Reactivity–Selectivity Correlations. 3. The α Effect at Saturated Carbon. Reactivity Studies of Methyl Phenyl Sulfates with Nucleophiles[1]

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Reaction of various nucleophiles with the series of methyl phenyl sulfates in methanol as solvent has been investigated as a probe of the importance of α effects at saturated carbon. The α nucleophiles hydrazine, hydroxylamine, and methoxyamine show a moderate rate enhancement in their reaction with methyl *p*-nitrophenyl sulfate, as exhibited by a positive deviation on the Brønsted plot of log k_{Nu} vs. pK_a. The results are in accord with a direct relationship between the magnitude of the α effect and the Brønsted β value. Additionally, the α effect as determined by the rate constant ratio $k_{H_2NNH_2}/k_{gly\text{-ester}}$ shows a dependence on the substituent in the phenyl moiety, increasing as the leaving group ability decreases. The trend in the magnitude of the α effect along the series is discussed on the basis of the applicability of the reactivity–selectivity principle (RSP). The Hammond postulate is also found to be applicable with respect to variation in extent of bond formation and bond rupture in the transition state as the leaving group is varied. An alternative approach to the α-effect problem, through consideration of contour diagrams, is presented. It is concluded that transition-state stabilization is an important factor contributing to α nucleophilicity in this system.

The often observed enhanced reactivity of nucleophilic reagents containing an atom bearing one or more unshared pairs of electrons adjacent to the reaction center has become known as the α effect.[3] These abnormally reactive species have also been called supernucleophiles.[4] Studies of this phenomenon have greatly widened in scope in recent years, from kinetic to synthetic and also to biochemical applications. The α effect has been observed for a number of reaction types at centers including carbon, oxygen, sulfur, silicon, and phosphorus. A number of reviews have been published.[5-7]

A continually puzzling aspect of the α-effect phenomenon is that in many systems it is, in fact, not observable. For example, a given α nucleophile may show enhanced reactivity with one substrate but not another. Also, the magnitude of the rate enhancement can vary widely, from factors of 10^3 or more to being essentially nonexistent, relative to the standard of comparison. Quantitatively, the α effect is generally expressed as the enhanced reactivity exceeding prediction as based on Brønsted basicity. It is readily manifested as a positive deviation on a plot of the logarithm of the rate constant vs. pK_a, where K_a refers to the conjugate acid of the nucleophiles, which should preferably be structurally related to the α nucleophiles. A common practice is to express the α effect as simply a rate constant ratio such as k_{HOO^-}/k_{HO^-}, $k_{H_2NNH_2}/k_{NH_3}$, or $k_{H_2NNH_2}/k_{glygly}$ or in the case of hydroxamic acids to use the phenoxide ion of comparable pK_a as the standard. Some caution needs to be applied to direct comparisons of this type since nucleophiles such as HO^- or NH_3 are often less reactive than would be predicted on the basis of pK_a values, possibly as a result of unusually strong solvation in hydroxylic media.

A number of theories have been proposed over the years in attempts to explain the α-effect phenomenon. In general, these have emphasized some single aspect as being

the underlying cause, and no all-embracing theory has so far been advanced. Thus the various theories are directed at one of the following factors as being at the origin of the enhanced rate: (a) ground-state destabilization of the nucleophile; (b) stabilization of the transition state; (c) enhanced thermodynamic stability of reaction products; (d) solvation effects. Within these somewhat arbitrary subdivisions are included specific mechanisms such as intramolecular general acid–base catalysis as well as fundamental theoretical treatments relating to orbital and molecular energetics. The concept of destabilization of the ground state as a result of repulsion between nonbonding electron pairs, which would then be relieved in the transition state through covalent bond formation, was initially proposed by Edwards and Pearson[3] and later modified by Ingold[8] and Hudson.[9] An explanation in terms of charge and frontier orbital control was provided by Klopman,[4] and recently Heaton[10] reported an ab initio quantum mechanical study of the problem. Other pertinent discussions relating to different facets of the classifications a–d can be found in several treatises[11-13] and numerous articles[14-20] (vide infra).

A particularly interesting aspect of the α-effect phenomenon is that for a given α effector there appears to be a strong dependence on hybridization type in nucleophilic attack at carbon centers. The largest α effect has been observed for reaction by hydroperoxide at the sp carbon of benzonitriles, $k_{HOO^-}/k_{HO^-} \approx 10^3-10^4$.[21,22] Nucleophilic

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attack at sp^2 carbon centers is typically associated with α effects of the order of 50–100.[23-25]

The possible importance of α effects in nucleophilic substitution at sp^3 carbon centers appears to be in some doubt, according to the widely varying reports which have appeared in the literature concerning such systems. In the first study with an alkyl halide, Pearson et al.[26] observed a moderate α effect for the reaction of benzyl bromide $(k_{HOO^-}/k_{HO^-} \approx 30$ in 50% aqueous acetone), and a similar effect was observed for α-bromo-p-toluic acid in water $(k_{HOO^-}/k_{HO^-} \approx 10).[27]$ Benzyl bromide was also found to exhibit a rate enhancement of ~ 10 relative to phenoxides of the same basicity in the reaction with amidoximes and N-methylhydroxamic acid in 50% aqueous acetone.[28] What appears to be a very large α effect has been given in an unpublished report[29] of the reaction of methyl iodide with N-chlorobenzenesulfonamide which occurs eightfold faster than the reaction of the much more strongly basic N-methylbenzenesulfonamide; correction for the basicity difference would lead to an α effect of 1800. However, in contrast to the above reports, several studies suggest that nucleophilic attack at an sp^3 carbon may be associated with only a very small α effect or even none at all. A threefold rate enhancement was observed in the reaction of methyl iodide with α diaza heteroaromatics in Me_2SO.[30] Reaction of hydrazine with methyl tosylate does not exhibit the α effect whereas HOO^- does.[31] Also, Bruice and Gregory[32] found no significant positive deviation for the reaction of methyl iodide in aqueous medium with hydrazine, hydroxylamine, and methoxyamine, from the Brønsted plot of a number of primary aliphatic amines, while methylhydrazine showed a twofold positive deviation from the line for secondary amines. Similarly, Oae et al.[33] detected no rate enhancement in the reactions of methyl iodide, isopropyl iodide, allyl iodide, and benzyl iodide in acetonitrile with hydrazine, relative to other amines.

In view of this variance in the literature reports concerning α effects at sp^3 carbon, it appeared desirable to reexamine the problem from another point of view. Thus a new class of methyl derivatives which has been available to us are the mixed alkyl aryl sulfates, and we had found, for example, that methyl p-nitrophenyl sulfate reacts with nucleophiles such as methoxide and halide ions solely at the methyl carbon, with $ArOSO_3^-$ as the leaving group.[34-36] In addition, reaction of a series of substitued aryl methyl sulfates shows interesting behavior in relation to the re-

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Table I. Second-Order Rate Coefficients (k_{Nu}) in Reactions of Nucleophiles with Methyl p-Nitrophenyl Sulfate in Methanol at 25 °C as Function of pK_a of the Conjugate Acids

Nu	pK_a^{NuH}	k_{Nu},[a] $M^{-1} s^{-1}$
Cl^-	1.23	0.011
$H_2NNH_3^+$	3.60	0.025
CH_3ONH_2	5.23	0.096
4-picoline	6.09	0.039
$HONH_2$	6.25	0.278
N_3^-	8.30	0.076
$C_2H_5O_2CCH_2NH_2$	9.20	0.140
H_2NNH_2	9.20	0.419
n-$BuNH_2$	11.60	0.220
CH_3O^-	16.70	0.513

[a] k_{Nu} data determined in the present work were obtained from slopes of plots of k_{obsd} vs. [Nu] in which [Nu] varied over the range 1×10^{-3} to 30×10^{-3} M, depending on the reactivity of Nu. Data for Cl^- and N_3^- are from ref 35, for $H_2NNH_3^+$ and H_2NNH_2 from ref 36, and for CH_3O^- from ref 34.
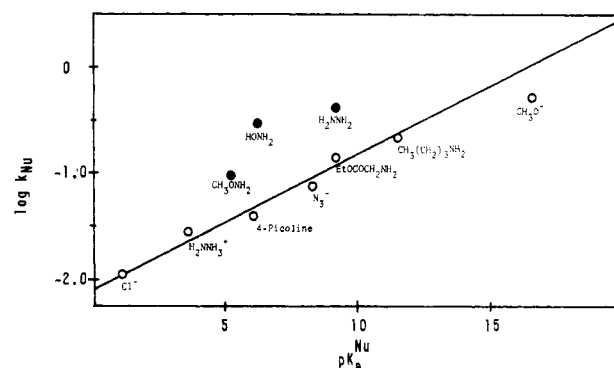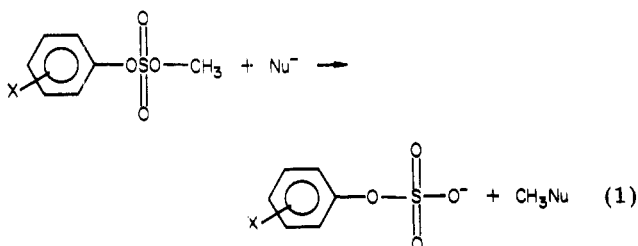

Figure 1. Brønsted plot of log k_{Nu} vs. pK_a for the reaction of nucleophiles with methyl p-nitrophenyl sulfate. The α nucleophiles are shown as solid circles.

activity–selectivity principle (RSP).[2] It thus appeared possible that a study of the α effect with these alkyl aryl sulfates could lead to useful information, especially through variation of the substituent in the aryl moiety. In this way, even though the magnitude of the effect might be small, any trends in the values should be significant. To our knowledge, this kind of study of the α effect as a function of substituent has not yet been reported for nucleophilic attack at sp^3 carbon. The results of our study have, in fact, revealed the anticipated variable α effect for hydrazine as the nucleophile.

Results and Discussion

Reactivity Toward Methyl p-Nitrophenyl Sulfate. The principal aim of this study was to evaluate the reactivities of some "α-effector" nucleophiles, relative to some common nucleophiles, at saturated carbon, as presented in the methyl phenyl sulfates. In our previous work with these mixed sulfates[2,34-36] we had investigated the reactivities of several nucleophiles, which had all been found to react at the methyl carbon center, with the aryl sulfate moiety, $ArOSO_3^-$, as the leaving group (eq 1). The range of nucleophiles has now been extended, with methyl p-nitrophenyl sulfate as the substrate in methanol solvent, to include also the reactivities of several α nucleophiles. In Table I are presented the second-order rate constants and the pertinent pK_a data, while in Figure 1 is shown the Brønsted plot of log k_{Nu} vs. pK_a.

It is evident from Figure 1 that hydrazine, hydroxylamine, and methoxyamine show a significant positive de-

$$\text{X} \cdots \text{—O—}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\displaystyle \|}{\underset{\displaystyle \|}{S}}}}\text{—O}^- + \text{CH}_3\text{Nu} \quad (1)$$

viation on this Brønsted plot; that is, the α effect is exhibited in this reaction. Thus the study has demonstrated that the nucleophilic substitution at saturated carbon in this system is subject to a moderate α effect. It can be noted that this result excludes certain specific explanations that have been proposed for the α effect, such as intramolecular acid–base catalysis[37] or stabilization of the transition state by means of an aromatic-type structure[38] which cannot readily operate in the saturated carbon case.

The slope, β, of the Brønsted plot in Figure 1 is 0.12, which shows that the process is characterized by low sensitivity to the basicity of the nucleophilic species. This kind of result is generally interpreted as implying that the extent of covalent bond formation to the nucleophilic species in the transition state is corresponding small.[39–41] Previous work shows that nucleophilic attack at saturated carbon is uniformly associated with low β values: 0.27 for methyl p-toluenesulfonate[31] and 0.20 for methyl iodide,[42] while the value 0.11 for reaction of substituted pyridines with ethyl p-toluenesulfonate[43] is apparently the lowest found.

A most significant result pertaining to the α effect was found by Dixon and Bruice,[40] since these authors observed a direct relationship between the magnitude of the α effect and the Brønsted β value for a wide-ranging variety of substrates. Thus the α effect, as measured by $k_{\text{H}_2\text{NNH}_2}/k_{\text{glygly}}$, was found to increase from 3 to 50 as β increased from 0.15 to 1.0. The result obtained in the present work, i.e., an α effect of 2–5 for a β value of 0.12, is in excellent agreement with the relationship observed by Bruice and Dixon.[40]

The requirement of a nucleophilic species to participate in the rate-determining step in order for an α effect to be observed is inherently a reasonable one. It was given a theoretical basis in the work of Klopman el al.[4] in their discussion of the phenomenon in terms of "charge-controlled" and "frontier-controlled" processes. The finding by Dixon and Bruice[40] of a direct relationship between β and the magnitude of the effect provides experimental confirmation for this, in light of the usual interpretation of β as a measure of the extent of bond formation to the nucleophilic species in the transition state. The present results corroborate these ideas, since the covalency limitation for nucleophilic attack at saturated carbon places a limit on nucleophilic participation in the transition state, relative to the situation for sp^2 or sp carbon centers.

Leaving Group Dependence of the α Effect. It seemed desirable in the sp^3 carbon case to introduce some variable which could bear upon the magnitude of the α effect. The leaving group potentially presents such a

Table II. Kinetic Data for Reaction of Hydrazine and Glycine Ethyl Ester with the Series of Aryl Methyl Sulfates in Methanol at 25 °C

substituent (substrate)[a]	$k_{\text{H}_2\text{NNH}_2}$[b]	$k_{\text{gly-ester}}$[c]	$k_{\text{H}_2\text{NNH}_2}/k_{\text{gly-ester}}$
p-NO$_2$ (p-NPMS)	0.419	0.140	3.00
m-NO$_2$ (m-NPMS)	0.380	0.122	3.11
p-Br (p-BPMS)	0.180	0.042	4.29
H (PMS)	0.125	0.024	5.21
p-CH$_3$ (p-MPMS)	0.095	0.019	5.01

[a] 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, PMS for phenyl methyl sulfate, p-MPMS for p-methylphenyl methyl sulfate. [b] Second-order rate constants obtained from measurements with solutions containing H$_2$NNH$_2$/H$_2$NNH$_3{}^+$Cl$^-$ by using the method described in ref 36. [c] Second-order rate constants: data obtained as in Table I.

variable for S$_N$2 processes, since one would expect that by causing a leaving group to be poorer, while keeping the nucleophile constant, the degree of participation of the nucleophile in the transition state would be effectively increased. The converse should likewise hold. One can also express these ideas in terms of the Hammond postulate,[44] since as the leaving group ability decreases, a later transition state would result, corresponding to a greater extent of bond formation between the nucleophile and the carbon center, thus leading to a larger α effect.

The study indicated above was thus undertaken, which in practice could be accomplished by varying the substituent on the aryl moiety. The α effect in this series of methyl phenyl sulfates was determined for the hydrazine case from the rates of reaction relative to the standard nucleophile glycine ethyl ester (Table II) which has a comparable pK_a value. The $k_{\text{H}_2\text{NNH}_2}/k_{\text{gly-ester}}$ data in fact show the anticipated trend: that is, an increasing α effect as the leaving group becomes poorer. As noted above, this is interpreted in terms of an increasingly larger interaction between the nucleophile and the sp^3 carbon reaction center in the transition state. Hence these results give further credence to our discussion and confirm that α effects at saturated carbon, albeit small in magnitude, have valid significance.[45]

α Nucleophiles and the Reactivity–Selectivity Principle (RSP). We had previously found that the RSP was applicable to the reactions of this series of aryl methyl sulfates with the oxygen nucleophiles MeOH, MeO$^-$, and PhO$^-$ (eq 1).[2] Thus it was found that log k_{Nu} (i.e., reactivity) increases in the order MeOH, MeO$^-$, PhO$^-$, while the Hammett ρ value (i.e., selectivity) decreases in the same order, so that reactivity bears an inverse relationship to selectivity as required by the RSP. In view of the current controversy concerning the applicability of the RSP,[46–53] it is noteworthy that when the system is designed

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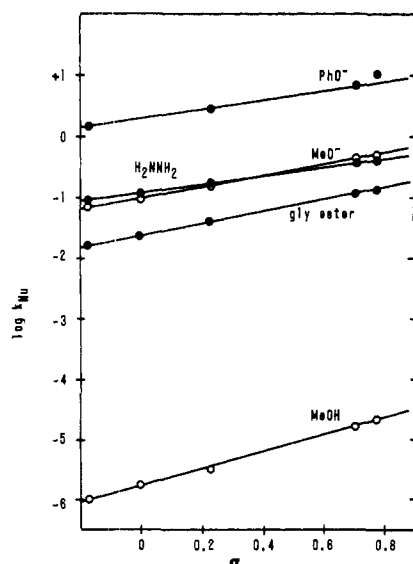(50) D. J. McLennan, *Aust. J. Chem.*, **31**, 1897 (1978).

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Figure 2. Plot of log k_{Nu} vs. σ for the reactions of the series of ring-substituted phenyl methyl sulfates with nucleophiles.

appropriately, that is, when the nature of the transition state is modulated through structural changes introduced at sites remote from the reaction center, and a constancy in mechanism is assured, the RSP is indeed followed.

Having established that the RSP is applicable in this reaction series for a set of common nucleophiles, we found it desirable to test the behavior of α nucleophiles in this regard. Our expectation was that α nucleophiles would not fit into the same pattern as common nucleophiles with regard to adherence to the RSP, since with the former some additional factor would be affecting their reactivity.

In Figure 2 are shown the plots of log k_{Nu} vs. σ for the series of methyl phenyl sulfates reacting with a number of nucleophiles pertinent to this problem. The lines for MeOH ($\rho = 1.39$), MeO$^-$ ($\rho = 0.92$), and PhO$^-$ ($\rho = 0.74$) anchor the system with regard to adherence to the RSP as discussed above.[2] Included also are the newly given data for glycine ethyl ester ($\rho = 1.00$) and for hydrazine ($\rho = 0.70$). The line for glycine ethyl ester fits well into the correlation expected if the RSP is also followed in this case, as with the other nucleophiles, since the reactivity parameter (log k_{Nu}) is intermediate between those for MeOH and MeO$^-$ while the selectivity parameter (ρ) enters in an inverse manner into the correlation. However, quite clearly, the line for hydrazine does not fit the correlation which governs the behavior of the other nucleophiles. It is also interesting that though H$_2$NNH$_2$ is closest in reactivity to MeO$^-$, the former exhibits greater reactivity with the substrates having poor leaving groups (PMS and p-MPMS; see Table II for the abbreviations) while for the substrates with relatively good leaving groups (m-NPMS and p-NPMS) the latter is more reactive, an inversion having occurred. Another point of interest is the smaller ρ value for hydrazine compared to glycine ethyl ester, which is reflected also in the increasing rate constant ratio $k_{H_2NNH_2}/k_{gly-ester}$ on going from p-NPMS to p-MPMS, that is, as the leaving group ability decreases. The observed trend in this rate constant ratio is a further manifestation of the RSP operating in this system; thus differentiation

between the reactivities of H$_2$NNH$_2$ and glycine ethyl ester is greatest with the least reactive substrates.

Analysis of α Effects via Brønsted Slope Parameters. A quantitative expression of the α effect can be derived as follows. With reference to Figure 1 for the reaction of p-NPMS with nucleophiles, one can define the Brønsted parameters β_1 and β_2 according to eq 2 and 3.

$$\beta_1 = \frac{\log (k_{gly-ester}/k_{H_2NNH_3{}^+})}{\Delta pK} \quad (2)$$

$$\beta_2 = \frac{\log (k_{H_2NNH_2}/k_{H_2NNH_3{}^+})}{\Delta pK} \quad (3)$$

Comparison of β_2 and β_1 affords a measure of the α effect in the Brønsted β parameter sense, as hydrazine and glycine ethyl ester have approximately equal pK's while comparison is made with respect to the common nucleophile, H$_2$NNH$_3{}^+$. The resulting values for the case of p-NPMS are $\beta_2 = 0.20$ and $\beta_1 = 0.12$. The latter value is equal to the slope of the overall plot, as expected on inspection of Figure 1.

α Effects and the Hammond Postulate. The observed variation in the α effect indicates that as the nucleophilic participation is increased and the Nu–R bond is tightened, so the bond between R and the leaving group X would become correspondingly looser, and this would occur with the poorer leaving groups. This conclusion follows from the generally accepted requirement of a direct relationship between the extent of bond formation to the nucleophile and the extent of bond rupture to the leaving group in S$_N$2 displacement at saturated carbon. One can also express this in terms of the Hammond postulate, since in the case of the substrates containing leaving groups with the smaller tendency for separation, a larger degree of bond formation between the nucleophile and the central carbon will be required for the rate-determining transition state to be reached, as one proceeds along the reaction coordinate. Thus for the more stable substrates a later transition state will occur, i.e., more bond formation and more bond rupture. Conversely, in the case of the better leaving group, the weaker R–X bond is easier to rupture, and the transition state can be reached with less nucleophilic participation, i.e., less expenditure of energy, so that an earlier transition state will result.

Study of the reactions of hydrazine and of N-methylhydrazine with triarylcarbonium ions has shown that the equilibrium constants for product formation are larger than those for primary amines of comparable pK_a; i.e., the reaction products derived from the α nucleophiles show the greater thermodynamic stability.[24] This result is pertinent to our argument concerning the effect of the leaving group on the magnitude of the α effect. Thus on comparison of the reactions of hydrazine and of glycine ethyl ester, the transition state will be reached later along the reaction coordinates for the less reactive substrates, containing the poorer leaving groups, as has been shown. Hence the difference in the free energies of activation for the normal and the α nucleophiles will be a greater fraction of the difference in the free energies of the products for the case of the poorer leaving group than for that of the better leaving group. Thus the larger α effect which is observed for the substrates with the poorer leaving groups is a further manifestation of the operation of the Hammond postulate as applied to the thermodynamic stability of the products.

Contour Diagrams and the α Effect. Our discussion of the α effect so far has not considered explicitly the possibility that the observed rate enhancement would be

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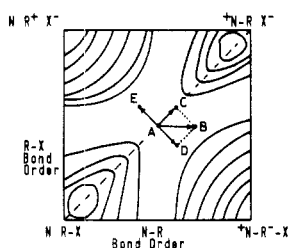
Figure 3. Reaction coordinate–energy contour diagram for S_N2 processes involving normal and α nucleophiles.

caused by stabilization of the transition state. The standard two-dimensional potential energy reaction coordinate representation implied in the discussion of the Hammond postulate, with its consideration of early/late transition states, is limited in scope in this regard. Thus a more general treatment of transition-state variation would allow for the possibility that in the case of α nucleophiles the Nu–R bond order would increase while the R–X bond order would remain unchanged, which contrasts with the previous discussion of a balance in bond formation and rupture.

Another approach to the consideration of transition-state changes with variation of substituents involves the use of virtual three-dimensional energy diagrams[52-57] in which potential energy is represented by contours, as indicated in Figure 3 for a hypothetical S_N2 process. The strength of this approach is that is permits consideration of not only movement of the transition state along the reaction coordinate (e.g., A → C) but also motion perpendicular to the reaction coordinate, i.e., A → E or A → D. The shift A → E would imply a shift toward a transition state with more S_N1 character, as, for example, in the reaction of benzylic derivatives.[52,53] An A → D shift would represent a mixing in of the influence of the hypothetical Doering–Zeiss pentacoordinate reaction intermediate.[58]

In the present system the potential energy surface perpendicular to the reaction coordinate at the saddle point is likely to be steep for the movement A → E as well as for A → D, in the former case due to the energetically unfavorable methyl carbenium ion and in the latter case due to the pentacoordinate carbon limitation.[59] However, as has been emphasized in previous applications of this method, even if such intermediates do not have actual existence, the potential energy surface and the transition state structure could still be influenced through their consideration.

To examine this approach to the α effect in more detail, we consider the situation that with a standard nucleophile the transition state would be along the normal reaction coordinate at point A. However, a change to an α nucleophile would lead to the motion A → B, corresponding to a greater degree of Nu–R bond formation, while the R–X bond order would remain essentially unchanged. The movement A → B can then be resolved into vectors, one along the reaction coordinate, A → C, and the other perpendicular to it, A → D. Moreover, the motion A → C would be favored by stabilizing the reactants, Nu and R–X, or by destabilizing the products, R–Nu$^+$ and X$^-$. Similarly, the motion A → D would be favored by causing the hy-

pothetical intermediates R$^+$X$^-$ and Nu to be destabilized and $^+$Nu–R$^-$–X to be stabilized. Thus, our finding of an α effect suggests that destabilization of the reactant nucleophile is unlikely to be a factor of major importance contributing to enhanced reactivity in this system, since this factor would disfavor the motion A → C along the reaction coordinate.

Considering next the leaving group effect, a poorer leaving group would destabilize $^+$Nu–R + X$^-$ and Nu + R$^+$X$^-$, which would favor the motions A → C and A → D, respectively. However, to the extent that the species $^+$Nu–R$^-$–X would be destabilized by the poorer leaving group, the motion A → D normal to the reaction coordinate could be disfavored.

Conclusions

Our study thus points to transition-state stabilization as a major factor for the enhanced reactivity of α nucleophiles in this system. Destabilization of the reactants is considered to be of lesser importance. This conclusion follows, in part, from our discussion of transition-state behavior as a function of leaving group variation which uses the standard two-dimensional potential energy reaction coordinate representation. In terms of the contour diagram (Figure 3) and the possibility of movement of the transition state perpendicular to the reaction coordinate, the suggestion that the Doering–Zeiss intermediate contributes to the transition-state properties is interpreted as an indication of a very tight transition-state structure rather than the formation of an actual pentacoordinate species.[59] The proposal of a tight S_N2 transition state in transmethylation is in conformity with the recent work of Schowen on such processes.[60]

Our consideration of transition-state stabilization as an important factor contributing to α nucleophilicity in this system is also in accord with the recent ab initio calculations by Heaton[10] and the earlier qualitative discussion by Ingold.[8] Thus it is shown[10] that hydrazine conforms to the main criterion of α nucleophilicity in possessing an antibonding HOMO of inhomogenous polarizability. Donation of these antibonding electrons to the electrophile stabilizes the composite system along the potential energy surface.[10] Our results and the interpretation of Figure 3 are in complete agreement with this view.

Experimental Section

Materials. The aryl methyl sulfates were prepared according to the previously published procedure.[61] Stock solutions of the sulfates were prepared in anhydrous ether and kept at 0 °C, under which conditions they are stable for prolonged periods of time. The methanol used in the kinetics was spectroquality Fisher reagent grade. Solutions of sodium methoxide were obtained by dissolving freshly cut sodium metal in dry methanol and standardized with 0.1 N HCl. The hydrochloride salt of picoline was prepared as a crystalline compound by the action of dry HCl gas on the ethereal solution of the amine. The hydrochloride salts of n-butylamine, hydroxylamine, methoxyamine, and glycine ethyl ester were commercially procured.

Kinetic Procedures. Kinetic data were obtained spectrophotometrically by using a Bausch and Lomb SP 505, a Unicam SP 800B, or a Beckman 25 spectrophotometer fitted with thermostated cell blocks. The reactions were followed either by

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repeated scanning between 220 and 370 nm or at constant wavelength. The detailed procedure follows that previously described for the hydrazinolysis of methyl *p*-nitrophenyl sulfate.[36]

Sulfonyl Radicals. 7.[1] Kinetics and Mechanism of the Thermal Decomposition of α-Phenylalkanesulfonyl Chlorides Proceeding via Ionic Intermediates

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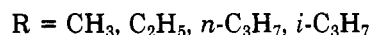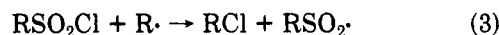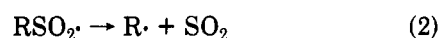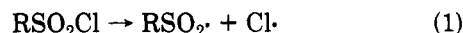
Kinetics and mechanism of the decomposition of α-phenylalkanesulfonyl chlorides [α-toluenesulfonyl chloride, TSC, and α-phenyl-β-(methanesulfonyl)ethanesulfonyl chloride, PMC] were studied. It was found that the rate of decomposition increased with increasing polarity of solvent or addition of LiCl, but the rate was not affected by addition of radical inhibitors. An ionic chain mechanism involving a heterolytic scission of a C–SO₂ bond was proposed for the thermal decomposition of the sulfonyl chlorides. The activation energies for the heterolytic scissions were found to be 33.7 and 27.3 kcal/mol for TSC and PMC, respectively.

The decomposition of alkanesulfonyl chlorides by a homolytic scission of a S–Cl bond has been used as a method for generation of sulfonyl radicals.[2-6] The homolytic scission requires certain reaction conditions such as high temperature,[7] induced by ultraviolet light[3] or γ-radiation,[5] or the addition of radical initiators, like peroxides[3] or copper chlorides.[6,8] The mechanistic study of the decomposition of alkanesulfonyl chloride was first made by Herbrandson et al.[9] By following the optical activity of 2-chlorooctane which was formed from optically active 2-octanesulfonyl chloride, they concluded that the thermal decomposition of the sulfonyl chloride in the absence of solvent, in diphenyl ether, in the presence of ultraviolet light, or in the presence of peroxide proceeds by a free-radical reaction. Furthermore, they suggested the formation of an adduct between the sulfonyl chloride and *N,N*-dimethylformamide solvent, which decomposed ionically. In a more detailed study on the kinetics and mechanism of the thermal decompositions of alkanesulfonyl chlorides in the gas phase, Geiseler and Kuschmiers[7] found that the overall activation energies for the decompositions were in the range of 42–46 kcal/mol. In view of their finding that the values of the activation energies were much less than the bond dissociation energies for the C–S bond (69–74 kcal/mol)[10] or the S–Cl bond (71

kcal/mol),[11] they proposed the radical chain mechanism shown in eq 1–5.

Scheme I

$$RSO_2Cl \rightarrow RSO_2\cdot + Cl\cdot \qquad (1)$$

$$RSO_2\cdot \rightarrow R\cdot + SO_2 \qquad (2)$$

$$RSO_2Cl + R\cdot \rightarrow RCl + RSO_2\cdot \qquad (3)$$

$$RSO_2Cl + Cl\cdot \rightarrow \cdot R'SO_2Cl + HCl \qquad (4)$$

$$\cdot R'SO_2Cl + wall \rightarrow olefin + SO_2 + Cl\cdot \qquad (5)$$

$$R = CH_3, C_2H_5, n\text{-}C_3H_7, i\text{-}C_3H_7$$

The key step in this chain mechanism is step 3 in which the R· radical abstracts a Cl atom from sulfonyl chloride to regenerate a sulfonyl radical. This mechanism (eq 1–3) has been accepted for the decomposition of methanesulfonyl chloride in the liquid phase.[5] The decomposition induced by ultraviolet light or radical initiators can be also explained by this mechanism with the modification that the RSO₂· radical in eq 1 is generated by photodecomposition of sulfonyl chloride or by Cl atom abstraction of radical initiators from sulfonyl chloride.

On the other hand, it is interesting to note that an α-phenyl substituent apparently favors the thermal decomposition of alkanesulfonyl chloride. Indeed, TSC decomposes at 95 °C[12] while methanesulfonyl chloride (MSC) is stable up to 150 °C.[13] Furthermore, the stabilities of the sulfonyl chlorides having an α-phenyl substituent strongly depend on their structures: while TSC is quite stable at room temperature, α-phenylethanesulfonyl chloride (PEC)

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