>
</tr>
<tr>
<td>1800</td>
<td>.270</td>
</tr>
<tr>
<td>2100</td>
<td>.229</td>
</tr>
<tr>
<td>0</td>
<td>.821</td>
</tr>
<tr>
<td>300</td>
<td>.704</td>
</tr>
<tr>
<td>600</td>
<td>.606</td>
</tr>
<tr>
<td>900</td>
<td>.509</td>
</tr>
<tr>
<td>1200</td>
<td>.444</td>
</tr>
<tr>
<td>1500</td>
<td>.381</td>
</tr>
<tr>
<td>1800</td>
<td>.328</td>
</tr>
<tr>
<td>2100</td>
<td>.285</td>
</tr>
<tr>
<td>0</td>
<td>.750</td>
</tr>
<tr>
<td>180</td>
<td>.702</td>
</tr>
<tr>
<td>360</td>
<td>.663</td>
</tr>
<tr>
<td>600</td>
<td>.618</td>
</tr>
<tr>
<td>900</td>
<td>.560</td>
</tr>
<tr>
<td>1260</td>
<td>.500</td>
</tr>
<tr>
<td>1800</td>
<td>.431</td>
</tr>
<tr>
<td>2280</td>
<td>.392</td>
</tr>
<tr>
<td>0</td>
<td>.879</td>
</tr>
<tr>
<td>300</td>
<td>.723</td>
</tr>
<tr>
<td>600</td>
<td>.573</td>
</tr>
<tr>
<td>900</td>
<td>.462</td>
</tr>
<tr>
<td>1200</td>
<td>.379</td>
</tr>
<tr>
<td>1500</td>
<td>.304</td>
</tr>
<tr>
<td>1800</td>
<td>.217</td>
</tr>
<tr>
<td>2100</td>
<td>.204</td>
</tr>
<tr>
<td>C:</td>
<td>45.8% (6.8M) D$_2$SO$_4$</td>
</tr>
<tr>
<td>---</td>
<td>----------------------</td>
</tr>
<tr>
<td>S:</td>
<td>0.0001 M/L</td>
</tr>
<tr>
<td>T:</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L:</td>
<td>300 nm</td>
</tr>
<tr>
<td>t:</td>
<td>5000 sec; A_i: 331</td>
</tr>
<tr>
<td>cc:</td>
<td>9997</td>
</tr>
<tr>
<td>rate:</td>
<td>1.94 x 10$^{-4}$ sec$^{-1}$</td>
</tr>
<tr>
<td>ti:</td>
<td>435 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C:</th>
<th>81.6% (11.75M) D$_2$SO$_4$</th>
<th>1.208</th>
</tr>
</thead>
<tbody>
<tr>
<td>S:</td>
<td>0.0001 M/L</td>
<td>1.128</td>
</tr>
<tr>
<td>T:</td>
<td>25.3°C</td>
<td>1.056</td>
</tr>
<tr>
<td>L:</td>
<td>290 nm</td>
<td>0.990</td>
</tr>
<tr>
<td>t:</td>
<td>6000 sec; A_i: 502</td>
<td>0.930</td>
</tr>
<tr>
<td>cc:</td>
<td>9999</td>
<td>0.882</td>
</tr>
<tr>
<td>rate:</td>
<td>1.66 x 10$^{-4}$ sec$^{-1}$</td>
<td>0.840</td>
</tr>
<tr>
<td>ti:</td>
<td>556 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C:</th>
<th>18.15M D$_2$SO$_4$</th>
<th>.758</th>
</tr>
</thead>
<tbody>
<tr>
<td>S:</td>
<td>0.0001 M/L</td>
<td>.575</td>
</tr>
<tr>
<td>T:</td>
<td>25.3°C</td>
<td>.437</td>
</tr>
<tr>
<td>L:</td>
<td>290 nm</td>
<td>.312</td>
</tr>
<tr>
<td>t(G):</td>
<td>1800 sec</td>
<td>.261</td>
</tr>
<tr>
<td>cc:</td>
<td>9994</td>
<td>.198</td>
</tr>
<tr>
<td>rate:</td>
<td>9.24 x 10$^{-4}$ sec$^{-1}$</td>
<td>.144</td>
</tr>
<tr>
<td>ti:</td>
<td>750 sec</td>
<td></td>
</tr>
<tr>
<td>t$_2^1$:</td>
<td>435 sec</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE XIX

<table>
<thead>
<tr>
<th>1-benzoyl-5-methyl-2-thiohydantoin</th>
<th>Time</th>
<th>(\text{dA})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>C:</strong> 58.0%</td>
<td>0</td>
<td>1.252</td>
</tr>
<tr>
<td>(S:) .0001M/L</td>
<td>60</td>
<td>1.077</td>
</tr>
<tr>
<td>(T:) 25.3(^\circ)C</td>
<td>120</td>
<td>0.932</td>
</tr>
<tr>
<td>(L:) 280 nm</td>
<td>180</td>
<td>0.812</td>
</tr>
<tr>
<td>(t:) 1500 sec; (A_i:) .298</td>
<td>240</td>
<td>0.715</td>
</tr>
<tr>
<td>(cc:) .9998</td>
<td>360</td>
<td>0.631</td>
</tr>
<tr>
<td>rate: (35.53 \times 10^{-4}) sec(^{-1})</td>
<td></td>
<td>0.566</td>
</tr>
<tr>
<td>sd: .21</td>
<td>420</td>
<td>0.513</td>
</tr>
<tr>
<td>(t_{1/2}:) 195 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C:</strong> 66.1%</td>
<td>0</td>
<td>1.123</td>
</tr>
<tr>
<td>(S:) .0001M/L</td>
<td>30</td>
<td>0.908</td>
</tr>
<tr>
<td>(T:) 25.3(^\circ)C</td>
<td>60</td>
<td>0.715</td>
</tr>
<tr>
<td>(L:) 280 nm</td>
<td>90</td>
<td>0.614</td>
</tr>
<tr>
<td>(t:) 1400 sec; (A_i:) .073</td>
<td>120</td>
<td>0.511</td>
</tr>
<tr>
<td>(cc:) .9999</td>
<td>150</td>
<td>0.428</td>
</tr>
<tr>
<td>rate: (71.77 \times 10^{-4}) sec(^{-1})</td>
<td></td>
<td>0.360</td>
</tr>
<tr>
<td>sd: .30</td>
<td>210</td>
<td>0.303</td>
</tr>
<tr>
<td>(t_{1/2}:) 97 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C:</strong> 68.0%</td>
<td>0</td>
<td>1.202</td>
</tr>
<tr>
<td>(S:) .0001M/L</td>
<td>30</td>
<td>0.914</td>
</tr>
<tr>
<td>(T:) 25.3(^\circ)C</td>
<td>60</td>
<td>0.715</td>
</tr>
<tr>
<td>(L:) 285 nm</td>
<td>90</td>
<td>0.562</td>
</tr>
<tr>
<td>(t:) 1000 sec; (A_i:) 0.037</td>
<td>120</td>
<td>0.418</td>
</tr>
<tr>
<td>(cc:) .9998</td>
<td>150</td>
<td>0.360</td>
</tr>
<tr>
<td>rate: (84.90 \times 10^{-4}) sec(^{-1})</td>
<td></td>
<td>0.282</td>
</tr>
<tr>
<td>sd: .61</td>
<td>210</td>
<td>0.231</td>
</tr>
<tr>
<td>(t_{1/2}:) 82 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C:</strong> 70.1%</td>
<td>0</td>
<td>1.402</td>
</tr>
<tr>
<td>(S:) .0001M/L</td>
<td>30</td>
<td>1.055</td>
</tr>
<tr>
<td>(T:) 25.3(^\circ)C</td>
<td>60</td>
<td>0.823</td>
</tr>
<tr>
<td>(L:) 285 nm</td>
<td>90</td>
<td>0.643</td>
</tr>
<tr>
<td>(t:) 1600 sec; (A_i:) .12</td>
<td>120</td>
<td>0.519</td>
</tr>
<tr>
<td>(cc:) .9995</td>
<td>150</td>
<td>0.421</td>
</tr>
<tr>
<td>rate: (93.10 \times 10^{-4}) sec(^{-1})</td>
<td></td>
<td>0.353</td>
</tr>
<tr>
<td>sd: 1.08</td>
<td>210</td>
<td>0.301</td>
</tr>
<tr>
<td>(t_{1/2}:) 74 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>C:</strong> 72.7%</td>
<td>0</td>
<td>1.263</td>
</tr>
<tr>
<td>(S:) .0001M/L</td>
<td>30</td>
<td>0.915</td>
</tr>
<tr>
<td>(T:) 25.3(^\circ)C</td>
<td>60</td>
<td>0.722</td>
</tr>
<tr>
<td>(L:) 285 nm</td>
<td>90</td>
<td>0.566</td>
</tr>
<tr>
<td>(t:) 600 sec</td>
<td>120</td>
<td>0.437</td>
</tr>
<tr>
<td>(cc:) .9996</td>
<td>150</td>
<td>0.348</td>
</tr>
<tr>
<td>rate: (84.13 \times 10^{-4}) sec(^{-1})</td>
<td></td>
<td>0.272</td>
</tr>
<tr>
<td>sd: .88</td>
<td>210</td>
<td>0.211</td>
</tr>
<tr>
<td>(t_{1/2}:) 82 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>dA</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.120</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1.110</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>.940</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>.786</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>.669</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>.569</td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>.491</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>.424</td>
<td></td>
</tr>
</tbody>
</table>

| C: 74.9% | 0 | 1.120 |
| S: .0001M/L | 30 | 1.110 |
| T: 25.3°C | 60 | .940  |
| L: 285 nm | 90 | .786  |
| t: 1500 sec; Ai: .135 | 120 | .669  |
| cc: .9995 | 150 | .569  |
| rate: 70.18 x 10^{-4} sec^{-1} | 180 | .491  |
| sd: .77 | 210 | .424  |
| $t_1/2$: 99 sec | | |

| C: 78.1% | 0 | .801 |
| S: .0001M/L | 100 | .638 |
| T: 25.3°C | 200 | .520 |
| L: 285 nm | 300 | .428 |
| t(G): 600 sec | 400 | .358 |
| cc: .9987 | 500 | .288 |
| rate: 19.13 x 10^{-4} sec^{-1} | 600 | .252 |
| sd: .34 | 700 | .207 |
| $t_1/2$: 362 sec | | |

| C: 96.1% | 0 | 1.007 |
| S: .0001M/L | 300 | .849 |
| T: 25.3°C | 600 | .726 |
| L: 310 nm | 900 | .620 |
| t(G): 3000 sec | 1200 | .528 |
| cc: .9994 | 1500 | .457 |
| rate: 5.08 x 10^{-4} sec^{-1} | 1800 | .399 |
| sd: .06 | 2100 | .316 |
| $t_1/2$: 1364 sec | | |

<p>| pH: 11.2 | 0 | 1.113 |
| B: .1M Na2HPO4, .025N NaOH, .075N NaCl | | |
| I: .45 | 150 | .905 |
| S: .0001M/L | 300 | .721 |
| T: 25.3°C | 450 | .617 |
| L: 300 nm | 900 | .514 |
| t(G): 900 sec | 750 | .424 |
| cc: .9998 | 900 | .352 |
| rate: 12.67 x 10^{-4} sec^{-1} | 1050 | .291 |
| sd: .07 | | |
| $t_1/2$: 547 sec | | |</p>
<table>
<thead>
<tr>
<th></th>
<th>1-benzoyl-5-isopropyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 62.4%</td>
<td>0</td>
<td>1.020</td>
<td></td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>100</td>
<td>.826</td>
<td></td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>200</td>
<td>.676</td>
<td></td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>300</td>
<td>.553</td>
<td></td>
</tr>
<tr>
<td>t(G): 500 sec</td>
<td>400</td>
<td>.555</td>
<td></td>
</tr>
<tr>
<td>cc: .9998</td>
<td>500</td>
<td>.376</td>
<td></td>
</tr>
<tr>
<td>rate: 19.60 x 10^-4 sec^-1</td>
<td>600</td>
<td>.311</td>
<td></td>
</tr>
<tr>
<td>sd: .13</td>
<td>700</td>
<td>.258</td>
<td></td>
</tr>
<tr>
<td>t_1/2: 394 sec</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| C: 66.1% | 0 | 1.183 |
| S: .0001M/L | 100 | .857 |
| T: 25.3°C | 200 | .634 |
| L: 285 nm | 300 | .179 |
| t(G): 500 sec | 400 | .357 |
| cc: .9999 | 500 | .264 |
| rate: 29.80 x 10^-4 sec^-1 | 600 | .197 |
| sd: .14 | 700 | .144 |
| t_1/2: 233 sec |   |    |

| C: 68.0% | 0 | 1.222 |
| S: .0001M/L | 100 | .864 |
| T: 25.3°C | 200 | .639 |
| L: 285 nm | 300 | .179 |
| t: 2000 sec; Ai: .066 | 400 | .360 |
| cc: .9998 | 500 | .280 |
| rate: 33.60 x 10^-4 sec^-1 | 600 | .172 |
| sd: .22 | 700 |    |
| t_1/2: 206 sec |   |    |

| C: 70.1% | 0 | 1.361 |
| S: .0001M/L | 50 | 1.112 |
| T: 25.3°C | 100 | .921 |
| L: 285 nm | 150 | .775 |
| t: 1700 sec; Ai: .116 | 200 | .661 |
| cc: .9996 | 250 | .565 |
| rate: 39.70 x 10^-4 sec^-1 | 300 | .188 |
| sd: .40 | 350 | .122 |
| t_1/2: 174 sec |   |    |

<p>| C: 72.7% | 0 | 1.501 |
| S: .0001M/L | 50 | 1.238 |
| T: 25.3°C | 100 | 1.031 |
| L: 285 nm | 150 | .863 |
| t: 2100 sec; Ai: .09 | 200 | .734 |
| cc: .9996 | 300 | .513 |
| rate: 36.56 x 10^-4 sec^-1 | 400 | .108 |
| sd: .38 | 500 | .314 |
| t_1/2: 190 sec |   |    |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.114</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 74.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 285 nm</td>
</tr>
<tr>
<td>t(G): 300 sec</td>
</tr>
<tr>
<td>cc: 0.9997</td>
</tr>
<tr>
<td>rate: $29.30 \times 10^{-4} \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>sd: 0.26</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 237 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 78.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 285 nm</td>
</tr>
<tr>
<td>t(G): 300 sec</td>
</tr>
<tr>
<td>cc: 0.9990</td>
</tr>
<tr>
<td>rate: $10.30 \times 10^{-4} \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>sd: 0.16</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 672 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C: 96.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S: 0.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 285 nm</td>
</tr>
<tr>
<td>t(G): 300 sec</td>
</tr>
<tr>
<td>cc: 0.9996</td>
</tr>
<tr>
<td>rate: $8.91 \times 10^{-4} \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>sd: 0.09</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 778 sec</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 11.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: 0.1M NaHPO$_4$, 0.025N NaCH, 0.07N NaCl</td>
</tr>
<tr>
<td>I: 0.15</td>
</tr>
<tr>
<td>S: 0.0001M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 285 nm</td>
</tr>
<tr>
<td>t(G): 300 sec</td>
</tr>
<tr>
<td>cc: 0.9994</td>
</tr>
<tr>
<td>rate: $4.77 \times 10^{-4} \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>sd: 0.06</td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 1453 sec</td>
</tr>
</tbody>
</table>
TABLE XXI

1-benzoyl-5-(sec)butyl-2-thiohydantoin

<table>
<thead>
<tr>
<th></th>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C: 58.0%</td>
<td>0</td>
<td>1.362</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>100</td>
<td>1.209</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>200</td>
<td>1.079</td>
</tr>
<tr>
<td>L: 285 nm</td>
<td>300</td>
<td>.964</td>
</tr>
<tr>
<td>t: 2500 sec; A1: .375</td>
<td>100</td>
<td>.869</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>500</td>
<td>.785</td>
</tr>
<tr>
<td>rate: 17.87 x 10^-4 sec^-1</td>
<td>600</td>
<td>.718</td>
</tr>
<tr>
<td>sd: .13</td>
<td>700</td>
<td>.657</td>
</tr>
<tr>
<td>t^-1/2: 388 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

C: 62.1% |
S: .0001M/L |
T: 25.3°C |
L: 285 nm |
t: 2800 sec; A1: .141 |
cc: .9999 |
rate: 24.77 x 10^-4 sec^-1 |
sd: .12 |
| t^-1/2: 280 sec |     |     |

C: 66.1% |
S: .0001M/L |
T: 25.3°C |
L: 285 nm |
t: 2000 sec; A1: .110 |
cc: .9998 |
rate: 35.54 x 10^-4 sec^-1 |
sd: .20 |
| t^-1/2: 195 sec |     |     |

C: 68.0% |
S: .0001M/L |
T: 25.3°C |
L: 285 nm |
t: 2200 sec; A1: .092 |
cc: .9998 |
rate: 40.76 x 10^-4 sec^-1 |
sd: .30 |
| t^-1/2: 170 sec |     |     |

C: 70.1% |
S: .0001M/L |
T: 25.3°C |
L: 285 nm |
t: 400 sec |
cc: .9999 |
rate: 47.30 x 10^-4 sec^-1 |
sd: .22 |
<p>| t^-1/2: 1147 sec |     |     |</p>
<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.230</td>
</tr>
<tr>
<td>50</td>
<td>1.008</td>
</tr>
<tr>
<td>100</td>
<td>.821</td>
</tr>
<tr>
<td>150</td>
<td>.683</td>
</tr>
<tr>
<td>200</td>
<td>.576</td>
</tr>
<tr>
<td>300</td>
<td>.420</td>
</tr>
<tr>
<td>400</td>
<td>.311</td>
</tr>
<tr>
<td>500</td>
<td>.239</td>
</tr>
<tr>
<td>167 sec</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.969</td>
</tr>
<tr>
<td>100</td>
<td>.680</td>
</tr>
<tr>
<td>200</td>
<td>.485</td>
</tr>
<tr>
<td>300</td>
<td>.343</td>
</tr>
<tr>
<td>400</td>
<td>.288</td>
</tr>
<tr>
<td>500</td>
<td>.239</td>
</tr>
<tr>
<td>600</td>
<td>.239</td>
</tr>
<tr>
<td>700</td>
<td>.100</td>
</tr>
<tr>
<td>214 sec</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.551</td>
</tr>
<tr>
<td>150</td>
<td>.374</td>
</tr>
<tr>
<td>300</td>
<td>.296</td>
</tr>
<tr>
<td>450</td>
<td>.259</td>
</tr>
<tr>
<td>600</td>
<td>.221</td>
</tr>
<tr>
<td>750</td>
<td>.188</td>
</tr>
<tr>
<td>1050</td>
<td>.769</td>
</tr>
<tr>
<td>675 sec</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>.658</td>
</tr>
<tr>
<td>300</td>
<td>.565</td>
</tr>
<tr>
<td>600</td>
<td>.491</td>
</tr>
<tr>
<td>900</td>
<td>.429</td>
</tr>
<tr>
<td>1200</td>
<td>.374</td>
</tr>
<tr>
<td>1500</td>
<td>.328</td>
</tr>
<tr>
<td>1800</td>
<td>.288</td>
</tr>
<tr>
<td>2100</td>
<td></td>
</tr>
<tr>
<td>1490 sec</td>
<td></td>
</tr>
</tbody>
</table>
## PART IV

### TABLE I

<table>
<thead>
<tr>
<th>1-acetyl-5,5-dimethyl-2-thiohydantoin</th>
<th>Time</th>
<th>$\Delta A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 14.0</td>
<td>0</td>
<td>1.498</td>
</tr>
<tr>
<td>B: 1N NaOH</td>
<td>3</td>
<td>0.990</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>6</td>
<td>0.697</td>
</tr>
<tr>
<td>S: 0.001M 7M/L</td>
<td>9</td>
<td>0.532</td>
</tr>
<tr>
<td>T: 25,4°C</td>
<td>12</td>
<td>0.432</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>15</td>
<td>0.366</td>
</tr>
<tr>
<td>$t$: 90 sec; $A_{i}$: 0.282</td>
<td>18</td>
<td>0.331</td>
</tr>
<tr>
<td>$cc$: 0.9998</td>
<td>21</td>
<td>0.310</td>
</tr>
<tr>
<td>rate: $1788 \times 10^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$sd$: 10.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{\frac{1}{2}}$: 3.88 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| pH: 14.0                             | 0    | 1.515      |
| B: 1N NaOH                            | 3    | 0.996      |
| I: 1.0                               | 6    | 0.678      |
| S: 0.001M 2M/L                       | 9    | 0.508      |
| T: 25,4°C                            | 12   | 0.406      |
| L: 300 nm                            | 15   | 0.343      |
| $t$: 90 sec; $A_{i}$: 0.250           | 18   | 0.303      |
| $cc$: 0.9999                         | 21   | 0.282      |
| rate: $1748 \times 10^{-4}$ sec$^{-1}$|      |            |
| $sd$: 7.6                            |      |            |
| $t_{\frac{1}{2}}$: 3.97 sec          |      |            |

| pH: 14.0                             | 0    | 1.110      |
| B: 1N NaOH                            | 3    | 0.750      |
| I: 1.0                               | 6    | 0.533      |
| S: 0.00135M/L                        | 9    | 0.110      |
| T: 25,4°C                            | 12   | 0.327      |
| L: 300 nm                            | 15   | 0.282      |
| $t$: 90 sec; $A_{i}$: 0.208           | 18   | 0.250      |
| $cc$: 0.9998                         | 21   | 0.235      |
| rate: $1679 \times 10^{-4}$ sec$^{-1}$|      |            |
| $sd$: 10.1                           |      |            |
| $t_{\frac{1}{2}}$: 5.13 sec          |      |            |
pH: 13.9
B: .8N NaOH, .2N KCl
I: 1.0
S: .00012 M/L
T: 25.4°C
L: 300 mm
t: 120 sec; Ai: .250
c: .9998
rate: 1357 x 10⁻⁴ sec⁻¹
sd: 9.06
t₁/₂: 5.11 sec

pH: 13.9
B: .8N NaOH, .2N KCl
I: 1.0
S: .00012 M/L
T: 25.4°C
L: 300 mm
t: 105 sec; Ai: .245
c: .9997
rate: 1331 x 10⁻⁴ sec⁻¹
sd: 10.0
t₁/₂: 5.21 sec

pH: 13.7
B: .5N NaOH, .5N KCl
I: 1.0
S: .0002 M/L
T: 25.4°C
L: 300 mm
t: 150 sec; Ai: .117
c: .9999
rate: 775 x 10⁻⁴ sec⁻¹
sd: 3.0
t₁/₂: 8.94 sec

pH: 13.7
B: .5N NaOH, .5N KCl
I: 1.0
S: .0002 M/L
T: 25.4°C
L: 300 mm
t: 150 sec; Ai: .127
c: .9998
rate: 753 x 10⁻⁴ sec⁻¹
sd: 4.4
 t₁/₂: 9.21 sec
<table>
<thead>
<tr>
<th>pH</th>
<th>B: .2N NaOH, .8N KCl</th>
<th>I: .0</th>
<th>S: .00015 M/L</th>
<th>T: 25.4°C</th>
<th>L: 300 mm</th>
<th>t: 300 sec; A1: 0.09</th>
<th>cc: .9998</th>
<th>rate: 302 x 10^-4 sec^-1</th>
<th>sd: 1.96</th>
<th>t_1/2: 22.9 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.3</td>
<td>0.2N NaOH, .8N KCl</td>
<td>1.0</td>
<td>0.00015 M/L</td>
<td>24</td>
<td>30</td>
<td>36</td>
<td>.9998</td>
<td>3.02 x 10^-4</td>
<td>1.96</td>
<td>22.9 sec</td>
</tr>
<tr>
<td>pH: 13.3</td>
<td>B: .2N NaOH, .8N KCl</td>
<td>I: 1.0</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t: 300 sec; A1: .09</td>
<td>cc: .9998</td>
<td>rate: 302 x 10^-4 sec^-1</td>
<td>sd: 1.96</td>
<td>t_1/2: 22.9 sec</td>
</tr>
<tr>
<td>pH: 13.3</td>
<td>B: .2N NaOH, .8N KCl</td>
<td>I: 1.0</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t: 300 sec; A1: .09</td>
<td>cc: .9998</td>
<td>rate: 302 x 10^-4 sec^-1</td>
<td>sd: 1.96</td>
<td>t_1/2: 22.9 sec</td>
</tr>
<tr>
<td>pH: 13.0</td>
<td>B: .1N NaOH, .4N KCl</td>
<td>I: .5</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t(G): 120 sec</td>
<td>cc: .9998</td>
<td>rate: 136.9 x 10^-4 sec^-1</td>
<td>sd: .7</td>
<td>t_1/2: 50.6 sec</td>
</tr>
<tr>
<td>pH: 13.0</td>
<td>B: .1N NaOH, .4N KCl</td>
<td>I: .5</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t(G): 120 sec</td>
<td>cc: .9998</td>
<td>rate: 136.9 x 10^-4 sec^-1</td>
<td>sd: .7</td>
<td>t_1/2: 50.6 sec</td>
</tr>
<tr>
<td>pH: 13.0</td>
<td>B: .1N NaOH, .4N KCl</td>
<td>I: .5</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t(G): 120 sec</td>
<td>cc: .9998</td>
<td>rate: 136.9 x 10^-4 sec^-1</td>
<td>sd: .7</td>
<td>t_1/2: 50.6 sec</td>
</tr>
<tr>
<td>pH: 13.0</td>
<td>B: .1N NaOH, .4N KCl</td>
<td>I: .5</td>
<td>S: .00015 M/L</td>
<td>T: 25.4°C</td>
<td>L: 300 mm</td>
<td>t(G): 120 sec</td>
<td>cc: .9998</td>
<td>rate: 136.9 x 10^-4 sec^-1</td>
<td>sd: .7</td>
<td>t_1/2: 50.6 sec</td>
</tr>
<tr>
<td>pH</td>
<td>Time (sec)</td>
<td>dA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>------------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>0</td>
<td>1.307</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.8</td>
<td>0</td>
<td>1.155</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.8</td>
<td>0</td>
<td>1.167</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.8</td>
<td>0</td>
<td>1.426</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>B: 1N NaOH, 0.9N KCl</th>
<th>I: 1.0</th>
<th>S: 0.0015M/L</th>
<th>T: 25.4°C</th>
<th>L: 300 mm</th>
<th>t: 530 sec; A1: 0.08</th>
<th>cc: 9999</th>
<th>rate: 1.49 x 10^{-4} sec^{-1}</th>
<th>sd: 0.7</th>
<th>t1/2: 46.4 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.0</td>
<td>0.1N NaOH, 0.9N KCl</td>
<td>0</td>
<td>0.155</td>
<td>0.723</td>
<td>0.382</td>
<td>120 sec</td>
<td>0.9998</td>
<td>1.47 x 10^{-4} sec^{-1}</td>
<td>0.9</td>
<td>46.9 sec</td>
</tr>
<tr>
<td>12.8</td>
<td>0.063N NaOH, 0.938N KCl</td>
<td>0</td>
<td>1.67</td>
<td>1.404</td>
<td>0.297</td>
<td>120 sec</td>
<td>0.9998</td>
<td>1.02 x 10^{-4} sec^{-1}</td>
<td>0.67</td>
<td>67.6 sec</td>
</tr>
<tr>
<td>12.8</td>
<td>0.063N NaOH, 0.938N KCl</td>
<td>0</td>
<td>1.426</td>
<td>0.368</td>
<td>0.237</td>
<td>135 sec</td>
<td>0.9996</td>
<td>1.02 x 10^{-4} sec^{-1}</td>
<td>1.07</td>
<td>67.8 sec</td>
</tr>
<tr>
<td>pH</td>
<td>B (NaOH)</td>
<td>I (KCl)</td>
<td>S (M/L)</td>
<td>T (°C)</td>
<td>L (nm)</td>
<td>t(G) (sec)</td>
<td>cc (%)</td>
<td>rate (sec⁻¹)</td>
<td>t½ (sec)</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>----------</td>
<td>---------</td>
<td>---------</td>
<td>--------</td>
<td>--------</td>
<td>------------</td>
<td>--------</td>
<td>--------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>12.4</td>
<td>.025N</td>
<td>1.0</td>
<td>.001M/L</td>
<td>25.4</td>
<td>300</td>
<td>270</td>
<td>.9997</td>
<td>4.12 x 10⁻⁴</td>
<td>168</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.001N</td>
<td>.975N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.4</td>
<td>.025N</td>
<td>1.0</td>
<td>.001M/L</td>
<td>25.4</td>
<td>300</td>
<td>450</td>
<td>.9998</td>
<td>4.16 x 10⁻⁴</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.001N</td>
<td>.975N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.25</td>
<td>.0175N</td>
<td>1.0</td>
<td>.001M/L</td>
<td>25.4</td>
<td>300</td>
<td>750</td>
<td>.9999</td>
<td>2.84 x 10⁻⁴</td>
<td>166</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.001N</td>
<td>.984N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>.01006N</td>
<td>.01</td>
<td>.0 x 10⁻⁵</td>
<td>25.4</td>
<td>280</td>
<td>4800</td>
<td>.9996</td>
<td>9.17 x 10⁻⁴</td>
<td>756</td>
<td></td>
</tr>
<tr>
<td></td>
<td>.01</td>
<td>.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH: 12.0</td>
<td>Time</td>
<td>( \Delta A )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B: ( 0.01006 \text{N NaOH} )</td>
<td>0</td>
<td>( 0.182 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I: ( 0.01 )</td>
<td>96</td>
<td>( 0.125 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S: ( 1.0 \times 10^{-5} \text{M} )</td>
<td>240</td>
<td>( 0.102 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>336</td>
<td>( 0.361 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>480</td>
<td>( 0.320 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( t(0) ): 300 sec</td>
<td>720</td>
<td>( 0.260 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cc: ( 0.9981 )</td>
<td>960</td>
<td>( 0.202 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rate: ( 8.71 \times 10^{-4} \text{sec}^{-1} )</td>
<td>1200</td>
<td>( 0.177 )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: ( 0.19 )</td>
<td>( t_{1/2} ): 796 sec</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 12.0</th>
<th>Time</th>
<th>( \Delta A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: ( 0.01006 \text{N NaOH, 0.03N KCl} )</td>
<td>0</td>
<td>( 0.793 )</td>
</tr>
<tr>
<td>I: ( 0.04 )</td>
<td>96</td>
<td>( 0.728 )</td>
</tr>
<tr>
<td>S: ( 1.0 \times 10^{-5} \text{M} )</td>
<td>240</td>
<td>( 0.624 )</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>336</td>
<td>( 0.589 )</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>480</td>
<td>( 0.512 )</td>
</tr>
<tr>
<td>( t(0) ): 4800 sec; ( A_i: 0.06 )</td>
<td>720</td>
<td>( 0.413 )</td>
</tr>
<tr>
<td>cc: ( 0.9997 )</td>
<td>960</td>
<td>( 0.327 )</td>
</tr>
<tr>
<td>rate: ( 10.42 \times 10^{-4} \text{sec}^{-1} )</td>
<td>1200</td>
<td>( 0.274 )</td>
</tr>
<tr>
<td>sd: ( 0.08 )</td>
<td>( t_{1/2} ): 665 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 12.0</th>
<th>Time</th>
<th>( \Delta A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: ( 0.01006 \text{N NaOH, 0.03N KCl} )</td>
<td>0</td>
<td>( 0.756 )</td>
</tr>
<tr>
<td>I: ( 0.09 )</td>
<td>96</td>
<td>( 0.696 )</td>
</tr>
<tr>
<td>S: ( 1.0 \times 10^{-5} \text{M} )</td>
<td>240</td>
<td>( 0.609 )</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>336</td>
<td>( 0.558 )</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>480</td>
<td>( 0.490 )</td>
</tr>
<tr>
<td>( t(0) ): 4320 sec; ( A_i: 0.061 )</td>
<td>720</td>
<td>( 0.390 )</td>
</tr>
<tr>
<td>cc: ( 0.9996 )</td>
<td>960</td>
<td>( 0.314 )</td>
</tr>
<tr>
<td>rate: ( 10.41 \times 10^{-4} \text{sec}^{-1} )</td>
<td>1200</td>
<td>( 0.264 )</td>
</tr>
<tr>
<td>sd: ( 0.13 )</td>
<td>( t_{1/2} ): 666 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 12.0</th>
<th>Time</th>
<th>( \Delta A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: ( 0.01006 \text{N NaOH, 0.08N KCl} )</td>
<td>0</td>
<td>( 0.862 )</td>
</tr>
<tr>
<td>I: ( 0.09 )</td>
<td>96</td>
<td>( 0.779 )</td>
</tr>
<tr>
<td>S: ( 1.0 \times 10^{-5} \text{M} )</td>
<td>240</td>
<td>( 0.683 )</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>336</td>
<td>( 0.618 )</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>480</td>
<td>( 0.535 )</td>
</tr>
<tr>
<td>( t(0) ): 4320 sec; ( A_i: 0.059 )</td>
<td>720</td>
<td>( 0.416 )</td>
</tr>
<tr>
<td>cc: ( 0.9994 )</td>
<td>960</td>
<td>( 0.325 )</td>
</tr>
<tr>
<td>rate: ( 11.0 \times 10^{-4} \text{sec}^{-1} )</td>
<td>1200</td>
<td>( 0.265 )</td>
</tr>
<tr>
<td>sd: ( 0.13 )</td>
<td>( t_{1/2} ): 630 sec</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>-------</td>
<td>------</td>
<td>-----</td>
</tr>
<tr>
<td>12.0</td>
<td>0</td>
<td>.567^p</td>
</tr>
<tr>
<td>B: .01006N NaOH, .08N KCl</td>
<td>96</td>
<td>.518</td>
</tr>
<tr>
<td>I: .09</td>
<td>210</td>
<td>.450</td>
</tr>
<tr>
<td>S: 1.0 x 10^{-5}M/L</td>
<td>336</td>
<td>.398</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>480</td>
<td>.340</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>576</td>
<td>.309</td>
</tr>
<tr>
<td>t(G): 480 sec</td>
<td>720</td>
<td>.260</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>816</td>
<td>.232</td>
</tr>
<tr>
<td>rate: 11.46 x 10^{-4} sec^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t:\bar{t}: 617 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 12.0</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .01006N NaOH, .15N KCl</td>
<td>96</td>
<td>.529^p</td>
</tr>
<tr>
<td>I: .16</td>
<td>240</td>
<td>.466</td>
</tr>
<tr>
<td>S: 1.0 x 10^{-5}M/L</td>
<td>336</td>
<td>.392</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>480</td>
<td>.351</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>576</td>
<td>.299</td>
</tr>
<tr>
<td>t(G): 480 sec</td>
<td>720</td>
<td>.260</td>
</tr>
<tr>
<td>cc: .9996</td>
<td>816</td>
<td>.216</td>
</tr>
<tr>
<td>rate: 12.2 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.195</td>
</tr>
<tr>
<td>sd: .11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t:\bar{t}: 566 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 12.0</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .01006N NaOH, .15N KCl</td>
<td>96</td>
<td>.560^p</td>
</tr>
<tr>
<td>I: .16</td>
<td>240</td>
<td>.433</td>
</tr>
<tr>
<td>S: 1.0 x 10^{-5}M/L</td>
<td>336</td>
<td>.390</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>480</td>
<td>.323</td>
</tr>
<tr>
<td>L: 280 mm</td>
<td>576</td>
<td>.285</td>
</tr>
<tr>
<td>t(G): 480 sec</td>
<td>720</td>
<td>.216</td>
</tr>
<tr>
<td>cc: .9993</td>
<td>816</td>
<td>.215</td>
</tr>
<tr>
<td>rate: 11.8 x 10^{-4} sec^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t:\bar{t}: 590 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 11.88^m</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .01M K_2HPO_4, .03M K_3PO_4, .79N KCl</td>
<td>350</td>
<td>1.088</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>300</td>
<td>.900</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>450</td>
<td>.744</td>
</tr>
<tr>
<td>T: 25.4°C</td>
<td>600</td>
<td>.622</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>750</td>
<td>.519</td>
</tr>
<tr>
<td>t(G): 1350 sec</td>
<td>900</td>
<td>.436</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>1050</td>
<td>.364</td>
</tr>
<tr>
<td>rate: 12.1 x 10^{-4} sec^{-1}</td>
<td></td>
<td>.302</td>
</tr>
<tr>
<td>sd: .05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t:\bar{t}: 572 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>B:</td>
<td>I:</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>11.56</td>
<td>.08 M K2HPO4, .08 M K3PO4, .28 N KCl</td>
<td>1.0</td>
</tr>
<tr>
<td>11.47</td>
<td>.04 M K2HPO4, .04 M K3PO4, .64 N KCl</td>
<td>1.0</td>
</tr>
<tr>
<td>11.4</td>
<td>.0025 N NaOH</td>
<td>1.80</td>
</tr>
<tr>
<td>10.95</td>
<td>.03 M K2HPO4, .01 M K3PO4, .85 N KCl</td>
<td>1.0</td>
</tr>
</tbody>
</table>
pH: 11.95  
B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl  
I: .55  
S: .0001M/L  
L: 300 nm  
t: 500 sec; A₁: .056  
c: .9998  
T: 58.1°C  
rate: 173.53 x 10⁻⁴ sec⁻¹  
sd: 1.23  
t₁/₂: 40 sec

pH: 11.95  
B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl  
I: .55  
S: .0001M/L  
L: 300 nm  
t: 480 sec; A₁: .031  
c: .9997  
T: 58.1°C  
rate: 176.66 x 10⁻⁴ sec⁻¹  
sd: 1.52  
t₁/₂: 39 sec

pH: 11.95  
B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl  
I: .55  
S: .0001M/L  
L: 300 nm  
t: 660 sec; A₁: .085  
c: .9999  
T: 58.1°C  
rate: 179.88 x 10⁻⁴ sec⁻¹  
sd: .94  
t₁/₂: 38.5 sec

pH: 11.95  
B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl  
I: .55  
S: .00023M/L  
L: 100 nm  
t: 870 sec; A₁: .149  
c: .9999  
T: 58.1°C  
rate: 94.58 x 10⁻⁴ sec⁻¹  
sd: .36  
t₁/₂: 73 sec
<table>
<thead>
<tr>
<th>pH</th>
<th>Time (sec)</th>
<th>Rate constant</th>
<th>t&lt;sub&gt;1/2&lt;/sub&gt; (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>95.69 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>72 sec</td>
</tr>
<tr>
<td>11.95</td>
<td>0</td>
<td>97.22 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>71 sec</td>
</tr>
<tr>
<td>11.95</td>
<td>0</td>
<td>12.85 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>71 sec</td>
</tr>
<tr>
<td>11.95</td>
<td>0</td>
<td>12.82 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>54.1 sec</td>
</tr>
</tbody>
</table>
**Time**

| pH: 11.95 | 0 |
| B: 1M Na<sub>2</sub>HPO<sub>4</sub>, 0.075M NaOH, 0.025M NaCl | 58 |
| I: 0.55 | 174 |
| L: 300 nm | 290 |
| T: 25.3°C | 406 |
| S: 0.0023M/L | 522 |
| t(0): 650 sec | 667 |
| cc: 0.9998 | 899 |
| rate: 12.91 x 10<sup>-4</sup> sec<sup>-1</sup> | |
| sd: 0.094 | |
| t<sub>½</sub>: 537 sec | |

| pH: 11.95 | 0 |
| B: 1M Na<sub>2</sub>HPO<sub>4</sub>, 0.075M NaOH, 0.025M NaCl | 116 |
| I: 0.55 | 290 |
| L: 300 nm | 522 |
| T: 11.0°C | 667 |
| S: 0.0023M/L | 899 |
| t(0): 4000 sec | 1015 |
| cc: 0.9999 | 1160 |
| rate: 3.663 x 10<sup>-4</sup> sec<sup>-1</sup> | |
| sd: 0.018 | |
| t<sub>½</sub>: 1892 sec | |

| pH: 11.95 | 0 |
| B: 1M Na<sub>2</sub>HPO<sub>4</sub>, 0.075M NaOH, 0.025M NaCl | 116 |
| I: 0.55 | 290 |
| L: 300 nm | 522 |
| T: 11.0°C | 667 |
| S: 0.0023M/L | 899 |
| t(0): 4000 sec | 1015 |
| cc: 0.9997 | 1160 |
| rate: 3.632 x 10<sup>-4</sup> sec<sup>-1</sup> | |
| sd: 0.034 | |
| t<sub>½</sub>: 1908 sec | |

<p>| pH: 11.2 | 0 |
| B: 1M Na&lt;sub&gt;2&lt;/sub&gt;HPO&lt;sub&gt;4&lt;/sub&gt;, 0.025M NaOH, 0.075M NaCl | 116 |
| I: 0.45 | 100 |
| T: 25.3°C | 200 |
| L: 300 nm | 100 |
| S: 0.001M/L | 600 |
| t(0): 3000 sec | 800 |
| cc: 0.9979 | 1000 |
| rate: 2.20 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt; | |
| sd: 0.05 | |
| t&lt;sub&gt;½&lt;/sub&gt;: 3148 sec | |</p>
<table>
<thead>
<tr>
<th>pH</th>
<th>B:</th>
<th>I:</th>
<th>S:</th>
<th>T:</th>
<th>L:</th>
<th>t(G):</th>
<th>cc:</th>
<th>rate:</th>
<th>sd:</th>
<th>t½:</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0.03M K₂HPO₄, 0.01M K₃PO₄, 0.85N KCl</td>
<td>1.0</td>
<td>0.0001M/L</td>
<td>20.0°C</td>
<td>300</td>
<td>2600 sec</td>
<td>9997</td>
<td>4.1 x 10⁻⁴ sec⁻¹</td>
<td>.035</td>
<td>1693 sec</td>
</tr>
<tr>
<td></td>
<td>0.03M K₂HPO₄, 0.01M K₃PO₄, 0.85N KCl</td>
<td>1.0</td>
<td>0.0001M/L</td>
<td>20.0°C</td>
<td>300</td>
<td>2500 sec</td>
<td>9972</td>
<td>3.85 x 10⁻⁴ sec⁻¹</td>
<td>.10</td>
<td>1800 sec</td>
</tr>
<tr>
<td></td>
<td>0.03M K₂HPO₄, 0.01M K₃PO₄, 0.85N KCl</td>
<td>1.0</td>
<td>0.0001M/L</td>
<td>20.0°C</td>
<td>300</td>
<td>2300 sec</td>
<td>9995</td>
<td>6.56 x 10⁻⁴ sec⁻¹</td>
<td>.07</td>
<td>1056 sec</td>
</tr>
<tr>
<td></td>
<td>0.03M K₂HPO₄, 0.01M K₃PO₄, 0.85N KCl</td>
<td>1.0</td>
<td>0.0001M/L</td>
<td>20.0°C</td>
<td>300</td>
<td>2000 sec</td>
<td>9975</td>
<td>7.37 x 10⁻⁴ sec⁻¹</td>
<td>.18</td>
<td>940 sec</td>
</tr>
</tbody>
</table>

The table above contains data on the reaction rates of 1-acetyl-2-thiohydantoin in different pH and concentration conditions. The reactions are measured at specific wavelengths (λ), temperatures (T), and reaction times (t). The rates are expressed in terms of the change in absorbance (ΔA) over time, with rates calculated using the first-order reaction kinetics. The standard deviation (sd) and the halflife (t½) are also provided for each run.
<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: 0.03M K$_2$HPO$_4$, 0.1M K$_3$PO$_4$, 0.85N KCl</td>
<td>0</td>
<td>.805</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.775</td>
</tr>
<tr>
<td>S: 0.0001M/L</td>
<td>60</td>
<td>.747</td>
</tr>
<tr>
<td>T: 30.4°C</td>
<td>90</td>
<td>.725</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>120</td>
<td>.702</td>
</tr>
<tr>
<td>t(0): 1000 sec</td>
<td>180</td>
<td>.654</td>
</tr>
<tr>
<td>cc: .9996</td>
<td>240</td>
<td>.608</td>
</tr>
<tr>
<td>rate: 11.3 x 10$^{-4}$ sec$^{-1}$</td>
<td>300</td>
<td>.566</td>
</tr>
<tr>
<td>sd: .076</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$: 614 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: 0.03M K$_2$HPO$_4$, 0.1M K$_3$PO$_4$, 0.85N KCl</td>
<td>0</td>
<td>.823</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.795</td>
</tr>
<tr>
<td>S: 0.0001M/L</td>
<td>60</td>
<td>.770</td>
</tr>
<tr>
<td>T: 30.4°C</td>
<td>90</td>
<td>.739</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>120</td>
<td>.718</td>
</tr>
<tr>
<td>t(0): 1200 sec</td>
<td>180</td>
<td>.670</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>240</td>
<td>.628</td>
</tr>
<tr>
<td>rate: 11.6 x 10$^{-4}$ sec$^{-1}$</td>
<td>300</td>
<td>.586</td>
</tr>
<tr>
<td>sd: .088</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$: 596 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: 0.03M K$_2$HPO$_4$, 0.1M K$_3$PO$_4$, 0.85N KCl</td>
<td>0</td>
<td>.879</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.831</td>
</tr>
<tr>
<td>S: 0.0001M/L</td>
<td>60</td>
<td>.789</td>
</tr>
<tr>
<td>T: 35.6°C</td>
<td>90</td>
<td>.745</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>120</td>
<td>.704</td>
</tr>
<tr>
<td>t(0): 750 sec</td>
<td>150</td>
<td>.660</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>180</td>
<td>.628</td>
</tr>
<tr>
<td>rate: 19.0 x 10$^{-4}$ sec$^{-1}$</td>
<td>210</td>
<td>.589</td>
</tr>
<tr>
<td>sd: .17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$: 364 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: 0.03M K$_2$HPO$_4$, 0.1M K$_3$PO$_4$, 0.85N KCl</td>
<td>0</td>
<td>.681</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.617</td>
</tr>
<tr>
<td>S: 0.0001M/L</td>
<td>60</td>
<td>.623</td>
</tr>
<tr>
<td>T: 35.6°C</td>
<td>90</td>
<td>.583</td>
</tr>
<tr>
<td>L: 300 mm</td>
<td>120</td>
<td>.551</td>
</tr>
<tr>
<td>t(0): 800 sec</td>
<td>150</td>
<td>.527</td>
</tr>
<tr>
<td>cc: .9998</td>
<td>180</td>
<td>.498</td>
</tr>
<tr>
<td>rate: 17.3 x 10$^{-4}$ sec$^{-1}$</td>
<td>210</td>
<td>.473</td>
</tr>
<tr>
<td>sd: .10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t$_{1/2}$: 400 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
pH: 10.95
B: .03M K₂HPO₄, .01M K₃PO₄, .85N KCl
I: 1.0
S: .0001M/L
T: h1.5°C
L: 300 nm
t(G): 400 sec
cc: .9998
rate: 29.4 x 10⁻¹ sec⁻¹
sd: .20
t₁/₂: 236 sec

dA

° 3 5 9 2 4 4 2 8 7 8 9 1 2 8 0 1 2 3 4 5 6 7

pH: 10.95
B: .03M K₂HPO₄, .01M K₃PO₄, .85N KCl
I: 1.0
S: .0001M/L
T: h1.5°C
L: 300 nm
t(G): 360 sec
cc: .9998
rate: 32.1 x 10⁻¹ sec⁻¹
sd: .21
t₁/₂: 216 sec
<table>
<thead>
<tr>
<th>TABLE III</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1-benzoyl-2-thiohydantoin</strong></td>
</tr>
<tr>
<td>pH: 10.95</td>
</tr>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
</tr>
<tr>
<td>I: 1.0</td>
</tr>
<tr>
<td>S: .0001M/L</td>
</tr>
<tr>
<td>L: 305 nm</td>
</tr>
<tr>
<td>T: 20.0°C</td>
</tr>
<tr>
<td>t(0): 1300 sec</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 8.74 x 10^{-4} sec$^{-1}$</td>
</tr>
<tr>
<td>sd: .04</td>
</tr>
<tr>
<td>t$_2$</td>
</tr>
<tr>
<td>pH: 10.95</td>
</tr>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
</tr>
<tr>
<td>I: 1.0</td>
</tr>
<tr>
<td>S: .0001M/L</td>
</tr>
<tr>
<td>L: 305 nm</td>
</tr>
<tr>
<td>T: 20.0°C</td>
</tr>
<tr>
<td>t(0): 1500 sec</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 8.82 x 10^{-4} sec$^{-1}$</td>
</tr>
<tr>
<td>sd: .11</td>
</tr>
<tr>
<td>t$_2$</td>
</tr>
<tr>
<td>pH: 10.95</td>
</tr>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
</tr>
<tr>
<td>I: 1.0</td>
</tr>
<tr>
<td>S: .0001M/L</td>
</tr>
<tr>
<td>L: 305 nm</td>
</tr>
<tr>
<td>T: 20.0°C</td>
</tr>
<tr>
<td>t(0): 1100 sec</td>
</tr>
<tr>
<td>cc: .9992</td>
</tr>
<tr>
<td>rate: 8.92 x 10^{-4} sec$^{-1}$</td>
</tr>
<tr>
<td>sd: .12</td>
</tr>
<tr>
<td>t$_2$</td>
</tr>
<tr>
<td>pH: 10.95</td>
</tr>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
</tr>
<tr>
<td>I: 1.0</td>
</tr>
<tr>
<td>S: .0001M/L</td>
</tr>
<tr>
<td>L: 305 nm</td>
</tr>
<tr>
<td>T: 25.4°C</td>
</tr>
<tr>
<td>t(0): 750 sec</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 16.6 x 10^{-4} sec$^{-1}$</td>
</tr>
<tr>
<td>sd: .06</td>
</tr>
<tr>
<td>t$_2$</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
<tr>
<td>10.95</td>
</tr>
</tbody>
</table>

Rate: 16.11 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>.900</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>.825</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.762</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.710</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.651</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.561</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.482</td>
</tr>
<tr>
<td>10.95</td>
<td>210</td>
<td>.392</td>
</tr>
</tbody>
</table>

Rate: 25.57 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>1.110</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>1.057</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.978</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.906</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.814</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.733</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.641</td>
</tr>
<tr>
<td>10.95</td>
<td>210</td>
<td>.560</td>
</tr>
</tbody>
</table>

Rate: 25.69 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>.791</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>.699</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.622</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.554</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.496</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.396</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.356</td>
</tr>
</tbody>
</table>

Rate: 40.3 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>.14</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>.18</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.13</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.11</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.09</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.08</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.06</td>
</tr>
<tr>
<td>10.95</td>
<td>210</td>
<td>.05</td>
</tr>
</tbody>
</table>

Rate: 40.3 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>.35</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>.28</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.24</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.22</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.20</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.19</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.18</td>
</tr>
<tr>
<td>10.95</td>
<td>210</td>
<td>.17</td>
</tr>
</tbody>
</table>

Rate: 40.3 x 10^-4 sec^-1

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.95</td>
<td>0</td>
<td>.17</td>
</tr>
<tr>
<td>10.95</td>
<td>30</td>
<td>.14</td>
</tr>
<tr>
<td>10.95</td>
<td>60</td>
<td>.12</td>
</tr>
<tr>
<td>10.95</td>
<td>90</td>
<td>.11</td>
</tr>
<tr>
<td>10.95</td>
<td>120</td>
<td>.10</td>
</tr>
<tr>
<td>10.95</td>
<td>150</td>
<td>.09</td>
</tr>
<tr>
<td>10.95</td>
<td>180</td>
<td>.08</td>
</tr>
<tr>
<td>10.95</td>
<td>210</td>
<td>.07</td>
</tr>
</tbody>
</table>

Rate: 40.3 x 10^-4 sec^-1
<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
<td>0</td>
<td>.991</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.886</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>60</td>
<td>.792</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>90</td>
<td>.711</td>
</tr>
<tr>
<td>T: 35.6°C</td>
<td>120</td>
<td>.640</td>
</tr>
<tr>
<td>$t$: 1250 sec; $A_i$: .086</td>
<td>150</td>
<td>.578</td>
</tr>
<tr>
<td>$c_i$: .9998</td>
<td>180</td>
<td>.523</td>
</tr>
<tr>
<td>rate: 37.9 x 10$^{-4}$ sec$^{-1}$</td>
<td>210</td>
<td>.474</td>
</tr>
<tr>
<td>sd: .25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$: 183 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
<td>0</td>
<td>.788</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>15</td>
<td>.708</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>30</td>
<td>.640</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>45</td>
<td>.577</td>
</tr>
<tr>
<td>T: 41.5°C</td>
<td>60</td>
<td>.524</td>
</tr>
<tr>
<td>$t(a)$: 120 sec</td>
<td>75</td>
<td>.479</td>
</tr>
<tr>
<td>$c_i$: .9998</td>
<td>90</td>
<td>.430</td>
</tr>
<tr>
<td>rate: 65.30 x 10$^{-4}$ sec$^{-1}$</td>
<td>105</td>
<td>.392</td>
</tr>
<tr>
<td>sd: .48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$: 106 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.95</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .03M K$_2$HPO$_4$, .01M K$_3$PO$_4$, .85N KCl</td>
<td>0</td>
<td>.998</td>
</tr>
<tr>
<td>I: 1.0</td>
<td>30</td>
<td>.825</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>60</td>
<td>.684</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>90</td>
<td>.566</td>
</tr>
<tr>
<td>T: 41.5°C</td>
<td>120</td>
<td>.566</td>
</tr>
<tr>
<td>$t(a)$: 250 sec</td>
<td>150</td>
<td>.382</td>
</tr>
<tr>
<td>$c_i$: .9998</td>
<td>180</td>
<td>.311</td>
</tr>
<tr>
<td>rate: 66.24 x 10$^{-4}$ sec$^{-1}$</td>
<td>210</td>
<td>.252</td>
</tr>
<tr>
<td>sd: .48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$: 105 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH: 10.75</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>B: .1M Na$_2$HPO$_4$, .01M NaOH, .09M NaCl</td>
<td>0</td>
<td>1.182</td>
</tr>
<tr>
<td>I: .12</td>
<td>300</td>
<td>.866</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>600</td>
<td>.650</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>900</td>
<td>.500</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>1200</td>
<td>.385</td>
</tr>
<tr>
<td>$t(a)$: 500 sec</td>
<td>1500</td>
<td>.289</td>
</tr>
<tr>
<td>$c_i$: .9998</td>
<td>1800</td>
<td>.216</td>
</tr>
<tr>
<td>rate: 9.31 x 10$^{-4}$ sec$^{-1}$</td>
<td>2100</td>
<td>.164</td>
</tr>
<tr>
<td>sd: .06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_{1/2}$: 745 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>1-p-methylbenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
<td>0</td>
<td>.811</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
<td>300</td>
<td>.659</td>
</tr>
<tr>
<td>I: .42</td>
<td>600</td>
<td>.516</td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>900</td>
<td>.461</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>1200</td>
<td>.389</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>1500</td>
<td>.318</td>
</tr>
<tr>
<td>t(G): 600 sec</td>
<td>1800</td>
<td>.261</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>2100</td>
<td>.218</td>
</tr>
<tr>
<td>rate: 6.17 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .052</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 1123 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1-m-methylbenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
<td>0</td>
<td>.903</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
<td>300</td>
<td>.710</td>
</tr>
<tr>
<td>I: .42</td>
<td>600</td>
<td>.566</td>
</tr>
<tr>
<td>S: .00007M/L</td>
<td>900</td>
<td>.459</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>1200</td>
<td>.369</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>1500</td>
<td>.296</td>
</tr>
<tr>
<td>t(G): 600 sec</td>
<td>1800</td>
<td>.228</td>
</tr>
<tr>
<td>cc: .9996</td>
<td>2100</td>
<td>.179</td>
</tr>
<tr>
<td>rate: 7.61 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .077</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 911 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1-m-methoxybenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
<td>0</td>
<td>1.260</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
<td>300</td>
<td>.869</td>
</tr>
<tr>
<td>I: .42</td>
<td>600</td>
<td>.618</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>900</td>
<td>.440</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>1200</td>
<td>.316</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>1500</td>
<td>.216</td>
</tr>
<tr>
<td>t(G): 400 sec</td>
<td>1800</td>
<td>.118</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>2100</td>
<td>.101</td>
</tr>
<tr>
<td>rate: 11.9 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 582 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1-p-fluorobenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
<td>0</td>
<td>1.167</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
<td>150</td>
<td>.936</td>
</tr>
<tr>
<td>I: .42</td>
<td>300</td>
<td>.761</td>
</tr>
<tr>
<td>S: .0001M/L</td>
<td>450</td>
<td>.628</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.517</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>750</td>
<td>.425</td>
</tr>
<tr>
<td>t(G): 800 sec</td>
<td>900</td>
<td>.354</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>1050</td>
<td>.284</td>
</tr>
<tr>
<td>rate: 13.25 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 523 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Time</td>
<td>dA</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>l-p-chlorobenzoyl-2-thiohydantoin</td>
<td>0</td>
<td>1.130</td>
</tr>
<tr>
<td>pH: 10.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl 150</td>
<td></td>
<td>.860</td>
</tr>
<tr>
<td>I: .42</td>
<td>300</td>
<td>.677</td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>150</td>
<td>.538</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>600</td>
<td>.431</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>750</td>
<td>.351</td>
</tr>
<tr>
<td>t: 3900 sec; Ai: .12</td>
<td>900</td>
<td>.293</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>1050</td>
<td>.251</td>
</tr>
<tr>
<td>rate: 19.14 x 10⁻⁶ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .068</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t₁/₂: 356 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| l-p-iodobenzoyl-2-thiohydantoin | 0     | 1.234     |
| pH: 10.75                |       |           |
| B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl 150 |       | .917      |
| I: .42                   | 300   | .706      |
| S: .00008M/L             | 150   | .558      |
| T: 25.3°C                | 600   | .439      |
| L: 305 nm                | 750   | .351      |
| t: 4800 sec; Ai: .119     | 900   | .290      |
| cc: .9999                | 1050  | .242      |
| rate: 20.82 x 10⁻⁴ sec⁻¹ |       |           |
| sd: .099                 |       |           |
| t₁/₂: 333 sec            |       |           |

| l-p-bromobenzoyl-2-thiohydantoin | 0     | 1.455     |
| pH: 10.75                |       |           |
| B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl 150 |       | 1.064     |
| I: .42                   | 300   | .796      |
| S: .00008M/L             | 150   | .511      |
| T: 25.3°C                | 600   | .476      |
| L: 305 nm                | 750   | .372      |
| t: 3900 sec; Ai: .12     | 900   | .306      |
| cc: .9999                | 1050  | .253      |
| rate: 21.87 x 10⁻⁴ sec⁻¹ |       |           |
| sd: .094                 |       |           |
| t₁/₂: 317 sec            |       |           |

<p>| l-m-chlorobenzoyl-2-thiohydantoin | 0     | 1.502     |
| pH: 10.75                |       |           |
| B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl 60 |       | 1.296     |
| I: .42                   | 90    | 1.196     |
| S: .00008M/L             | 180   | .950      |
| T: 25.3°C                | 300   | .735      |
| L: 305 nm                | 450   | .538      |
| t: 3600 sec; Ai: .108    | 600   | .400      |
| cc: .9998                | 750   | .306      |
| rate: 25.89 x 10⁻⁴ sec⁻¹ |       |           |
| sd: .15                  |       |           |
| t₁/₂: 268 sec            |       |           |</p>
<table>
<thead>
<tr>
<th>1-m-bromobenzoyl-2-thiohydantoin</th>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
<td>0</td>
<td>1.310</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
<td>60</td>
<td>1.112</td>
</tr>
<tr>
<td>I: .42</td>
<td>90</td>
<td>1.030</td>
</tr>
<tr>
<td>S: .00008M/L</td>
<td>180</td>
<td>.829</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>300</td>
<td>.634</td>
</tr>
<tr>
<td>L: 305 nm</td>
<td>450</td>
<td>.462</td>
</tr>
<tr>
<td>t: 3600 sec; Aλ: .11</td>
<td>600</td>
<td>.342</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>750</td>
<td>.266</td>
</tr>
<tr>
<td>rate: 27.05 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .106</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½: 256 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1-m-trifluoromethylbenzoyl-2-thiohydantoin</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH: 10.75</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .01M NaOH, .09M NaCl</td>
</tr>
<tr>
<td>I: .42</td>
</tr>
<tr>
<td>S: .00008M/L</td>
</tr>
<tr>
<td>T: 25.3°C</td>
</tr>
<tr>
<td>L: 305 nm</td>
</tr>
<tr>
<td>t: 3000 sec; Aλ: .119</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 32.89 x 10⁻⁴ sec⁻¹</td>
</tr>
<tr>
<td>sd: .137</td>
</tr>
<tr>
<td>t½: 211 sec</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>11.95</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
</tr>
<tr>
<td>I: .55</td>
</tr>
<tr>
<td>T: 58.1°C</td>
</tr>
<tr>
<td>S: .0002M/L</td>
</tr>
<tr>
<td>t: 510 sec; A₁: .103</td>
</tr>
<tr>
<td>cc: .9999</td>
</tr>
<tr>
<td>rate: 178.37 x 10⁻³ sec⁻¹</td>
</tr>
<tr>
<td>sd: .75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (min)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>6</td>
<td>1.316</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>15</td>
<td>1.128</td>
</tr>
<tr>
<td>I: .55</td>
<td>30</td>
<td>.888</td>
</tr>
<tr>
<td>T: 58.1°C</td>
<td>45</td>
<td>.705</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>60</td>
<td>.564</td>
</tr>
<tr>
<td>t: 540 sec; A₁: .0999</td>
<td></td>
<td>.452</td>
</tr>
<tr>
<td>cc: .9986</td>
<td>90</td>
<td>.365</td>
</tr>
<tr>
<td>rate: 175.05 x 10⁻³ sec⁻¹</td>
<td>105</td>
<td>.301</td>
</tr>
<tr>
<td>sd: 3.2</td>
<td>t₁/₂: 40 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (min)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.151</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>15</td>
<td>.906</td>
</tr>
<tr>
<td>I: .55</td>
<td>30</td>
<td>.728</td>
</tr>
<tr>
<td>T: 58.1°C</td>
<td>45</td>
<td>.583</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>60</td>
<td>.469</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>75</td>
<td>.384</td>
</tr>
<tr>
<td>t: 540 sec; A₁: .106</td>
<td></td>
<td>.319</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>105</td>
<td>.268</td>
</tr>
<tr>
<td>rate: 177.62 x 10⁻³ sec⁻¹</td>
<td></td>
<td>.251</td>
</tr>
<tr>
<td>sd: .59</td>
<td>t₁/₂: 39 sec</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (min)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.149</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>29</td>
<td>.890</td>
</tr>
<tr>
<td>I: .55</td>
<td>58</td>
<td>.702</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>87</td>
<td>.562</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>116</td>
<td>.453</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>145</td>
<td>.364</td>
</tr>
<tr>
<td>t: 1000 sec; A₁: .092</td>
<td></td>
<td>.302</td>
</tr>
<tr>
<td>cc: .9999</td>
<td>203</td>
<td>.251</td>
</tr>
<tr>
<td>rate: 97.10 x 10⁻³ sec⁻¹</td>
<td></td>
<td>.251</td>
</tr>
<tr>
<td>sd: .68</td>
<td>t₁/₂: 71 sec</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE V**

1-acetyl(d₃)-5,5-dimethyl-2-thiohydantoin
<table>
<thead>
<tr>
<th>pH</th>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.1476</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>29</td>
<td>1.1426</td>
</tr>
<tr>
<td>I: .55</td>
<td>58</td>
<td>.883</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>87</td>
<td>.704</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.568</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>145</td>
<td>.165</td>
</tr>
<tr>
<td>t: 800 sec</td>
<td>174</td>
<td>.378</td>
</tr>
<tr>
<td>cc: .99999</td>
<td>203</td>
<td>.317</td>
</tr>
<tr>
<td>rate: 98.39 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½: 70 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.2144</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>29</td>
<td>1.2144</td>
</tr>
<tr>
<td>I: .55</td>
<td>58</td>
<td>.944</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>87</td>
<td>.735</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.588</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>145</td>
<td>.171</td>
</tr>
<tr>
<td>t: 800 sec</td>
<td>174</td>
<td>.378</td>
</tr>
<tr>
<td>cc: .99999</td>
<td>203</td>
<td>.314</td>
</tr>
<tr>
<td>rate: 99.51 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½: 70 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95 (I suspect this is CH₃)</td>
<td>0</td>
<td>1.2225</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>29</td>
<td>1.2225</td>
</tr>
<tr>
<td>I: .55</td>
<td>58</td>
<td>.935</td>
</tr>
<tr>
<td>T: 49.6°C</td>
<td>87</td>
<td>.723</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>116</td>
<td>.580</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>145</td>
<td>.462</td>
</tr>
<tr>
<td>t: 800 sec</td>
<td>174</td>
<td>.372</td>
</tr>
<tr>
<td>cc: .99999</td>
<td>203</td>
<td>.304</td>
</tr>
<tr>
<td>rate: 92.87 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½: 75 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time (sec)</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>.898</td>
</tr>
<tr>
<td>B: .1M Na₂HPO₄, .075M NaOH, .025M NaCl</td>
<td>29</td>
<td>.823</td>
</tr>
<tr>
<td>I: .55</td>
<td>174</td>
<td>.697</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>290</td>
<td>.593</td>
</tr>
<tr>
<td>L: 300 nm</td>
<td>406</td>
<td>.515</td>
</tr>
<tr>
<td>S: .0002M/L</td>
<td>522</td>
<td>.144</td>
</tr>
<tr>
<td>t(0): 580 sec</td>
<td></td>
<td>.366</td>
</tr>
<tr>
<td>cc: .9997</td>
<td>899</td>
<td>.270</td>
</tr>
<tr>
<td>rate: 13.27 x 10⁻⁴ sec⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: .10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½: 522 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>Time</td>
<td>DA</td>
</tr>
<tr>
<td>----</td>
<td>------</td>
<td>----</td>
</tr>
<tr>
<td>11.95</td>
<td>0</td>
<td>0.980</td>
</tr>
<tr>
<td>B: 1M Na$_2$HPO$_4$, 0.075M NaOH, 0.025M NaCl</td>
<td>58</td>
<td>0.897</td>
</tr>
<tr>
<td>I: 0.55</td>
<td>174</td>
<td>0.762</td>
</tr>
<tr>
<td>T: 25.3°C</td>
<td>290</td>
<td>0.650</td>
</tr>
<tr>
<td>λ: 300 nm</td>
<td>606</td>
<td>0.563</td>
</tr>
<tr>
<td>S: 0.002M/L</td>
<td>522</td>
<td>0.488</td>
</tr>
<tr>
<td>t(G): 800 sec</td>
<td>667</td>
<td>0.404</td>
</tr>
<tr>
<td>cc: 0.9997</td>
<td>899</td>
<td>0.294</td>
</tr>
<tr>
<td>rate: 1.323 x 10$^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: 0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 524 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.057</td>
</tr>
<tr>
<td>B: 1M Na$_2$HPO$_4$, 0.075M NaOH, 0.025M NaCl</td>
<td>16</td>
<td>0.989</td>
</tr>
<tr>
<td>I: 0.55</td>
<td>290</td>
<td>0.920</td>
</tr>
<tr>
<td>T: 11.0°C</td>
<td>522</td>
<td>0.836</td>
</tr>
<tr>
<td>λ: 300 nm</td>
<td>667</td>
<td>0.796</td>
</tr>
<tr>
<td>S: 0.002M/L</td>
<td>899</td>
<td>0.732</td>
</tr>
<tr>
<td>t(G): 3500 sec</td>
<td>1015</td>
<td>0.704</td>
</tr>
<tr>
<td>cc: 0.9977</td>
<td>1160</td>
<td>0.673</td>
</tr>
<tr>
<td>rate: 3.84 x 10$^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: 0.093</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 1804 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>0.910</td>
</tr>
<tr>
<td>B: 1M Na$_2$HPO$_4$, 0.075M NaOH, 0.025M NaCl</td>
<td>16</td>
<td>0.865</td>
</tr>
<tr>
<td>I: 0.55</td>
<td>290</td>
<td>0.813</td>
</tr>
<tr>
<td>T: 11.0°C</td>
<td>522</td>
<td>0.753</td>
</tr>
<tr>
<td>λ: 300 nm</td>
<td>667</td>
<td>0.711</td>
</tr>
<tr>
<td>S: 0.002M/L</td>
<td>899</td>
<td>0.660</td>
</tr>
<tr>
<td>t(G): 4000 sec</td>
<td>1015</td>
<td>0.636</td>
</tr>
<tr>
<td>cc: 0.9998</td>
<td>1160</td>
<td>0.608</td>
</tr>
<tr>
<td>rate: 3.46 x 10$^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: 0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 2005 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>Time</th>
<th>DA</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.95</td>
<td>0</td>
<td>1.178</td>
</tr>
<tr>
<td>B: 1M Na$_2$HPO$_4$, 0.075M NaOH, 0.025M NaCl</td>
<td>16</td>
<td>1.018</td>
</tr>
<tr>
<td>I: 0.55</td>
<td>290</td>
<td>0.911</td>
</tr>
<tr>
<td>T: 11.0°C</td>
<td>522</td>
<td>0.770</td>
</tr>
<tr>
<td>λ: 300 nm</td>
<td>667</td>
<td>0.690</td>
</tr>
<tr>
<td>S: 0.002M/L</td>
<td>899</td>
<td>0.583</td>
</tr>
<tr>
<td>t(G): 4000 sec</td>
<td>1015</td>
<td>0.538</td>
</tr>
<tr>
<td>cc: 0.9998</td>
<td>1160</td>
<td>0.483</td>
</tr>
<tr>
<td>rate: 3.63 x 10$^{-4}$ sec$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sd: 0.026</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_\frac{1}{2}$: 1908 sec</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table VI

#### 1-benzoyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.510</td>
</tr>
</tbody>
</table>

- **pH:** 11.2
- **B:** .1M Na₂HPO₄, .025N NaOH, .075N NaCl
- **I:** .7N
- **T:** 25.3°C
- **L:** 300 nm
- **S:** .0001M/L
- **t:** 2200 sec; **A**₁: .128
- **cc:** .9999
- **rate:** 31.40 x 10⁻⁴ sec⁻¹
- **sd:** .13
- **t½:** 221 sec

#### 1-benzoyl-5-phenyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.021</td>
</tr>
</tbody>
</table>

- **pH:** 11.2
- **B:** .1M Na₂HPO₄, .025N NaOH, .075N NaCl
- **I:** .45
- **T:** 25.3°C
- **L:** 310 nm
- **S:** .001M/L
- **t(G):** 600 sec
- **cc:** .9982
- **rate:** 10.15 x 10⁻⁴ sec⁻¹
- **sd:** .22
- **t½:** 683 sec

#### 1-benzoyl-5-isobutyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.967</td>
</tr>
</tbody>
</table>

- **pH:** 11.2
- **B:** .1M Na₂HPO₄, .025N NaOH, .075N NaCl
- **I:** .45
- **T:** 25.3°C
- **L:** 305 nm
- **S:** .001M/L
- **t(G):** 1200 sec
- **cc:** .9997
- **rate:** 6.64 x 10⁻⁴ sec⁻¹
- **sd:** .05
- **t½:** 1044 sec
1-benzoyl-5,5-dimethyl-2-thiodydantoain

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.687</td>
</tr>
<tr>
<td>2913 sec</td>
<td>.822</td>
</tr>
<tr>
<td>2100</td>
<td>1.234</td>
</tr>
<tr>
<td>700</td>
<td>1.021</td>
</tr>
<tr>
<td>500</td>
<td>.862</td>
</tr>
<tr>
<td>400</td>
<td>.744</td>
</tr>
<tr>
<td>500</td>
<td>.651</td>
</tr>
<tr>
<td>400</td>
<td>.580</td>
</tr>
<tr>
<td>400</td>
<td>.522</td>
</tr>
<tr>
<td>369</td>
<td>.476</td>
</tr>
<tr>
<td>300</td>
<td>.476</td>
</tr>
<tr>
<td>2400 sec; Ai: .369</td>
<td>1.234</td>
</tr>
<tr>
<td>1500</td>
<td>1.021</td>
</tr>
<tr>
<td>1000</td>
<td>.862</td>
</tr>
<tr>
<td>600</td>
<td>.744</td>
</tr>
<tr>
<td>500</td>
<td>.651</td>
</tr>
<tr>
<td>500</td>
<td>.580</td>
</tr>
<tr>
<td>400</td>
<td>.522</td>
</tr>
<tr>
<td>400</td>
<td>.476</td>
</tr>
<tr>
<td>300</td>
<td>.476</td>
</tr>
<tr>
<td>2913 sec</td>
<td>.822</td>
</tr>
<tr>
<td>2100</td>
<td>1.234</td>
</tr>
<tr>
<td>700</td>
<td>1.021</td>
</tr>
<tr>
<td>500</td>
<td>.862</td>
</tr>
<tr>
<td>400</td>
<td>.744</td>
</tr>
<tr>
<td>300</td>
<td>.651</td>
</tr>
<tr>
<td>400</td>
<td>.580</td>
</tr>
<tr>
<td>300</td>
<td>.522</td>
</tr>
<tr>
<td>300</td>
<td>.476</td>
</tr>
</tbody>
</table>
### 1-acetyl-5,5-dimethyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.2</td>
</tr>
<tr>
<td>Buffer</td>
<td>0.1M Na&lt;sub&gt;2&lt;/sub&gt;HPO&lt;sub&gt;4&lt;/sub&gt;, 0.025N NaOH, 0.075N NaCl</td>
</tr>
<tr>
<td>I</td>
<td>45</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L</td>
<td>305 nm</td>
</tr>
<tr>
<td>S</td>
<td>0.001M/L</td>
</tr>
<tr>
<td>t(g)</td>
<td>1600 sec</td>
</tr>
<tr>
<td>cc</td>
<td>0.9977</td>
</tr>
<tr>
<td>rate</td>
<td>2.008 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>sd</td>
<td>0.05</td>
</tr>
<tr>
<td>t&lt;sub&gt;1/2&lt;/sub&gt;</td>
<td>3452 sec</td>
</tr>
</tbody>
</table>

### 1-acetyl-5-methyl-2-thiohydantoin

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>11.2</td>
</tr>
<tr>
<td>Buffer</td>
<td>0.1M Na&lt;sub&gt;2&lt;/sub&gt;HPO&lt;sub&gt;4&lt;/sub&gt;, 0.025N NaOH, 0.075N NaCl</td>
</tr>
<tr>
<td>I</td>
<td>45</td>
</tr>
<tr>
<td>T</td>
<td>25.3°C</td>
</tr>
<tr>
<td>L</td>
<td>305 nm</td>
</tr>
<tr>
<td>S</td>
<td>0.001M/L</td>
</tr>
<tr>
<td>t(g)</td>
<td>450 sec</td>
</tr>
<tr>
<td>cc</td>
<td>0.9994</td>
</tr>
<tr>
<td>rate</td>
<td>12.04 x 10&lt;sup&gt;-4&lt;/sup&gt; sec&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>sd</td>
<td>0.15</td>
</tr>
<tr>
<td>t&lt;sub&gt;1/2&lt;/sub&gt;</td>
<td>576 sec</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.431</td>
</tr>
<tr>
<td>60</td>
<td>0.407</td>
</tr>
<tr>
<td>120</td>
<td>0.379</td>
</tr>
<tr>
<td>180</td>
<td>0.357</td>
</tr>
<tr>
<td>240</td>
<td>0.330</td>
</tr>
<tr>
<td>300</td>
<td>0.316</td>
</tr>
<tr>
<td>360</td>
<td>0.302</td>
</tr>
<tr>
<td>420</td>
<td>0.283</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.716</td>
</tr>
<tr>
<td>60</td>
<td>0.639</td>
</tr>
<tr>
<td>120</td>
<td>0.563</td>
</tr>
<tr>
<td>180</td>
<td>0.503</td>
</tr>
<tr>
<td>240</td>
<td>0.466</td>
</tr>
<tr>
<td>300</td>
<td>0.400</td>
</tr>
<tr>
<td>360</td>
<td>0.353</td>
</tr>
<tr>
<td>420</td>
<td>0.304</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Time</th>
<th>dA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.404</td>
</tr>
<tr>
<td>60</td>
<td>1.150</td>
</tr>
<tr>
<td>120</td>
<td>1.061</td>
</tr>
<tr>
<td>180</td>
<td>0.977</td>
</tr>
<tr>
<td>240</td>
<td>0.859</td>
</tr>
<tr>
<td>300</td>
<td>0.740</td>
</tr>
<tr>
<td>360</td>
<td>0.666</td>
</tr>
<tr>
<td>420</td>
<td>0.622</td>
</tr>
</tbody>
</table>

---