References

1. (a) Juris, A.; Balzani, V.; Bargelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Review* **1988**, *84*, 279. (b) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
2. Ghosh, K. B. *Coord. Chem. Review* **1989**, *95*, 239.
3. (a) Bock, C. R.; Conner, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815. (b) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94.
4. (a) Haq, I.; Lincoln, P.; Suh, D.; Norden, B.; Chowdhry, B. Z.; Chaires, J. B. *J. Am. Chem. Soc.* **1995**, *117*, 4788. (b) Pyle, A. M.; Barton, J. K. *Progress Inorg. Chem.: Bioinorg. Chem.* **1990**, *38*, 413 and references therein.
5. (a) Constable, E. C. *Tetrahedron* **1992**, *46*, 10013. (b) Morgan, R. J.; Baker, A. D. *J. Org. Chem.* **1990**, *55*, 1986.
6. Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980, p 228.
7. Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.
8. Jahng, Y.; Kim, J.-I., Na, Y. H. *Bull. Kor. Chem. Soc.* **1992**, *13*, 211.
9. Thummel, R. P.; Jahng, Y. *J. Org. Chem.* **1985**, *50*, 2407.
10. Thummel, R. P.; Jahng, Y. *Inorg. Chem.* **1986**, *25*, 2527 and references therein.
11. Bierig, K.; Morgan, R. J.; Tysoe, S.; Gafney, H. D.; Strekas, T. C.; Baker, A. D. *Inorg. Chem.* **1991**, *30*, 4898 and references therein.
12. Nakamoto, K. *J. Phys. Chem.* **1960**, *64*, 1420.
13. Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69.
14. Elliott, C. M.; Hershenhart, E. J. *J. Am. Chem. Soc.* **1982**, *104*, 7519.
15. Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J. *Chem. Phys. Lett.* **1978**, *58*, 389.

Transition-State Variation in the Solvolysis of Cyclopentyl *para*-Substituted Benzenesulfonates

In Sun Koo, Kiyull Yang, Keumduck Kang, Jong Keun Park,
Hyuck Keun Oh*, and Ikchoon Lee**

Department of Chemical Education, Gyeongsang National University, Chinju 660-701, Korea
*Department of Chemistry, Chonbuk National University, Chunju 560-756, Korea
**Department of Chemistry, Inha University, Inchon 402-751, Korea
Received October 22, 1996

Rate constants for solvolyses of cyclopentyl *para*-substituted benzenesulfonates are reported for aqueous binary mixtures with acetone, ethanol and methanol. These data are interpreted using the equations of original and extended Grunwald-Winstein relationship, Hammett equation, potential energy surface model, and quantum mechanical model. The Grunwald-Winstein plots of first-order rate constants for cyclopentyl benzenesulfonates with Y_{OTs} (based on 2-adamantyl tosylate) show a dispersion phenomenon while the extended Grunwald-Winstein plots show a good correlation ($r > 0.997$) for the solvolyses of cyclopentyl tosylate, benzensulfonate, and *para*-chlorobenzenesulfonate. This study has shown that (i) the magnitudes of *m*, *l* and *m/l* associated with a change of solvent composition indicate a relatively advanced bond-breaking in the transition state for the solvolysis of cyclopentyl tosylate, (ii) the decrease of ρ_L value with solvent change from pure ethanol to pure water implies a product-like transition state, where bond breaking is much more progressed than bond formation (iii) both the potential energy surface and quantum mechanical models are applicable for the prediction of the transition state variation involving more product-like S_N2 transition state, and (iv) the S_N2 reaction via product-like transition state appears to cause the dispersions in the original Grunwald-Winstein correlations.

Introduction

Dispersion into separate lines in the correlation of the specific rates of solvoysis of a substrate in various binary mixtures was documented[1-3] in early treatments using the Grunwald-Winstein Eq. (1).

$$\log(k/k_o) = mY + c \tag{1}$$

In Eq. (1), k and k_o are specific rates of solvolysis of a substrate in a given solvent, of solvent ionizing power Y, and in 80% ethanol, respectively, m is the sensitivity to changes in Y values, and c is a residual (constant) term. Eq. (1) is commonly written without the intercept (c), which is

180　*Bull. Korean Chem. Soc.* **1997**, Vol. 18, No. 2

In Sun Koo et al.

not required for typical interpretations, but it is often considered as a "hidden" adjustable parameter in the correlations.[4]

In general, dispersion effects in unimolecular solvolyses[5,6] make smaller contribution to the overall linear free energy relationship (LFER) than solvent nucleophilicity effects in bimolecular solvolyses. It was suggested[2] that a second term which is governed by the sensitivity l to solvent nucleophilicity N, should be added to Eq. (1) for bimolecular solvolyses. The resulting Eq. (2) is often referred to as an extended Grunwald-Winstein equation.

$$\log(k/k_o)=mY+lN \tag{2}$$

It was also suggested that a Y scale based on 2-adamantyl tosylate solvolysis[7-9] (Y_{OTs}) should be the most appropriate, and N_{OTs} values can be obtained from Eq. (3).

$$N_{OTs}=\log(k/k_o)_{MeOTs}-0.3Y_{OTs} \tag{3}$$

The main cause of dispersion in the Grunwald-Winstein plots using Eq. (1) is the different leaving group in the solvoysis of a given substrate from that of the standard substrate used to establish the Y scale being used in the correlation.[10] Other causes of dispersion phenomenon are the resonance stabilization within benzylic carbocations and appreciable crowding in the vicinity of the reaction center.[11]

The potential energy surface (PES) model[12] for predicting transition state variation is based on the application of the Hammond postulate[13] and the Thornton's rule[14] to the reaction of a nucleophile (N) attacking a substrate (RL),

$$N(B) + RL(A) \longrightarrow [N\cdots R\cdots L]^{\ddagger} \longrightarrow N^+\text{-}R + L^- \tag{4}$$
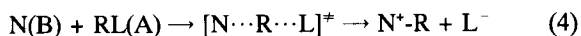
While the PES model has been successful in many applications, one of the prominent failures of this model involved the inability of predicting the effect of changing the leaving group on transition-state structure of nucleophilic substitution reactions.[15]

Pross[16] *et al.*, and Lee *et al.*,[17] however, solved this difficulty by analyzing the effect of leaving groups on transition-state structure using a simplified quantum mechanical (QM) model. In the method of Pross *et al.*,[16] 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, transition state variation in the solvolysis of some cyclopentyl *para*-substituted benzenesulfonates in EtOH-H$_2$O, MeOH-H$_2$O and Acetone-H$_2$O mixtures is investigated by applying the extended Grunwald-Winstein equation, the Hammett equation, the potential energy surface model and the quantum mechanical model.

Results and Discussion

Solvent Effects. Rate constants for solvolyses of cyclopentyl tosylate, cyclopentyl benzenesulfonate, cyclopentyl *para*-chlorobenzenesulfonate, and cyclopentyl *para*-nitrobenzenesulfonate in aqueous binary mixtures of acetone, ethanol, and methanol are reported in Table 1. In order to eliminate the dispersion phenomenon due to variation of leaving group in Grunwald-Winstein plots, we tried to correlate log k with Y_{OTs} using k values obtained in this work. The Grunwald-Winstein plots of first-order rate constants for cyclopentyl tosylate with Y_{OTs} (based on 2-adamantyl tosylate) still showed dispersions for cyclopentyl tosylate, cyclopentyl benzenesulfonate, and cyclopentyl *para*-chlorobenzenesulfonate (Figures 1, 2, and 3). However, the plot of first-order rate constants for cyclopentyl para-nitrobenzenesulfonate with Y_{OTs} (based on 2-adamantyl tosylate) showed a little dispersions (Figure 4).

Since cyclopentyl para-substituted benzenesulfonates are neither conjugated systems nor aromatic rings adjacent to the reaction center in the substrate, it can not be explained by phenomenon of the dispersion caused by differential solvation effect on the stabilized reaction center by conjugation with adjacent conjugated system or aromatic rings. Therefore such phenomenon can be explained as dispersion effect caused by other specific solvent effect or a change of reaction mechanisms according to the variation of solvent composition. In order to examine the cause of this dispersion phenomenon, we correlated using extended Grunwald-Winstein equation with the rate data in Table 1. The extended Grunwald-Winstein plots showed good correlations for cyclopentyl benzenesulfonates solvolysis (Figures.

Table 1. Rate constants(k) solvolyses of cyclopentyltosylates in aqueous binary mixtures at 25 °C

v/v%	$k \times 10^4$ sec^{-1}											
	MeOH				EtOH				Acetone			
	p-CH$_3$	H	*p*-Cl	*p*-NO$_2$	p-CH$_3$	H	*p*-Cl	*p*-NO$_2$	p-CH$_3$	H	*p*-Cl	*p*-NO$_2$
100	0.115	0.171	0.407	2.59	0.0325	0.0732	0.128	0.820				
90	0.242	0.388	0.993	4.09	0.103	0.181	0.560	3.68				
80	0.515	0.908	2.26	15.8	0.254	0.430	1.34	10.4	0.0288	0.066	0.202	1.93
70	1.05	1.86	4.62	29.6	0.496	0.865	2.64	20.6	0.112	0.207	0.670	5.72
60	2.20	3.72	9.20	57.6	0.907	1.55	5.04	39.2	0.321	0.526	1.84	15.4
50	4.56	7.51	18.7	108	1.93	3.05	9.52	72.0	0.919	2.06	4.82	37.7
40	9.17	16.0	36.2	207	4.35	7.53	20.0	147	2.48	4.91	12.6	91.7
30	19.3	33.1	70.0	378	12.0	22.8	48.6	310	7.69	18.2	33.0	211
20	36.8	65.6	126	635	32.7	47.9	115	635	21.9	35.8	74.8	442
10	69.1	110	186	944	63.9	112	189	1010	59.3	84.7	148	836
0	101	177	282	1380	101	177	282	1380	101	177	282	1380

Transition-State Variation in the Solvolysis Reaction

Bull. Korean Chem. Soc. 1997, Vol. 18, No. 2   181
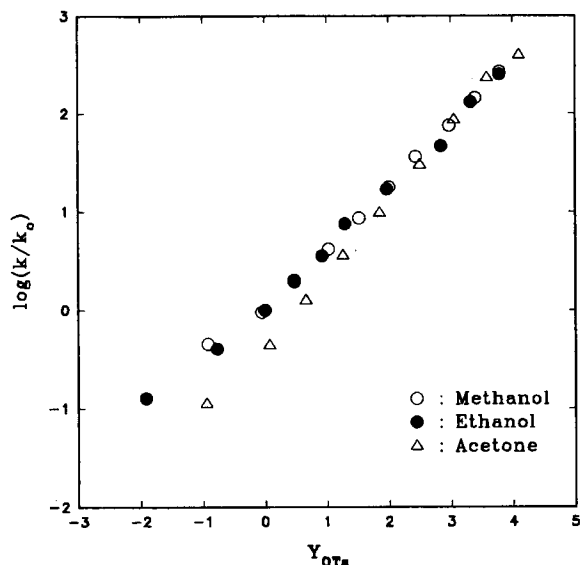

Figure 1. Logarithms of first-order rate constants for solvolyses of cyclopentyl tosylate at 25°C vs. Y_{OTs}.
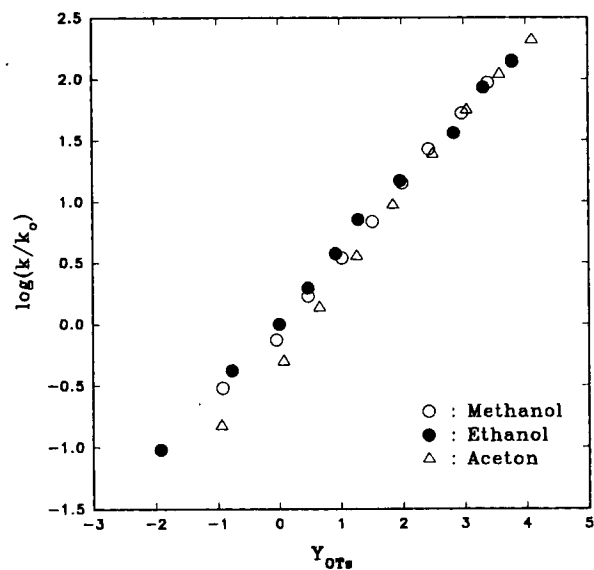

Figure 3. Logarithms of first-order rate constats for solvolyses of cyclopentyl para-chlorobenzenesulfonate at 25 °C vs. Y_{OTs}.
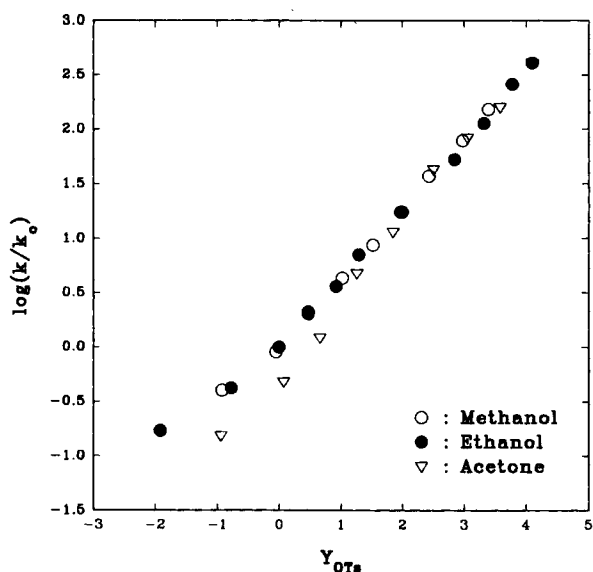

Figure 2. Logarithms of first-order rate constants for solvolyses of cyclopentyl benzenesulfonate at 25 °C vs. Y_{OTs}.
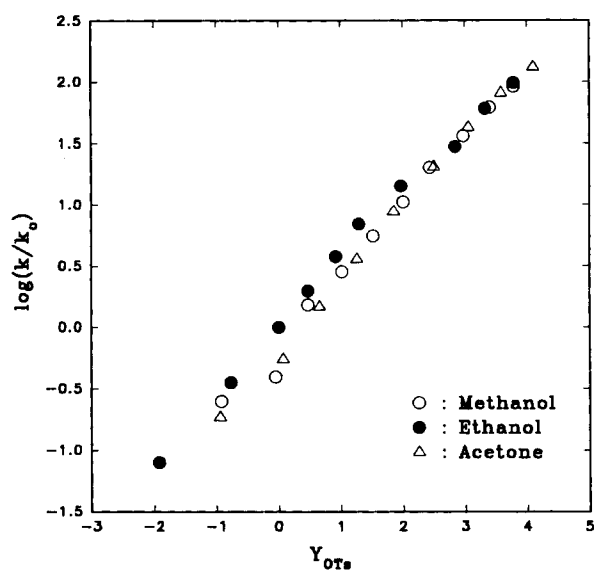

Figure 4. Logarithms of first-order rate constants for solvolyses of cyclopentyl para-nitrobenzenesulfonate at 25 °C vs. Y_{OTs}.

5, 6, 7, and 8).

The nucleophilicity parameter (N) has previously been shown to give considerable improvement when an lN term is added to the original Grunwald-Winstein correlations of the solvolyses reactions. The m value is changed slightly after removal of dispersion, but the associated standard errors are substantially reduced. The correlation coefficient of 0.989 in the absence of the lN term was improved to 0.996 with the lN term for cyclopentyl tosylate solvolysis. Therefore, it shows the importance of solvent nucleophilicity compared to solvent ionizing power for the solvolysis of cyclopentyl tosylate. And also, same linear free energy relationships for the solvolysis of cyclopentyl benzenesulfonate and cyclopentyl para-chlorobenzenesulfonate were improved with good linear correlation coefficients.

This indicates that the solvolysis of cyclopentyl derivatives proceeds by predominantly S_N2 pathway with a more product-like transition state (asymmetric TS, $[N^{\delta+} \cdots C \cdots L^{\delta-}]^+$), where bond breaking is much more progressed than bond formation (vide infra). The S_N2 reaction via product-like transition state appears to cause the dispersions in the present Grunwald-Winstein correlations.

Substituent Effects. The Hammett plot (Figure 9) for the variation of substituents of leaving group shows a good linearity ($r \geq 0.997$) with large positive slopes, $\rho_L = 0.90$-1.7 in various alcohol-water solvents at 25 °C (Table 3). Relatively large ρ_L values suggest that bond breaking tends to be advanced in the transition state of the solvolysis of cyclopentyl benzenesulfonates. If we assume virtually separate ρ values for bond formation ($\rho_L < 0$) and bond breaking ($\rho_L > 0$),[18] positive ρ_L values obtained suggest predom-
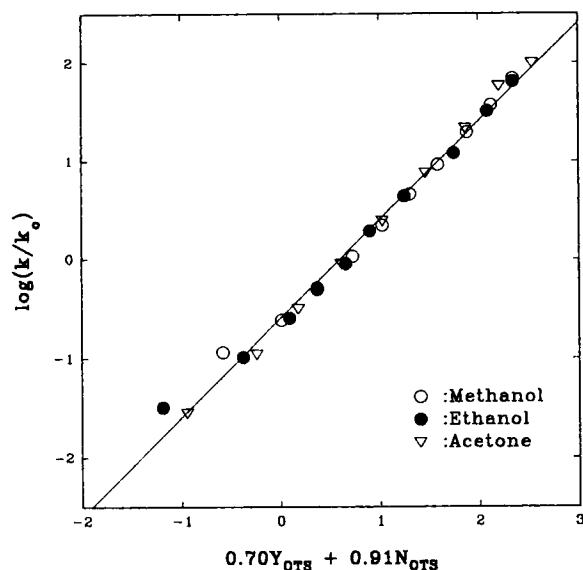
Figure 5. Plot of log(k/k_o) for cyclopentyl tosylate against $0.70Y_{\text{OTS}}+0.91N_{\text{OTS}}$ (r=0.996).
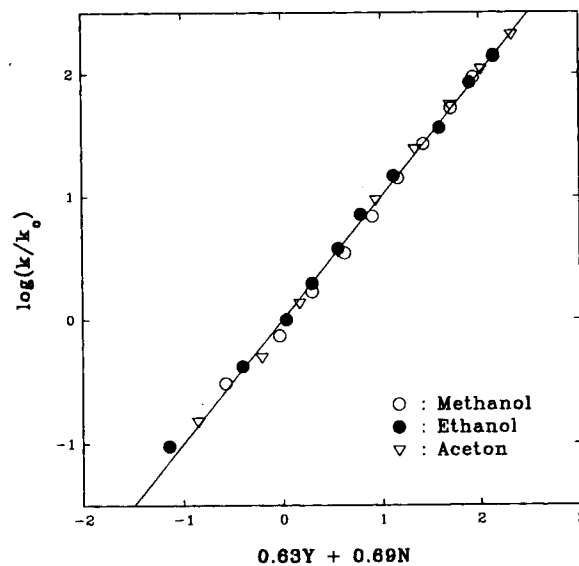

Figure 7. Plot of log (k/k_o) for cyclopentyl *para*-chlorobenzenesulfonate against $0.63Y+0.69N$ (r=0.999).
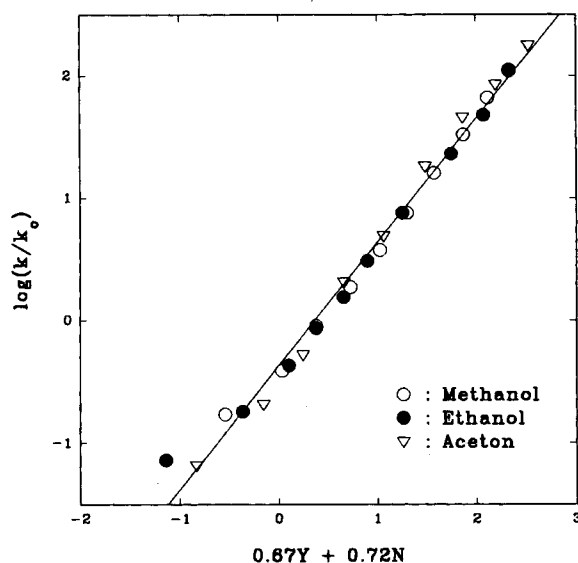

Figure 6. Plot of log (k/k_o) for cyclopentyl benzenesulfonate against $0.67Y+0.72N$ (r=0.994).
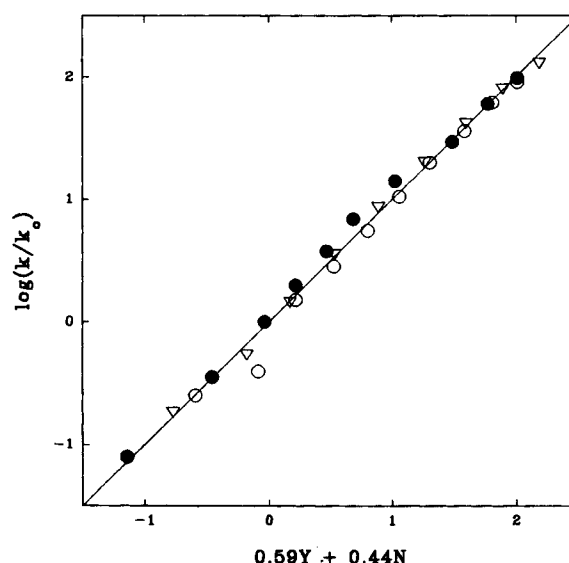

Figure 8. Plot of log (k/k_o) for cyclopentyl *para*-nitro benzenesulfonate against $0.59Y+0.44N$ (r=0.998).

inance of the bond-breaking in the transition state. The relatively loose transition state with a large degree of bond cleavage predicted for the solvolysis of cyclopentyl arenesulfonates in this work is consistent with the relatively small ρ_{XZ} values found for the S_N2 reactions of cycloalkyl derivatives.[19a] It has been shown that the magnitude of ρ_{XZ}, which is defined by Eqs. (5),[20] is inversely proportional to the tightness of the S_N2 transition state (or to the distance between reaction centers on nucleophile (X) and leaving group (Z)), $\gamma_{XZ}{}^{\neq}$, which is the same

$$\log(k_{XZ}/k_{HA}) = \rho_X\,\sigma_X + \rho_Z\,\sigma_Z + \rho_{XZ}\,\sigma_X\,\sigma_Z \qquad (5a)$$

$$\rho_{XZ} = \frac{\partial \rho_Z}{\partial \sigma_X} = \frac{\partial \rho_X}{\partial \sigma_Z} \qquad (5b)$$

as $\gamma_{NL}{}^{\neq}$ Eq. (4); the larger the magnitude of ρ_{XZ}, the tighter

is the transition state, *i.e.*, the shorter is the $\gamma_{XZ}{}^{\neq}$ (or $\gamma_{NL}{}^{\neq}$).[21] Moreover, the ρ_{XZ} value has been found to be a relatively large constant value for the S_N2 reaction at a primary carbon ($\rho_{XZ}\cong 0.3$), whereas it is a smaller constant at a secondary carbon center ($\rho_{XZ}\cong 0.1$), irrespective of the size of the group attached to the reaction center. These constant ρ_{XZ} values suggest that the transition state tightness of the S_N2 reactions is tight or loose *i.e.*, $\gamma_{XZ}{}^{\neq}$ (or $\gamma_{NL}{}^{\neq}$) is short or long, depending on whether the reaction center carbon is primary or secondary, but the transition state tightness varies very little with regard to the group attached to the reaction center.[19] The constancy of the transition state tightness has been confirmed by the experimental ρ_{XZ} values as well as by a high level *ab initio* MO calculations,[22] the difference in the experimental ρ_{XZ} values between the primary and secondary carbon centers of *ca.* 0.2 ($\Delta\rho_{XZ}\cong 0.2$) corresponded to the
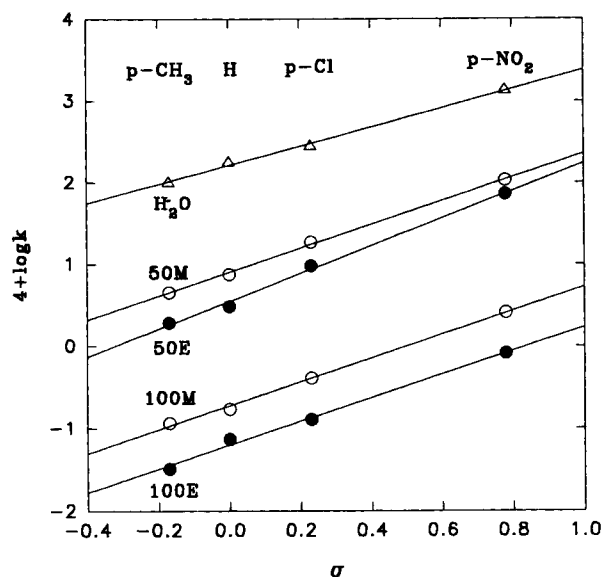
Transition-State Variation in the Solvolysis Reaction

Bull. Korean Chem. Soc. 1997, Vol. 18, No. 2   183

Figure 9. Hanmmet plot for the solvolysis of cyclopentyl benzenesulfonates in alcohol-water at 25 °C.

Table 2. Correlation of the specific rates of solvolysis of cyclopentyl benzenesulfonates at 25 °C

Substituents	m	l	m/l	r
p-CH$_3$	0.70	0.91	0.77	0.996
H	0.67	0.72	0.93	0.994
p-Cl	0.63	0.69	0.91	0.999
p-NO$_2$	0.59	0.44	1.34	0.999

Table 3. Hammett ρ_L values for the solvolysis of cylopentyl para-substituted benzenesulfonates in alcohol-water at 25 °C

Sovlents	100E	100M	50E	50M	H$_2$O
ρ_L	1.74	1.54	1.55	1.26	0.92
r	0.998	1.00	0.998	0.998	0.997

$\Delta\gamma_{xz}^{\neq}$ values of *ca.* 0.1 Å ($\Delta\gamma_{xz}^{\neq} \cong 0.1$ Å).[19]

Since cyclopentyl derivatives used in this work have a secondary carbon reaction center and react by the S_N2 mechanism,[19a] the transition state is expected to have a rather loose structure, as evidence by the large component of S_N2 character (large l values) as well as by the large ρ_L values ($\rho_L \cong 1.0$-1.7). The decrease of ρ_L from pure ethanol to water ($1.7 \rightarrow 0.90$) implies an increasing importance of bond making in the transition state. The transition state is therefore more product-like (more asymmetric transition state, [N$^{\delta+}\cdots$C$\cdots$L$^{\delta-}$]$^{\neq}$), where bond breaking is much more progressed than bond formation in ethanol than water. This is again in line with a relatively constant transition state tightness, *i.e.*, $\gamma_{NL}^{\neq} \cong constant$, since a stronger nucleophile (EtOH) should lead to a shorter $\gamma_{NC}^{\neq}$ with a larger $\gamma_{CL}^{\neq}$ (larger γ_L), whereas a weaker nucleopile (H$_2$O) leads to a longer $\gamma_{NC}^{\neq}$ with a shorter $\gamma_{CL}^{\neq}$, with approximately constant total tightness, *i.e.*, $\gamma_{NL}^{\neq} = \gamma_{CL}^{\neq} + \gamma_{CL}^{\neq} \cong$ constant.

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[12] (Figure 10) in predicting the changes in the structure of the transition
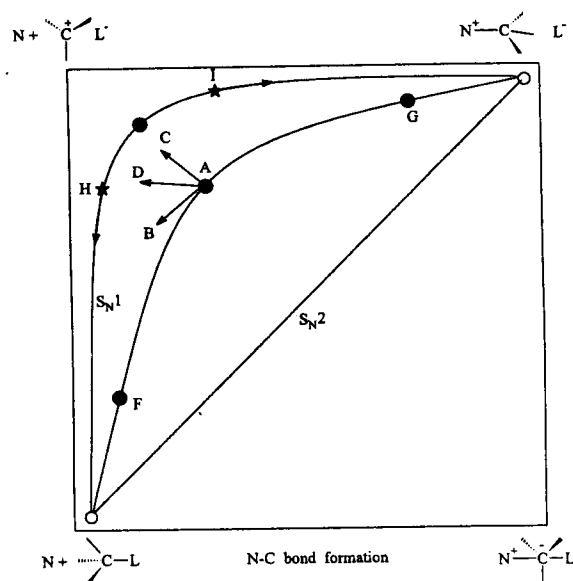

Figure 10. Potential energy surface for nucleophilic substitution of cyclopentyl benzenesulfonates; N is the nucleophile, and energy minima and maxima are repreented by circles and star marks, respectively.

state as a sustituent in the substrate, the nucleophile, or the leaving group is changed. Since it is well established that bond-breaking is more ahead of bond-making in the transition state of nucleophilic cyclopentyl sulfonates substitution, the transition state will lie on the reaction coordinate between S_N1 and S_N2 paths. It can be readily shown that both an early, F, and a late, G, transition states 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_N1 mechanism as untenable; an electron-withdrawing substituent in the leaving group should stabilize the upper left corner which is on the reaction coordinate of the S_N1 path and the first transition state H will move toward reactants corner (the second transition state, I, away from products corner) hence C-L bond cleavage should decrease in contrary to the experimental results; the small ρ_L values obtained for a higher ionizing power solvent suggest a shorter C-L bond in the transition state. The increase in ionizing power of solvent mixture should enhance the leaving ability by assisting the leaving group L to depart more easily causing a slight increase in the length of the C-L bond. On the PES diagram, the increase in the ionizing power stabilizes the upper corner, and this should cause the transition state A to move to, *e.g.* D which is obtained as a vector sum of AB and AC. Thus vector AD will be somewhere in between the vector AB and AC 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-C bonds irrespective of whether perpendicular or parallel effect is stronger. This is consistent with the experimental results since smaller ρ_L values clearly indicated a shorter C-L together with a longer N-C bond (keeping approximately constant $\gamma_{NL}^{\neq}$) as the ionizing power of solvents is increased in water. Thus we conclude that the PES model predicts transition state variation correctly for S_N2 reaction of cy-

Table 4. 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

clopentyl benzenesulfonates.

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.[17,23] The former two are long range whereas the latter two are short range components of intersystem interactions. Pross and Shaik[16] considered only the two, polarization and charge transfer, in their quantum mechanical description of transition state structure. They expressed 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 VB description led Pross and Shaik to a set of simple rules for prediction the structural effects of the three configurations on the reaction complex as presented in Table 4. 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 and sulfonyl system.[15,24] An increase in the nucleophile strength (ethanol) will increase electron donating ability of the nucleophile and hence increase the contribution of the B⁺A⁻ configuration to the transition state. Reference to Table 4 suggests that as a consequence both nucleophile-substrate (N-C) bond formation and substrate-leaving group (C-L) bond should increase. The experimental results obtained in this work support these predictions. It can be seen that the ρ_L value increases in the order of nucleophilicity (Table 3). Increasing electron withdrawing ability in the leaving group has the effect of increasing leaving ability, which will result in lowering the energy of the B⁺A⁻ and BA* configuration 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 4 also suggests a looser C-L bond while the effect on N-C bond length is uncertain since two opposing effects are predicted. The experimental m/l values increase in the order X=p-CH₃<H<p-Cl<p-NO₂, where X is the substituent in the leaving group ring since the bond-breaking is slightly more advanced in the transition state. Therefore, quantum mechanical approach is well established to propose the product like transition state for the solvolysis of cyclopentyl benzenesulfonates.

Conclusions

This study has shown: (i) the magnitudes of m, l and m/l associated with a change of solvent composition indicate that bond-breaking in the transition state is relatively more advanced, (ii) the decrease in ρ_L from pure ethanol to pure water suggests that a more product-like transition state (asymmetric TS, [N^{δ+}···C···L^{δ-}]^{≠}), where bond breaking is much more progressed than bond formation is obtained upon increasing solvent nucleophilicity, (iii) both the PES and QM models correctly predict the transition state variation to a more product-like S_N2 transition state, and (iv) the dispersions in the Grunwald-Winstein correlations in the present studies are caused by the product-like S_N2 transition state structure.

Experimental

Cyclopentyl para-substituted benzenesulfonates were prepared by the previous method.[25] Gr grade methanol, ethanol and acetone (Merck) were used without further purification. Water was used after purification as described in the previous report.[26] Kinetic measurements were done conductometrically using the same apparatus and thermostatic bath as before.[26] Pseudo-first order rate constants were determined by the LSKIN program.[27] Rate constants were accurate to ±3%.

References

1. Winstein, S.; Grunwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 846.
2. Winstein, S.; Grunwald E.; Jones, H. W. *J. Am. Chem. Soc.* **1951**, *73*, 2700.
3. Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2770.
4. Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.
5. Winstein, S.; Fainberg, A. H.; Grunwald, E. *J. Am. Chem. Soc.* **1957**, *79*, 4146.
6. Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*, 1597.
7. Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121.
8. Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
9. Bentley. T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7656.
10. Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1957**, *79*. (a) 1602; (b) 1608.
11. Liu, K.-T.; Sheu, H.-C. *J. Org. Chem.* **1991**, *56*, 3021.
12. More O'Ferrall, R. A. *J. Chem. Soc.(B)* **1970**, 274.
13. Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
14. Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915.
15. Westaway, K. C.; Ali, S. F. *Can. J. Chem.* **1979**, *57*, 1354.
16. Pross, A.; Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.
17. Lee, I.; Song, C. H. *Bull. Korean Chem. Soc.* **1986**, *7*,

186.

18. Johnson, C. D. *The Hammett Equation*; Cambrige Univ. Press: Cambrige, 1973; Chap. 1.
19. (a) Oh, H. K.; Kwon, Y. B.; Cho, I. H.; Lee, I. *J. Chem. Soc. Perkin Trans. 2*, **1994**, 1697. (b) Oh, H. K.; Kwon, Y. B.; Chung, D. S.; Lee, I. *Bull. Korean Chem. Soc.* **1995**, *16*, 827. (c) Lee, I. *Chem. Soc. Rev.* **1995**, *24*, 223.
20. (a) Lee, I. *Chem. Soc. Rev.* **1990**, *19*, 317. (b) Lee, I. *Adv. Phys. Org. Chem.* **1992**, *27*, 57.
21. Lee, I. *J. Phys. Org. Chem.* **1992**, *5*, 736.
22. Lee, I.; Kim, C. K.; Chung, D. S.; L, B. S. *J. Org. Chem.* **1994**, *59*, 4490.
23. (a) Murrell, J. M.; Randic, M.; Williams, D. *J. Proc.*

Roy. Soc. **1965**, *A284*, 566. (b) Fueno, T.; Nagase, S.; Tatsumi, K.; Yamaguchi, K. *Theoret. Chim. Acta* **1972**, *26*, 48. (c) Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1989. (d) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (e) Kollman, P. *Accounts Chem. Res.* **1977**, *10*, 365. (f) Lee, I. *Prog. Chem. and Chem. Industry* **1977**, *17*, 383.
24. Lee, I.; Koo, I. S. *Tetrahedron* **1983**, *39*, 1803.
25. Oh, H, K.; Kwon, Y. B.; Cho, I. H.; Lee, I. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1697.
26. Koo, I. S.; Yang, K.; Kang, K.; Oh, H. K.; Lee, I. *Bull. Korean Chem. Soc.* **1996**, *17*, 520.
27. Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 938.

pH and Micellar Effects on the Quenching of Tris(2,2'-bipyridine)Ruthenium(II) Luminescence by 1-Alkyl-4,4'-bipyridinium: Evidence of Deep Embedment of the Quencher Cations in Sodium Dodecyl Sulfate Micelle

Joon Woo Park* and Yu Na Kim

*Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea*
Received October 28, 1996

The effects of pH and sodium dodecyl sulfate (SDS) micelle on the quenching of Ru(bpy)₃²⁺ luminescnce by N-alkyl-4,4'-bipyridinium ions (RBPY⁺: R=methyl, octyl, dodecyl, benzyl) were investigated. In the absence of SDS, the quenching rate at pH 2 is similar to that of the corresponding methylalkyl viologens and much greater than that in pH 8 solution due to greater reducibility of the protonated form of RBPY⁺ (HRBPY²⁺). The quenching rate at pH 2 is strongly enhanced by the presence of SDS, while that at basic pH is greatly retarded. These observations are explained by deep embedment of RBPY⁺ into the hydrophobic hydrocarbon region of the micelle, whereas Ru(bpy)₃²⁺ and HRBPY²⁺ locate in the Stern layer of the micelle.

Introduction

The electron transfer quenching of luminescence from tris (α,α'-diimine)ruthenium(II) complexes by viologens has been extensively investigated in relation to the development of light to chemical energy conversion schemes[1-9] and photosensitized reductive transformation of organic compounds[10,11] where viologens behave as electron mediators. The rate of the quenching reactions is greatly enhanced by the presence of anionic micelles such as sodium dodecyl sulfate (SDS), largely due to condensation of the electron donor and acceptor pairs in the potential field of the anionic microparticles by electrostatic interaction.[3-9] However, different degree of embedment of viologens into micellar interface depending on the alkyl chain length also influences the surface diffusion of the viologens in micelles and thus the quenching rate.[4,6,7]

Basic Form (RBPY⁺)   Acidic Form (HRBPY²⁺)

1-alkyl-4,4'-bipyridinium ions (RBPY⁺) undergo the following acid-base equilibrium. The acidic form (HRBPY²⁺) has structural similarity to viologens, while the basic form is a substituted pyridinium ion which can be considered as an analog of coenzyme NAD⁺.[12] Because of these interesting characteristics, the pH-dependent electrochemical[13-16] and spectroscopic[14,15,17] behaviors of the compounds as well as the ability of the compounds as electron mediators in redox reactions in homogeneous media have been investigated.[18-20] An nmr study indicated that the bipyridine moiety of RBPY⁺ intercalates between the hydrocarbon chains of the SDS micelle.[21] In this paper, we have studied the emission quenching of Ru(bpy)₃²⁺ by various RBPY⁺ in acidic and basic solutions. The opposite effect of SDS on the quenching reaction rate depending on pH is discussed in terms of difference of the locations of HRBPY²⁺ and RBPY⁺ in the micelle.
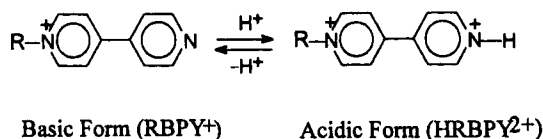
Experimental Section

Sodium dodecyl sulfate was obtained from Fluka and was purified by recrystallization from ethyl alcohol after washing with diethyl ether. Chloride salts of 1-alkyl-4,4'-bi-