Methanolyses of *para*-Substituted Benzoyl Chlorides in Isodielectric Binary Mixtures

Ikchoon Lee *
Department of Chemistry, Inha University, Inchon, 402-751, Korea
Dae Dong Sung, Tae Seop Uhm, and Zoon Ha Ryu
Department of Chemistry, Dong-A University, Pusan, 604-714, Korea

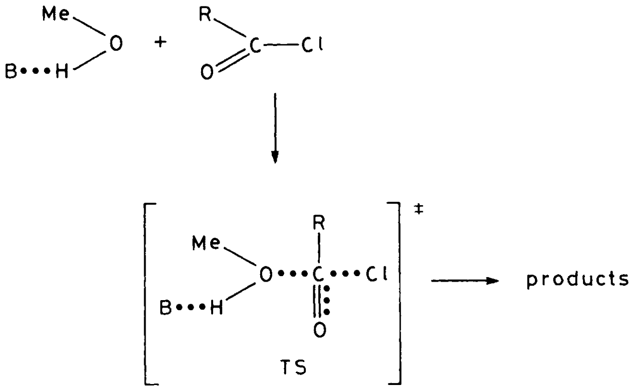
The kinetics and mechanism of solvolysis of *p*-substituted benzoyl chlorides have been investigated in three isodielectric systems: methanol–acetonitrile, methanol–nitrobenzene, and methanol–nitromethane mixtures. Only S_N1–S_N2 processes are favoured by electron-donating substituents in all binary systems, but carbonyl addition processes become dominant in the low basicity (β) region of binary mixtures, especially in methanol–nitromethane for compounds with electron-withdrawing substituents. The rates for unsubstituted substrates as well as those substitutes with electron-withdrawing groups are higher than those for *p*-methyl substituted substrates, suggesting the contribution of a combined S_N1–S_N2 and carbonyl addition pathway, rather than the involvement of a concerted displacement with variable transition state.

Solvolyses of aromatic and aliphatic acyl halides have been studied extensively.[1] However, the reaction mechanism is not well established.

A unimolecular mechanism with the formation of an acylium ion (RCO^+) is believed to operate under certain conditions.[2] Bimolecular mechanisms are less well defined, the two most commonly cited variations being a concerted S_N2 displacement and an addition–elimination (S_AN) mechanism.

In ethanolysis studies of aliphatic acyl chlorides, Kevill *et al.*[3] concluded that the reaction proceeds through either a synchronous displacement mechanism, incorporating a variable transition state (TS) structure, or as a combination of this type of mechanism with (especially for electron-withdrawing substituents, EWS) an addition–elimination mechanism. They proposed the involvement of considerable carbocation character in the rate-determining TS of the methanolysis of acetyl chloride;[4a,b] a loose S_N2 TS allows for nucleophilic assistance by a methanol molecule, which is subject to general base catalysis by a second methanol molecule, by added chloride ion, or by an acetonitrile molecule (Scheme). More recently, Bentley *et al.*[5] have proposed concurrent concerted (S_N2) and addition–elimination (S_AN) processes for the solvolysis of benzoyl chlorides, with the S_N2 concerted mechanism being favoured in the more ionizing aqueous–organic mixtures due to low solvent nucleophilicity and by an electron-donating substituent (EDS) in the substrate.

This survey shows that there are two controversial aspects which still need to be resolved regarding the bimolecular mechanism of solvolysis of acyl chlorides. (*a*) Is the tetrahedral species found along the reaction co-ordinate an intermediate (*i.e.*, S_AN mechanism) or a TS (*i.e.*, S_N2 mechanism)?[6] In this respect, results of recent studies on the nucleophilic displacement reactions of acyl halides in the gas phase [7a–f] together with MO theoretical [7g–k] analyses have been helpful in unravelling mechanisms occurring in solution. The stability of the tetrahedral adduct has been proposed to depend on (i) the energy difference between the π^* orbital of the carbonyl group and the σ^*_{Cx} orbital of the bond between the carbonyl carbon and the leaving group (X), and (ii) the difference in gas-phase basicities between the attacking nucleophile and the tetrahedral anion.[7] This means that the tetrahedral species is likely to become a tetrahedral TS, in which weak nucleophiles and good leaving groups (LG) are involved, whereas tetrahedral intermediates can be expected when strong nucleophiles and poor LG are involved. (b) Secondly, if both the S_N2 and S_AN mechanisms are compatible under certain conditions, is synchronous displacement operative with a variable TS structure (possibly with an intermediate TS structure) or are they concurrent with a combination of the two mechanisms contributing to the overall reaction? Kevill *et al.*[3,4] were indecisive, while Bentley *et al.*,[5] favoured the concurrent mechanisms of S_N1–S_N2 and addition–elimination.



Scheme.

Methanol (MeOH), acetonitrile (MeCN), nitrobenzene ($PhNO_2$), and nitromethane ($MeNO_2$) have very similar dielectric constants[8] and provide us with isodielectric binary mixtures. Although bulk properties of the four solvents are nearly the same, specific solvation properties such as hydrogen-bond donor acidity, α, and hydrogen-bond acceptor basicity, β, as well as polarity–polarizability, π^*, parameters[9] are quite different, as shown in Table 1.[9c,d]

The Lewis basicity parameter (β) of the binary mixture MeOH–MeCN increases linearly from 0.37 to 0.62 as the MeOH content is increased from 0 to 100%;[11] in contrast, however, MeOH and $MeNO_2$ form regular mixtures with negative deviation which corresponds to a negative deviation of the β values from the ideal straight line.[11] This reflects a smaller β with a relatively greater α value of $MeNO_2$. The effects of weak bases and ions on bulk methanol structure have been discussed

Table 1. Solvatochromic parameters of pure solvents.[8,9c,d,10]

	MeOH	MeCN	$PhNO_2$	$MeNO_2$	EtOH	TFE
α	0.93	0.19	0.00	0.22	0.83	1.51
β	0.62	0.37	0.30	0.22	0.77	0.00
π^*	0.60	0.75	1.01	0.85	0.54	0.73
ε^a	3.36 (20)	37.5 (20)	34.8 (20)	35.9 (35)	24.3 (25)	26.1 (25)

[a] Values in parentheses are temperatures/°C.

Table 2. Pseudo-first-order rate constants ($k_{obs}/10^{-4}$ s^{-1}) for the solvolysis of substituted benzoyl chlorides in MeOH–MeCN at 10.0 °C.

	Substituents				
Solvent[a]	p-OCH_3	p-CH_3	p-H	p-F	p-Cl
100	22.8	8.91	10.4	10.6	19.1
95	19.5	9.97	11.1	10.9	20.0
90	19.0	9.33	11.6	11.2	20.2
85	18.2	9.10	11.1	12.2	19.4
80	17.8	8.57	10.9	11.8	18.4
70	16.3	7.65	9.44	10.1	16.2
50	10.8	5.60	7.72	8.29	11.5
40	7.16	4.31	5.71	6.13	8.34
30	4.49	2.79	3.85	4.33	4.61

[a] MeOH composition (%).

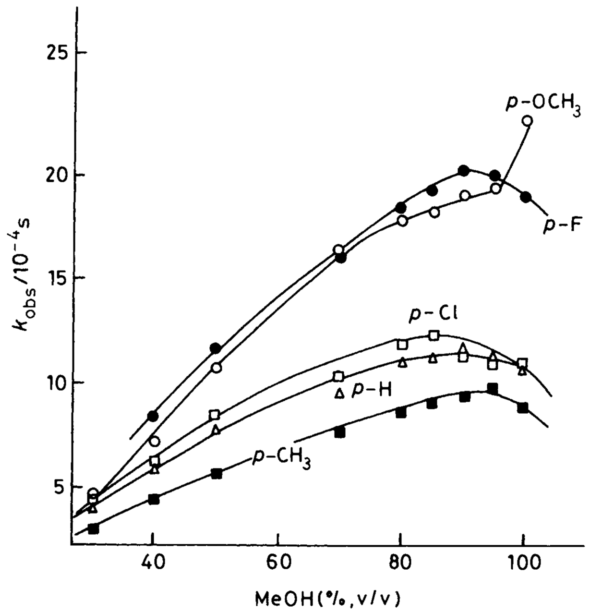


Figure 1. Plots of k_{obs} *versus* methanol composition (%, v/v) in MeOH–MeCN at 10.0 °C.

in great detail by Symons *et al.*[12] in terms of free OH group, $[OH]_{free}$, and free lone-pair group $[LP]_{free}$, production.

Trifluoroethanol (TFE) has the greatest hydrogen-bond donor acidity known (α = 1.51) but also has a negligibly low solvent basicity (β = 0), although it has nearly the same dielectric constant as EtOH[8] (Table 1). Thus solvation properties of EtOH–TFE binary mixtures will be, in some respects, similar to those of $MeOH–MeNO_2$ systems. In our previous work[13] on the solvolyses of benzoyl chlorides (YC_6H_4COCl) in TFE–EtOH systems, however, we concluded that the reaction proceeds by a concerted displacement mechanism with a variable TS depending on the substituent Y; a more EWS (Y = p-NO_2) had a greater degree of bond formation while a more EDS (Y = p-CH_3) led to a greater degree of bond breaking in the TS.

Table 3. Pseudo-first-order rate constants ($k_{obs}/10^{-4}$ s^{-1}) for the solvolysis of substituted benzoyl chlorides in $MeOH–PhNO_2$ at 5.0 °C.

	Substituents				
Solvent[a]	p-OCH_3	p-CH_3	p-H	p-F	p-Cl
100	12.4	5.37	6.45	6.79	12.5
95	13.1	5.00	6.29	6.75	12.3
90	12.9	4.70	5.96	6.45	12.0
85	11.9	4.51	5.64	6.22	11.8
80	10.9	4.10	5.30	5.94	11.0
70	8.73	3.62	4.68	5.14	9.83
50	4.17	2.51	3.11	3.52	7.14

[a] MeOH composition (%).

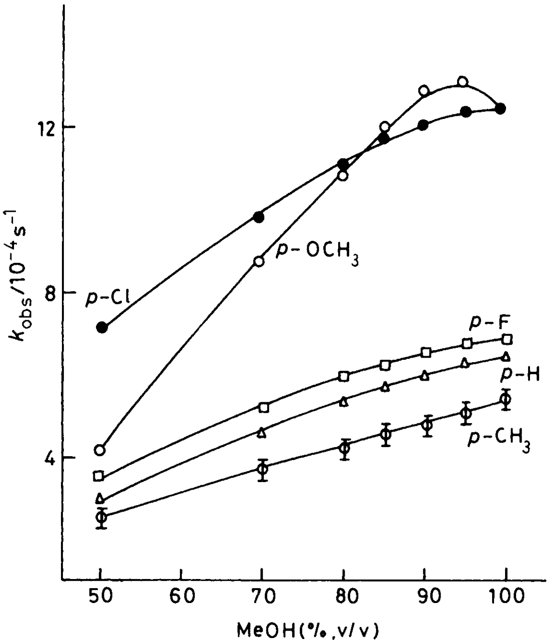


Figure 2. Plots of k_{obs} *versus* methanol composition (%, v/v) in $MeOH–PhNO_2$ at 5.0 °C.

On the other hand, the solvolyses of t-butyl halides exhibited rate maxima,[14] *e.g.* at 50–60%, 70–80%, and 80–100% (v/v) for $MeOH–MeNO_2$, MeOH–MeCN, and $MeOH–PhNO_2$, respectively, in the range 25–45 °C.[14c]

In this work, we report the methanolyses of *para*-substituted benzoyl chlorides (YC_6H_4COCl) in the three isodielectric binary mixtures of MeOH–MeCN, $MeOH–PhNO_2$, and $MeOH–MeNO_2$.

Results and Discussion

Pseudo-first-order rate constants, k_{obs}, for the solvolyses of Y-substituted benzoyl chlorides are summarized in Tables 2–4 and rate profiles with MeOH composition are presented in Figures 1–3. Rough estimates show that the reactivities in binary mixtures are in the order $MeOH–MeNO_2$ > MeOH–MeCN > $MeOH–PhNO_2$, which is the same as the reactivity order of t-butyl halide solvolysis in the binary mixtures.[14] There are clear trends in maximum rate behaviour for MeCN binary mixtures and for $PhNO_2$, albeit somewhat obscured, at 80–90% and 90–100% (v/v) MeOH, respectively. The fact that the rate maxima appeared for the benzoyl chlorides solvolysis over nearly the same range of MeOH composition as for the t-butyl halide solvolysis[14c] suggests that in MeCN and $PhNO_2$ binary

Table 4. Pseudo first-order rate constants ($k_{obs}/10^{-4}$ s^{-1}) for the solvolysis of substituted benzoyl chlorides and 1-adamantyl (1-AdCl) in MeOH–$MeNO_2$ at various temperatures.

	p-OCH$_3$			p-CH$_3$				p-H				o-F			p-Cl			1-AdCl
Solvent[a]	−5 °C	0 °C	5 °C	10 °C	−5 °C	0 °C	5 °C	10 °C	−5 °C	0 °C	5 °C	−5 °C	0 °C	5 °C	−10 °C	−5 °C	0 °C	80 °C
100	3.52	6.54	12.3	22.8	1.80	3.13	5.37	8.91	2.16	3.85	6.45	2.49	4.56	6.79	3.09	5.04	7.97	—
90	4.67	9.00	15.6	28.3	2.28	3.68	5.94	9.79	2.76	4.54	7.74	3.22	5.04	8.18	3.59	6.03	9.60	0.106
80	5.18	9.65	16.5	29.2	2.37	3.96	6.43	10.4	3.04	4.88	8.29	3.68	5.67	8.89	3.96	6.77	11.2	0.109
70	6.52	9.12	17.2	30.2	2.30	3.85	6.45	10.5	3.22	4.93	8.48	3.85	5.96	9.19	4.70	7.55	12.6	0.116
60	5.37	8.94	14.5	23.5	2.19	3.62	6.15	9.58	3.29	5.23	8.57	3.87	6.08	9.30	6.17	9.40	14.0	0.103
50	4.51	7.44	13.6	22.2	2.14	3.41	5.44	8.33	3.34	5.16	8.29	4.40	6.38	9.44	6.59	10.0	14.9	0.0736
40	3.92	6.72	11.5	19.3	1.84	2.97	5.00	7.55	3.43	5.11	8.11	4.58	6.45	9.53	8.06	11.5	16.5	—
30	2.86	4.58	7.88	13.3	1.54	2.65	4.42	7.30	3.45	4.86	7.44	4.68	6.61	9.76	9.53	13.4	19.7	0.0487
20	2.33	3.40	5.37	7.97	—	—	—	—	—	—	—	5.34	8.13	10.8	—	—	—	—
10	—	—	—	—	—	—	—	—	—	—	—	7.67	10.9	15.6	—	—	—	—

[a] MeOH composition (%).

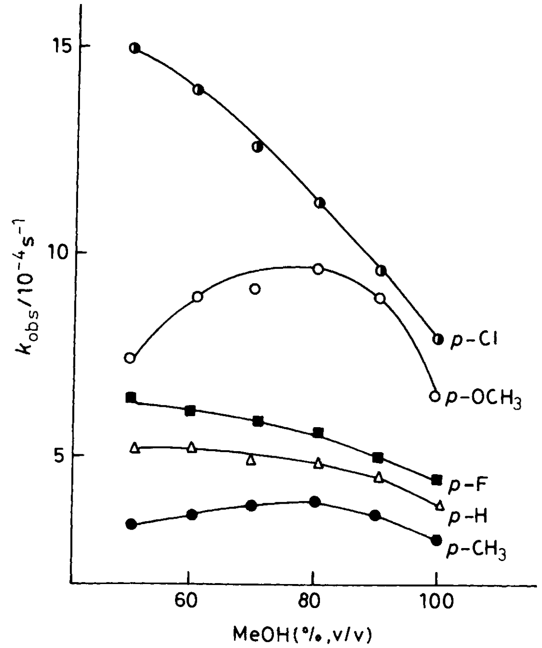


Figure 3. Plots of k_{obs} *versus* methanol composition (%, v/v) in MeOH–$MeNO_2$ at 0.0 °C.

mixtures, the solvolyses proceed largely by an S_N1–S_N2 mechanism, since t-butyl halides are known to solvolyse by mostly S_N1 but with some solvent nucleophilic assistance.[15]

In striking contrast, rate maxima are only found with EDS (Y = p-OCH$_3$ or p-CH$_3$) at 70–80% MeOH in MeOH–$MeNO_2$ binary mixtures; for EWS (Y = p-F or p-Cl) there are no rate maxima but the rate increases steadily as the composition of cosolvent ($MeNO_2$) increases. This is in marked contrast to the rate profiles found for the solvolysis of benzoyl chlorides in EtOH–TFE binary mixtures.[13] No rate maximum was observed in this system, but a steady increase in the rate was found with the TFE content for Y = EDS while the trend reversed to a decrease for Y = EWS. This indicates that bond breaking is important for Y = EDS but bond formation becomes more important for Y = EWS, since the ionizing power increases but the solvent nucleophilicity decreases with the TFE content. The rate profiles for EDS in MeOH–$MeNO_2$ (Figure 3) as well as in other binary mixtures (Figures 1 and 2) are consistent with the S_N1–S_N2 processes because only this mechanism permits positive charge development on the carbonyl atom, as implied by the obvious similarities between the rate profiles with those of t-butyl halide solvolysis in the corresponding binary mixtures.[14c]

The abnormal rate increases with $MeNO_2$ content observed for EWS in $MeNO_2$ binary mixtures, however, strongly suggest that another mechanistic pathway, presumably carbonyl addition (as Bentley[15] has proposed) becomes predominant for these compounds. The addition–elimination pathway is known to be particularly effective in nucleophilic solvents of low ionizing power.[5] However, as we have noted above, $MeNO_2$ has a relatively large α (albeit quite smaller than that for MeOH) but has the smallest β value among the three cosolvents studied in this work. This means that the mechanism, which is dominant for EWS in $MeNO_2$ binary mixtures, is insensitive to the hydrogen-bond donor acidity, α, but is operative in a solvent of low basicity (β) and high polarity (π^*). The S_N2 reactivity will be low if β is small, since the base cannot accept a hydrogen bond effectively.

The low β value is also relevant to the low concentration of $[LP]_{free}$, owing to inefficient solvation of the methanolic OH group, resulting in the lowest solvent nucleophilicity and the lowest disrupting ability of any MeOH polymer structure with $MeNO_2$. In this respect the similarities between EtOH–TFE and MeOH–$MeNO_2$ binary mixtures end. TFE has a greater α than EtOH so that the ionizing power should increase with the TFE content while in $MeNO_2$ binary mixtures the α value decreases continuously with the $MeNO_2$ content, although the solvent nucleophilicity (β) decreases in both binary mixtures with the cosolvent, TFE and $MeNO_2$, content. Thus for the TFE binary mixtures the rate decrease with the TFE content for Y = EWS can be equally well interpreted in terms of the concurrent carbonyl addition and S_N1–S_N2 mechanisms, since an increase in α accompanied by a decrease in β should result in some increase in the competing S_N1–S_N2 contribution with a concomitant relative decrease in the contribution of the major component, carbonyl addition, to the overall solvolyses when the TFE content is increased. It should be noted that, although the two mechanistic pathways are competing, the reactivity of the S_N1–S_N2 path is low while that of the carbonyl addition path is high for Y = EWS, whereas the opposite is true for Y = EDS.

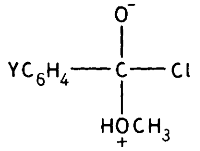
The fact that the carbonyl addition mechanism becomes dominant in a relatively high polarity (π^*) medium is in accord with the stabilization of the tetrahedral intermediate, which is either zwitterionic (**1**) or anionic (**2**), if proton transfer precedes the carbonyl addition pathway,[7c] by more 'physical' *i.e.*, electrostatic, solvation.[16]

Examination of Figure 3 reveals that the unsubstituted benzoyl chloride has a rate profile with a nature intermediate

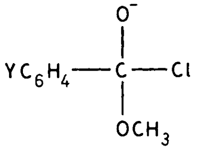
Table 5. Activation parameters, $\Delta H^{\ddagger}$/kcal mol^{-1}, and $\Delta S^{\ddagger}$ (e.u.) for the solvolysis of substituted benzoyl chlorides in MeOH–MeNO$_2$ at 5.0 °C.

	p-OCH$_3$		*p*-CH$_3$		*p*-H		*p*-F		*p*-Cl[a]	
Solvent[b]	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$\Delta H^{\ddagger c}$	$-\Delta S^{\ddagger}$
100	18.2	6.27	15.5	17.6	15.6	16.9	14.3	21.5	13.0	25.0
90	17.4	8.65	14.0	22.8	14.7	19.8	13.2	25.1	13.6	22.4
80	16.7	11.1	14.3	21.6	14.3	21.1	15.5	27.4	14.4	19.2
70	15.2	16.4	14.7	20.2	13.7	23.2	12.3	28.1	13.6	21.8
60	14.2	20.3	14.4	21.3	13.6	23.5	12.4	27.7	13.2	23.1
50	15.6	15.4	14.6	20.9	12.9	26.1	10.7	33.8	11.2	30.3
40	15.4	16.5	13.8	23.9	12.1	29.0	10.3	35.2	9.66	35.7
30	14.9	19.0	15.0	19.8	10.8	33.9	10.3	35.2	9.86	34.7
20	12.0	30.2	—	—	—	—	9.85	36.6	—	—
10	—	—	—	—	—	—	9.95	35.5	—	—

[a] Calculated at 0 °C. [b] MeOH composition (%).



(1)



(2)

Tetrahedral intermediates

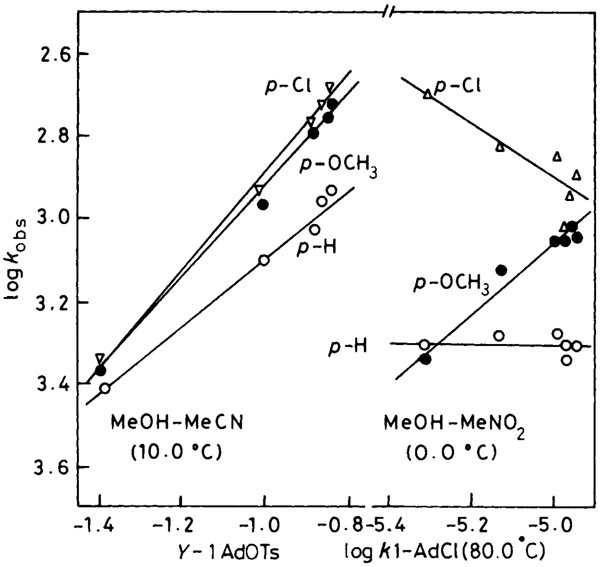


Figure 4. Plots of $\log k_{\text{obs}}$ *versus* $\log(k/k_0)$ for the solvolysis of 1-adamantyl toluene-*p*-sulphonate in MeOH–MeCN mixtures. (For MeOH–MeNO$_2$ binary mixtures, the solvolysis rate constants for 1-adamantyl chloride at 80.0 °C are used in the plots.)

between that of an S$_N$1–S$_N$2 (*p*-OCH$_3$) and a carbonyl addition (*p*-Cl) mechanism, with a higher rate than the *p*-CH$_3$ compound. The rates are enhanced by a strong EDS (*p*-OCH$_3$) and by all EWS. The higher rate of the unsubstituted compound as compared with the rate of *p*-CH$_3$ (an EDS for which only the S$_N$1–S$_N$2 process will be favoured)[5] suggests again that the carbonyl addition pathway is concurrent with the S$_N$1–S$_N$2 mechanism. Consequently, the higher reactivity of benzoyl chloride solvolyses in MeNO$_2$ relative to other binary mixtures can be readily explained by the carbonyl addition mechanism concurrent with the S$_N$1–S$_N$2 path. The plot of $\log k_{\text{obs}}$ *versus* $\log(k/k_0)$ ($= Y_{1-\text{AdOTs}}$) for 1-adamantyl toluene-*p*-sulphate solvolysis[17] gave near unit slopes, *i.e. m ca.* 1.0 in the *mY* plot, equation (1), for benzoyl chloride solvolyses in MeOH–MeCN mixtures (S$_N$1–S$_N$2 mechanism with an 'exploded' type TS) but

$$\log(k/k_0) = mY \qquad (1)$$

had a negative *m* value ($m = -0.48$) for the carbonyl addition process of *p*-Cl compounds in MeNO$_2$ binary mixtures, as shown in Figure 4. The change in *m* with change in mechanism is shown clearly for *p*-CH$_3$O and *p*-Cl, but is less clear for the unsubstituted benzoyl chloride in MeOH–MeNO$_2$ mixtures.

In all binary mixtures, the rate was found to increase in the order, *p*-CH$_3$ < *p*-H < *p*-F < *p*-OCH$_3$ < *p*-Cl in the low MeOH composition region (<80%, v/v), indicating that the concurrent carbonyl addition pathway plays an increasingly greater role with a more EWS, while the S$_N$1–S$_N$2 reactivity reaches a peak with a strong EDS, *p*-OCH$_3$, especially in the highly ionizing, MeOH-rich region in all cases.

The Hammett plots were curved concave downward with EDS and EWS forming two separate branches of negative and positive slopes, respectively; this is considered typical of a mechanistic changeover.[18] The use of σ^+ instead of σ did not improve the linearity of the Hammett plots.

Activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, for the solvolyses of benzoyl chlorides in MeOH–MeNO$_2$ binary mixtures are shown in Table 5; it can be seen that both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ decrease gradually as the substituent (Y) is varied from electron-donating (Y = *p*-CH$_3$O) to electron-withdrawing (Y = *p*-Cl). Since in the S$_N$1–S$_N$2 mechanism, a σ bond (C–Cl) is partially broken whereas in the carbonyl addition a weaker π bond of the C=O group is partially broken in the TS, a greater energy barrier (greater $\Delta H^{\ddagger}$) will be involved in the former mechanism, which is favoured by a more EDS, than in the latter, which is favoured by a more EWS.

Calculation of isokinetic temperatures[19] gave values in the range 270–290 K as the substituent was varied from electron donating to electron withdrawing, at the average experimental temperature of *ca.* 273 K. This indicates that for EDS the reaction is entropy-controlled whereas for EWS it becomes enthalpy-controlled.[19] These trends were also maintained for the solvolyses of benzoyl chlorides in EtOH–H$_2$O and EtOH–TFE binary mixtures.[13] It is well known that the S$_N$1–S$_N$2 solvolytic processes involve extensive solvent reorganization in the TS due to strong specific solute–solvent interactions[20] so that the processes are normally entropy-controlled, as we found with EDS.[21] On the other hand, in reactions in which bond formation is more important than bond breaking in the TS, exothermicity (or endothermicity) controls the activation barrier, *i.e.*, the process is thermodynamically controlled.[22]

Thus we can understand why the reaction becomes enthalpy-controlled for EWS for which the carbonyl addition mechanism is dominant.

Experimental

Material.—Solvents, MeOH, MeCN, $PhNO_2$ and $MeNO_2$, and benzoyl chlorides were purified as described previously.[14c] Solvent mixtures were prepared in volume percentages (v/v). Benzoyl chlorides were commercial samples, which were used after purification as described.[13,20]

Kinetic Methods.—The rates were followed conductimetrically[14c] and the k_{obs} values were obtained by the Guggenheim method.[23] The values listed in Tables 2–4 are the averages of several runs with a reproducibility of $> \pm 5\%$ in all cases.

Acknowledgements

We thank the Korea Science and Engineering Foundation for support of this work.

References

1 (*a*) A. Kivinen, in 'The Chemistry of Acyl Halides,' ed. S. Patai, Interscience, New York, 1972, ch. 6; (*b*) R. J. E. Talbot, in 'Comprehensive Chemical Kinetics,' ed. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, vol. 10, p. 226.

2 D. P. N. Satchell and R. S. Satchell, in 'The Chemistry of Acyl Halides,' ed. S. Patai, Interscience, New York, 1972, ch. 4.

3 D. N. Kevill, P. H. Daum, and R. Sapre, *J. Chem. Soc., Perkin Trans. 2*, 1975, 963.

4 (*a*) D. N. Kevill and C.-B. Kim, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1353; (*b*) D. N. Kevill and C.-B. Kim, *Bull. Soc. Chim. France*, 1988, 383; (*c*) H. Neuvonev, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1141.

5 (*a*) T. W. Bentley, G. E. Carter, and H. C. Harris, *J. Chem. Soc., Perkin Trans. 2*, 1985, 983; (*b*) T. W. Bentley and H. C. Harris, *ibid.*, 1986, 619; (*c*) T. W. Bentley and H. C. Harris, *J. Org. Chem.*, 1988, **53**, 724.

6 (*a*) E. Chrystiuk and A. Williams, *J. Am. Chem. Soc.*, 1987, **109**, 3040; (*b*) S. Ba-Saif, A. K. Luthra, and A. Williams, *ibid.*, 1987, **109**, 6362; (*c*) S. Ba-Saif, A. K. Luthra, and A. Williams, *ibid.*, 1989, **111**, 2647.

7 (*a*) H. van der Wel and N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 479, 491; (*b*) H. van der Wel, G. T. J. M. Bruin, S. J. J. van der Linde and N. M. M. Nibbering, *ibid.*, 1988, **107**, 370; (*c*) O. I. Asubiojo and J. I. Brauman, *J. Am. Chem. Soc.*, 1979, **101**, 3715; (*d*) C. L. Johlman and C. L. Wilkins, *ibid.*, 1985, **107**, 327; (*e*) C. H. Depuy, J. J. Grabowski, V. M. Bierbaum, S. Ingemann, and N. M. M. Nibbering, *ibid.*, 1985, **107**, 1093; (*f*) K. Takashima, S. M. Jose, A. T. do Amaral, and J. M. Riveros, *J. Chem. Soc., Chem. Commun.*, 1983, 1255; (*g*) S. Yamabe and T. Minato, *J. Org. Chem.*, 1983, **48**, 2972; (*h*) S. Yamabe, T. Minato, and Y. Kawabata, *Can. J. Chem.*, 1984, **62**, 235; (*i*) F. Blake and W. L. Jorgensen, *J. Am. Chem. Soc.*, 1987, **109**, 3856; (*j*) I. H. Williams, D. Spangler, G. M. Maggiora, and R. L. Schowen, *ibid.*, 1985, **107**, 7717.

8 J. A. Dean, 'Handbook of Organic Chemistry,' McGraw-Hill, New York 1987, Tables 4–10.

9 (*a*) M. J. Kamlet, J.-L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, 1981, **13**, 485; (*b*) M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877; (*c*) M. H. Abraham, R. M. Doherty, M. J. Kamlet, J. M. Harris, and R. W. Taft, *J. Chem. Soc., Perkin Trans. 2*, 1987, 913; (*d*) M. H. Abraham, P. L. Grelliers, A. Nasehzadeh, and R. A. C. Walker, *ibid.*, 1988, 1717.

10 L. M. Mukherjee and E. Grunwald, *J. Phys. Chem.*, 1958, **62**, 1311.

11 T. M. Krygowski, C. Reichardt, P. Wrona, C. Wyszomirska, and U. Zeilkowska, *J. Chem. Res. (S)*, 1983, 116.

12 (*a*) M. C. R. Symons, *Acc. Chem. Res.*, 1981, **14**, 179; (*b*) M. C. R. Symons and V. K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1883, 1891; (*c*) M. C. R. Symons, V. K. Thomas, N. J. Fletcher, and N. G. Pay, *ibid.*, 1981, **77**, 1899; (*d*) H. L. Robinson and M. C. R. Symons, *ibid.*, 1985, **81**, 2131.

13 I. Lee, I. S. Koo, C. S. Sohn, and H. H. Lee, *Bull. Korean Chem. Soc.*, 1982, **3**, 92.

14 (*a*) I. Lee, S.-M. La, B.-S. Lee, and S. C. Sohn, *J. Korean Chem. Soc.*, 1984, **28**, 210; (*b*) I. Lee, B.-S. Lee, I. S. Koo, and S. C. Sohn, *Bull. Korean Chem. Soc.*, 1983, **4**, 189; (*c*) I. Lee, H. W. Lee, T. S. Uhm, D. D. Sung, and Z. H. Ryu, *J. Korean Chem. Soc.*, 1988, **32**, 85.

15 (*a*) T. W. Bentley, C. T. Bowen, D. H. Morton, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 5466; (*b*) T. W. Bentley and G. E. Carter, *ibid.*, 1982, **104**, 5741; (*c*) T. W. Bentley and G. E. Carter, *J. Org. Chem.*, 1983, **48**, 579; (*d*) D. N. Kevill, W. A. Kamil, and S. W. Anderson, *Tetrahedron Lett.*, 1982, **23**, 4635.

16 Y. Kondo, K. Yuki, T. Yashika, and N. Tokura, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 812.

17 I. Lee, B.-S. Lee, S. C. Sohn, and B. C. Lee *Bull. Korean Chem. Soc.*, 1985, **6**, 19.

18 N. S. Isaas, 'Physical Organic Chemistry,' Longman, Harlow, 1987, p. 146.

19 R. D. Gilliom, 'Introduction to Physical Organic Chemistry,' Addison–Wesley, New York, 1969, ch. 9.

20 H. W. Lee, S.-M. La, and I. Lee, *J. Korean Chem. Soc.*, 1980, **24**, 115.

21 (*a*) J. H. Kim, I. Lee, S. C. Sohn, and T. S. Uhm, *J. Korean Chem. Soc.*, 1983, **27**, 95; (*b*) H. T. Kim, S. D. Yoh, and I. Lee, *ibid.*, 1983, **27**, 167; (*c*) J. P. Lee, D. D. Sung, T. S. Uhm, I. Lee, and S. C. Sohn, *ibid.*, 1985, **29**, 465.

22 (*a*) I. Lee, *J. Chem. Soc., Perkin Trans. 2*, in the press; (*b*) I. Lee, C. S. Shim, S. Y. Chung, and H. W. Lee, *ibid.*, 1988, 975; (*c*) I. Lee, Y. H. Choi, H. W. Lee, and B. C. Lee, *ibid.*, 1988, 1537; (*d*) I. Lee, Y. H. Choi, K. W. Ryu, and C. S. Shim, *ibid.*, in press; (*e*) I. Lee, C. S. Shim, S. Y. Chung, H. Y. Kim, and H. W. Lee, *ibid.*, 1988, 1919.

23 E. A. Guggenheim, *Philos. Mag.*, 1928, **2**, 538.

Received 6*th February* 1989; *Paper* 9/00554D