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VARIATION OF TRANSITION STATE IN REACTIONS OF BENZENSULFONYL CHLORIDES WITH ANILINES IN MeOH–MeCN SOLVENTS

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Abstract—Kinetic studies of nucleophilic substitution reactions of substituted benzensulfonyl chlorides with anilines were conducted at 35° in a range of methanol-acetonitrile solvent mixtures. Results showed that (i) the magnitudes of ρ_N and β associated with a change of substituent in the nucleophile are large and indicate a relatively advanced bond-formation in the transition state, (ii) maximum size of ρ_N, ρ_S and β at the solvent composition of the maximum ionizing power, together with a positive cross-interaction coefficient, suggest S_N2 transition state of a "synchronous push-pull" type, and (iii) the potential energy surface model is unstable to predict the transition state variation to a more product-like transition state, where bond formation is much more progressed and bond-breaking is slightly more advanced, upon changing the solvent to a more ionizing one enhancing leaving ability. In this respect the quantum mechanical model is superior to the potential energy surface model.

The nucleophilic substitution of sulfonyl halide is an extensively studied class of reaction in organic chemistry.[1] Applications of various mechanistic criteria have lead different groups of investigators to propose mainly two types of mechanisms for this reaction; S_N2^{1a-e} and S_AN^{1f-k} the former mechanism being more preferred lately. Important potential energy surface(PES) models for predicting changes in transition-state structure of organic reactions have been developed over recent years,[2] in which perturbations both parallel and perpendicular to the reaction coordinate are considered.

While these PES models have been successful in many applications, one of the prominent failures of these models involved the inability of predicting the effect of changing the leaving group on transition-state structure of nucleophilic substitution reactions[3].

Pross and Shaik[4], however, were able to overcome this difficulty by analyzing the effect of leaving groups on transition-state structure using a simplified quantum mechanical (QM) model in which transition states are defined in terms of linear combinations of reactant configurations. This model has been shown to predict correctly the effects of nucleophiles and substrates as well as of leaving groups when applied to a limited family of reactions such as the S_N2 reaction of benzyl derivatives.

In this work we investigated transition-state variations in the nucleophilic substitution reaction of benzensulfonyl chlorides with anilines, (1), in a range of solvent mixtures of MeOH and MeCN. Both the PES and QM models are applied in some detail in this work to probe the structure of the transition state of the nucleophilic substitution reactions.

$$\begin{aligned} &YC_6H_4SO_2Cl + 2H_2NC_6H_4X \\ &\quad \rightarrow YC_6H_4SO_2NHC_6H_4X + H_3\overset{+}{N}C_6H_4X + Cl^-. \qquad (1) \end{aligned}$$

RESULTS AND DISCUSSION

The reactions, carried out in a large excess of aniline, followed a pseudo-first-order kinetics to at least 70% completion. k_{obsd} values are linearly correlated with the aniline concentration, indicating the second order kinetics, first-order with respect to each reactant, according to the simple rate law

$$k_{obsd} = k_2[\text{aniline}]. \qquad (2)$$

Second-order rate constants, k_2, were determined from the slope of the plot of k_{obsd} vs aniline concentration, obtained from 4–6 kinetic runs. The k_2 values obtained in various solvent mixtures are summarized in Table 1. In general the rate increases with the MeOH content; similar trend was noted for the rate of the benzylation of aniline in MeOH–MeCN[5].

Effects of the nucleophile and substrate. The reactions of benzensulfonyl chlorides with the series of anilines show linear Hammett plots with large negative slopes, $\rho_N = -2.0 \sim -2.9$, and good Brønsted relationships with β values of $0.6 \sim 0.9$ in various MeOH–MeCN mixtures as summarized in Tables 2 and 3. Relatively large magnitudes of these selectivity parameters suggest that bond-making tends to be advanced in the transition state of the reactions of benzensulfonyl chlorides with anilines.[1e] The greater magnitudes of these parameters for substrates with the more electron-withdrawing substituent indicate that larger portion of electron density is transferred and N–S bond-making is more advanced, and hence the selectivity for nucleophiles is greater, with the more electron-withdrawing ring substituent. On the other hand, Hammett ρ values, ρ_S in Table 4, for the reactions of the series of benzensulfonyl chlorides with anilines varied from 0.5 for the reaction with *m*-nitroaniline to 1.0 for *p*-methylaniline indicating less N–S bond-making with nucleophiles with the more electron-withdrawing substituent. This means that the S atom is less negatively charged and the N–S bond must be longer in the transition state with the nucleophile.

Since the size of ρ is an indication of the extent of charge development at the atom of the reacting side chain adjacent to the ring in passing from ground to transition state,[1e,6] the greater size of ρ_N relative to that of ρ_S may be interpreted as much less negative charge development at the S atom despite the large amount of

Table 1. Second-order rate constants for the reaction of substituted benzensulfonyl chlorides with anilines in MeOH-MeCN mixtures at 35° ($10^2 \times k_2$ l mole^{-1} s^{-1})

MeOH (v/v %)	$X-C_6H_4NH_2$	$Y-C_6H_4SO_2Cl$			
		p-CH_3	H	p-Cl	p-NO_2
50	p-CH_3	10.6	15.7	29.4	114
	H	5.33	7.77	10.4	37.3
	p-Cl	2.04	2.59	3.12	11.0
	m-NO_2	0.192	0.203	0.237	0.555
70	p-CH_3	16.0	24.5	35.7	148
	H	6.25	8.68	13.2	45.6
	p-Cl	2.54	3.15	3.79	12.6
	m-NO_2	0.238	0.263	0.293	0.743
80	p-CH_3	16.4	28.6	47.2	198
	H	6.68	9.67	14.2	55.0
	p-Cl	2.51	3.22	4.34	14.1
	m-NO_2	0.250	0.297	0.323	0.760
90	p-CH_3	17.3	31.7	43.7	223
	H	7.41	10.8	15.8	57.3
	p-Cl	2.81	3.92	5.00	16.2
	m-NO_2	0.310	0.323	0.333	0.835
100	p-CH_3	18.4	26.6	40.8	186
	H	7.85	10.6	16.0	63.2
	p-Cl	2.87	4.36	5.59	18.6
	m-NO_2	0.336	0.320	0.336	0.839

Table 2. Slopes(ρ_N) and correlation coefficient(r) of the Hammett plots for the reactions of the series of anilines with sulfonyl chlorides in MeOH-MeCN mixtures

MeOH (v/v %)	Sulfonyl derivatives	ρ_N	r
50	p-CH_3	- 2.00	0.999
	H	- 2.17	0.999
	p-Cl	- 2.35	0.998
	p-NO_2	- 2.60	0.999
70	p-CH_3	- 2.04	0.999
	H	- 2.20	0.999
	p-Cl	- 2.36	0.999
	p-NO_2	- 2.58	0.999
80	p-CH_3	- 2.04	0.999
	H	- 2.23	0.999
	p-Cl	- 2.41	0.999
	p-NO_2	- 2.71	0.999
90	p-CH_3	- 1.97	0.999
	H	- 2.23	0.999
	p-Cl	- 2.39	0.999
	p-NO_2	- 2.71	0.999
100	p-CH_3	- 1.96	0.999
	H	- 2.16	0.998
	p-Cl	- 2.36	0.999
	p-NO_2	- 2.65	0.999

Table 3. Slopes(β) and correlation coefficients(r) of the Brønsted plots for the reaction of the anilines with sulfonyl chlorides in MeOH-MeCN mixtures

MeOH (v/v %)	Sulfonyl derivatives	β	r
50	p-CH_3	0.66	0.982
	H	0.70	0.981
	p-Cl	0.75	0.976
	p-NO_2	0.84	0.982
70	p-CH_3	0.66	0.981
	H	0.71	0.985
	p-Cl	0.76	0.989
	p-NO_2	0.83	0.984
80	p-CH_3	0.66	0.984
	H	0.71	0.989
	p-Cl	0.78	0.987
	p-NO_2	0.88	0.988
90	p-CH_3	0.64	0.985
	H	0.72	0.984
	p-Cl	0.77	0.984
	p-NO_2	0.87	0.985
100	p-CH_3	0.63	0.987
	H	0.69	0.976
	p-Cl	0.76	0.978
	p-NO_2	0.85	0.981

Table 4. Slopes (ρ_S) and correlation coefficients(r) of the Hammett plots for the reactions of the series of sulfonyl chlorides with anilines in MeOH-MeCN mixtures

MeOH (v/v %)	Aniline derivatives	ρ_S	r
50	p-CH_3	1.03	0.997
	H	0.88	0.996
	p-Cl	0.78	0.999
	m-NO_2	0.51	0.975
70	p-CH_3	1.01	0.997
	H	0.91	0.999
	p-Cl	0.78	0.981
	m-NO_2	0.53	0.969
80	p-CH_3	1.12	0.998
	H	0.96	0.997
	p-Cl	0.80	0.994
	m-NO_2	0.55	0.978
90	p-CH_3	1.14	0.994
	H	0.93	0.997
	p-Cl	0.80	0.994
	m-NO_2	0.57	0.966
100	p-CH_3	1.07	0.997
	H	0.96	0.996
	p-Cl	0.84	0.995
	m-NO_2	0.57	0.986

charge transferred from the N atom of the nucleophile due mainly to the partial transfer of electron density toward the leaving group which should have started to cleave in an S_N2 transition state. If we assume virtually separate ρ values for bond formation ($\rho_S > 0$) and bond-breaking ($\rho_S < 0$)[6], positive ρ_S values obtained suggest predominance of bond-making in the transition state. The large difference in the size of ρ_N and ρ_S can thus be taken as an indication that S–Cl bond-breaking is in progress at the transition state and an S_N2 mechanism is operative in the reactions studied. This conclusion is supported by a positive cross-interaction coefficient P_{xy} of Jencks,[7] which is a measure of the coupling between the N–S bond-formation and S-Cl bond-breaking processes.

$$p_{xy'} = \frac{\partial \rho_N}{-\partial \sigma_y} = \frac{\partial \rho_S}{-\partial \sigma_x}. \quad (3)$$

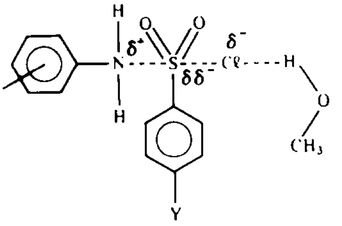
The reaction is predicted to proceed along a diagonal reaction coordinate in the potential energy surface diagram, i.e. the reaction proceeds via a concerted bond-forming and -breaking process as in the S_N2 reaction, when the $P_{xy'}$ is positive.[7] Thus the $P_{xy'}$ value of 0.41 ~ 0.54 obtained in this study for various MeOH-MeCN solutions in Table 5 lends support to the S_N2 mechanism for the reaction (1). On the other hand, Litvinenko *et al.*[18] have observed an inverse D kinetic isotope effect of $k_H/k_D = 0.78$ in the reaction between p-$CH_3C_6H_4SO_2Cl$ and p-$CH_3OC_6H_4NH_2$ (and p-$CH_3OC_6H_4ND_2$), and concluded that the S-Cl bond cleavage is involved in the rate determining step.

Effect of solvent. Various anomalies in physico-chemical properties of MeOH-MeCN mixtures have been noted at the composition of 80 – 90% (v/v%) MeOH, which are often associated with the broken down polymer chain structure of MeOH.[1c–e,8,9]. Solvolysis rate constants of t-BuBr in MeOH-MeCN solution exhibited a maximum at this solvent composition[8c] demonstrating that ionizing power of the mixture is maximum at this solvent composition[10]. Since the S–Cl bond cleavage is in progress in the transition state, we would expect the leaving ability of the leaving group Cl to be at a maximum and hence, the S–Cl bond to become the longest in the transition state at this most ionizing solvent composition. This means that changes in selectivity parameters ρ and β, which are normally measures of extent of bond formation in the transition state, as the solvent ionizing power is varied should also reflect the change in bond cleavage with the solvent. Inspection of Tables 2–4 reveals that all the three selectivity parameters, ρ_N, ρ_S and β, show definite trends of exhibiting maximum behavior at the maximum ionizing solvent composition. A similar increase in selectivity as solvent ionizing power is increased has also been noted for nucleophilic substitution of benzyl and 1-methylheptyl chlorides and bromides by competing nucleophiles, *m*-chloroaniline and ethanol, in aqueous ethanol.[11] However the result is surprising because it is contrary to what we would expect normally from the "push–pull" mechanism of S_N2 reactions;[12] an increased leaving ability due to an increase in solvent ionizing power would require less assistance from the nucleophile,[13] i.e. less N–S bond formation, resulting in a longer N–S bond and a slightly longer S–Cl bond. Our result of an enhanced leaving ability in a more strongly ionizing solvent leading to a transition state with a much shorter N–S and a slightly longer S–Cl bond suggests a "synchronous push–pull" type of transition state (I) for the nucleophilic substitution reactions of benzensulfonyl chlorides with anilines in the MeOH-MeCN solvent mixtures. By the "synchronous" we mean that bond formation and cleavage take place to the same extent in all stages along the reaction coordinate. The results are quite similar to those of Westway and Ali[3] who found a better leaving group leading to a transition state with a shorter nucleophile–substrate bond in the nucleophilic substitution reaction of a series of 4-substituted phenylbenzyldimethylammonium ions with thiophenoxide ions in N,N-dimethylformamide.

Table 5. Jencks' cross interaction coefficients ($P_{xy'}$) and correlation coefficients(r) for the reaction of sulfonyl chlorides with anilines in MeOH-MeCN mixtures

MeOH (v/v %)	$P_{xy'}$	r
50	0.40	0.936
70	0.45	0.952
80	0.53	0.931
90	0.54	0.865
100	0.50	0.899

$$P_{xy'} = \frac{\partial \rho_S}{-\partial \sigma_X} = \frac{\partial \rho_N}{-\partial \sigma_Y}$$



(I)

Application of the PES model. The most recent and convenient method of application of the PES model is to use a More O'Ferrall type of energy surface[2d] (Fig. 1) in predicting the changes in the structure of the transition state when a substituent in the substrate, the nuclephile, or the leaving group is changed. Since it is well established that bond-making is somewhat ahead of bond-breaking in the transition state of nucleophilic sulfonyl substitutions,[1] the transition state will lie on the reaction coordinate between S_N2 and S_AN paths. It can be readily shown that both an early, F, and a late, G, transition state would not be consistent with the experimental results. Similarly simple considerations of the effects of substituents in the substrate lead us to reject the S_AN mechanism as untenable; an electron-withdrawing(electron-releasing) substituent should

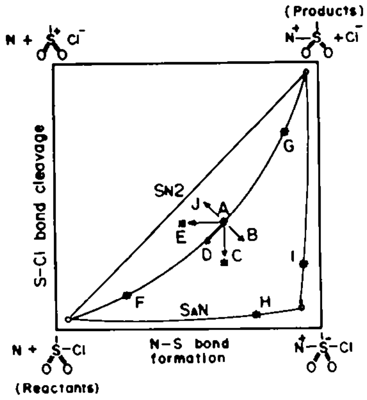


Fig. 1. Potential energy surface for a nucleophilic substitution of sulfonyl chlorides, where N is the nucleophile and energy minima and maxima are represented by circles and star marks, respectively.

stabilize(destabilize) the lower right corner which is on the reaction coordinate of the S_AN path and the first transition state H will move toward reactants corner (the second transition state, I, away from products corner) hence N-S bond formation(S-Cl bond cleavage) should decrease it contrary to the experimental results; the large β and ρ_N values obtained for an electron-withdrawing substituent suggest a shorter N-S (a larger S-Cl) bond in the transition state. A better nucleophile will stabilize the right hand corners and the transition state will move from A to C assuming approximately the same perpendicular(vector AB) and parallel(vector AD) effects[14]; the transition state should then have a shorter S-Cl bond with little change in N-S bond length, which again disagrees with the experiments, since the ρ_N is larger for p-Me-aniline indicating greater bond formation. This discrepancy can only be reconciled with the assumption of stronger perpendicular effect relative to parallel effect. The increase in the ionizing power of solvent mixture should enhance the leaving ability by assisting the leaving group Cl to depart more easily causing a slight increase in the length of the S-Cl bond. On the PES diagram, the increase in the ionizing power stabilizes the upper corners and this should cause the transition state A to move to, e.g. E which is obtained as a vector sum of AD and AJ. Thus the vector AE will be somewhere in between the vectors AD and AJ depending on the magnitudes of the two vectors. The PES model now predicts that the increase in the ionizing power should always lead to a longer N-S bond irrespective of whether perpendicular or parallel effect is stronger. This is contrary to the experimental results since greater size of β and ρ values clearly indicated a shorter N-S bond with a longer S-Cl bond as the ionizing power of solvent is increased. Thus we conclude that the PES model fails to predict transition state variation correctly for the reaction (1). In particular the PES model is ambiguous with regards to the transition state variation when two opposing effects, parallel and perpendicular to the reaction coordinate, are involved.

Application of the QM model. In general four types of interactions are involved in the perturbation of a system, A, by another, B: electrostatic, polarization, exchange repulsion and charge transfer interactions[15]. The former two are long range whereas the latter two are short range components of intersystem interactions. Pross and Shaik[4] considered only the two, polarization and charge transfer, in their quantum mechanical description of transition state structure. They rationalized this simplification with the fact that actual intra- and intersystem electron shifts occur only in these two interactions. Accordingly they expressed the various states of the reaction complex as a linear combination of the three configurations; ground BA, polarized BA* and charge transferred B^+A^- configurations. In a nucleophilic substitution reaction, B may be a nucleophile N and A a substrate RX with a leaving group X. Analysis of bonding characteristics and the relative contribution to the structure of the transition state of the three key configurations allow us to predict how the transition state will change as a result of a given perturbation. Examination of the structural implications associated with each configuration using an MO and a VB description lead Pross and Shaik to a set of simple rules for predicting the structural effects of the three configurations on the reaction complex as presented in Table 6. Let us now apply the QM model based on these rules of structural effects.

Application of the model to the predictions of effects of the nucleophile and substrate is entirely analogous to that for the benzyl system[3]. An increase in the nucleophile strength (p-Me-aniline) will increase electron donating (CT) ability of the nucleophile and hence increase the contribution of the B^+A^- configuration to the transition state. Reference to Table 6 suggests that as a consequence both nucleophile-substrate (N-S) bond formation and substrate-leaving group (S-Cl) bond cleavage should increase. The experimental results obtained in this work are in support of these predictions. It can be seen that the ρ_S value increases in the order $X = m\text{-}NO_2 < p\text{-}Cl < H < p\text{-}Me$, where X is the substituent in the aniline ring; since the reaction was found to proceed via the "synchronous push-pull" mechanism the ρ value can be utilized here as a measure of the degree of both bond formation and bond breaking. The experimental results agree with the predictions based on the QM model, but are not in agreement with the predictions of the PES model, according to which an increase in the nucleophile strength should lead to a decrease in the degree of S-Cl bond cleavage and have little effect on the degree of N-S bond formation.

An electron-withdrawing substituent on the substrate(p-NO_2-$C_6H_4SO_2Cl$) will stabilize the B^+A^- and destabilize the BA* configuration. Inspection of Table 6 suggests that increased participation of B^+A^- will lead to a tighter N-S and a looser S-Cl bond. An electron-donating substituent on the other hand will favor BA* over BA and B^+A^- and is expected to loosen both the N-S and S-Cl bond. The effect of substituents predicted with the QM model on the degree of N-S bond formation, i.e. a tighter N-S bond with the more electron-withdrawing substituent, is supported by the increasing size of ρ_N and β values in the order $Y = p\text{-}Me < H < p\text{-}Cl < p\text{-}NO_2$ in Table 2 and 3.

Increasing ionizing power of solvent has the effect of increasing leaving ability, which will result in lowering the energy of the B^+A^- and BA* configurations in which electrons are already largely localized on the leaving group. Thus the contributions of these two configurations to the transition state will increase. Reference to Table 6 suggests a looser S-Cl bond while the effect on N-S bond length is uncertain since two opposing effects are predicted. For S_N2 reactions however the B^+A^- configuration contributes into the transition state to a greater extent than the BA* due to the greater stability of the configuration;[4] a tighter N-S bond is thus expected as a result of the increase in the ionizing power of solvent. The experimental results of maxima in ρ_N, ρ_S and β values at the solvent composition of maximum ionizing power are in accord with this prediction.

CONCLUSIONS

This study has shown that; (i) the magnitudes of ρ_N and β associated with a change of substituent in the nucleophile are large and indicate a relatively advanced

Table 6. 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

bond-formation in the transition state, (ii) maximum size of ρ_N, ρ_S and β at the solvent composition of the maximum ionizing power, together with a positive ,cross-interaction coefficient, suggest S_N2 transition state of a "synchronous push-pull" type, and (iii) the potential energy surface model is unable to predict the transition state variation to a more product-like transition state, where bond formation is much more progressed and bond-breaking is slightly more advanced, upon changing the solvent to a more ionizing one enhancing leaving ability. In this respect the quantum mechanical model is superior to the potential energy surface model.

EXPERIMENTAL

Materials. Sulfonyl chlorides and anilines were fresh samples of GR grade(Tokyo Kasei) and were used as supplied. Merck GR methanol was used throughout. Acetonitrile was fractionally distilled after successive dehydration with KOH and P_2O_5 (b.p. 82°).

Kinetic measurements. The rate was followed conductometrically. Other procedures and treatment of data to derive rate constants were similar to those reported in Ref. 1e for the kinetic studies of benzensulfonyl chlorides with anilines in MeOH. Accuracy of rate constants were estimated to be ±5%. The various Hammett and Brønsted slopes and correlation coefficients were calculated by a least-squares treatment of log k vs σ or pK_a.

Product analysis. Products in 50% MeOH solvent were isolated and analyzed in a few cases following the procedure in Ref. 1e, and in every case single product only was found.

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REFERENCES

[1a] M. L. Tonnet and A. N. Hambly, *Aust. J. Chem.* **24**, 703 (1971); [b] R. Foon and A. N. Hambly, *Ibid.* **24**, 713 (1971); [c] I. Lee and I. S. Koo, *J. Korean Chem. Soc.* **25**, 7 (1981); [d] I. Lee and I. S. Koo, *Bull. Korean Chem. Soc.* **2**, 41 (1981); [e] O. Rogne, *J. Chem. Soc.* (B), 1294 (1968); *Ibid.* 663 (1969); *Ibid.* 1855 (1971), *Ibid.* Perkin II, 472 (1972); [f] L. M. Litvinenko, A. F. Popov and V. A. Savelova, *Ukr. Khim. Zh.* **33**, 57 (1967); [g] L. M. Litvinenko, N. T. Maleeva, V. A. Savelova and T. D. Kovach, *Zh. Obshch. Khim.* **41**, 2615 (1971); [h] E. Ciuffarin, L. Senatore and M. Isola, *J. Chem. Soc.* Perkin II, 468 (1972); [i] L. J. Stangeland, L. Senatore and E. Ciuffarin, *Ibid.* 852 (1972); [j] A. Arcoria, E. Maccarone, G. Musumarra and G. A. Tomaselli, *J. Org. Chem.* **24**, 3595 (1974); [k] A. Arcoria, F. P. Ballistreri, G. Musummarra and G. A. Tomaselli, *J. Chem. Soc.* Perkin II, 221 (1981).

[2a] E. R. Thornton, *J. Am. Chem. Soc.* **89**, 2915 (1969); [b] J. C. Harris and J. L. Kurz, *Ibid.* **92**, 349 (1970); [c] J. E. Critchlow, *J. Chem. Soc.*, Faraday I, **68**, 1774 (1972); [d] R. A. More O'Ferrall, *Ibid.* (B), 274 (1970).

[3] K. C. Westaway and S. F. Ali, *Can. J. Chem.* **57**, 1354 (1979).

[4] A. Pross and S. S. Shaik, *J. Am. Chem. Soc.* **103**, 3702 (1981).

[5] F. P. Ballistreri, E. Maccarone and A. Mamo, *J. Org. Chem.* **41**, 3364 (1976).

[6] C. D. Johnson, *The Hammett Equation* Chap. 1. Cambridge Univ. Press, Cambridge, (1973).

[7a] D. A. Jencks and W. P. Jencks, *J. Am. Chem. Soc.* **99**, 7948 (1977); [b] P. R. Young and W. P. Jencks, *Ibid.* **101**, 3288 (1979).

[8a] M. A. Coplan and R. M. Fuoss, *J. Phys. Chem.* **68**, 1181 (1964); [b] A. D'Aprano, M. Gofferdi, and R. Triols, *J. Chem. Soc.* Faraday, **72**, 79 (1976); [c] H. W. Lee, S. La, and I. Lee, *J. Korean Chem. Soc.* **24**, 115 (1980); [d] H. W. Lee, K. S. Song, H. B. Song and I. Lee, *Bull. Inst. Basic Soc.* Inha Univ. **2**, 27 (1981); [e] A. Arcoria, V. Librando, E. Maccarone, G. Musumarra and G. A. Tomaselli, *Tetrahedron* **33**, 105 (1977).

[9] M. C. R. Symons, V. K. Thomas, N. J. Fletcher and N. G. Pay, *J. Chem. Soc.* Faraday I, **77**, 1899 (1981).

[10] Our recent unpublished studies of t-BuCl solvolysis in MeOH-MeCN also showed a rate maximum at the same composition.

[11] Y. Karton and A. Pross, *J. Chem. Soc.* Perkin II, 250 (1980).

[12] R. W. Alder, R. Baker and J. M. Brown, *Mechanism in Organic Chemistry*, Chap. 3. Wiley-Interscience, London (1971).

[13] M. J. Kamlet and R. W. Taft, *J. Chem. Soc.* Perkin II, 349 (1979).

[14] J. M. Harris, S. G. Shafer, T. R. Moffatt and A. R. Becker, *J. Am. Chem. Soc.* **101**, 3295 (1979).

[15a] J. M. Murrell, M. Randic and D. R. Williams, *Proc. Roy. Soc.* A**284**, 566 (1965); [b] T. Fueno, S. Nagase, K. Tatsumi and K. Yamaguchi, *Theoret. Chim. Acta* **26**, 48 (1972); [c] K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.* **41**, 1989 (1968); [d] K. Morokuma, *J. Chem. Phys.* **55**, 1236 (1971); [e] P. Kollman, *Accounts Chem. Res.* **10**, 365 (1977); [f] I. Lee, *Prog. Chem. and Chem. Industry* **17**, 383 (1977).