The Menschutkin reaction of benzyl *p*-toluenesulfonates with *N,N*-dimethylanilines. Evidence for the duality of S_N1 and S_N2 mechanisms

Sung Hong Kim,[1] Soo-Dong Yoh,[2] Chultack Lim,[1] Masaaki Mishima,[1] Mizue Fujio[1]* and Yuho Tsuno[1]

[1]Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812, Japan
[2]Department of Chemistry, Teachers College, Kyungpook National University, Taegu 702-701, Korea

ABSTRACT: The rate data for the Menschutkin reaction between strongly activated Z-substituted benzyl *p*-toluenesulfonates and Y-substituted *N,N*-dimethylanilines in acetonitrile at 35 °C fit the equation, $k_{obs} = k_1 + k_2$ [DMA], which is consistent with concurrent first- and second-order processes. The k_1 and k_2 values for each substrate were separated based on the above equation. The S_N1 rate constant, k_1, is unaffected by the nature of the nucleophile, whereas the S_N2 rate constant, k_2, increased with the electron-donating substituent of the *N,N*-dimethylaniline. The substituent effect on the k_1 values is linearly correlated by the Yukawa–Tsuno equation with $\rho = -5.2$ and $r = 1.3$. The unimolecular reaction can be regarded as a classical S_N1 mechanism. In contrast, that on the k_2 values shows an upward curvature when analyzed by the Brown σ^+ treatment. These results are ascribed to the simultaneous and independent occurrence of S_N1 and S_N2 mechanisms in the present Menschutkin reaction. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: Menschutkin reaction; duality of S_N1, S_N2 mechanisms; benzyl tosylates; Yukawa–Tsuno equation

INTRODUCTION

Ever since the designation of S_N1 and S_N2 mechanisms by Ingold and Rothstein[1] in nucleophilic displacement at saturated carbon attached to an aromatic ring, a vast number of studies have been carried out in this area. The mechanism of borderline reactions was controversial for a long time, especially concerning the question whether they proceed by a dual process of independent S_N1 and S_N2 mechanisms or by a merged S_N1/S_N2 mechanism, which means that there is no sharp line of demarcation between them.[2–5]

Mechanistic studies on the Menschutkin reaction of benzylic systems mostly led to the conclusion that the reaction proceeds by a typical S_N2 mechanism with a concerted displacement transition state.[6–9] In previous papers,[10,11] we discussed the mechanism of the Menschutkin reaction of Z-substituted benzyl tosylates with Y-substituted *N,N*-dimethylanilines in acetone or acetonitrile based on the substituent effect analysis. Electron-donating Z-substituents enhance the reaction, indicating an appreciable development of positive charge at the benzylic reaction center in the transition state. The

negative ρ_Z value for the whole range of substituents indicates the dominance of bond fission in the transition state. The curved Hammett plot indicates the change in the cationic transition state, which becomes looser (or tighter) as the substituent Z becomes more electron donating (or withdrawing). This substituent effect in the Menschutkin reaction resembles the behavior in the solvolysis of the corresponding benzyl tosylates.[12] There is general agreement that the solvolysis of benzyl tosylates covers a mechanistic spectrum ranging from the classical unimolecular S_N1 mechanism for electron-donating substituents to typical S_N2 mechanism for electron-withdrawing substituents. It is difficult to elucidate the way of the mechanistic transition using the solvolysis system owing to ambiguity of molecularity.

The Menschutkin reaction should occur in a non-solvolyzing solvent by a bimolecular mechanism with nucleophiles and the concerted S_N2 displacement transition state can be discussed in terms of the varying contributions of bond formation and bond fission from the dependence on the electronic effect of the substituent Z. Our interest is how S_N1-like the behavior of benzyl derivatives carrying a strong electron-donating Z is. We report here the precise kinetic form of the Menschutkin reaction between strongly activated benzyl tosylates and substituted *N,N*-dimethylanilines in acetonitrile based on

*Correspondence to: M. Fujio, Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812, Japan Email: fujio@ms.ifoc.kyushu-u.ac.jp
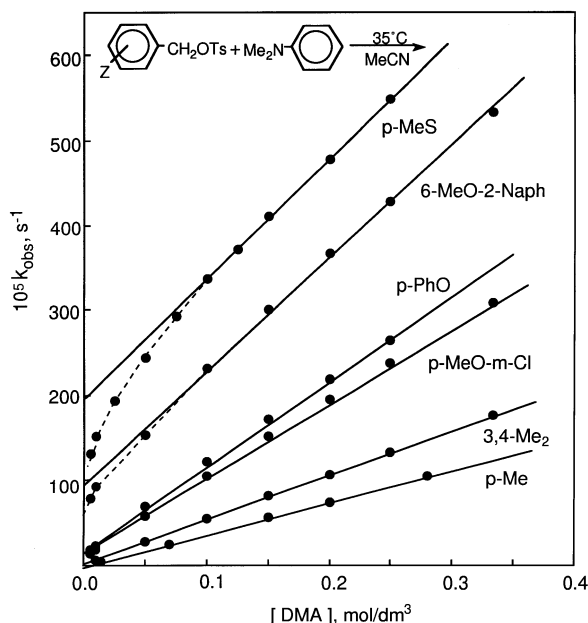
Figure 1. Plot of k_{obs} vs nucleophile concentration for the reactions of Z-substituted benzyl tosylates with unsubstituted N,N-dimethylaniline in acetonitrile at 35 °C

a detailed examination of the dependence of the rate on the concentration of the nucleophile to clarify the behavior of mechanistic borderline reaction in benzyl system.

RESULTS AND DISCUSSION

The reaction rates of 0.0005 M Z-substituted benzyl tosylates with 0.01 to 0.3 M Y-substituted N,N-dimethylanilines were measured in acetonitrile at 35 °C by following the increase in conductance of the quaternary anilinium salts produced.[10,11] The precision of the fit to pseudo-first-order kinetics was generally satisfactory, with correlation coefficients > 0.99995 over 2.5 half-lives of the reaction.

The pseudo-first-order rate constants, k_{obs}, were in direct proportion to the concentrations of the N,N-dimethylaniline for the benzyl tosylates less activated than the p-methylbenzyl derivative (Fig. 1); the correlation line passes through the origin within the experimental uncertainty. Consequently, the reactions are exactly first order in N,N-dimethylaniline concentration, [DMA]:

$$k_{obs} = k_2 \text{ [DMA]} \tag{1}$$

In contrast, for benzyl tosylates substituted by typical electron-donating groups, significant positive intercepts were observed in the plots of k_{obs} vs [DMA], as shown in Fig. 1. The reaction was carried out in the non-solvolyzing solvent acetonitrile, and no product indicat-

ing the operation of the solvent as a nucleophile was observed. Consequently, the positive intercept which is independent of nucleophile concentration corresponds to an S_N1 rate constant, k_1, via the rate-determining unimolecular ionization. These results can be fitted to a kinetic equation as the sum of zero and first-order terms in N,N-dimethylaniline concentration:

$$k_{obs} = k_1 + k_2 \text{ [DMA]} \tag{2}$$

The kinetic dependence of Eqn (2) implies the simultaneous and competitive operation of independent S_N1 and S_N2 processes in the reaction of benzyl tosylates carrying strongly electron-donating substituents with N,N-dimethylaniline in acetonitrile.

The plots of k_{obs} vs nucleophile concentrations for the reaction of p-methylthiobenzyl tosylate with Y-substituted N,N-dimethylanilines in acetonitrile at 35 °C are illustrated in Fig. 2. The second-order rate constant, k_2, obtained from the slope of the linear parts of plots, decreases with decreasing nucleophilicity of N,N-dimethylanilines (Y: p-MeO > H > m-Cl > m-NO$_2$), whereas the first-order rate constant, k_1, remains constant and invariant with the nature of nucleophile, as demonstrated by the convergence at the same intercept in the k_{obs} vs [DMA] plots for the various Y-substituents. For the reactions of 6-methoxy-2-naphthylmethyl, 3-chloro-4-methoxybenzyl, 4-phenoxybenzyl, 2-fluorenylmethyl, 3,4,5-trimethylbenzyl and 3,4-dimethylbenzyl tosylates, the plots were similar to that for Z = p-MeS in Fig. 2. It is therefore seen that the bimolecular substitution reaction of strongly activated benzyl tosylates with N,N-dimethylanilines is accompanied by a competitive unimolecular substitution reaction, which is first-order in the substrate but independent of the nature and concentration of the
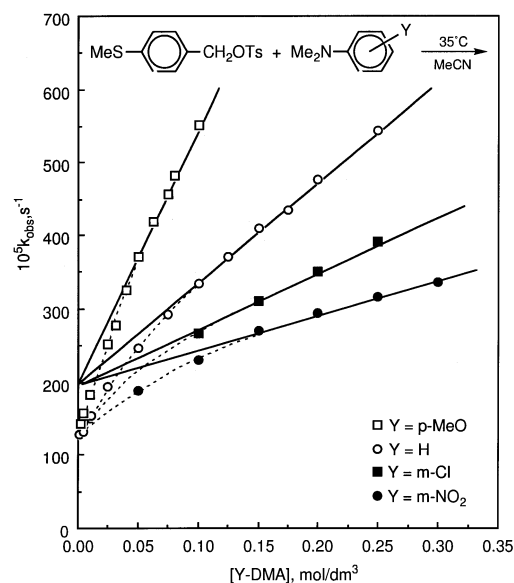

Figure 2. Plot of k_{obs} vs nucleophile concentration for the reactions of p-methylthiobenzyl tosylate with Y-substituted N,N-dimethylanilines in acetonitrile at 35 °C

Table 1. First- and second-order rate constants for the reaction of Z-substituted benzyl tosylates with Y-substituted *N, N*-dimethylanilines in acetonitrile at 35 °C

Substituent Z	Y	$10^4 k_2 (s^{-1} lmol^{-1})$	$10^5 k_1 (s^{-1})$	$100 k_1/(0.1 k_2 + k_1)$[a]
p-MeS	*p*-MeO	350.6 ± 9.4	191.1 ± 1.4	35
	H	137.0 ± 3.8	202.5 ± 7.8	60
	m-Cl	79.80 ± 0.69	191.5 ± 1.4	69
	m-NO$_2$	48.30 ± 1.56	198.6 ± 3.2	80
	p-CHO	48.56 ± 2.44	206.5 ± 5.8	81
6-MeO-2-Naph	*p*-MeO	499.5 ± 8.1	89.08 ± 7.73	15
	H	131.0 ± 3.5	97.85 ± 7.1	43
	m-NO$_2$	35.62 ± 1.42	97.47 ± 3.67	73
p-PhO	*p*-MeO	336.8 ± 4.7	22.41 ± 3.95	6
	H	98.06 ± 2.11	22.53 ± 3.51	19
	m-NO$_2$	14.05 ± 0.56	20.18 ± 1.51	58
	p-CHO	12.09 ± 0.51	19.83 ± 1.08	62
p-MeO-*m*-Cl	*p*-MeO	336.5 ± 2.0	22.87 ± 1.80	6
	H	86.84 ± 0.89	20.53 ± 1.97	19
	m-NO$_2$	10.44 ± 0.62	17.59 ± 1.74	63
2-Fl	*p*-MeO	431.1 ± 4.9	11.65 ± 3.38	3
	H	106.9 ± 0.6	11.13 ± 1.26	9
	m-NO$_2$	11.57 ± 0.46	9.722 ± 1.104	46
3,4,5-Me$_3$	*p*-MeO	374.8 ± 2.9	3.479 ± 1.609	0.9
	H	90.66 ± 0.94	3.762 ± 1.210	4
	m-NO$_2$	11.83 ± 0.32	3.016 ± 0.626	15
3,4-Me$_2$	*p*-MeO	228.0 ± 0.9	1.175 ± 0.622	0.5
	H	52.87 ± 0.34	1.546 ± 0.510	3
	m-NO$_2$	5.047 ± 0.940	1.595 ± 0.244	24
p-Me	H	37.60 ± 0.46	0	0

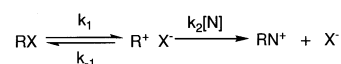[a] Percent reaction by S_N1 route at [nucleophile] = 0.1 M.

nucleophile. The k_1 and k_2 values for the reactions of the activated benzyl tosylates with *N,N*-dimethylanilines were calculated by means of Eqn (2) from the best linear parts of k_{obs} vs at least four concentrations of *N,N*-dimethylanilines with correlation coefficients > 0.999, and the rate data are summarized in Table 1. The

Figure 3. Plot of k (= k_{obs} - k_2 [DMA]) vs nucleophile concentration for the reactions of *p*-methylthiobenzyl and 6-methoxy-2-naphthylmethyl tosylates with *N,N*-dimethylanilines in acetonitrile at 35 °C

percentage of S_N1 in the overall reaction at [DMA] = 0.1 M (>100 molar equivalents of [ArCH$_2$-OTs]) are listed in the last column of Table 1. The S_N1 contribution increases with the weaker nucleophiles and the more electron-donating substituent Z.

In Figs 1 and 2 we can observe a steep drop of the k_{obs} vs [DMA] curves in the region of low concentrations of *N,N*-dimethylanilines. This may be rationalized in terms of the return from the intermediate(s) and its capture by the *N,N*-dimethylanilines. The k_1 values involved in k_{obs} can be estimated by subtraction of k_2 [DMA] from k_{obs}:

$$k = k_{obs} - k_2 \text{ [DMA]} \tag{2'}$$

The k values calculated for the *p*-MeS-benzyl and 6-MeO-2-naphthyl substrates are plotted against nucleophile concentrations in Fig. 3 and their decrease at low nucleophile concentrations indicates a characteristic behavior of an ion-pair mechanism (Scheme 1).
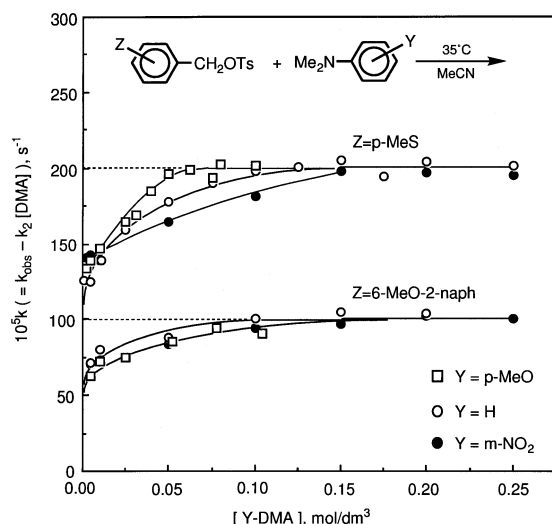
$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} R^+ X^- \overset{k_2[N]}{\longrightarrow} RN^+ + X^-$$

Scheme 1

Under a steady-state approximation, this mechanism would lead to the following kinetic dependence:

$$k = k_1 k_2 \text{ [N]}/(k_{-1} + k_2[N]) \tag{3}$$

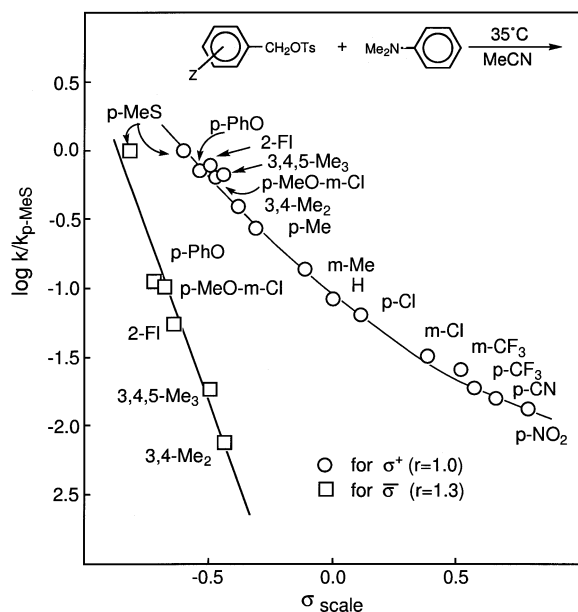In the unimolecular process given in Scheme 1, the

Figure 4. Plot of $\log k/k_{p\text{-MeS}}$ vs $\bar{\sigma}$ in the reaction of Z-substituted benzyl tosylates with *N,N*-dimethylaniline in acetonitrile at 35 °C: open squares for k_1 against $\bar{\sigma}$ ($r = 1.3$) and open circles for k_2 against σ^+

intermediate formed can undergo return to the starting substrate before reacting with the *N,N*-dimethylaniline, whereas at high concentrations of the nucleophile (k_2 [N] $\gg k_{-1}$) the intermediate can be captured by the nucleophile in its immediate vicinity before returning to the starting substrate, shown by the plateau region in Fig. 3; $k = k_1$. If the availability of the *N,N*-dimethylaniline around the intermediate is insufficient, the return process, k_{-1}, may compete with the nucleophilic capture by *N,N*-dimethylaniline leading to a lower S_N1 rate, $k < k_1$, shown by the initial steep increase in Fig. 3.

The data in Table 1 show that the k_1 value is markedly enhanced by electron-donating Z-substituents in the benzyl tosylates compared with the k_2 values. The substituent effect on k_1 can be described in terms of the Yukawa–Tsuno equation:
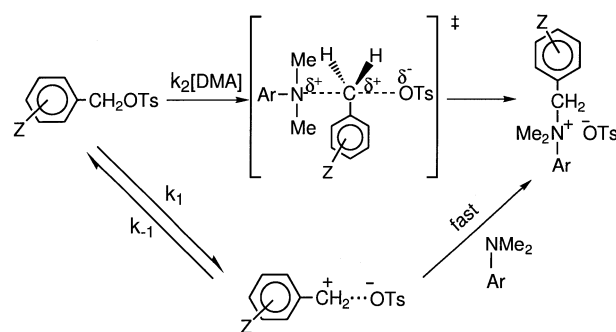
$$\log (k/k_0) = \rho \left(\sigma^0 + r \Delta \bar{\sigma}_R^+ \right) \qquad (4)$$

where the r value is a parameter measuring resonance demand, i.e. the degree of resonance interaction between the aryl group and the carbocationic reaction site in the rate-determining transition state. We have reported that the S_N1 solvolysis of substituted benzyl tosylates can well be approximated by means of Eqn (4) with $r = 1.3$.[12] Although the k_1 values in Table 1 were obtained for only a limited range of electron-donating substituents, application of Eqn (4) to $\log k_1$ values shows a linear correlation with $\rho_Z = -5.2$ with $r = 1.3$ ($R = 0.976$), as shown in the squares in Fig. 4. The substituent effect for k_1 is comparable to or even identical with those of the

solvolyses of benzyl tosylates; $\rho = -5.23$ and $r = 1.29$ for the hydrolysis in 80% aqueous acetone and $\rho = -5.39$ and $r = 1.29$ for the acetolysis at 25 °C.[12] In fact, there is an interrelation ($R = 0.981$) between the k_1 values in the present Menschutkin reaction and the k_t values for the hydrolysis of benzyl tosylates in 80% aqueous acetone with a slope of 0.97.

On the other hand, a plot of $\log k_2$ vs σ^+ gives a smooth curved correlation as demonstrated by the circles in Fig. 4. The curved Hammett plot is ascribed to a continuous change in the accumulated positive charge of the central carbon in the pentacoordinate S_N2 transition state caused by the contribution of decreased bond formation to the nucleophile and/or increased bond fission. However, the slope of the k_2 curve, i.e. the ρ value, for a bimolecular process at the activated end is still smaller than that of the k_1 correlation line, as shown in Fig. 4 and the carbocationic character of the k_2 process at the most activated end is still far from that of the S_N1 transition state.[10,11] Nevertheless, it should be noted that the r value for the bimolecular process is still close to that for the unimolecular process, which should be characteristic of the intermediate carbocation. The mechanism of the bimolecular Menschutkin reaction will be discussed in more detail in a forthcoming paper.

The detailed mechanism of nucleophilic substitution, especially the mechanistic transition from S_N2 to S_N1, has been the subject of considerable controversy. Sneen[4] had proposed a unification of the S_N1 and S_N2 mechanisms in which all nucleophilic substitutions involve the formation of ion pairs. This merged mechanism is given by Scheme 1 and Eqn (3), and corresponds to that of the S_N2 reaction when $k_{-1} \gg k_2$ [N] and to the S_N1 reaction when $k_{-1} \ll k_2$ [N]. We have taken the present results in Table 1 and Fig. 1, Fig. 2 and Fig. 3 as convincing evidence for the occurrence of simultaneous S_N1 and S_N2 mechanisms in the reaction between the activated benzyl tosylates and amines (Scheme 2) rather than a single process involving a common intermediate.[4,13]

Scheme 2

The present results do not support the Sneen unified ion-pair merged mechanism of nucleophilic substitution. We believe that our results provide evidence for a duality of mechanisms for highly activated benzyl tosylates in

the presence of nucleophiles in acetonitrile. Sneen's two-step mechanism may be valid for an ion-pair mechanism within the S_N1 process of the present reaction in Scheme 2, and the whole relationship should be described by the equation

$$k = k_1 k_2' \, [\text{DMA}]/(k_{-1} + k_2' \, [\text{DMA}]) + k_2 \, [\text{DMA}] \quad (3)$$

Schleyer and co-workers[13] proposed the concept of a continuous spectrum of S_N1–S_N2 mechanisms, involving a continuity of solvolytic mechanisms from S_N1, via S_N2 (intermediate), to the conventional S_N2 mechanism. This approach, which argues against the duality of mechanisms, seems not to apply to our system, based on the present experimental evidence. Whereas we see a continuous spectrum of S_N2 mechanisms of varying tightness for the bimolecular process of changing the Z-substituents, this process is completely discrete from the unimolecular process. Its loosest end is still a bimolecular S_N2C^+ mechanism,[14] even though it closely resembles in structure the transition state of S_N1 mechanism.

The simultaneous operation of independent S_N1 and S_N2 mechanisms is believed to be fairly general and not specific to the present system. Concurrent S_N1 and S_N2 mechanisms in borderline nucleophilic displacement reactions have been published. Katritzky and co-workers[2,15] studied extensively the substitution of *N*-benzylpyridinium salts with a neutral piperidine nucleophile in non-polar solvents. In plots of the rate constant vs the nucleophile concentration, they found that the *p*-methoxybenzyl derivative showed a positive intercept which was invariant with the nature of the nucleophile, while benzyl derivatives which carry less electron-donating substituents than *p*-methyl did not give such significant intercepts. Katritzky and co-workers amine exchange of benzylammonium ion is virtually an identity reaction, which is conceivably an ideal system to be described by a continuous spectrum of S_N2 mechanisms of varying tightness. The reaction of *p*-methoxybenzyl bromide with pyridine or thiourea in aqueous acetone also proceeds by simultaneous independent S_N1 and S_N2 mechanisms.[16] The duality of the S_N1–S_N2 mechanism has been preferentially observed for secondary benzylic systems for a wide range of substituents. In the Menschutkin reaction of 1-phenylethyl bromide with pyridines and *N,N*-dimethylanilines in acetonitrile, the same behavior as that in Fig. 4 was observed for a range of substituents from *p*-MeO to H.[17] The isotopic exchange between substituted benzhydryl thiocyanates and labeled ionic thiocyanate was measured in acetonitrile by Ceccon *et al.*,[18] indicating that the substituent effect on k_1 values were correlated by the Brown σ^+ value with $\rho^+ = -4.5$, in contrast to the shallow U-shaped Hammett plot of k_2 for the electron-attracting substituent range. In the isotopic exchange reaction of benzylic chlorides with radioactive lithium chloride in dimethyl-formamide, no detectable first-order contribution to the exchange was found with benzyl chloride whereas with

diphenylmethyl chloride the first- and second-order processes were found to contribute equally to the overall exchange at a concentration of ca. 0.1 M lithium chloride.[19] Further, the ratio of first-order rate constant increases with increase in the dielectric constant of the solvent. These observations parallel our observations on the present reaction of benzyl tosylates.

Detection of the return process from the ionic intermediate(s) to the reactant can be direct evidence of the S_N1 ionization process.[5,20–24] Recently we have detected ^{18}O scrambling of the alkoxy oxygen within doubly labeled $[^{13}C]$ benzyl $[S^{18}O_2]$ tosylates in the reaction with or without *N, N*-dimethylanilines in acetonitrile by means of ^{13}C-NMR spectroscopy.[25] These findings provide further strong support for the k_1 ionization pathway in the present reaction and the S_N1 and S_N2 mechanisms remain distinct without merging at the mechanistic borderline.

EXPERIMENTAL

Materials

Acetonitrile was refluxed over P_2O_5 for 1 day and fractionated. After three repetitions with fresh P_2O_5, it was dried over anhydrous sodium carbonate and fractionated, b.p. 82 °C.

N, N-Dimethylaniline dried over NaOH pellets was distilled under a nitrogen atmosphere immediately before use, b.p. 116–116.5 °C/128 mmHg. The *m*-NO_2 and *p*-CHO derivatives were purified by recrystallization before use. *N, N*-Dimethyl-*p*-methoxyaniline, m.p. 45.2–45.9 °C (lit.[26,27] m.p. 47 °C, 48–49 °C)[28] was synthesized[29] by $LiAlH_4$ reduction of *N, N, N*-trimethyl(*p*-methoxyphenyl)ammonium iodide, which was prepared from *p*-anisidine and methyl iodide.[27,30] Similarly, *N, N*-dimethyl-*m*-chloroaniline, b.p. 80.5 °C/2.5 mmHg (lit.[26] 90 °C/2 mmHg) was prepared from *m*-chloroaniline.

Benzyl tosylates were prepared by the Schotten–Bauman method according to the procedure described in earlier papers.[12] To a solution of benzyl alcohol (13.0 mmol) and *p*-methylbenzenesulfonyl chloride (13.0 mmol) in 15 ml of dioxane in an ice-bath under stirring, 33% aqueous NaOH (4 equiv.) was added dropwise. After stirring for 2 h in an ice-bath, the mixture was poured into ice–water and the solid product was filtered. The crude benzyl tosylates were purified by recrystallization from diethyl ether–hexane. The analytical data were in good agreement with the established values.[12]

N, N-Dimethylaniline (3 g, 0.02 mol) and *p*-methylbenzyl tosylate (1.5 g, 0.0054 mol) in acetonitrile (50 ml) were refluxed for 1 day. The solvent was evaporated and the *N*-(*p*-methylbenzyl)-*N, N*-dimethylanilinium tosylate obtained was washed with dry diethyl ether and recrystallized from propan-2-ol; m.p. 161–162 °C. Ana-

lysis: calculated for $C_{23}H_{27}NO_3S$, C 69.49, H 6.85, N 3.52; found, C 69.28, H 6.87, N 3.58%.

Kinetic measurements

The reaction rates of substituted benzyl tosylates with *N, N*-dimethylanilines in acetonitrile at 35 °C were measured by a conductimetric method. Conductance measurements were made in a cell with bright platinum electrodes and conductivity readings were carried out by using a conductivity meter (CM-60S, equipped with interval time unit and printer; Toa Electric).

The typical procedure for kinetic measurements is as follows. A 50 ml volume of a stock solution of *N, N*-dimethylaniline (0.12 M) in acetonitrile, which was prepared at 35 °C, was equilibrated in the reaction cell at 35 ± 0.01 °C in a thermostated bath for 30 min and then 10 ml of benzyl ester solution (0.003 M) were added. The resulting solution of 0.0005 M ester and 0.1 M amine in the cell was shaken thoroughly. The reactions were generally followed by taking at least 100 points at appropriate time intervals for 2.5 half-lives and the infinity reading was taken after 10 half-lives. All kinetic runs were carried out under pseudo-first-order conditions with 0.01–0.30 M concentrations of amine, which are 20–600 times larger than that of the substrate (0.0005 M). The pseudo-first-order rate constants were calculated by a least-squares computer program. At an ester concentration of 0.0005 M, the precision of the fit to first-order kinetics was generally satisfactory over 2.5 half-lives with a correlation coefficient > 0.99995 by the direct employment of the apparent conductivity of the ammonium salt produced. Duplicate kinetic runs showed that the rate constant was reproducible to within ± 1.5%.

In previous studies,[10,31] we found that the rate plot of $\log(S_\infty - S_t)$ vs time *t* did not give a good straight line when the concentration of benzyl ester was 0.015–0.0025 M. At such high ester concentrations, the conductances were not linearly related to the salt concentration owing to ionic aggregation. Therefore, conductance readings were converted into concentrations of quaternary ammonium salt with the aid of a conductance–concentration relationship and this calibration gave good linear first-order rate plots with correlation coefficients > 0.99993.[31] The rate constants with or without calibration at the low ester concentration of 0.0005 M agreed well with each other, to within 1.5%, and also agreed with those at high concentrations of 0.015–0.0025 M after the calibration.

For all the substituted benzyl tosylates more deactivating than *p*-Me, the plot of pseudo-first-order rate constants k_{obs} vs [DMA] passed through the origin within experimental uncertainty. Second-order rate constants, k_2, were obtained by dividing the pseudo-first-order rate constants by the initial DMA concentration. For substrates more reactive than 3,4-dimethylbenzyl tosylate, second- and first-order rate constants were determined

from the slope and the intercept of the linear part of the plot of pseudo-first-order rate constants vs [DMA] with Eqn (2), with correlation coefficients ≥ 0.999.

REFERENCES

1. C. K. Ingold and E. Rothstein. *J. Chem. Soc.* 1217 (1928).
2. A. R. Katritzky and B. E. Brycki. *Chem. Soc. Rev.* **19,** 83 (1990).
3. D. J. McLennan. *Acc. Chem. Res.* **9,** 281 (1976).
4. R. A. Sneen. *Acc. Chem. Res.* **6,** 46 (1973).
5. J. M. Harris. *Prog. Phys. Org. Chem.* **11,** 89 (1974).
6. J. W. Baker and W. W. Nathan. *J. Chem. Soc.* 236 (1936).
7. C. G. Swain and W. P. Langsdorf. *J. Am. Chem. Soc.* **73,** 2813 (1951).
8. F. P. Ballistreri, E. Maccarone and A. Mamo. *J. Org. Chem.* **41,** 3364 (1976).
9. T. Ando, H. Tanabe and H. Yamataka. *J. Am. Chem. Soc.* **106,** 2084 (1984).
10. S.-D. Yoh, Y. Tsuno, M. Fujio, M. Sawada and Y. Yukawa. *J. Chem. Soc., Perkin Trans.* 27 (1989); S.-D. Yoh, PhD Thesis, Osaka University (1973).
11. S. H. Kim. PhD Thesis, Kyungpook National University Taegu Korea (1992); D.-Y. Cheong, S. H. Kim, M.-H. Lee, S.-D. Yoh, M. Fujio and Y. Tsuno. *J. Korean Chem. Soc.* **39,** 643 (1995); S. H. Kim, S.-D. Yoh, M. Fujio, H. Imahori, M. Mishima and Y. Tsuno. *Bull. Korean Chem. Soc.* **16,** 760 (1995).
12. M. Fujio, M. Goto, T. Susuki, I. Akasaka, M. Mishima and Y. Tsuno. *Bull. Chem. Soc. Jpn.* **63,** 1146 (1990); M. Fujio, M. Goto, T. Susuki, M. Mishima and Y. Tsuno. *J. Phys. Org. Chem.* **3,** 449 (1990); M. Fujio, I. Akasaka, S. H. Kim, M. Mishima, Y. Tsuji and Y. Tsuno. *Mem. Fac. Sci. Kyushu Univ., Ser. C* **18** 131 (1991).
13. F. L. Schadt, T. W. Bentley and P. v. R. Schleyer. *J. Am. Chem. Soc.* **98,** 7667 (1976); T. W. Bentley, C. T. Bowen, D. H. Morten and P. v. R. Schleyer. *J. Am. Chem. Soc.* **103,** 5466 (1981).
14. E. Gelles, E. D. Hughes and C. K. Ingold. *J. Chem. Soc.* 2918 (1954).
15. A. R. Katritzky, G. Musumarra, K. Sakizadeh, S. M. M. El-Shafie and B. Jovanovic. *Tetrahedron Lett.* **21,** 2697 (1980); A. R. Katritzky, A. M. El-Mowafy, G. Musumarra, K. Sakizadeh, C. Sana-Ullah, S. M. M. El-Shafie and S. S. Thind. *J. Org. Chem.* **46,** 3823 (1981); A. R. Katritzky, G. Musumarra and K. Sakizadeh. *J. Org. Chem.* **46,** 3831 (1981); A. R. Katritzky and G. Musumarra. *Chem. Soc. Rev.* **13,** 47 (1984).
16. A. Queen. *Can. J. Chem.* **57,** 2646 (1979).
17. C. Lim, S. H. Kim, S.-D. Yoh, M. Fujio and Y. Tsuno. *Tetrahedron Lett.* **38,** 3243 (1997).
18. A. Ceccon, I. Papa and A. Fava. *J. Am. Chem. Soc.* **88,** 4643 (1966).
19. P. Casapieri and E. R. Swart. *J. Chem. Soc.* 4342 (1961); 1254 (1963).
20. C. J. Lancelot, D. J. Cram and P. v. R. Schleyer. *in Carbonium Ions,* edited by G. A. Olah and P. v. R. Schleyer, Vol. 3, Chapt. 27, pp. 1347–1483. Wiley, New York (1972).
21. D. J. Raber, J. M. Harris and P. v. R. Schleyer. *in Ions and Ion Pairs in Organic Reactions,* edited by M. Szwarc, Vol. 2, Chapt. 3, pp. 247–374. Wiley, New York (1974).
22. C. Paradisi and J. F. Bunnett. *J. Am. Chem. Soc.* **103,** 946 (1981); **107,** 8223 (1985).
23. H. J. Koh, H. W. Lee and I. Lee. *J. Chem. Soc., Perkin Trans.* 2 125 (1994).
24. M. Fujio, F. Sanematsu, Y. Tsuno, M. Sawada and Y. Takai. *Tetrahedron Lett.* **29** 93 (1988); Y. Tsuji, K. Yatsugi, M. Fujio and Y. Tsuno. *Tetrahedron Lett.* **36,** 1461 (1995); Y. Tsuji, S. H. Kim,

Y. Saeki, K. Yatsugi, M. Fujio and Y. Tsuno. *Tetrahedron Lett.* **36,** 1465 (1995); A. D. Allen, M. Fujio, O. S. Tee, T. T. Tidwell, Y. Tsuji, Y. Tsuno and K. Yatsugi. *J. Am. Chem. Soc.* **117,** 8974 (1995).

25. Y. Tsuji, Y. Saeki, K. Yatsugi, S.-G. Kim, M. Fujio and Y. Tsuno. *Mem. Fac. Sci. Kyushu Univ., Ser. C* **19,** 47 (1993); Y. Tsuji, S.-G Kim, M. Fujio and Y. Tsuno. to be published

26. H. P. Crocker and B. Jones. *J. Chem. Soc.* 1808 (1959).

27. B. B. P. Tice, I. Lee and F. H. Kendall. *J. Am. Chem. Soc.* **85,** 329 (1963).

28. F. G. Bordwell and P. J. Boutan. *J. Am. Chem. Soc.* **78** 87 (1956).

29. A. C. Cope, E. Ciganek, L. J. Fleckenstein and M. A. P. Meisinger. *J. Am. Chem. Soc.* **82,** 4651 (1960).

30. S. R. Sandler and W. Karo. *Organic Functional Group Preparations,* pp. 325–327. Academic Press, New York (1968).

31. M. Fujio, K. Ikeda and Y. Tsuno. *Mem. Fac. Sci. Kyushu Univ., Ser. C* **11,** 75 (1978).