Kinetics of the Hydrolysis of 1-Naphthyl N-Phenylecarbamates

Jae-Seul Jeung, Chang-Suk Kim, and Soon-Yung Hong*

Department of Science Education, Chungbuk National University, Cheonju 360-763, Korea
Department of Chemistry, Hanyang University, Seoul 133-791, Korea

(Received July 13, 1987)

Several N-alkylcarbamates (Ar OCONHR, Ar = 1-naphthyl, 2-naphthyl, substituted phenyl; R = methyl, ethyl) are known to be an important class of biodegradable insecticides. Recently, an effect of the moiety of haloalkylcarbamate as amino protecting group has been reported.

In the present study, we have synthesized eight new carbamates (Ar OCONHAr', Ar = 1-naphthyl; Ar' = m- or p-substituted phenyl), 1a-1h, and investigated kinetically the hydrolysis of these compounds at pH 5-6 (Ep. 1). Kinetic data, derived from Arrhenius plots and absolute rate theory, are summarized in Table 1. The hydrolysis obeyed a ρα Hammett relationship (correlation coefficient γ = 0.986) with the rate decreasing consistently as the substituents made more electron-attracting (reaction constant ρ = -0.35). This suggests that the reaction proceeds through a typical \( A_{N-2} \) mechanism with a rate-determining protonation to carbonyl oxygen of the carbamate. Plots of \( ΔH^\ddagger \)'s against \( ΔS^\ddagger \)'s revealed a good isokinetic relationship (\( \delta ΔH^\ddagger = \beta ΔS^\ddagger \); correlation coefficient γ = 0.998) with isokinetic temperature (\( β \)) of 298°K. This value falls in the range observed in acid-catalyzed hydrolyses of some alkyl esters.

EXPERIMENTAL SECTION

Melting points were determined on a Yamato MP-1 capillary melting point apparatus and are uncorrected. UV and IR spectra were recorded on a Shimadzu UV-210A spectrophotometer and a Perkin-Elmer 567 spectrophotometer, respectively. A Varian FT-80 nuclear magnetic resonance spectrometer was used for \(^1\)H NMR spectra with tetramethylsilane as an internal standard.

Synthesis of 1-Naphthyl N-Substitutedphenylecarbamates (1a-1h). Synthetic procedures are similar to those applied to phenyl N-methylecarbamate synthesis with a slight modification. The following procedure for 1b is a repr...
Table 1. Kinetic data for the hydrolysis of Carbamates. 1-naph-OCONH-C₆H₅-X at 27°C

<table>
<thead>
<tr>
<th>X(Carbamate)</th>
<th>$k \times 10^2$(sec⁻¹)</th>
<th>$E_a$ (kcal/mol)</th>
<th>$\Delta H^*$ (kcal/mol)</th>
<th>$\Delta G^*$ (kcal/mol)</th>
<th>$-\Delta S^*$ (eu)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>17°C</td>
<td>27°C</td>
<td>37°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$p$-CH₃O(1a)</td>
<td>1.681</td>
<td>2.066</td>
<td>3.626</td>
<td>7.8</td>
<td>21.18</td>
</tr>
<tr>
<td>H(1b)</td>
<td>1.343</td>
<td>1.938</td>
<td>3.047</td>
<td>7.62</td>
<td>21.27</td>
</tr>
<tr>
<td>$m$-ClCH₃O(1c)</td>
<td>1.168</td>
<td>1.601</td>
<td>2.602</td>
<td>7.96</td>
<td>21.37</td>
</tr>
<tr>
<td>$p$-Cl(1d)</td>
<td>1.634</td>
<td>2.074</td>
<td>2.737</td>
<td>4.83</td>
<td>21.24</td>
</tr>
<tr>
<td>$p$-Br(1e)</td>
<td>1.515</td>
<td>2.024</td>
<td>2.410</td>
<td>4.23</td>
<td>21.30</td>
</tr>
<tr>
<td>$m$-Cl(1f)</td>
<td>1.904</td>
<td>1.985</td>
<td>2.320</td>
<td>1.82</td>
<td>21.25</td>
</tr>
<tr>
<td>$m$-NO₂(1g)</td>
<td>1.034</td>
<td>1.209</td>
<td>1.669</td>
<td>4.91</td>
<td>21.54</td>
</tr>
<tr>
<td>$p$-NO₂(1h)</td>
<td>*</td>
<td>*</td>
<td>1.532</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Not reproducible data were obtained.

Essential of all other syntheses of carbamates.

First, obtained a quantitative amount of triethylammonium naphthoate by simply mixing equimolar amount of 1-naphthol (4.3g, 0.03mol) and triethylamine (3.0g, 0.03mol) in ethanol (60mL). Dissolved triethylammonium naphthoate (4.9g, 0.02mol) in dry ether (60mL). To this solution, phenylisocyanate (2.4g, 0.02mol) was added slowly and refluxed for 1 hr. By chilling the solution, obtained brown precipitates. Recrystallization from ethanol gave 1b (4.28g, 0.016mol).

1-Naphthyl-N-p-Methoxyphenoxy carbamate (1a): 91.5% yield, brown solid, mp 122–124°C; IR(KBr) 1590, 1750, 3010, 3330cm⁻¹; ¹H NMR(DMSO) δ3.7 (s, 2H), 7.1–7.7 (m, 13H), 7.8 (s, 1H). Anal. Caled for C₁₆H₁₄NO₂: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.82; H, 5.43; N, 4.92.

1-Naphthyl N-p-Bromophenoxy carbamate (1d): 41.4% yield, brown solid, mp 158–159°C; IR(KBr) 660, 1710, 3050, 3320cm⁻¹; ¹H NMR (DMSO) δ7.0–7.9 (m, 11H), 8.1 (s, 1H). Anal. Caled for C₁₆H₁₄NO₂Br: C, 59.67; H, 3.53; N, 4.09. Found: C, 59.80; H, 3.60; N, 4.08.

1-Naphthyl N-p-Chlorophenoxy carbamate (1e): 45.1% yield, brown solid, mp 156–158°C; IR(KBr) 780, 1710, 3010, 3430cm⁻¹; ¹H NMR (DMSO) δ7.1–7.7 (m, 11H), 7.8 (s, 1H). Anal. Caled for C₁₆H₁₄NO₂Cl: C, 68.58; H, 4.66; N, 4.70. Found: C, 68.32; H, 4.32; N, 4.25.

1-Naphthyl N-m-Chlorophenoxy carbamate (1f): 45.0% yield, brown solid, mp 210°C; IR(KBr) 780, 1700, 3050, 3300cm⁻¹; ¹H NMR (DMSO) δ7.2–8.0 (m, 11H), 8.25 (s, 1H). Anal. Caled for C₁₆H₁₂NO₂Cl: C, 68.58; H, 4.06; N, 4.70. Found: C, 68.18; H, 4.21; N, 4.31.

1-Naphthyl N-m-Nitrophenoxy carbamate (1g): 41.8% yield, yellow solid, mp 210°C; IR(KBr) 1350, 1720, 3060, 3360cm⁻¹; ¹H NMR (DMSO) δ7.1–7.8 (m, 11H), 8.21 (s, 1H). Anal. Caled for C₁₆H₁₂NO₂: C, 66.23; H, 3.92; N,
1-Naphthyl N-Phenylcarbamate 유도체의 가수분해에 관한 반응속도동적 연구

9.09. Found: C, 66.03; H, 3.70; N, 9.21.

1-Naphthyl N-p-Nitrophenylcarbamate (1b) : 68.6% yield, yellow solid, mp 220°C; IR (KBr) 1350, 1750, 3100, 3360 cm⁻¹; H NMR (DMSO) δ 7.0~7.8 (m, 11H), 8.4 (s, 1H). Anal. Calcd for C₁₇H₁₂N₂O₄: C, 66.23; H, 3.92; N, 9.09. Found: C, 66.11; H, 3.73; N, 9.32.

Kinetic Measurements. Rates of hydrolysis of 1a-1h at pH 5.6 were measured by a UV spectrophotometer. Concentrations of these carbamates vs. UV absorbance at λmax obeyed the Beer-Lambert law. Typically, 1ml of ethanol solution (2×10⁻³M) of the substrate, 1b (λmax = 292nm, ε = 9.4×10³), was mixed with 10ml of acetate buffer (AcOH=0.025M, AcONa=0.176 M; pH5.6). At appropriate times, absorbances of 292nm for the mixture were measured at each of 17, 27 and 37°C. Pseudo first-order rate constants were obtained from the plots of UV absorbance against time.


Vol. 32, No. 3, 1988