Reactivity–Selectivity Correlations. 4. [1] The α Effect in S_N2 Reactions at sp³ Carbon. The Reactions of Hydrogen Peroxide Anion with Methyl Phenyl Sulfates

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Abstract: A kinetic study is reported of the reaction of substituted phenyl methyl sulfates with hydrogen peroxide and methoxide ion in methanol solvent at 25 °C. Dissection of the rate data for the $H_2O_2/MeONa$ system allows the specific coefficients k_{HOO^-} and k_{MeO^-} to be evaluated. Hydroperoxide anion is found to be more reactive than methoxide ion (k_{HOO^-}/k_{MeO^-} varies from 6 to 11 depending on the substrate), indicating than an α effect is operating for this nucleophilic attack at saturated carbon. This is in agreement with earlier results on the enhanced reactivity of hydrazine relative to glycine ethyl ester. The results further show that the Hammett ρ value for the α nucleophiles is smaller than for the normal nucleophiles; however an inverse order is found for the respective Brønsted β values. Analysis of these contrasting relationships in terms of reaction coordinate diagrams leads to the conclusion that the ordinary two-dimensional reaction coordinate is not applicable to the α nucleophiles and that significant anti-Hammond effects arise in these cases. The shift in the transition state perpendicular to the diagonal is discussed in terms of destabilization of the α nucleophile or via a tight transition-state structure as previously suggested for transmethylation. It is concluded that the Hammett ρ value is a valid criterion of the reactivity–selectivity principle (RSP) for the normal nucleophiles which conform to the two-dimensional representation but not for the α nucleophiles. This leads to a limitation on the applicability of the RSP as a measure of transition-state structure.

In this paper we examine two reactivity relationships which are currently under critical discussion, namely, the reactivity–selectivity principle (RSP) and the α effect of certain nucleophiles. The system under study enables one to place these factors in juxtaposition for the first time. Limitations on the applicability of certain criteria pertaining to these relationships have thus come to light.

The reactivity–selectivity principle which had generally been accepted as a guiding principle of chemical behavior has come under increasing critical attention.[3-5] The most recent review[5] of the topic is thus subtitled "fact or fiction". It is possible, however, that many of the so-called "failures" of the RSP could be attributed to faulty experimental design. For example, in order for the inverse relationship between reactivity and selectivity to be observed, it is essential that the reaction series being investigated involves no mechanistic changeover. Equally important is constancy of solvent and steric effects along the reaction series. One system that appears to meet these demanding criteria is the reaction of aryl methyl sulfates with nucleophiles, eq 1.[6,7]
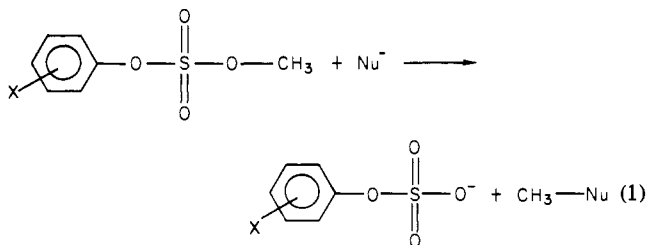
The results of kinetic spectrophotometric studies of this system have demonstrated that nucleophilic displacement occurs exclusively on the methyl carbon as shown in eq 1. A classical Hammett treatment of the reactions of oxygen nucleophiles with a series

of aryl-substituted sulfates gave ρ values (a measure of selectivity)[8] of 1.39, 0.92, and 0.74 for the reactions of MeOH, MeO⁻, and PhO⁻.[6] This order of selectivity is the reverse of the reactivities of the nucleophiles, as measured by their specific rate constants, and thus the RSP is shown to operate in this system.

Having established the applicability of the RSP in this case, it was decided to investigate the enhanced reactivity of the so-called α nucleophiles[9] when attacking an sp³-hybridized carbon. There are widely varying reports in the literature concerning such systems. Several studies have even suggested that nucleophilic attack at sp³ carbon will exhibit no α effect.[10-14]

The reactions of the substituted aryl methyl sulfates with the α nucleophile hydrazine and the normal nucleophile glycine ethyl ester of comparable pK_a were investigated,[2] and a small α effect, $k_{H_2NNH_2}/k_{EtOCOCH_2NH_2}$ varying between 3 and 5, was measured. The observation was made that the α effect increased as the nucleofugicity of the leaving group decreased. This kind of result had not been reported previously.

In an attempt to corroborate these results, it was decided to use the α nucleophile HO_2^-. Many studies of the α effect have shown the hydroperoxide anion to be the most effective α nucleophile; indeed, Heaton[15] in a theoretical treatment of the phenomenon considered it to possess all of the characteristics leading to α nucleophilicity. However, recently Wolfe and co-workers[16] in a theoretical treatment of the gas-phase S_N2 reaction found a remarkable correlation between the enthalpy change and the intrinsic barriers to reaction calculated on the basis of Marcus theory.[17] An intriguing aspect of this work was that HOO^- followed the same correlation as other nucleophiles, suggesting the nonexistence of the α effect in the gas phase. This calls for a reexamination of the origin of the α effect.

A number of suggestions have been put forth to account for the often observed rate enhancement in reactions of α nucleophiles, particularly at sp² and sp carbon centers. The explanations usually

(1) For part 3 in this series see ref 2. This is also part 14 in the series "Bond Scission in Sulfur Compounds".
(2) Buncel, E.; Chuaqui, C.; Wilson, H. *J. Org. Chem.* **1980**, *45*, 3621.
(3) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.
(4) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 25.
(5) Johnson, C. D. *Tetrahedron* **1980**, *36*, 1461.
(6) Buncel, E.; Chuaqui, C. *J. Org. Chem.* **1980**, *45*, 2825.
(7) (a) Buncel, E.; Chuaqui, C.; Lynn, K. R.; Raoult, A. *Bioorg. Chem.* **1978**, *7*, 1. (b) Buncel, E.; Raoult, A.; Wiltshire, J. F. *J. Am. Chem. Soc.* **1973**, *95*, 799. (c) Buncel, E.; Raoult, A.; Wiltshire, J. F. *J. Chem. Educ.* **1974**, *51*, 814. (d) Buncel, E.; Chuaqui, C.; Forsythe, P.; Mahoney, S.; Raoult, A.; Wiltshire, J. F. *J. Chem. Soc., Perkin Trans. 2* **1975**, 478.

(8) McLennan, D. J. *Tetrahedron* **1978**, *34*, 2331.
(9) Edwards, J. O.; Pearson, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 16.
(10) McIsaacs, J. E., Jr.; Subbaraman, L. R.; Subbaraman, J.; Mulhausen, H. A.; Behrman, E. J. *J. Org. Chem.* **1972**, *37*, 1037.
(11) Aubort, J. D.; Hudson, R. F. *Chem. Commun.* **1970**, 1378.
(12) Zoltewicz, J. A.; Deady, L. W. *J. Am. Chem. Soc.* **1972**, *94*, 2765.
(13) Gregory, M. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1967**, *89*, 4400.
(14) Oae, S.; Kadoma, Y.; Yano, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1110.
(15) Heaton, M. M. *J. Am. Chem. Soc.* **1978**, *100*, 2004.
(16) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7694. We acknowledge a preview of this manuscript.
(17) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

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Table I. Kinetic Data for Reactions of Aryl Methyl Sulfates with HOOH/MeONa in Methanol at 25 °C Obtained on Varying [MeO⁻] in Case of m-NPMS (Two Sets of [HOOH] Values) and Varying [HOOH] in Case of p-BPMS, PMS, and p-MPMS (Constant [MeO⁻])[a]

substituent (substrate)	$10^3 \cdot [HOOH]_0$, M	$10^3 \cdot [MeO^-]$, M	$10^4 \cdot k_\psi$, s⁻¹
m-NO₂ (m-NPMS)	1.38	0.84	6.07
		1.34	7.68
		1.67	9.06
		2.00	10.9
	5.70	3.90	25.6
		4.55	28.2
		6.50	38.9
		7.15	46.1
		7.75	50.7
		10.40	61.0
		11.70	68.5
		13.01	75.0
	0	13.01	63.3
p-Br (p-BPMS)	0	25.8	45.4
	1.43		48.0
	2.85		50.4
	4.28		52.8
	5.70		54.3
	7.13		58.0
	8.55		60.9
H (PMS)	0	25.8	23.1
	1.43		25.2
	2.85		27.4
	3.40		28.7
	4.28		29.8
	4.80		30.5
	5.70		32.1
Me (p-MPMS)	0	25.8	19.2
	1.43		22.0
	2.00		22.1
	2.85		23.4
	3.40		24.0
	4.28		24.9
	4.80		25.7
	5.70		27.1

[a] For m-NPMS the procedure used allowed direct comparison with p-NPMS.[26] The second method was chosen for the other substrates because it resulted in greater variation in k_ψ.

consider one or more of the following factors:[18-24] (a) destabilization of the ground state of the α nucleophile; (b) stabilization of the transition state; (c) stabilization of the products; (d) solvation effects. The relative importance of these factors has remained undetermined. It appeared that the present work would provide further experimental evidence and hence contribute to our understanding of this problem.

Results

Reaction of the series of substituted phenyl methyl sulfates[25] with hydrogen peroxide and sodium methoxide in methanol solution was studied under pseudo-first-order conditions using a spectrophotometric method. The results obtained are presented in Table I.

Our previous studies have established that the aryl methyl sulfates react with a variety of nucleophiles according to eq 1.

(18) Fina, N. J.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, 5, 1.
(19) Gregov, A. P.; Veselov, V. Y. *Usp. Khim.* **1978**, 47, 1200.
(20) Bruice, T. C.; Donzel, A.; Huffman, R. W.; Butler, A. *J. Am. Chem. Soc.* **1967**, 89, 2106.
(21) Kice, J. L.; Mullen, L. F. *J. Am. Chem. Soc.* **1976**, 98, 4259.
(22) Dessolin, M.; Laloi-Diard, M.; Vilkas, M. *Tetrahedron Lett.* **1974**, 2405.
(23) Guillot-Edelheit, G.; Laloi-Diard, M.; Eisenstein, O. *Tetrahedron* **1978**, 34, 523.
(24) Aubort, J. D.; Hudson, R. F. *Chem. Commun.* **1970**, 937, 938.
(25) The following notation is adopted for brevity: p-NPMS for p-nitrophenyl methyl sulfate; m-NPMS for m-nitrophenyl methyl sulfate; p-BPMS for p-bromophenyl methyl sulfate; p-MPMS for p-methylphenyl methyl sulfate; PMS for phenyl methyl sulfate.
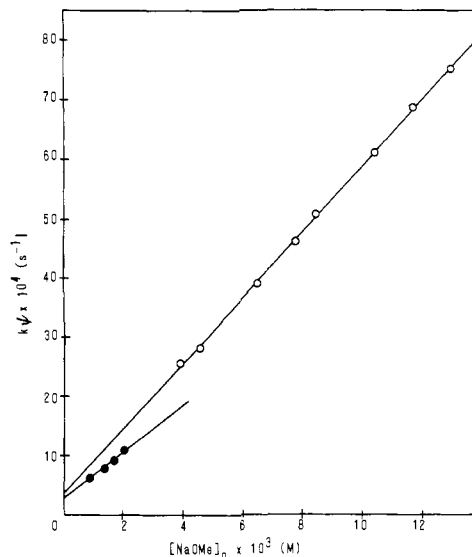

Figure 1. Dependence of pseudo-first-order rate constants for reaction of methyl m-nitrophenyl sulfate with HOOH/MeONa on [HOOH]₀ and [MeONa]₀, in methanol at 25 °C: full circles, [HOOH]₀ = 1.38 × 10⁻³ M; open circles, [HOOH]₀ = 5.70 × 10⁻³ M.

Table II. Rate Constants for Hydroperoxide and Methoxide Anions in Methanol at 25 °C and Values of the α Effect for the Series of Aryl Methyl Sulfates

	k_{HOO^-},[a] M⁻¹ s⁻¹	k_{MeO^-},[b] M⁻¹ s⁻¹	k_{HOO^-}/k_{MeO^-}[c]	$k_{H_2NNH_2}/k_{gly\ ester}$[d]
p-NO₂ (p-NPMS)	4.6	0.513	8.8	3.00
m-NO₂ (m-NPMS)	2.6	0.459	5.7	3.11
p-Br (p-BPMS)	1.3	0.165	7.9	4.29
H (PMS)	1.0	0.091	11.0	5.21
p-Me (p-MPMS)	0.72	0.073	9.9	5.01

[a] Derived from data in Table I using kinetic analysis of ref 26 which also gives complete data for p-NPMS, as well as the uncertainty in the value of k_{HOO^-} associated with measurement of K for eq 3. [b] Data from ref 6. [c] Error limit is ca. 10%. [d] Data from ref 2.

In the present system the observed pseudo-first-order constants are governed by the relationship in eq 2. k_S is the solvolytic rate

$$k_\psi = k_S + k_{MeO^-} [MeO^-]_e + k_{HOO^-}[HOO^-]_e \qquad (2)$$

constant, k_{MeO^-} and k_{HOO^-} are the specific rate constants for the two nucleophiles, and the concentration terms [MeO⁻]ₑ and [HOO⁻]ₑ are the equilibrium values established via eq 3.

$$HOOH + MeO^- \rightleftarrows HOO^- + MeOH \qquad (3)$$

Using the kinetic data for the reaction of p-NPMS with HOOH/CH₃ONa/CH₃OH, the value of K for the equilibrium (3) was evaluated as 9 ± 3 M⁻¹ by means of an iterative procedure.[26] Data recorded in Table I for m-NPMS and illustrated in Figure 1 show striking similarity to those previously observed for p-NPMS.[26] Application of the slope/intercept procedure[26] gave a value of K in close agreement with the mean value obtained in the case of p-NPMS.

It is possible to treat the data for the other substrates (Table I) in terms of eq 4.[27] The slope of a plot of $(k_\psi - k_S)/[HOO^-]_e$

$$\frac{k_\psi - k_S}{[HOO^-]_e} = k_{HOO^-} + \frac{k_{MeO^-}}{K} \frac{1}{[HOOH]_e} \qquad (4)$$

vs. $1/[HOOH]_e$ gives the ratio k_{MeO^-}/K. Using a K value of 9

(26) Buncel, E.; Chuaqui, C.; Wilson, H. *Int. J. Chem. Kinet.*, in press.
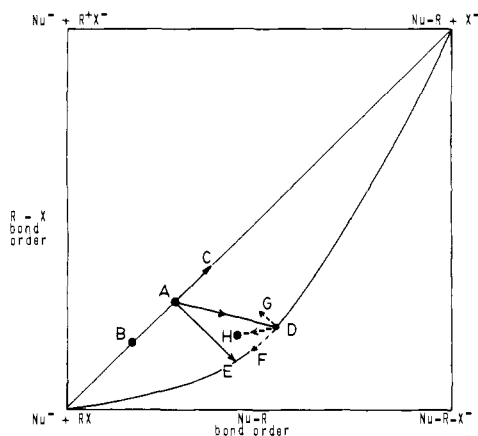(27) Bunnett, J. F.; Retallick, L. A. *J. Am. Chem. Soc.* **1967**, 89, 423.

Figure 2. Schematic reaction coordinate diagram for S_N2 process involving normal and α nucleophiles illustrating transition-state movement along and perpendicular to the diagonal.

M^{-1} resulted in values of k_{MeO^-} which agreed within experimental error with those obtained directly by using MeO^- as the nucleophile.[6] This agreement reinforced the choice of K value as 9 M^{-1}.

The values of the specific rate constants for the hydrogen peroxide anion, k_{HOO^-}, for p-BPMS, p-MPMS, and PMS were then obtained from intercepts of the plots of $(k_\psi - k_S)/[HOO^-]_e$ vs. $1/[HOOH]_e$. The rate constants for p-NPMS and m-NPMS were determined by the slope/intercept procedure.[26] The derived values of k_{HOO^-} are given in Table II, together with the previously determined k_{MeO^-} values. The rate constant ratio k_{HOO^-}/k_{MeO^-} provides a measure of the α effect and the values obtained (Table II) are listed alongside those for hydrazine[2] for comparison.

Discussion

The results given in Table II show that reaction of the methyl phenyl sulfates with hydrogen peroxide anion in methanol solvent is subject to a rate enhancement in comparison with methoxide ion. Such a rate enhancement has been considered as indicative of the α effect. Since HO_2^- is a somewhat weaker base in methanol than CH_3O^-, correction for this pK_a difference would lead to an even larger value of the α effect. Thus the present results, when coupled with our previous work on hydrazine[2] (Table II), lend strong evidence for the existence of an α effect in this system. This is significant in view of the controversy in the literature (vide supra) as to whether reaction at sp^3 carbon does, or does not, exhibit the α effect.

In our previous paper[2] we showed that further insight into the origin of the effect could be gleaned through consideration of three-dimensional potential energy surface diagrams[28-32] rather than the two-dimensional diagrams typically used in discussions of S_N2 displacement processes. This is continued in the present study (Figure 2) in order to enable us to consider transition state movement in a direction perpendicular to the reaction coordinate ("anti-Hammond" effects), as well as along (parallel to) the reaction coordinate. Anti-Hammond effects arise when intermediates on alternative routes from reactants to products exert perpendicular (antiparallel) effects on the transition state. The magnitudes of these effects are directly related to the stabilities of the intermediates involved. Since in the present system these species are CH_3^+ and the hypothetical Doering–Zeiss pentacoordinate intermediate[33] (top left and bottom right corners, respectively, in Figure 2), their inclusion could perhaps be regarded as superfluous. However, even if these intermediates are of high
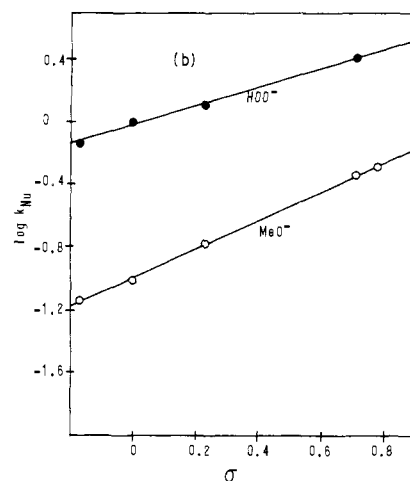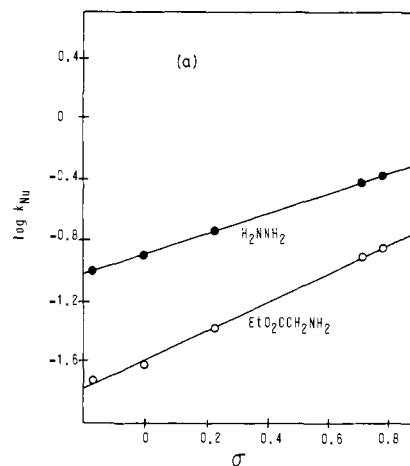
(28) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, *274*.
(29) Winey, D. A. Thornton, E. R. *J. Am. Chem. Soc.* **1975**, *97*, 3102; Thornton, E. K.; Thornton, E. R. "Transition States of Biochemical Processes"; Gandour, R. D.; Schowen, R. L.; Eds.; Plenum Press: New York, 1978.
(30) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288. Knier, B. L.; Jencks, W. P. *Ibid.* **1980**, *102*, 6789.
(31) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295.
(32) Buncel, E.; Wilson, H. *J. Chem. Educ.* **1980**, *57*, 629.
(33) Doering, W. E.; Zeiss, H. H.; *J. Am. Chem. Soc.* **1953**, *75*, 4733.

Figure 3. Hammett log k_{Nu} vs. σ plots for reactions of nucleophiles with substituted phenyl methyl sulfates: (a) glycine ethyl ester vs. hydrazine; (b) methoxide vs. hydroperoxide anion.

energy, the potential energy surface and transition-state structure could still be influenced by them. In fact, it is shown that analysis of the system in terms of the standard two-dimensional diagram leads to inconsistencies, whereas the three-dimensional approach provides a self-consistent explanation of the results.

Interpretation of ρ and β via Reaction Coordinate Diagrams. We consider first a possible explanation of the results on the basis of the diagonal in Figure 2, which is equivalent to the two-dimensional approach. Let A correspond to the position of the transition state for a normal nucleophile, then what would be the effect of changing to a more reactive nucleophile? According to the Leffler–Hammond postulate,[34,35] the transition state for the more reactive nucleophile would come earlier, i.e., a movement from A to B, corresponding to a lower Nu–R bond order and a greater R–X bond order. It should then follow that the smaller Nu–R bond order would be reflected in a smaller value of the Brønsted β coefficient in the log k vs. pK_a (nucleophile) plot. On the other hand, with a greater R–X bond order there should be less charge development on the leaving group, which would manifest itself in a lower Hammett ρ value for substitution on the phenyl moiety.

As shown by the Hammett plot in Figure 3a, the data for reaction of the methyl phenyl sulfates with hydrazine as the α nucleophile do indeed yield a lower ρ value (0.70) compared to the normal nucleophile glycine ethyl ester (1.00). A similar relationship is found in the corresponding plots for HO_2^- and MeO^- (Figure 3b) which give ρ values of 0.61 and 0.92, respectively.

(34) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.
(35) Leffler, J. E. *Science (Washington, D.C.)* **1953**, *117*, 340. Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions" Wiley: New York, 1963; p 162.

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In Figure 3b the point for *p*-NPMS has been omitted as this would show an unreasonably large positive deviation from the plot when using the normal σ value for *p*-NO$_2$.[36] Use of σ^- for *p*-NO$_2$ in the HO$_2^-$ reaction brings the point on line but it is not clear why a σ^- value should be operative in this system. Possibly this highly reactive substrate is associated with an unusually large uncertainty in measurement compared to the hydrazine reaction where rate constants can be obtained more directly.[37] A similar deviation was observed previously for *p*-NPMS with the highly reactive phenoxide anion.[6]

The decrease in ρ on going to the α nucleophiles would be in accord with movement of the transition state along the diagonal toward the reactant (A → B) in the two-dimensional representation. However, consideration of Brønsted β values brings this interpretation into question. For the reaction of *p*-NPMS with the normal nucleophiles the Brønsted β value may be obtained from eq 5,[38] where ΔpK_a is the difference in the pK_a values of the

$$\beta_1 = \frac{\log k_{MeO^-} - \log k_{gly\,ester}}{\Delta pK_a} \tag{5}$$

two nucleophiles. Similarly, the kinetic data for hydroperoxide anion and hydrazine[2] yield the Brønsted β value for these α nucleophiles according to eq 6.[38] One hence obtains the values

$$\beta_2 = \frac{\log k_{HOO^-} - \log k_{H_2NNH_2}}{\Delta pK_a} \tag{6}$$

$\beta_1 = 0.07_5$ and $\beta_2 = 0.16$, i.e., an appreciably larger β value for the α nucleophiles. Comparable results are obtained on calculating β values for the other methyl aryl sulfates ($\beta_1 = 0.075-0.080$, $\beta_2 = 0.13-0.14$).

The higher β values obtained for the α nucleophiles indicate a greater extent of bond formation (greater Nu–R bond order) compared to the normal nucleophile. This, however, is contrary to what would be expected if change from normal to the α nucleophile caused movement of the transition state from A to B along the diagonal in Figure 2, as indicated above on the basis of consideration of ρ values.

Reaction Coordinates for α Nucleophiles. To account for the lower measured ρ value and the higher measured Brønsted β value in the case of the α nucleophile, the transition state must move in a direction with increased R–X and increased Nu–R bond order, i.e., A → D. Thus the transition state for the α nucleophile must lie on a coordinate which deviates from the diagonal. At this point D, Nu–R bond formation has progressed to greater extent than R–X bond cleavage, which is in contrast to the behavior of the normal nucleophiles.

Thus reaction of the α nucleophile is associated with increased R–X and Nu–R bond order, while the normal S$_N$2 reaction would proceed with simultaneous Nu–R bond formation and R–X bond cleavage, i.e., increased Nu–R and decreased R–X bond order. Other S$_N$2 processes have also been discussed in terms of non-simultaneous bond formation and rupture. For substitution in benzylic halides it is considered that the reaction coordinate deviates from the diagonal toward the carbonium ion intermediate, corresponding to decreased R–X and Nu–R bond orders.[30,31] In the case of the Menschutkin reaction, however, differing views

have been expressed whether the transition state should be described as "loose" or "tight"[40-44] corresponding to motion toward the top left or bottom right corners respectively.

The movement of the transition state A → D can be discussed in terms of two vectors, one along the reaction coordinate, A → C, and one perpendicular to it, A → E. The lower value of ρ for the α nucleophile requires that the vector A → C be of smaller magnitude than A → E. The motion A → C could occur as a consequence of relative stabilization of the reactants in the case of the α nucleophile or destabilization of the products. Neither of these possibilities seem tenable as the origin of α nucleophilicity.

The dominant anti-Hammond motion A → E would occur if the potential energy surface perpendicular to the diagonal were tilted so that the top left corner would be raised in energy and the bottom right corner lowered. The former effect would correspond to the α nucleophile being destabilized relative to the normal nucleophile since RX is invariant. The latter effect requires that the potential energy associated with the hypothetical Doering–Zeiss intermediate is lower for the α nucleophile than for a normal nucleophile. This lowering in energy will have the effect of decreasing the slope of the energy surface in the predicted direction. It should be emphasized that the Doering–Zeiss intermediate is invoked merely as a contributor to the transition structure and is not considered as a feasible intermediate.

Previous studies of the origin of the α effect have generally emphasized the special properties associated with the nucleophile. The present work can be interpreted as providing support for that view since destabilization of the nucleophile would account for the motion A → E as noted above. However, our alternative explanation of the origin of the α effect deserves consideration as well, namely, that the α nucleophile causes rate acceleration through formation of a tighter transition state compared to a normal nucleophile. Support for this contention derives in part from Schowen's[45] conclusion (see also ref 43) that transmethylation typically is associated with a tight transition-state structure and that such transition-state compression can be an important source of enzymatic rate acceleration. This alternative interpretation of α nucleophilicity would hence ascribe the origin of the effect to transition-state stabilization.

Schowen's studies[45] have indicated that transition-state compression is more effective for methyl than for other alkyl groups. This in turn suggests that α effects would be larger for methyl derivatives than for higher alkyl analogues. No systematic studies of this kind have as yet been reported to test this hypothesis.

The Influence of the Leaving Group. The tightness of the transition state can in principle be influenced by varying the leaving group. As a consequence, if the α effect is related to this tightness, there should be a correlation between the magnitude of the α effect and the nucleofugicity of the leaving group.

Thus consider the effect on the transition-state D of using a better leaving group, i.e., more stable X$^-$. Motion along the curved coordinate would result in a shift D → F while a perpendicular motion would cause the shift D → G. Irrespective of the relative magnitudes of these two effects, the result would be a loosening of the transition state. One would then predict that a lower α effect would result with the better leaving group.

The data in Table II show that for hydrazine as the α nucleophile, the $k_{H_2NNH_2}/k_{gly\,ester}$ ratio, representing the magnitude of the α effect, shows a decreasing tendency with increasing nucleofugicity of the leaving group. This is in accord with the above prediction. For the more reactive hydroperoxide anion the α effects are larger and with the exception of the para nitro substituent show the same trend. The uncertainty in the value

(36) Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley: New York, 1975; p 66.

(37) Buncel. E.; Chuaqui, C. *Can. J. Chem.* **1975**, *53*, 1275.

(38) Ideally, it would be desirable to evaluate Brønsted β values from studies with a series of normal nucleophiles and, correspondingly, with a series of α nucleophiles. This is extremely difficult to do in practice because of differences in α-effect compounds that affect reactivity and basicity differently. The present method of calculating two-point slope values via eq 5 and 6[39] is used until a much more comprehensive study with several series of α nucleophiles and normal nucleophiles can be undertaken.

(39) Previously[2] eq 7 was used to calculate a "β" value for hydrazine but, as pointed out by a referee of the present paper, this slope (0.20) provides merely another measure of the greater reactivity of the α nucleophile rather than yielding a true Brønsted β parameter. We are grateful to this reviewer for bringing this to our attention.

$$\beta = \frac{\log(k_{H_2NNH_2}/k_{H_2NNH_3^+})}{\Delta pK} \tag{7}$$

(40) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

(41) le Noble, W. J.; Miller, A. R. *J. Org. Chem.* **1979**, *44*, 889.

(42) Kevill, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, *421.*

(43) Abraham, M. H.; Nasehzadeh, A. *J. Chem. Soc., Chem. Commun.* **1981**, *905.*

(44) Harris, J. M.; Paley, M. S.; Prasthofer, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5915.

(45) Gray, C. H.; Coward, J. K.; Schowen, K. B.; Schowen, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 4351.

for p-NO$_2$ was noted previously. Although a firm conclusion cannot be drawn because of this uncertainty, a trend in the predicted direction is indicated by the results in Table II.

Hammett ρ as a Criterion of Selectivity. The Hammett ρ value has frequently been used as a selectivity parameter in discussions of the RSP. In general, higher ρ values are associated with lower reactivities in systems where the RSP is applicable. This is apparently the case for reaction of the methyl phenyl sulfates with the normal nucleophiles.[6]

At first glance the α nucleophiles would appear to follow the RSP as well, since these have associated higher reactivities than the normal nucleophiles but have lower ρ values. However, our discussion has shown that the lower ρ value for the α nucleophile is not brought about by the motion A → B corresponding to lower selectivity but rather by a change in transition-state character dominated by anti-Hammond effects. This obviously brings into question the use of ρ as a selectivity parameter. In principle it would be valid to use ρ for systems which can be represented by two-dimensional diagrams but not for systems in which anti-Hammond effects are believed to be important.

Conclusion Concerning Validity of the RSP. The overall conclusion that may be drawn from this study is that the RSP will hold whenever (and only whenever) "perpendicular" or "anti-Hammond" effects are absent or when they are of subordinate importance. When this is so, any valid measure of transition-state structure should reflect the RSP, but not otherwise. In that sense,

the RSP should be understood as a rule of restricted applicability.

Experimental Section

Materials. The aryl methyl sulfates were prepared according to previously described procedures.[7] The methanol used in the kinetics was spectroquality Fisher reagent grade. Methanolic stock solutions of hydrogen peroxide were prepared from 30% Anachimia reagent grade solution, and the solutions were standardized iodometrically. Solutions of sodium methoxide were obtained by dissolving clean sodium metal in dry methanol and standardized by titration with 0.100 N HCl.

Kinetic Procedures. Kinetic data were obtained spectrophotometrically by using a Bausch and Lomb SP505, a Unicam SP800B, or a Beckman 25 spectrophotometer fitted with thermostated cell blocks. The reactions were followed either by repeated scanning between 220 and 370 nm or at a constant wavelength (λ$_{max}$ for ArOSO$_3^-$). Details of treatment of the kinetic data are given elsewhere.[37]

In a typical run the reaction medium was prepared by addition of aliquots of methanolic solutions of hydrogen peroxide and sodium methoxide and completing volume up to 3.00 mL with methanol. The reaction was started by adding 50 μL of an ethereal 3.60×10^{-3} M stock solution of the substrate to the H$_2$O$_2$/MeONa/MeOH solution contained in the cuvette at constant temperature.

Mechanistic Study of Thermal Z–E Isomerization of Azobenzenes by High-Pressure Kinetics

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Abstract: Pressure effects for the thermal Z–E isomerization of several azobenzenes were measured in various solvents. The activation volumes for 4-(dimethylamino)-4'-nitroazobenzene indicate that the reaction mechanism changes from inversion in n-hexane to rotation in benzene and other relatively polar solvents. The same change in mechanism takes place in the case of 4-anilino-4'-nitroazobenzene when the solvent is changed from benzene to acetone; for 4-methoxy-4'-nitroazobenzene and unsubstituted azobenzene, the reaction mechanism does not change greatly with solvent polarity. The activation enthalpy for azobenzene was redetermined; the result suggests that the original dipole moment is reduced by about 40% in the activation step.

Interest in the mechanism of thermal Z–E isomerizations of azobenzenes has recently revived. The majority of the new studies have been kinetic,[1,3-7] but molecular orbital calculations[1,8] and thermochemical measurements[2] have also been made. The inversion mechanism is accepted for most cases;[7,9] in this pathway, the double bond between the nitrogen atoms remains intact, but one of them undergoes rehybridization from sp^2 to sp in the transition state 1. However, for push–pull substituted azobenzenes
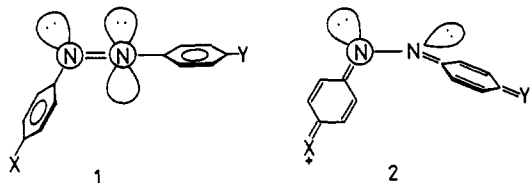
(i.e., which have strong electron-donating and -attracting substituents in the 4- and 4'-positions, respectively) considerable dependence of the rate constant on the solvent polarity was observed; in such instances, a rotation mechanism via the dipolar transition state 2 is postulated.[10] Since 1 and 2 greatly differ in their polarities, the activation volume,[11] obtained from the pressure effects on the rate constant, is expected to provide unequivocal evidence for the operating mechanism. In the inversion mechanism, neither bond formation nor bond scission occurs during activation, and the polarity of the Z isomer may be only

(1) Brown, E. V.; Granneman, G. R. J. Am. Chem. Soc. 1975, 97, 621.
(2) Haberfield, P.; Block, P. M.; Lux, M. S. J. Am. Chem. Soc. 1975, 97, 5804.
(3) Nishimura, N.; Sueyoshi, T.; Yamanaka, H.; Imai, E.; Yamamoto, S.; Hasegawa, S. Bull. Chem. Soc. Jpn. 1976, 49, 1381.
(4) Wolf, E.; Cammenga, H. K. Z. Phys. Chem. (Wiesbaden) 1977, 107, 21.
(5) Nerbonne, J. M.; Weiss, R. G. J. Am. Chem. Soc. 1978, 100, 5953.
(6) Görner, H.; Gruen, H.; Schulte-Frolinde, D. J. Phys. Chem. 1980, 84, 3031.
(7) Asano, T.; Okada, T.; Shinkai, S.; Shigematsu, K.; Kusano, Y.; Manabe, O. J. Am. Chem. Soc. 1981, 103, 5161.
(8) Ljunggren, S.; Wettermark, G. Acta Chem. Scand. 1971, 25, 1599.
(9) Weiss, who has advocated the rotational mechanism,[5] writes in a private communication that he now has results supporting the inversion mechanism.

(10) Wildes, P. D.; Pacifici, J. G.; Irick, G.; Whitten, D. G. J. Am. Chem. Soc. 1971, 93, 2004.
(11) Asano, T.; le Noble, W. J. Chem. Rev. 1978, 78, 407.