Pergamon

TETRAHEDRON

Tetrahedron 57 (2001) 3343–3347

Application of Grunwald–Winstein correlation analyses with Y_{BnBr} scales to the solvolysis of benzoyl bromides

Kwang-Ting Liu* and Iuan-Jye Hou

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

Received 26 December 2000; accepted 19 February 2001

Abstract—The solvolysis of 4-methoxy-(**1**), 4-methyl-(**2**), unsubstituted (**3**) and 4-chloro-(**4**) benzoyl bromide in a variety of solvents was studied. The linear log k–Y_{BnBr} plots for **1** indicates limiting S_N1 mechanism, whereas the splitting of lines for nucleophilic solvents and poorly nucleophilic solvents in the case of **2** suggests significant nucleophilic solvent participation. The mechanism for the solvolysis of **3** and **4** probably varies with solvents, similar to that of the corresponding chlorides. Good linear Hammett log k–σ^+ plot could be found in a few solvents. A comparison of the solvolytic behavior for aromatic acyl bromides and chlorides will be discussed. © 2001 Elsevier Science Ltd. All rights reserved.

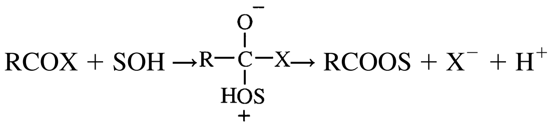
1. Introduction

Acyl halides are fundamental organic substrates with very high reactivity. Although acyl chlorides were continuously studied from mechanistic[1] and synthetic[2] points of view, much less attention was paid to the corresponding bromides. Nucleophilic substitution of substituted aromatic acyl bromides with methanol in acetonitrile solution was examined and the mechanism was found substituent-dependent.[3] To our knowledge, little work on the solvent effect for the solvolysis of acyl bromides has been performed.

Early mechanistic studies led to a conclusion of three possible pathways for the solvolysis of acyl halides,[4] namely, the unimolecular dissociation (Eq. (1)), the bimolecular synchronous S_N2-type (Eq. (2)) and the addition–elimination (Eq. (3)) mechanisms.

$$\mathrm{RCOX} \rightarrow \mathrm{R\overset{+}{C}{=}O} + \mathrm{X^-} \xrightarrow{\mathrm{SOH}} \mathrm{RCOOS} + \mathrm{H^+} \tag{1}$$

$$\mathrm{RCOX} + \mathrm{SOH} \rightarrow [\mathrm{TS}]^{\ddagger} \rightarrow \mathrm{RCOOS} + \mathrm{X^-} + \mathrm{H^+} \tag{2}$$



$$\mathrm{RCOX} + \mathrm{SOH} \rightarrow \mathrm{R{-}\underset{\underset{+}{HOS}}{\overset{O^-}{C}}{-}X} \rightarrow \mathrm{RCOOS} + \mathrm{X^-} + \mathrm{H^+} \tag{3}$$

Previously, based on the observation of linear correlation between logarithms of rate constants in a number of solvents for 4-methoxybenzyl chloride, which was proposed to solvolyzed via limiting S_N1 mechanism from linear Grunwald–Winstein plots with Y_{Cl} scales,[5] 2,6-dimethylbenzoyl chloride and 4-methoxybenzoyl chloride were both considered to solvolyze with S_N1 mechanism similar to the 1-adamantyl system.[6] Non-linear log k–mY_{Cl} plots suggested different mechanisms of solvolysis for other aromatic acyl chlorides.[7] However, by employing the single-[8] and the dual-parameter[9] Grunwald–Winstein (Eqs. (4)[8] and (5)[9]) with Y_{BnCl}[10] and N_{OTs}[11] scales to examine solvolytic mechanisms for a series of benzoyl chlorides, and in association with the results of Hammett-type correlation analyses and of ab initio calculations, we concluded[1a] that 2,6-dimethylbenzoyl chloride solvolyzed with limiting S_N1 mechanism (Eq. (1)), while 2-methyl-, 4-methoxy- and 4-methylbenzoyl chloride proceeded with nucleophilic solvent participation.

$$\log(k/k_0) = mY \tag{4}$$

$$\log(k/k_0) = mY + lN \tag{5}$$

More complicated mechanisms were involved for other benzoyl chlorides.

Obviously, correlation analysis using Y_{BnCl} scales will provide a better understanding to the solvolytic mechanism for benzoyl chlorides. We therefore undertook to explore the applicability of using Y_{BnBr}[12] in a similar approach for studying the solvolysis of benzoyl bromides. The results are reported in the present paper.

2. Results

4-Methoxybenzoyl bromide (**1**), 4-methylbenzoyl bromide (**2**), benzoyl bromide (**3**), and 4-chlorobenzoyl bromide (**4**),

---

Keywords: solvolysis; Y_{BnBr}; Grunwald–Winstein correlation.

* Corresponding author. Tel.: +886-2-2369-4966; fax: +886-2-2363-6359; e-mail: ktlui@ccms.ntu.edu.tw

PII: S0040-4020(01)00204-6

Table 1. Solvolysis rate constants (×10^2) for aromatic acyl bromides (**1**–**4**) at 25°C

Solvent[a]	**1**	**2**	**3**	**4**
100E	9.53	3.16	5.90	9.22
90E	50.2[b]	8.87	7.12	20.4[b]
80E	130[b]	19.5[b]	8.44	
90A	4.09	1.96	3.26	2.52
80A	34.3[b]	6.94	5.77	6.10
70A	113[b]	16.6[b]	8.38	
100M	84.5[b]	18.3[b]	12.8[b]	43.8[b]
90M		32.7[b]	18.9[b]	
80M			35.5[b]	
100T			8.12	2.03
80T20E		33.8[b]	6.07	2.78
60T40E	327[b]	19.2[b]	5.51	3.54
40T60E	117[b]	9.88	4.71	4.73

[a] For abbreviation of solvents: A=acetone, E=ethanol, M=methanol, T=2,2,2-trifluoroethanol. Figures shown are percentages of volume in water; 80T20E indicates T–E of 80:20 v/v and likewise for 60T40E and 40T60E.

[b] From data at other temperatures.

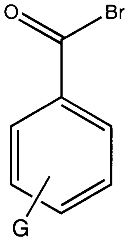
Table 2. Correlation analyses using single parameter Eq. (1)

Substrate	Parameters	n[a] (solvent)	R	m (S.D.)[b]
1	Y_{BnBr}	9 (All)	0.993	0.702 (0.031)
		7 (AEM)	0.995	0.745 (0.032)
2	Y_{BnBr}	11 (All)	0.926	0.359 (0.049)
		8 (AEM)	0.995	0.509 (0.020)
3	Y_{BnBr}	13 (All)	0.397	0.086 (0.060)
		9(AEM)	0.923	0.299 (0.047)
4	Y_{BnBr}	9 (All)	0.383	−0.115 (0.105)
		5 (AEM)	0.882	0.597 (0.184)

[a] Number of data points.

[b] Standard deviation.

were solvolysed in a variety of solvents, and the rate constants were measured by conductimetric method as described.[10a] Because of the high reactivity and the low solubility at temperature below −10°C, the rate of solvolysis in solvents of relatively large solvent ionizing power could not be measured accurately. Pertinent data at 25°C are given in Table 1.



1 G = 4-OCH$_3$
2 G = 4-CH$_3$
3 G = H
4 G = 4-Cl

Correlation analyses of log k values against Y_{Br}[13] using Eq. (4) or against Y_{Br} and N_{OTs} using Eq. (5) showed poor correlation with scattered data points in every case. The results of the analysis against Y_{BnBr} are shown in Table 2. An excellent linear relationship[14] (R=0.993) was found in log k–Y_{BnBr} plots for acyl bromide **1** in all solvents where k could be measured (Fig. 1). In the case of compound **2**, two lines, one in nucleophilic solvents (R=0.995 in aqueous acetone, ethanol and methanol) and the other in poorly nucleophilic ethanol–trifluoroethanol, were observed against Y_{BnBr} (Fig. 2). Only dispersed log k–Y_{BnBr} plots were found for **3** and **4**, even if only nucleophilic solvents were considered. The analysis for log k against Y_{BnBr} and N_{OTs} or N_{T}[15] by using Eq. (5) revealed no good linear relationship for acyl bromides **2**, **3** and **4** either.

Hammett-type correlation analyses of log k values against σ^+ constants[16] (Eq. (6)) were carried out for substrates if three or four rate constants in same solvent were available (Table 3).

$$\log(k/k_0) = \sigma^+ \rho \qquad (6)$$

Among the limited number of solvent systems under examination, excellent linear correlation (R=0.994) was observed for all four substrates in 60T40E with ρ of −2.20 (Fig. 3).

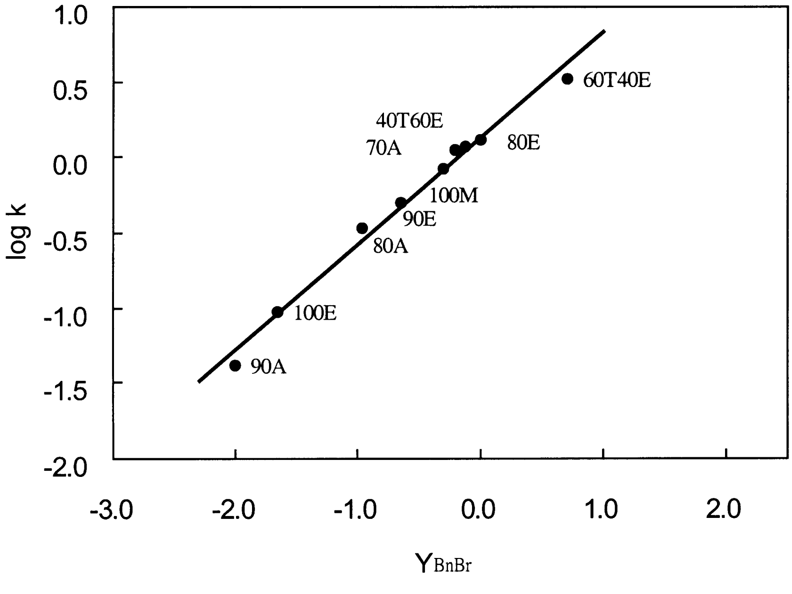


Figure 1. Plots of log k for **1** against Y_{BnBr}.

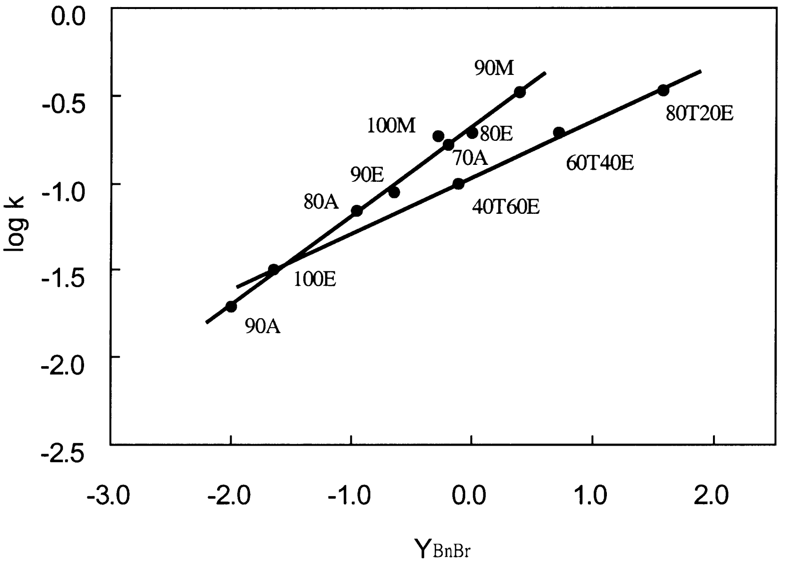


Figure 2. Plots of log k for **2** against Y_{BnBr}.

Table 3. Hammett plots of selective log k values against σ^+ constants

Solvent	Substrate	n	ρ	R
90E	**1–3**	3	−1.13	0.954
80E	**1–3**	3	−2.03	0.995
80A	**1–4**	4	−0.859	0.927
80A	**1–3**	3	−1.03	0.951
70A	**1–3**	3	−1.48	0.988
100M	**1–3**	3	−1.08	0.974
80T20E	**2–4**	3	−2.52	0.999
60T40E	**1–4**	4	−2.20	0.994
40T60E	**1–4**	4	−1.60	0.968
40T60E	**1–3**	3	−1.83	0.983

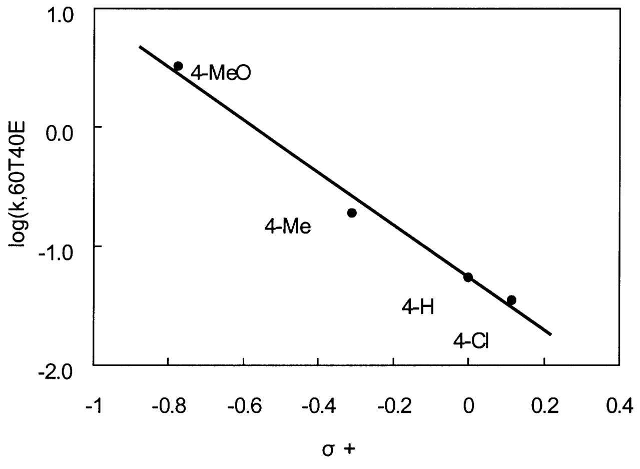


Figure 3. Plots of log k in 60T40E for **1–4** against σ^+ constants.

3. Discussion

Correlation of rates of solvolysis using Grunwald–Winstein Eqs. (4) and/or (5) with appropriate scales of solvent ionizing power (Y) and solvent nucleophilicity (N) has been generally applied to mechanistic studies for the solvolysis of substrates at saturated carbons.[17] Recently, it was also employed in the elucidation of solvolytic mechanisms for unsaturated systems, such as styryliodonium salt,[18] *N*,*N*-diphenylcarbamoyl chloride[19] and aromatic acyl chlorides.[1a,c,d,6] The usefulness of Y_{BnCl} scale in studying the solvolysis of substituted benzoyl chlorides[1a] suggested an extension to the study of the corresponding benzoyl bromides with Y_{BnBr} would be worthwhile. Indeed, valuable information about the solvolytic mechanism for benzoyl bromides was obtained.

Owing to the high reactivity, only limited number of aromatic acyl bromides were found suitable for the study of solvent effects. Although seven substituted benzoyl chlorides were examined in the previous work,[1a] the reaction kinetics for only four bromides (**1**–**4**) could be monitored in reasonable varieties of solvent systems, including both highly nucleophilic and poorly nucleophilic ones, for correlation analyses. In spite of their low solubility in solvents of high water-content, **1**–**4** could still be solvolyzed in solvent systems with sufficiently large difference in solvent ionizing power (ΔY_{BnBr}=2.7–4.6) and made the interpretation meaningful. However, due to insufficient kinetic data in the non-nucleophilic trifluoroethanol (100T) available, which was found necessary in correlating experimental reactivity with the energy of isodesmic reaction,[1a] ab initio calculation for the formation of acylium ion ($ArCO^+$) from benzoyl bromides (RCOBr) was not performed. Besides, the three-parameter Eq. (7) suggested by Kevill and coworkers[20] was not tested, as it would be meaningless to treat such regression with less than ten variables.

$$\log(k/k_0) = mY_{Cl} + lN_T + hI \qquad (7)$$

In the previous study,[1a] the solvolyses of 4-methoxy- and 4-methylbenzoyl chlorides were considered to proceed with non-limiting S_N1 mechanisms, while the unsubstituted benzoyl chloride was on the borderline of unimolecular dissociation (Eq. (1)) and the addition–elimination (Eq. (3)) mechanisms. Moreover, the solvolyses of 4-chloro- and 4-nitrobenzoyl chlorides were likely to involve an S_N2 mechanism (Eq. (2)) in nucleophilic solvents, and an addition–elimination (Eq. (3)) mechanism in trifluoroethanol–ethanol.[1a] Similar to the corresponding chlorides, no linear correlation with Y_{Br} (Eq. (5)), or Y_{Br} and N_{OTs} (Eq. (6)) was found for **1** to **4** in the present work. On the other hand, log k–Y_{BnBr} plots showed excellent linear correlation (Fig. 1; R=0.993, Table 2) for the solvolysis of 4-methoxybenzoyl bromide (**1**), and therefore, a limiting $\mathrm{S_N1}$ mechanism could be deduced. The lack of significant nucleophilic solvent participation as compared with the analogous 4-methoxybenzoyl chloride[1a] is likely due to the better leaving ability of bromide ion in **1**.

In the case of the 4-methyl derivative (**2**), two separate lines, one for nucleophilic solvents (AEM) and the other for poorly nucleophilic solvents (TE), were observed (Fig. 2). The use of isodielectric trifluoroethanol–ethanol mixture[21] has been shown to be a diagnostic probe for nucleophilic solvent participation in solvolyses of various substrates.[22] Therefore, the downward splitting of line for data points obtained in TE from that in AEM suggests the intervention of nucleophilic solvents in the solvolysis of **2**. The poor regression for **2** with respect to all solvents (R=0.926, n=11, Table 2) by using the single-parameter Eq. (4) could be improved (R=0.964, n=9) from the dual-parameter Eq. (5), $\log (k/k_0)=0.458Y_{\mathrm{BnBr}}+0.301\ N_{\mathrm{OTs}}$. Although no excellent linear correlation ($R\geq0.99$)[14] was obtained, the low m value and the high l value could also indicate significant nucleophilic solvent participation in the solvolysis of **2**. Unlike 4-methoxybenzoyl bromide **1** and the corresponding chloride (vide supra), but similar to 4-methoxybenzyl halides,[22c] the reactivity of the bromide leaving group is still not good enough to yield an unassisted solvolysis.

The solvolysis of benzoyl bromides **3** and **4** gave nonlinear relationship for Eqs. (4) or (5). Scattered data points were resulted from log k–Y_{BnBr} plots. Poor correlation with Y_{BnBr} and N_{OTs} by using the dual-parameter Eq. (5), R=0.7–0.8, was found in both cases. The results show some similarities with those found for the corresponding benzoyl chlorides,[1a] indicating a variation of mechanisms in different solvent. Logarithm plots of rate data for **3** and **4**, respectively, against those for the corresponding chlorides[1a] showed fair linear relationships (R=0.96). Probably different types of non-$\mathrm{S_N1}$ reactions were involved in the solvolysis of **3** and **4** in nucleophilic solvents, similar to the corresponding chlorides.[1a]

The results of Hammett plots against σ^+ constants (Table 3) are also interesting. The solvolysis of **1** to **4** showed linear log k–σ^+ relationship in 60T40E (Fig. 3), but not in other nucleophilic solvents. Bromide **1** was too reactive in 80T20E to yield a reliable rate constant. Nevertheless, linear plot was observed for **2**–**4** in 80T20E, and presumably for **1**–**4** as well. In 40T60E, linear regression for **1**–**3** was realized as a marginal case, but significant deviation was found for the 4-chloro derivative **4**. The rate constant for **4** in 70A or in 80E could not be measured conductimetrically due to the low solubility at the temperature below 0°C. But linear plots were obtained for **1**–**3** in these solvents. Pertinent data for log k–σ^+ regression are listed in Table 3. For acyl chlorides corresponding to **1**–**4**, linear relationships were found only in solvents containing high percentage of water (50A, 50E and 60M) or high percentage of trifluoroethanol (100T and 80T20E).[1a] But for those corresponding to **1**–**3**, linear log k–σ^+ plots were observed in solvents containing less water (60A, 60E and 70M) or less trifluoroethanol (60T40E).[1a] Apparently, the more reactive acyl bromides **1**–**4** will display linear Hammett log k–σ^+ plots in solvents of smaller ionizing power, such as 70A and 80E, as compared with corresponding chlorides. The small negative ρ values in 60T40E and 80T20E, and even smaller in nucleophilic solvents could also be attributed to the less extent of charge development at the transition state, similarly to that found in the solvolysis of acyl chlorides.[1a]

4. Conclusions

In summary, solvolytic mechanisms for benzoyl bromides could be understood by means of Grunwald–Winstein type correlation analysis using Y_{BnBr} scales, in association with Hammett-type plots against σ^+ constants. 4-Methoxybenzoyl bromide (**1**) solvolyzes with limiting $\mathrm{S_N1}$ mechanism (Eq. (1)), whereas 4-methylbenzoyl bromide (**2**) proceeds with nucleophilic solvent participation. Different types of $\mathrm{S_N1}$ and non-$\mathrm{S_N1}$ reactions are probably involved in the solvolysis of benzoyl bromide (**3**) and 4-chlorobenzoyl bromide (**4**). The presence of the better leaving group, bromide as compared with chloride, could make benzoyl halides more likely to solvolyze via limiting or non-limiting $\mathrm{S_N1}$ mechanism and to exhibit linear Hammett-type plots, log k–σ^+ in solvents of smaller ionizing power.

5. Experimental

5.1. Materials

Spectral-grade or reagent-grade solvents (E. Merck) were purified following conventional methods[23] for kinetic studies. Doubly deionized water was used to prepare aqueous solvent mixtures for solvolytic studies. Benzoyl bromide (**3**) was commercially available (across) and other acid bromides **1**, **2** and **4** were prepared from corresponding acids and thionyl bromide,[24] respectively. The IR and NMR spectra were found to agree with the assigned structure. All of the acid bromides were freshly distilled for kinetic studies.

5.2. Kinetic measurements

Rate constants were measured by conductimetric method at least in duplicate. The conductivity cells containing about 1.8 mL of 1×10^{-4}–1×10^{-5} M solution of substrate and 1 μL of 2,6-lutidine were placed in a thermostat with a temperature variation of ±0.02°C. The maximum error for the measurement of k is ±2%.

Rate constants (in $\mathrm{s^{-1}}$) were monitored at 25°C or at appropriate temperatures. The rate constants (in $\mathrm{s^{-1}}$) measured at low temperatures are listed as follows:

For **1** in 90E, $k(-10°\mathrm{C})=1.79\times10^{-2}$, $k(-5°\mathrm{C})=3.04\times10^{-2}$ and $k(0°\mathrm{C})=5.10\times10^{-2}$; in 80E, $k(-10°\mathrm{C})=2.77\times10^{-2}$, $k(-5°\mathrm{C})=5.10\times10^{-2}$ and $k(0°\mathrm{C})=9.19\times10^{-2}$; in 80A, k

$(-10°\mathrm{C})=1.62\times10^{-2}$, $k(-5°\mathrm{C})=2.63\times10^{-2}$ and $k(0°\mathrm{C})=4.20\times10^{-2}$; in 70A, $k(-10°\mathrm{C})=2.54\times10^{-2}$. $k(-5°\mathrm{C})=4.46\times10^{-2}$ and $k(0°\mathrm{C})=8.30\times10^{-2}$; in 100M, $k(-10°\mathrm{C})=3.15\times10^{-2}$, $k(-5°\mathrm{C})=5.31\times10^{-2}$ and $k(0°\mathrm{C})=8.79\times10^{-2}$; in 60T40E, k $(-10°\mathrm{C})=4.02\times10^{-2}$ and $k(-5°\mathrm{C})=8.08\times10^{-2}$; in 40T60E, $k(-10°\mathrm{C})=2.92\times10^{-2}$, $k(-5°\mathrm{C})=5.24\times10^{-2}$ and $k(0°\mathrm{C})=9.22\times10^{-2}$.

For **2**, in 80E, $k(-10°\mathrm{C})=5.03\times10^{-3}$, $k(-5°\mathrm{C})=8.99\times10^{-3}$ and $k(0°\mathrm{C})=1.57\times10^{-2}$; in 70A, $k(-10°\mathrm{C})=4.83\times10^{-3}$, $k(-5°\mathrm{C})=8.47\times10^{-3}$ and $k(0°\mathrm{C})=1.46\times10^{-2}$; in 100M, $k(-10°\mathrm{C})=4.48\times10^{-3}$, $k(-5°\mathrm{C})=8.07\times10^{-3}$ and $k(0°\mathrm{C})=1.42\times10^{-2}$; in 90M, $k(-10°\mathrm{C})=6.05\times10^{-3}$, $k(-5°\mathrm{C})=1.14\times10^{-2}$ and $k(0°\mathrm{C})=2.10\times10^{-2}$; in 80T20E, $k(-10°\mathrm{C})=5.64\times10^{-3}$, $k(-5°\mathrm{C})=1.08\times10^{-2}$ and $k(0°\mathrm{C})=2.10\times10^{-2}$; in 60T40E, $k(-10°\mathrm{C})=4.47\times10^{-3}$, $k(-5°\mathrm{C})=8.03\times10^{-3}$ and $k(0°\mathrm{C})=1.43\times10^{-2}$.

For **3**, in 100M, $k(-10°\mathrm{C})=4.67\times10^{-3}$, $k(-5°\mathrm{C})=7.90\times10^{-3}$ and $k(0°\mathrm{C})=1.31\times10^{-2}$; in 90M, $k(-10°\mathrm{C})=5.54\times10^{-3}$, $k(-5°\mathrm{C})=9.71\times10^{-3}$ and $k(0°\mathrm{C})=1.67\times10^{-2}$; in 80M, $k(-10°\mathrm{C})=7.03\times10^{-3}$, $k(-5°\mathrm{C})=1.31\times10^{-2}$, $k(0°\mathrm{C})=2.39\times10^{-2}$.

For **4**, in 90E, $k(-10°\mathrm{C})=3.14\times10^{-3}$, $k(-5°\mathrm{C})=6.09\times10^{-3}$ and $k(0°\mathrm{C})=1.15\times10^{-2}$; in 100M, k $(-10°\mathrm{C})=7.31\times10^{-3}$, $k(-5°\mathrm{C})=1.40\times10^{-2}$ and $k(0°\mathrm{C})=2.62\times10^{-2}$.

The rate constants measured at 25°C and those from extrapolation to 25°C by using Arrhenius plot are given in Table 1.

Acknowledgements

The authors acknowledge the financial support from the National Science Council, Republic of China (Grants NSC88-2113-M-002-014 and NSC89-2113-M-002-012).

References

1. For some recent studies, see: (a) Liu, K.-T.; Chen, H.-I. *J. Chem. Soc., Perkin Trans. 2* **2000**, 893. (b) Garcia-Riu, L.; Leis, J. R. *Chem. Commun.* **2000**, 455. (c) Koo, I. S.; Kim, J-S.; An, S. K.; Yang, K.; Lee, I. *J. Korean Chem. Soc.* **1999**, *43*, 527 (*Chem. Abstr.* **2000**, *132*, 107619e). (d) Koo, I. S.; Lee, S. I.; An, S. K.; Yang, K.; Lee, I. *Bull. Korean Chem. Soc.* **1999**, *20*, 1451 (*Chem. Abstr.* **2000**, *132*, 236663p).
2. For a recent example, see: Kabalka, G. W.; Malladi, R. R.; Tejedor, D.; Kelley, S. *Tetrahedron Lett.* **2000**, *41*, 1001.
3. Kevill, D. N.; Knauss, D. C. *J. Chem. Soc., Perkin Trans. 2* **1993**, 307.
4. For a review of early work on the mechanisms of substitution at carbonyl carbon in acyl halides, see: Kivinen, A. In *The Chemistry of Acyl Halides*, Patai, S., Ed.; Interscience: New York, 1972; pp 177–230.
5. Bentley, T. W.; Koo, I. S.; Norman, S. J. *J. Org. Chem.* **1991**, *56*, 1604.
6. Bentley, T. W.; Harris, H. C.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1988**, 783.
7. Bentley, T. W.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1986**, 619.
8. Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.
9. Winstein, S.; Grunwald, E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700.
10. (a) Liu, K.-T.; Sheu, H.-C. *J. Org. Chem.* **1991**, *56*, 3021. (b) Liu, K.-T.; Chang, L.-W.; Yu, D.-G.; Chen, P.-S.; Fan, J.-D. *J. Phys. Org. Chem.* **1997**, *10*, 879.
11. Fujio, M.; Susuki, T.; Goto, M.; Tsuji, Y.; Yatsugi, K.; Saeki, Y.; Kim, S. H.; Tsuno, Y. *Bull. Chem. Soc. Jpn* **1994**, *67*, 2233.
12. Liu, K.-T.; Chin, C.-P.; Yu, D.-G.; Duann, Y.-F. *J. Chinese Chem. Soc. (Taipei)* **1999**, *46*, 789.
13. Bentley, T. W.; Llewellyn, G. *Progr. Phys. Org. Chem.* **1990**, *17*, 121.
14. Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.
15. Kevill, D. N.; D'Souza, M. J. *J. Chem. Res. (S)* **1993**, 174.
16. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
17. For recent examples, see: (a) Nakashima, T.; Fujiyama, R.; Kim, H.-J.; Fujio, M.; Tsuno, Y. *Bull. Chem. Soc. Jpn* **2000**, *73*, 429. (b) Kevill, D. N.; Abduljaber, M. H. *J. Org. Chem.* **2000**, *65*, 2548. (c) Liu, K.-T.; Chang, C.-W.; Chen, H.-I.; Chin, C.-P.; Duann, Y.-F. *J. Phys. Org. Chem.* **2000**, *13*, 203.
18. Okuyama, T.; Ishida, Y.; Ochiai, M. *Bull. Chem. Soc. Jpn* **1999**, *72*, 163.
19. Liu, K.-T.; Chen, H.-I; Lin, Y.-S.; Jin, B.-Y. *J. Phys. Org. Chem.* **2000**, *13*, 322.
20. Kevill, D. N.; D'Souza, M. J. *J. Chem. Soc., Perkin Trans. 2* **1995**, 973.
21. Kaspi, L.; Rappoport, Z. *J. Am. Chem. Soc.* **1980**, *102*, 3829.
22. For recent examples, see: (a) Ref. 1a. (b) Liu, K.-T.; Hou, S.-J.; Tsao, M.-L. *J. Org. Chem.* **1998**, *63*, 1360. (c) Liu, K.-T.; Duann, Y.-F.; Hou, S.-J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2181. (d) Bentley, T. W.; Llewellyn, G.; Ryu, Z. H. *J. Org. Chem.* **1998**, *63*, 4654.
23. Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: London, 1996.
24. Saraf, S. D.; Zaki, M. *Synthesis* **1973**, 612.