(14) F. Kern and W. D. Walters, *Proc. Natl. Acad. Sci. U. S. A.*, **38**, 937 (1952).

(15) T. Fujimoto, F. M. Wang and B. S. Rabinovitch, *Canad. J. Chem.*, **50**, 3251 (1972).

(16) K. A. Holbrook and R. A. Scott, *J. Chem. Soc. Faraday Trans.*, **71**, 1849 (1975).

(17) D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.*, **77**, 1849 (1977).

(18) M. Szwarc, *J. Chem. Phys.*, **17**, 284 (1949).

(19) D. M. Golden, C. N. Spokes and S. W. Benson, *Angew. Chem. Intl. Edit.*, **12**, 434 (1973).

(20) K. Y. Choo, D. M. Golden and S. W. Benson, *Intl. J. Chem. Kinet.*, **7**, 713 (1975).

(21) G. Allen and H. J. Bernstein, *Canad. J. Chem.*, **32**, 1044 (1954).

(22) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **71**, 2903 (1967).

(23) P. Cadman and W. J. Engelbrecht, *Chem. Comm.*, 453 (1970).

(24) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1967).

(25) S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, **87**, 4036 (1965).

(26) S. W. Benson and G. R. Haugen, *J. Phys. Chem.*, **70**, 3336 (1966).

(27) J. D. Cox and G. Pilcher, "Thermochemistry of organic and organometallic compounds," Academic Press, London, 1970.

(28) J. M. Simmie and W. J. Quiring and E. Tschukow-Roux, *J. Phys. Chem.*, **74**, 992 (1970).

(29) M. Kh. Karapet'yants and M. L. Karapet'yants, "Thermodynamic constants of inorganic and organic compounds," Ann Arbor-Humphrey Science Publisher, Ann Arbor, 1970.

Kinetics of Reactions Between Substituted Benzyl Chlorides and Anilines in MeOH-MeCN Mixtures

Ikchoon Lee and Se Chul Sohn†

Department of Chemistry, Inha University, Inchon 160, Korea

Byung Choon Lee

Department of Chemical Education, Choongbuk National University, Cheung Joo 310, Korea

Ho Bong Song

Department of Chemistry, Kyunggi University, Suwon 170, Korea (*Received June 10, 1983*)

Kinetic studies of nucleophilic substitution reactions of *para*-substituted benzylchlorides with anilines were conducted in a range of MeOH–MeCN mixtures at 55.1 °C. Hammett ρ_C, ρ_N values and Brönsted β values were determined, in other to examine the transition state variations caused by changes in nucleophiles, substituents and solvents properties (π^* and α). Applications of potential energy surface (PES) and quantum mechanical (QM) models of transition state characterization lead us to conclude that the reaction proceeds *via* the dissociative S_N2 mechanism.

Introduction

Although benzylation of tertiary amines (Menschutkin reaction1) were widely studied as one of the best examples of solvent effects on reaction rates, the reaction with primary amines has not been investigated to the same extent. Moreover nucleophilic substitution reaction of benzylchloride attracted considerable interest with special regards to the detailed transition state (TS) analysis.[2,3] Hill *et al.*[3a] and Ballistreri *et al.*[2a–b] reported that electron-donating substituent, *e.g.*, *p*-OCH_3 on the benzene ring promotes S_N1 nature while electron-withdrawing group, *e.g.*, *p*-NO_2 increases e_N2 character of the reaction.

Recently reacting bond rules[4] in a form of More O'Ferrall[5]–Jencks[6] type plot have been applied to interpretation of TS variation accompanying substituent and medium changes. Harris *et al.*[3d] used the More O'Ferrall plot for predicting TS variation in the nucleophilic substitution of benzyl compounds. Lee *et al.*[7] also applied the potential energy surface (PES) model to the characterization of TS in the S_N2 reactions of benzoyl and benzenesulfonyl halides. It has been demonstrated that the PES model predicts TS variation correctly in most cases but it fails to account for TS variation due to leaving group changes.[2d]

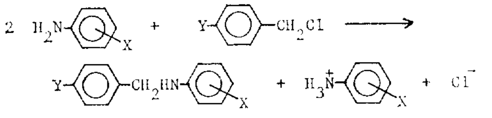
This difficulty has been overcome by Shaik[8] *et al.*, using a simple quantum mechanical (QM) model of TS characterization.

Solvatochromic equation, (1), developed by Taft[9] has been successfully applied to elucidation of various solvent effects.

$$XYX = XYZ_0 + s\pi^* + b\beta + a\alpha \qquad (1)$$

where XYZ is a physicochemical property or reaction rate constant, π^* is the polarity-polarizability parameter, β and α are the hydrogen bond (HB) acceptor basicity and HB donor acidity parameters, and s, b, and a are the susceptibilities of XYZ to the various solvent parameters. Using the solvatochromic correlation, Lee et al.[10] determined π^* and α scales for MeOH–MeCN binaries and demonstrated that π^* increases whereas α decreases with the increase of MeCN content.

In this paper we report a systematic kinetic study on the substituent and medium effects in the reaction of benzylchlorides with anilines, (2), in MeOH–MeCN mixtures to obtain further informations on the reaction mechanism.



(2)

where X = p-CH$_3$O, p-CH$_3$, H, p-Cl, m-NO$_2$

Y = p-CH$_3$O, p-CH$_3$, H, p-Cl, p-NO$_2$

Experimental

All materials were recrystallized or distilled before use as needed, except *p*-toluidine and aniline which were Merck GR grade. Methanol, Merck GR, and acetonitrile, J. T. Baker GR, were used without further purification. The rate was followed conductometrically using Beckmann RC 18-A conductometer.

The reactions were carried out in a large excess of nucleophile, aniline, (0.025–0.15*M*) and a pseudo-first-order rate constants, k_{obs}, were determined using Guggenheim plot. The k_{obs} values obtained from 4 to 6 kinetics runs were then linearly correlated with the aniline concentration, (3), and second-order rate constants were calculated from the slope of the linear plot, (3). Methanolysis rate constant, k_{MeOH}, obtained from

$$k_{obs} = k_{MeOH} + k_2\,[\text{aniline}] \qquad (3)$$

the intercept of the linear plot agreed with those obtained by independent solvolysis runs. In most of the cases, k_{MeOH} values were small and negligible compared to k_2.

Results and Discussion

The k_2 values obtained are summarized in Table 1. The rate increases in general with the increase of MeOH content and with the electron-donating ability of substituents on benzylchloride. The rate also increases with the increase of nucleophilicity by increasing electron-donating power of substituents on aniline.

Substituent and Solvent Effects

The Brönsted β and the Hammett ρ_N and ρ_C values obtained using second order rate constants are summarized in Tables 2, 3 and 4. The β values for 100 % MeOH solvent vary very little with substituents on benzylchloride except for *p*-CH$_3$O compound. In other solvent mixtures, the β values tend to increase in general for the more electron-withdrawing substituent. This can be interpreted as an increase in bond formation with the more electron-withdrawing group on the substrate. Reference to Table 2 reveals that the β value also increases with the increase of MeCN content of the medium. This increase in β values with the increase in MeCN content is an indicative of the increase in bond formation; bond formation is favored in more polar (greater π^*) solvent. Considerably smaller β values for *p*-CH$_3$O compound, especially in 100% MeOH, indicate that the electron-donating group makes the TS looser, *i.e.*, bond-

TABLE 1: Second-order Rate Constants ($k_2 \times 10^4\ M^{-1}\ s^{-1}$) for the Reactions of Benzyl Chlorides with Anilines at 55.1 °C in MeOH-MeCN Mixtures

MeOH (v/v %)	XC$_6$H$_4$NH$_2$	YC$_6$H$_4$CH$_2$Cl				
		p-CH$_3$O	*p*-CH$_3$	H	*p*-Cl	*p*-NO$_2$
100	*p*-CH$_3$O	120	11.6	5.18	4.78	2.80
	p-CH$_3$	101	8.40	3.72	3.34	1.85
	H	89.5	5.74	2.37	2.08	1.30
	p-Cl	82.0	3.70	1.55	1.32	0.823
	m-NO$_2$	73.5	1.42	0.682	0.562	0.363
80	*p*-CH$_3$O	99.7	9.21	4.92	4.55	2.68
	p-CH$_3$	82.6	6.69	3.33	3.25	1.83
	H	68.1	5.05	2.05	1.92	1.10
	p-Cl	59.6	2.29	1.16	0.845	0.451
	m-NO$_2$	44.8	1.05	0.226	—	—
50	*p*-CH$_3$O	49.0	6.77	4.36	3.79	2.16
	p-CH$_3$	44.6	4.86	2.71	2.40	1.48
	H	35.9	2.82	1.79	1.43	0.764
	p-Cl	28.5	1.53	0.784	0.621	0.355
	m-NO$_2$	14.2	—	—	—	—

Correlation coefficients; $r = 0.995 \pm 0.004$.

TABLE 2: Brönsted β Values for the Reactions of Benzyl Chlorides with Anlilines at 55.1 °C in MeOH-MeCN Mixtures

MeOH (v/v %)	$YC_6H_4CH_2Cl$				
	p-CH_3O	p-CH_3	H	p-Cl	p-NO_2
100	0.06	0.35	0.38	0.40	0.37
80	0.11	0.45	0.42	0.52	0.55
50	0.19	0.49	0.52	0.56	0.58

Correlation coefficients; $r=0.991\pm0.007$.

TABLE 3: Hammett ρ_N Values for the Reactions of Benzyl Chlorides with Anilines at 55.1 °C in MeOH-MeCN Mixtures

MeOH (v/v %)	$YC_6H_4CH_2Cl$				
	p-CH_3O	p-CH_3	H	p-Cl	p-NO_2
100	−0.19	−0.97	−1.04	−1.10	−1.02
80	−0.34	−1.17	−1.23	−1.45	−1.52
50	−0.55	−1.29	−1.44	−1.54	−1.57

Correlation coefficients; $r=0.993\pm0.006$.

TABLE 4: Hammett ρ_C Values for the Reactions of Benzyl Chlorides with Anilines at 55.1 °C in MeOH-MeCN Mixtures

MeOH (v/v %)	$XC_6H_4NH_2$			
	p-CH_3O	p-CH_3	H	p-Cl
100	−0.57	−0.60	−0.58	−0.59
80	−0.50	−0.51	−0.59	−0.68
50	−0.48	−0.49	−0.56	−0.60

Correlation coefficients; $r=0.950\pm0.028$.

breaking precedes bond formation.

Table 3 shows the ρ_N values are all negative, indicating positive charge development on the N atom of aniline at the TS owing to the charge transfer to benzylic carbon. The magnitude of ρ_N value, $|\rho_N|$ is increased, and hence bond formation is increased, by electron-withdrawing substituents on substrate. Here again the $|\rho_N|$ values are considerably smaller for p-CH_3O compound than those for other substituents, which is in accord with the results for β values. Solvent composition dependence of $|\rho_N|$ is also in line with that found for β values; $|\rho_N|$ is increased by the increase of MeCN content indicating more effective stabilization of bulky cation by the more polar (greater π^*) solvent.

Table 4 shows that benzylic carbon is weakly positive at the TS since ρ_C values are small and negative. In the S_N2 TS bond formation and bond breaking are synchronous, and hence assuming separate ρ values for the two processes, ρ_{form} and ρ_{break}, the prevailing contribution to the TS should be bond breaking, since ρ_C is negative in eq (4).

$$\rho_C=\rho_{break}+\rho_{form} \tag{4}$$

where $\rho_{break}<0$ and $\rho_{form}>0$.
In other words, $\rho_C<0$ is a net effect of $|\rho_{break}|>|\rho_{form}|$, and confirms the conclusion reached by other workers that the reaction proceeds *via* a dissociative S_N2 mechanism.

Reference to Table 4 reveals that the degree of bond formation is little effected by substituents on aniline in 100% MeOH solvent, since ρ_C differs little. This is a natural consequence of the low π^* and high α values of 100 % MeOH; a loose TS formed in this solvent is more favored by a strong HB donor acidity rather than a more polar (greater π^*) solvent. For other solvents, however, $|\rho_C|$ value is decreased by the increase in MeCN content of the solvent mixture. This is consistent with other results discussed above; increasing MeCN content increases polarity (π^*) of the solvent and stabilization of bulky cation is favored causing further bond formation. An increase in bond formation gives a greater contribution of ρ_{form} in eq (4) and will reduce $|\rho_C|$ value. The TS for typical solvents, 50% and 100% MeOH, can therefore be represented as (I) and (II) respectively.

$$\overset{\delta^+}{N}\text{——}\overset{\delta\delta^+}{C}\text{——}\overset{\delta^-}{L} \qquad\qquad \overset{\delta\delta^+}{N}\text{——}\overset{\delta^-}{C}\text{——}\overset{\delta^-}{L}$$

50 % MeOH (I)

100 % MeOH (II)

Structure (I) should have greater dipole moment compared with (II) and hence the stabilization will be more effective in a more polar medium. We therefore conclude that greater degree of bond formation is favored by more polar (greater π^*) solvents due to the well developed bulky cation solvation.

The cross interaction coefficients $p_{xy'}$ of Jencks[2c, 11], defined as eq (5), obtained in this work were 0.38 and 0.26 for 80 % and 50 % MeOH solvents respectively.

$$p_{xy'}=\frac{\partial\rho_N}{-\partial\sigma_Y}=\frac{\partial\rho_C}{-\partial\sigma_X} \tag{5}$$

The positive values of $p_{xy'}$ support the contention that the reaction preceeds by an S_N2 mechanism, in which bond formation and bond breaking are synchronous.

Application of PES Model

Let us examine TS variation accompanying substituent and medium changes applying the PES model. As we have already concluded, the reaction of benzylchloride with aniline in MeOH-MeCN proceeds *via* a dissociative S_N2 path, which will be located between S_N1 and S_N2 paths as shown in Fig. 1. An electron-donating substituent on the substrate ring will stabilize the upper left corner of the PES diagram, and the TS A will move to B in accordance with the anti-Hammond rule. The PES diagram predicts that this TS variation will cause the decrease in bond formation and increase in bond breaking. Our experimental results in Tables 2 and 3 show that β and $|\rho_N|$ values are decreased by electron-donating substituents. This is consistent with the prediction of the PES model since the decrease in β and $|\rho_N|$ values can be taken as the decrease in bond formation. The rate acceleration effect of electron-donating substituent (Table 1) can be interpreted as an indication of an incerased bond breaking at the TS. Substitution of electron-withdrawing group on aniline should destabilize the right corners, and the TS A will now move to D which is a resultant sum of vectors AC (Hammond rule) and AB (anti-Hammond rule). The variation of TS expected from this movement to *D* is: no change in bond formation, $\Delta\rho_{form}\cong0$ and increased bond breaking,

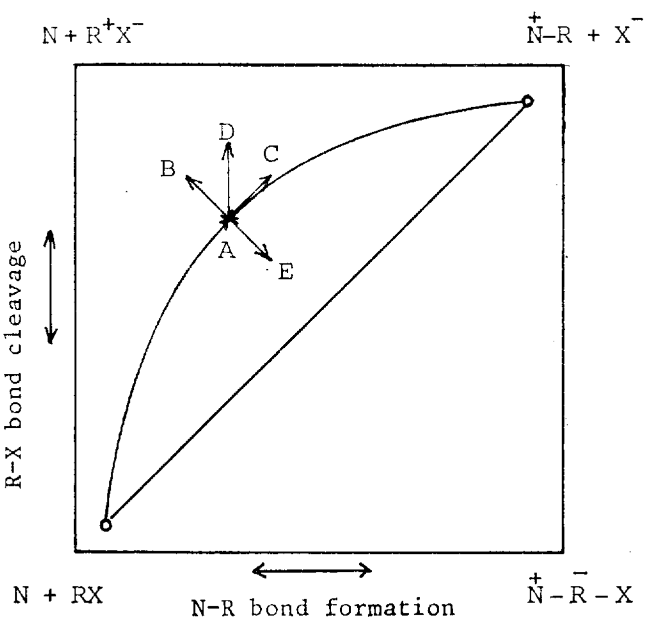


Figure 1. PES diagram for the nucleophilic substitution reaction of benzyl chlorides.

$\Delta\rho_{break}<0$. This is consistent with the experimental results, since Table 4 shows the $|\rho_C|$ is increased, *i.e.*, $\Delta\rho<0$, by electron-withdrawing substituents on aniline which is in accord with the expected trend from eq (4), $\Delta\rho_C=\Delta\rho_{form}+\Delta\rho_{break}<0$.

On the other hand, the increase in polarity (π^*) of solvent (with the increase in MeCN content) will stabilize the lower right corner and the TS will move to E by the anti-Hammond rule. The expected increase in β and $|\rho_N|$ as well as the decrease in $|\rho_C|$ are borne out by the experimental results in Tables 2, 3 and 4. The PES model therefore correctly predicts the TS variations in general for the reaction studied in this work.

Application of QM Model

Shaik *et al.*[8] discussed the TS variation in the reaction of nucleophile N(B) and substrate RX(A) quantum mechanically, using linear combination of three principal configurations: BA (ground), BA* (polarized) and B^+A^-(charge-transfered). The effects of these three configurations on the TS variation are summarized in Table 5. Substitution of electron-withdrawing groups on substrate benzene ring will stabilize B^+A^- but will destabilize BA* configuration. The expected effects from the stabilization of B^+A^- configuration are, according to Table 5, a tight nucleophile-substrate (N-R) bond and a loose substrate-leaving group (R-X) bond. However the expected effects from the destabilization of BA* configuration are tight N-R and R-X bonds. Thus the overall effect will be a tight N-R with little change in R-X bond, in agreement with the experimental results.

Substitution of electron-donating groups on the substrate benzene ring will stabilize more the BA* relative to the BA and B^+A^- configurations; the loose structures for both N-R and R-X bonds expected are again born out by our results in Tables 2, 3 and 4.

TABLE 5: The Structural Effects of the Key Configurations on the Reaction Complex, N··R··X

Configuration	Structural effect	
	N-R	R-X
BA	loose	tight
B^+A^-	tight	loose
BA*	loose	loose

The increase in HB donor acidity of the medium accompanied with the increase in MeOH content will stabilize BA* configuration. The expected loose TS formation (Table 5) is again borne out by a relatively large $|\rho_C|$ of nearly constant magnitude in 100% MeOH solvent shown in Table 4.

We therefore conclude that for the reaction studied both the PES and QM models can give correct predictions for the TS variation.

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

Reference

(1) N. Menschutkin, *Z. Phys. Chem. (Leipzig)*, **5**, 589 (1890).

(2) (a) F. P. Ballistreri, E. Maccarone, and A. Mamo, *J. Org. Chem.*, **41**, 3364 (1976); (b) F. P. Ballistreri, E. Maccarone, G. Musumarra, and G. A. Tomaselli, *J. Org. Chem.*, **42**, 1415 (1977); (c) P. R. Young and W. P. Jencks, *J. Amer. Chem. Soc.*, **101**, 3288 (1979); (d) K.C. Westaway and S. F. Ali, *Can. J. Chem.*, **57**, 1354(1979); (e) K. C. Westaway and Z. Waszczylo, *Can. J. Chem.*, **60**, 2500 (1982).

(3) (a) J. W. Hill and A. Fry, *J. Amer. Chem. Soc.*, **84**, 2763 (1962); (b) D. A. da Roza, L. T. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, **95**, 7003 (1973); (c) P. Haberfield, A. Nudelman, A. Bloom, R. Romm, and H. Ginsberg., *J. Org. Chem.*, **36**, 1792 (1971); (d) J. M. Harris, S. G. Shafer, J. R. Moffatt,and A. R. Becker, *J. Amer. Chem. Soc.*, **101**, 3295 (1979).

(4) E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 2915 (1967).

(5) R. A. More O'Ferrall, *J. Chem. Soc., B*, 274 (1970).

(6) W. P. Jencks, *Chem. Rev.*, **72**, 705 (1972).

(7) (a) I. Lee, I. S. Koo, and H. K. Kang, *Bull. Korean Chem. Soc.*, **2**, 41 (1981); (b) I. Lee, I. S. Koo, S. C. Sohn, and H. H. Lee, *Bull. Korean Chem. Soc.*, **2**, 92 (1982); (c) I. Lee and I. S. Koo, *Tetrahedron*, **39**, 1803 (1983).

(8) A. Pross and S. S. Shaik, *J. Amer. Chem. Soc.*, **103**, 3702 (1981).

(9) M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, "Progress in Physical Organic Chemistry," Ed. by R. W. Taft, Vol. 13, P 485-630, John Wiley & Sons, 1981.

(10) I. Lee, B. Lee, I. S. Koo, and S. C. Sohn, *Bull. Korean Chem. Soc.*, **4**, 189 (1983).

(11) D. A. Jencks and W. P. Jencks, *J. Amer. Chem. Soc.*, **89**, 7948 (1977).