

단 신

1-Naphthyl N-Phenylcarbamate 유도체의 가수분해에 관한 반응속도론적 연구

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Kinetics of the Hydrolysis of 1-Naphthyl N-Phenylcarbamates

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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^{1,2}. Recently, an effect of the moiety of haloalkylcarbamate as amino protecting group has been reported.³

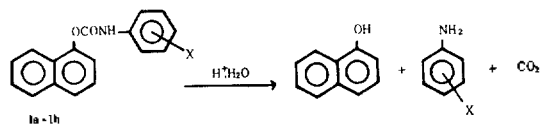
In the present study, we have synthesized eight new carbamates (Ar OCONHAr', Ar = 1-naphthyl; Ar' = *m*- or *p*-substituted phenyl), **1a-1h**, and investigated kinetically the hydrolysis of these compounds at pH 5.6 (Ep. 1). Kinetic data, derived from Arrhenius plots and absolute rate theory, are summarized in Table 1. The hydrolysis obeyed a $\rho\sigma$ Hammett relation-

a rate-determining protonation to carbonyl oxygen of the carbamate. Plots of ΔH^\ddagger 's against ΔS^\ddagger 's revealed a good isokinetic relationship⁶ ($\delta\Delta H^\ddagger = \beta\delta\Delta S^\ddagger$; correlation coefficient $r = 0.998$) with isokinetic temperature (β) of 298°K. This value falls in the range observed in acid-catalyzed hydrolyses of some alkyl esters.⁷

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 ¹H NMR spectra with tetramethylsilane as an internal standard.

Synthesis of 1-Naphthyl N-Substitutedphenylcarbamates (1a-1h). Synthetic procedures are similar to those applied to phenyl *N*-methylcarbamate synthesis⁸ with a slight modification. The following procedure for **1b** is a repr-



ship⁴ (correlation coefficient $r = 0.985$) with the rate decreasing consistently as the substituents made more electron-attracting (reaction constant $\rho = -0.35$). This suggests that the reaction proceeds through a typical $A_{AC}2$ mechanism⁵ with

Table 1. Kinetic data for the hydrolysis of Carbamate, 1-naph-OCONH-C₆H₄-X at 27°C

X(Carbamate)	$k \times 10^3 (\text{sec}^{-1})$			E_a (kcal/mol)	ΔH^\ddagger (kcal/mol)	ΔG^\ddagger (kcal/mol)	$-\Delta S^\ddagger$ (eu)
	17°C	27°C	37°C				
<i>p</i> -CH ₃ O(1a)	1.681	2.060	3.620	7.81	7.21	21.18	46.53
H(1b)	1.343	1.938	3.047	7.62	7.02	21.27	47.49
<i>m</i> -CH ₃ O(1c)	1.168	1.601	2.602	7.96	7.36	21.37	46.68
<i>p</i> -Cl(1d)	1.634	2.074	2.737	4.83	4.23	21.24	56.69
<i>p</i> -Br(1e)	1.515	2.024	2.410	4.23	3.63	21.30	58.88
<i>m</i> -Cl(1f)	1.904	1.985	2.320	1.82	1.22	21.25	66.73
<i>m</i> -NO ₂ (1g)	1.034	1.209	1.669	4.91	4.31	21.54	57.42
<i>p</i> -NO ₂ (1h)	*	*	1.532	—	—	—	—

*Not reproducible data were obtained.

esentative 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*-Methoxyphenylcarbamate (1a): 91.5% yield, brown solid, *mp* 122–124°C; IR (KBr) 1590, 1750, 3010, 3430cm⁻¹; ¹H NMR (DMSO) δ 3.7 (*s*, 3H), 7.1~7.7 (*m*, 1H), 7.8 (*s*, 1H). Anal. Calcd for C₁₈H₁₅NO₃: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.90; H, 5.50; N, 4.81.

1-Naphthyl N-Phenylcarbamate (1b): 81.0% yield, brown solid, *mp* 164°C; IR (KBr) 1720, 3060, 3350cm⁻¹; ¹H NMR (DMSO) δ 6.8~7.8 (*m*, 12H), 8.8 (*s*, 1H). Anal. Calcd for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.36; H, 4.82; N, 5.05.

1-Naphthyl N-*m*-Methoxyphenylcarbamate (1c): 88.3% yield, brown solid, *mp* 120–121°C; IR (KBr) 1600, 1710, 3020, 3430cm⁻¹; ¹H NMR (CDCl₃+DMSO) δ 3.6 (*s*, 3H), 6.9~7.6

(*m*, 11H), 7.8 (*s*, 1H). Anal. Calcd for C₁₈H₁₅NO₃: C, 73.71; H, 5.15; N, 4.78. Found: C, 73.82; H, 5.43; N, 4.92.

1-Naphthyl N-*p*-Bromophenylcarbamate (1d): 41.4% yield, brown solid, *mp* 158~159°C; IR (KBr) 660, 1710, 3050, 3320cm⁻¹; ¹H NMR (DMSO) δ 7.0~7.9 (*m*, 11H), 8.1 (*s*, 1H). Anal. Calcd for C₁₇H₁₂NO₂Br: C, 59.67; H, 3.53; N, 4.09. Found: C, 59.80; H, 3.60; N, 4.08.

1-Naphthyl N-*p*-Chlorophenylcarbamate (1e): 45.1% yield, brown solid, *mp* 156~158°C; IR (KBr) 780, 1710, 3010, 3430cm⁻¹; ¹H NMR (CDCl₃+DMSO) δ 7.1~7.7 (*m*, 11H), 7.8 (*s*, 1H). Anal. Calcd for C₁₇H₁₂NO₂Cl: C, 68.58; H, 4.06; N, 4.70. Found: C, 68.32; H, 4.32; N, 4.25.

1-Naphthyl N-*m*-Chlorophenylcarbamate (1f): 45.0% yield, brown solid, *mp* 210°C; IR (KBr) 780, 1700, 3050, 3300cm⁻¹; ¹H NMR (DMSO) δ 7.2~8.0 (*m*, 11H), 8.25 (*s*, 1H). Anal. Calcd for C₁₇H₁₂NO₂Cl: C, 68.58; H, 4.06; N, 4.70. Found: C, 68.18; H, 4.21; N, 4.31.

1-Naphthyl N-*m*-Nitrophenylcarbamate (1g): 41.8% yield, yellow solid, *mp* 210°C; IR (KBr) 1350, 1720, 3080, 3380cm⁻¹; ¹H NMR (DMSO) δ 7.1~7.8 (*m*, 11H), 8.2 (*s*, 1H). Anal. Calcd for C₁₇H₁₂N₂O₄: C, 66.23; H, 3.92; N,

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

1-Naphthyl N-*p*-Nitrophenylcarbamate(1h): 69.6% yield, yellow solid, *mp* 220°C; IR (KBr) 1350, 1750, 3100, 3360 cm^{-1} ; ^1H NMR (DMSO) δ 7.0~7.8 (*m*, 11H), 8.4(*s*, 1H). Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_4$: 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 λ_{max} obeyed the Beer-Lambert law. Typically, 1ml of ethanol solution ($2 \times 10^{-3}\text{M}$) of the substrate, **1b** ($\lambda_{\text{max}} = 292\text{nm}$, $\epsilon = 9.4 \times 10^3$), was mixed with 19ml of acetate buffer ($\text{AcOH} = 0.025\text{M}$, $\text{AcONa} = 0.176\text{M}$; pH 5.6). 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.

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