Equilibration of the Butyl Butenyl Sulfones. Sulfone mixtures were analyzed by a combined GLC–NMR method. The *cis*-1-butenyl isomer is eluted more rapidly on a 6-ft 10% diisodecyl phthalate column at 140 °C than the trans isomer, whose peak overlaps badly with the peak for the 2-butenyl isomers. The amount of *trans*-1-butenyl isomer present was determined from the area of the vinyl hydrogen peak at δ 6.87 related to the total area for vinyl hydrogen atoms. The ratio of *cis*- to *trans*-2-butenyl isomer was determined from the ratio of the areas of the SO_2C-H_2C=C peaks at δ 3.81 and 3.65, respectively.

In a typical equilibration 100 mL of 0.10 M butyl *trans*-1-butenyl sulfone (>99% pure) and 100 mL of 0.10 M potassium *tert*-butoxide, both in *tert*-butyl alcohol solution, were mixed and placed in a 25 °C bath. After 20 h an 80-mL sample was withdrawn and added to 100 mL of standard pH 7 phosphate buffer to which 0.5 mL of 12 M hydrochloric acid had been added. (Earlier experiments had shown that the reaction goes more than 90% to equilibrium in 2 h under these conditions.) Two 100-mL methylene chloride extracts of this solution were combined, washed with saturated sodium chloride, dried over magnesium sulfate, and concentrated to 1–2 mL. The 60-MHz ^{1}H NMR spectrum of the residue at normal amplitude was essentially identical with that of the butyl 2-butenyl sulfone mixture that had been synthesized. The GLC revealed no *cis*-1-butenyl sulfone. The high amplitude 100-MHz NMR showed that 2.3 ± 0.5% *trans*-1-butenyl sulfone was present.

Equilibrium was also approached by starting from 5% trans–95% cis butyl 1-butenyl sulfone and from 82% cis–18% trans butyl 2-butenyl sulfone. In all cases 18 ± 2% *cis*-2-butenyl, 80 ± 2% *trans*-2-butenyl, and 2.1 ± 0.3% *trans*-1-butenyl sulfone were found at equilibrium.

When the *cis*-1-butenyl sulfone was the starting material, about 1.2% of it still seemed to be present after 20 and 95 h. With the other two starting materials no *cis*-1-butenyl sulfone could be detected; 0.5% would have been detectable.

When initial concentrations of 0.13 M sulfone and 0.05 M potassium *tert*-butoxide were used, 1.7 ± 0.3% *trans*-1-butenyl, 18 ± 1% *cis*-2-butenyl, and 80 ± 1% *trans*-2-butenyl sulfone were found at equilibrium. Experiments carried out at 35 °C gave essentially the same results.

***cis*- and *trans*-4-Hexen-2-one.** A 6-ft Carbowax 20M column was used at 70 °C to separate 4-hexen-2-one.[14] For the more rapidly eluted trans isomer: ^{1}H NMR (360 MHz, benzene-d_6) δ 5.46 (m, 1, $CHCH_2CO$), 5.28 (m, 1, CH_2CH), 2.68 (br d, 2, CH_2CO), 1.65 (s, 3, CH_3CO), and 1.50 (br d, 3, CH_3CH). Decoupling experiments confirmed these assignments and gave the following coupling constants: $J_{3,4}$ = 6.9, $J_{3,5}$ = 1.0, $J_{4,5}$ = 15.3, $J_{4,6}$ = 1.6, and $J_{5,6}$ = 6.3 Hz. For the cis isomer: ^{1}H NMR (360/MHz, benzene-d_6) δ 5.59 (m, 1, $CHCH_2CO$), 5.47 (m, 1, CH_3CH), 2.72 (br d, 2, CH_2CO), 1.62 (s, 3, CH_3CO), and 1.37 (br d, 3, CH_3CH). These assignments were confirmed by decoupling which showed the following: $J_{3,4}$ = 6.8, $J_{3,5}$ = 1.5, $J_{4,5}$ = 10.9, $J_{4,6}$ = 1.6, and $J_{5,6}$ = 6.5 Hz.

***trans*-3-Hexen-2-one.** A solution of 11 g of cis–trans 4-hexen-2-one and 10.5 g of triethylamine in 100 mL of *tert*-butyl alcohol was refluxed and analyzed at various times by GLC. After 50 h its content was essentially the same as it had been after 10 h. The remaining solution was fractionally distilled, first at atmospheric pressure and then at reduced pressure. The best fraction contained 9% 4-hexen-2-ones and 91% *trans*-3-hexen-2-one: ^{1}H NMR (60 MHz, $CDCl_3$) δ 6.58 (d of t's, 1, J = 15, J' = 6 Hz, COC=CH), 5.97 (d of t's, 1 J = 15, J' = 1.5 Hz, COCH=C), 2.18 (s, ~3, CH_3CO), 2.15 (~q, ~2, J ~ 7 Hz, CH_3CH_2), and 1.05 (t, 3, J = 7 Hz, CH_3CH_2).

Equilibration of Hexen-2-ones. A mixture of 2 mL of 2.2 M 4-hexen-2-one (6.6% cis and 93.4% trans) and 2 mL of 2.0 M 1,8-diazabicyclo[5.4.0]-7-undecene, both in *tert*-butyl alcohol, was kept at 25 °C. Samples were analyzed by GLC using a 6-ft Carbowax 20M column, where *trans*-3-hexen-2-one has a considerably longer retention time than that of either of the 4-hexen-2-ones.

Samples taken after 11, 11.5, 32, and 50 h showed that 16.6 ± 0.5% *trans*-4-ene, 7.0 ± 0.4% *cis*-4-ene, 76.4 ± 0.6% *trans*-3-ene, and no detectable *cis*-3-ene were present.[24] Starting from trans-3-ene gave 15.5 ± 0.6% *trans*-4-ene, 7.4 ± 0.4% *cis*-4-ene, and 77.0 ± 0.4% *trans*-3-ene after 24–29 h. The reaction went about 90% to equilibrium in 4 h under these conditions.

Registry No. 1, 42817-44-7; 2, 73687-55-5; hydrocinnamaldehyde 2,4-dinitrophenylhydrazone, 73687-56-6; hydrocinnamaldehyde, 104-53-0; butyl *cis*-1-butenyl sulfide, 73687-57-7; butyl *trans*-1-butenyl sulfide, 73687-58-8; butyl *cis*-1-butenyl sulfone, 73687-59-9; butyl *trans*-1-butenyl sulfone, 73687-60-2; butyl *cis*-2-butenyl sulfone, 73687-61-3; butyl *trans*-2-butenyl sulfone, 73687-62-4; butyl *cis*-2-butenyl sulfide, 73687-63-5; butyl *trans*-2-butenyl sulfide, 3001-22-7; butyl 1-methylallyl sulfide, 689-90-7; butyl 1-methylallyl sulfone, 73687-64-6; *cis*-4-hexen-2-one, 51024-76-1; *trans*-4-hexen-2-one, 763-92-8; *trans*-3-hexen-2-one, 4376-23-2.

(24) If *cis*-3-hexen-2-one has the same GLC retention time as its trans isomer, as much as 5% could have been present in the equilibrium mixture (limit established by NMR measurements).

Reactivity–Selectivity Correlations. 2.[1] Reactivity of Alkyl Aryl Sulfates toward Oxygen Nucleophiles and the Reactivity–Selectivity Principle

Erwin Buncel* and Claudio Chuaqui

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received January 11, 1980

The reaction of a series of alkyl aryl sulfates with oxygen nucleophiles (methanol, methoxide ion, phenoxide ion), in methanol at 25 °C, has been investigated spectrophotometrically. The results show that the mode of reaction along the series is uniformly by alkyl–oxygen scission, i.e., nucleophilic displacement on the methyl carbon with $ArOSO_3^-$ as the leaving group. The Hammett σ plots yield ρ values of 1.39, 0.90, and 0.74 for the reactions of MeOH, MeO^-, and PhO^-, respectively. Since reactivity in these processes increases in this order, taking ρ as a selectivity parameter, it follows that selectivity bears an inverse relationship to reactivity. This result is in accord with the reactivity–selectivity principle (RSP). It is suggested that a number of studies in which the RSP has apparently failed to hold are subject to certain inherent problems in experimental design, e.g., differential solvent, structural or steric effects along the reaction series, or mechanistic variation, which could lead to a variety of patterns of reactivity and selectivity. The design of the present system allows one to modulate the nature of the nucleophilic and the nucleofugic moieties, ensuring a constancy of mechanism within a series of transition states whose structures and properties should vary in uniform fashion.

The reactivity–selectivity principle (RSP) would seem intuitively to be one of the fundamental guiding principles of chemical behavior, as expressed in its basic form that selectivity in a series of related processes on varying the

0022-3263/80/1945-2825$01.00/0

reagent or substrate bears an inverse relationship to reactivity. Furthermore, the RSP can be related by deductive arguments to transition-state (TS) structure and variation along such reaction series, by way of postulates introduced by Hammond[2] and Leffler,[3] and in somewhat different form earlier by Bell, Evans, and Polanyi.[4-6] Moreover, by means of linear free-energy relationships (LFER's) of the Hammett or Bronsted type,[7-10] the reactivity trends along the series can then be quantitatively related to transition-state variation, via the derived ρ and α or β parameters. Thus, apparent "failure" of the RSP could adversely affect our interpretive and predictive power concerning structure–reactivity relationships in general and transition-state behavior in particular.

There is in fact an intense ongoing controversy concerning the validity of the RSP, as can be seen from the concluding statements in several articles dealing with this topic. In a critical evaluation of the RSP, Johnson in 1975 stated:[11] "It is quite clear that selectivity is independent of reactivity from which the theoretical deduction may be made that TS structure is independent of reaction rate." Two years later, Giesse concluded thus:[12] "The fact that the RSP does not hold for many series of reactions does not necessarily render the Hammond postulate useless, as frequently presumed." Concurrently, another optimistic view was expressed by Pross:[13] "in spite of many apparent failures the RSP is fundamentally valid".

However, just 2 years following the latter statements, the current viewpoints are once again more skeptical of the RSP. Thus quite recently Jencks and co-workers have stated:[14] "we believe that all reactions should not be expected to follow the RSP and that the RSP should be abandoned as a general principle". Similarly, Harris and co-workers have asserted:[15a] "it seems obvious that the RSP is not a basic principle in chemistry". Interestingly, both Jencks and Harris have qualified their conclusions with some penetrating statements concerning the light which apparent failures to the RSP may shed on the properties of transition states and on reactivity–selectivity relationships.

The question arises, what are the reasons for the widely ranging views concerning the validity of the RSP? We select here a few pertinent factors, starting with solvation effects and structural variation, and point out how these factors can affect the outcome of reactivity studies.

Solvent could conceivably interact with reactants, products, transition states, and intermediates along a reaction series in a differential manner,[15] thereby giving rise to artifacts which could lead to apparent failure of the RSP. Pross[13,16] has in fact attributed a solvation effect as the factor responsible for the apparent failure of the RSP as embodied in Ritchie's $\log k/k_0 = N_+$ relationship.[17] It appears that solvation effects in general, and interactions of solvation shells of entering and leaving groups in particular, are primarily responsible for deviation from an ideal situation and can lead to a variety of patterns of reactivity and selectivity.[18-20]

That appreciable structural changes along a reaction series, in either the substrate or the reagent, at or near the reaction site, could lead to ambiguity and conflicting results can readily be shown. Thus changes in steric interactions, e.g., for S_N processes, between the nucleophile and the electrophilic center, between nucleophile and leaving group (nucleofuge) in the transition state, and the consequent variation in solvation phenomena (vide supra), could profoundly influence the observed structure–reactivity relationships, rendering these uninterpretable in terms of the RSP or TS variation.

However, even relatively subtle structural changes could have the effect of a *change in mechanism*. For example, in the case of S_N reactions, transition from S_N1 to S_N2 mechanisms could occur or, less easily detectable, a change in the balance of ion-pairing phenomena (contact, solvent-separated ion pairs, or free ions).[21-24] In the case of reaction at carbonyl centers, structural variation could result in a change in the rate-determining step (formation of tetrahedral intermediate or its decomposition).[9] Reaction at sulfonyl centers could also conceivably be complicated by the intervention of pentacoordinate intermediates; this in fact has been invoked as an explanation of the failure of the RSP in the reaction of arenesulfonyl chlorides with aromatic amines.[12,25]

The possible effect of leaving-group variation in S_N reactions is less easy to predict. An appreciable change in leaving group, for example, from bromide to tosylate, could change the transition-state properties appreciably, including interactions by London forces[19,26] and its solvation properties. Nevertheless, in a recent study of the reactions between aryl oxide ions and various CH_3X derivatives with X ranging widely, i.e., OMe_2^+, OSO_2CF_3, OSO_2OMe, $OPMe(OMe)_2^+$, OTs, and I, with some exceptions, definite trends in reactivity were observed, in accord with the RSP.[27,28]

The dilemma posed by these considerations is that most, or possibly all, systems available to the physical organic chemist so far have been lacking in one or another of the conditions which are required for the RSP to be strictly

(1) Part I. E. Buncel, C. Chuaqui, K. R. Lynn, and A. Raoult, *Bioorg. Chem.* **7**, 1 (1978).
(2) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(3) J. E. Leffler, *Science*, **117**, 340 (1953); J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, p 162.
(4) R. P. Bell, *Proc. R. Soc. London, Ser. A*, **154**, 414 (1936).
(5) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1340 (1936).
(6) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw Hill, New York, 1969, p 284.
(7) L. P. Hammett, "Physical Organic Chemistry", 2nd ed., McGraw Hill, New York, 1970.
(8) C. D. Johnson, "The Hammett Equation", Cambridge University Press, New York, 1973.
(9) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw Hill, New York, 1969.
(10) W. J. LeNoble, "Highlights of Organic Chemistry", Marcel Dekker, New York, 1974.
(11) C. D. Johnson, *Chem. Rev.*, **75**, 755 (1975).
(12) B. Giese, *Angew Chem., Int. Ed. Engl.*, **16**, 125 (1977).
(13) A. Pross, *Adv. Phys. Org. Chem.*, **14**, 69 (1977).
(14) P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, **101**, 3288 (1979).
(15) (a) J. M. Harris, S. G. Shafer, J. R. Moffatt, and A. R. Becker, *J. Am. Chem. Soc.*, **101**, 3295 (1979); (b) E. Buncel and H. Wilson, *Acc. Chem. Res.*, **12**, 42 (1979); (c) E. Buncel and H. Wilson, *Adv. Phys. Org. Chem.*, **14**, 133 (1977).
(16) A. Pross, *J. Am. Chem. Soc.*, **98**, 776 (1976).
(17) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).
(18) C. D. Ritchie in "Solute–Solvent Interactions", Vol. 2, J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1976.
(19) D. J. McLennan, *Aust. J. Chem.*, **31**, 1897 (1978).
(20) A. J. Parker, *Chem. Rev.* **69**, 1 (1969).
(21) D. J. Raber, J. M. Harris, and P. v. R. Schleyer in "Ions and Ion Pairs in Organic Reactions", Vol. 2, M. Szwarc, Ed., Wiley, New York, 1974.
(22) R. A. Sneen, *Acc. Chem. Res.*, **6**, 46 (1973).
(23) R. E. Robertson, A. Annesa, and J. M. W. Scott, *Can. J. Chem.*, **53**, 3106 (1975).
(24) E. Buncel and B. C. Menon, *J. Org. Chem.*, **44**, 317 (1979).
(25) O. Rogne, *J. Chem. Soc. B*, 1855 (1971).
(26) J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962).
(27) E. S. Lewis and S. H. Vanderpool, *J. Am. Chem. Soc.*, **99**, 1946 (1977).
(28) E. S. Lewis and S. H. Vanderpool, *J. Am. Chem. Soc.*, **100**, 6421 (1978).

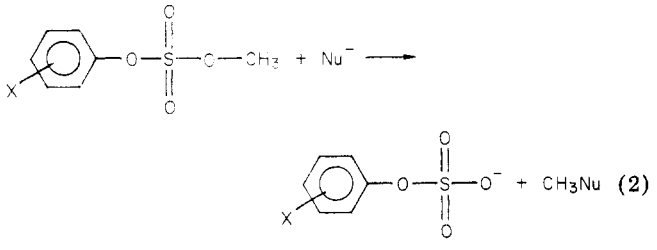
applicable.[29] Under these circumstances, observations of apparent "failure" of the RSP could be misleading and hardly surprising. Moreover, in the eventuality that actual systems for testing the RSP could not be devised, then this concept would have little practical utility. Fortunately this is not the case, as we show in the present study.

A system which should be suited for testing the RSP for S_N processes is that depicted in eq 1. In this reaction,

$$X\text{-}Ar\text{-}Z\text{-}E + N\text{-}Ar'\text{-}Y \rightarrow X\text{-}Ar\text{-}Z + E\text{-}N\text{-}Ar'\text{-}Y \quad (1)$$

substitution by a nucleophilic atom N occurs at an electrophilic center E such that structural variation in the substrate and the nucleophile can be remotely effected via the substituents X and Y. In this way one can modulate the nature of the nucleophilic and the nucleofugic moieties while ensuring a constancy of mechanism within a series of transition states whose structures and properties should vary in uniform fashion. The results of reactivity studies should thus be subject to unambiguous interpretation, including the testing of the RSP.

In the present study, we describe a system which fulfills most of the criteria considered above. The reaction concerned is that of alkyl aryl sulfates with nucleophiles, specifically of aryl methyl sulfates with oxygen nucleophiles[30] (see eq 2). In such a reaction series, constancy



of mechanism is virtually assured; nucleophilic substitution at a methyl carbon should proceed by the bimolecular (S_N2) mechanism regardless of the nature of the substituent X or the nucleophile Nu (cf. ref 21–24, 28, 29).

We have already shown[30] that reaction of methyl *p*-nitrophenyl sulfate with methoxide ion and with methanol occurs exclusively at the methyl carbon; neither reaction at the sulfur center nor reaction at the aromatic carbon could be detected. It would hence appear that the series of aryl methyl sulfates bearing different phenyl substituents should provide opportunity for evaluating the role of leaving-group ability while preserving the structural relationship among members of the series. In view of the suitability of such a series, it is somewhat surprising that the $ArOSO_3^-$ leaving group has so far received so little attention.[31,32] With a view of exploring the potential of this system, we have now completed the study of nucleophilic reactivity of the aryl methyl sulfates with methanol, methoxide ion, and phenoxide ion as nucleophiles.[33] The results have a bearing on the question of the validity of the RSP in these systems.

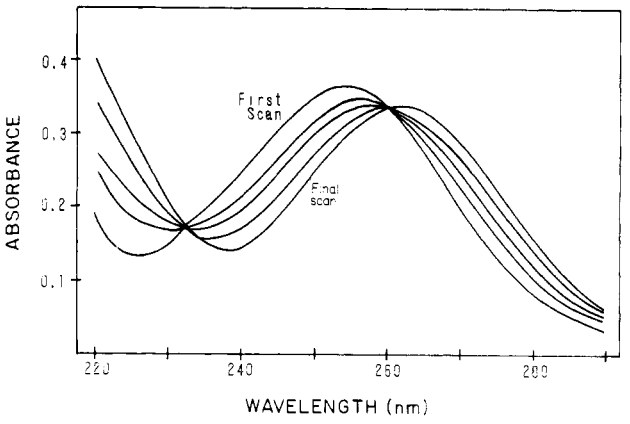
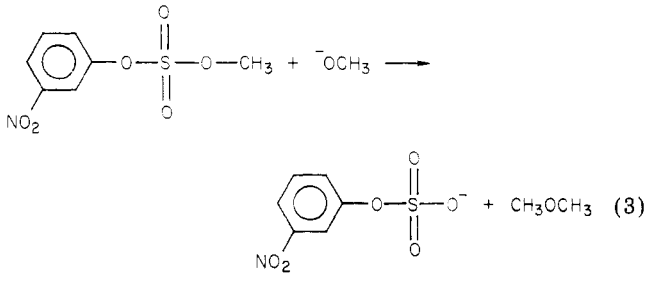


Figure 1. Spectral scans for the conversion of methyl *m*-nitrophenyl sulfate to *m*-nitrophenyl sulfate by methanolic sodium methoxide at 25 °C.

Results and Discussion

The first requirement in this study was to establish that the mode of reaction throughout the series of aryl methyl sulfates in their reactions with the nucleophiles investigated was indeed by attack at the methyl carbon with $ArOSO_3^-$ as the leaving group. It is recalled that this had been found[30] to be the case with methyl *p*-nitrophenyl sulfate, which should be the most activated substrate in this series toward nucleophilic attack at aromatic carbon (see also ref 34 and 35). It was probable, therefore, that attack at this center would persist throughout the present reaction series. In fact the following experiments confirm this expectation for the series of sulfates reacting with MeOH, MeO^-, and PhO^- as nucleophiles. Moreover, the possibility of attack at sulfur (with ArO^- as leaving group) could readily be eliminated as a possible reaction mode.

Methoxide Ion and Methanol Reactivity. The reaction of *m*-NPMS[36] with methoxide ion, as followed spectrophotometrically, was found to be straightforward in behavior. The spectral changes which occurred during a kinetic run are illustrated in Figure 1 and show that the absorption maximum at 254 nm, due to substrate, decreases with time while an absorption at 262 nm correspondingly increases, with a well-defined isosbestic point appearing at 260 nm. The 262-nm absorption corresponds accurately to authentic *m*-NPS, which is formed in quantitative yield. The reaction path under study is hence shown to be as in eq 3, i.e., nucleophilic displacement at



the methyl carbon with $ArOSO_3^-$ as the leaving group. As noted above, this is analogous to the reaction observed previously with *p*-NPMS; indeed the spectral changes

(29) D. J. McLennan, *Tetrahedron*, **34**, 2331 (1978).
(30) E. Buncel, A. Raoult, and J. F. Wiltshire, *J. Am. Chem. Soc.*, **95**, 799 (1973).
(31) G. Bartoli and P. E. Todesco, *Acc. Chem. Res.*, **10**, 125 (1977).
(32) C. J. M. Stirling, *Acc. Chem. Res.*, **12**, 198 (1979).
(33) At the outset of this study it was hoped to extend the range of nucleophiles to various substituted aryl oxides in accord with eq 1, which would have afforded a wider test of the applicability of the RSP to these systems. However, it was not possible to resolve problems arising from overlap of spectral absorptions between substrate and the nucleophilic species, which was especially severe in the case of *p*-nitrophenoxide ion. Another experimental method for following the reaction kinetics, such as GLC analysis of reaction products, could perhaps be used to overcome the problem but then this would have other disadvantages (e.g., concentration factor) with respect to the spectrophotometric method.[28]

(34) E. Buncel and C. Chuaqui, *Can. J. Chem.*, **53**, 1275 (1975).
(35) E. Buncel, C. Chuaqui, P. Forsythe, S. Mahoney, A. Raoult, and J. F. Wiltshire, *J. Chem. Soc., Perkin Trans. 2*, 478 (1975).
(36) 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; the corresponding aryl sulfates are denoted by *p*-NPS, *m*-NPS, *p*-BPS, *p*-MPS, and PS, respectively.

Table I. Kinetic Data for Alkaline Methanolysis of Aryl Methyl Sulfates at 25 °C

substituent (substrate)	$10^3 \times$ [MeO⁻], M	$10^4 \times k_{obsd}$, s^{-1}	$10^5 \times k_{MeOH}$,[a] $M^{-1}\ s^{-1}$	k_{MeO^-},[b] $M^{-1}\ s^{-1}$
p-NO_2 (*p*-NPMS)			2.11[c]	0.513[c]
m-NO_2 (*m*-NPMS)	0.412	6.04	1.64	0.459
	0.836	7.98		
	1.34	10.2		
	1.67	11.7		
	2.01	13.4		
p-Br (*p*-BPMS)	3.31	6.26	0.320	0.165
	4.92	9.32		
	6.89	11.6		
	8.36	14.5		
	9.84	17.3		
	10.8	18.0		
H (PMS)	18.2	16.9	0.172	0.091
	48.5	44.7		
	74.1	67.8		
	94.9	86.6		
p-Me (*p*-MPMS)	2.21	1.71	0.100	0.073
	4.80	3.78		
	6.40	4.88		
	9.60	7.24		
	10.8	8.32		
	11.2	8.63		

[a] Second-order rate constant calculated from k_{sol} for methanolysis and [CH_3OH] = 25.0 M. [b] Slope of plot of k_{obsd} vs. [MeO⁻]. [c] Data from ref 30.

displayed in Figure 1 are analogous to those observed in the reaction of *p*-NPMS with CH_3ONa/CH_3OH.[30] Moreover, addition of acid at the completion of the *m*-NPMS/MeO⁻ reaction caused a shift in the spectral absorption to 269 nm, corresponding to the formation of *m*-nitrophenol, which was again formed in quantitative yield. The acid-catalyzed conversion of aryl sulfates to the phenols was observed also in the previous work[30,34,35] (see also ref 37–40).

A plot of log ($A_\infty - A_t$) vs. time using the absorbance data at 254 nm in the *m*-NPMS/MeO⁻ kinetic run was linear, yielding k_{obsd}, the pseudo-first-order rate constant. A series of kinetic runs performed over a range of initial base concentrations yielded the results in Table I, shown graphically in Figure 2 as a plot of k_{obsd} vs. [MeO⁻]. The slope of this plot gives the rate coefficient for the methoxide ion reaction, k_{MeO^-}, while the intercept yields the rate constant for the solvolytic process, k_{sol}. A similar plot was obtained previously with *p*-NPMS.[30] Also, as with *p*-NPMS, one could obtain confirmation of the k_{sol} value for *m*-NPMS by performing the solvolytic experiment in initially neutral methanol and analyzing the spectral data as previously.[30,41]

The methanolysis reactions of the other members of the series, i.e., *p*-BPMS, *p*-MPMS, and PMS, were similarly investigated spectrophotometrically. However, the spectral changes observed with these compounds were quite different from the behavior found for *m*-NPMS (Figure 1). As an example, Figure 3 shows the evolution of the spectra in the *p*-MPMS/MeO⁻ reaction. Unlike the situation in Figure 1, no isosbestic behavior is found in Figure 3. However, this lack of isosbestic behavior is an incidental

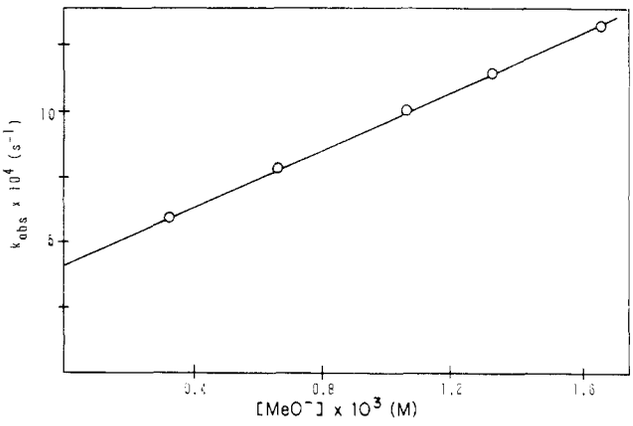


Figure 2. Plot of k_{obsd} vs. [CH_3ONa] for reaction of methyl *m*-nitrophenyl sulfate with methoxide ion at 25 °C.

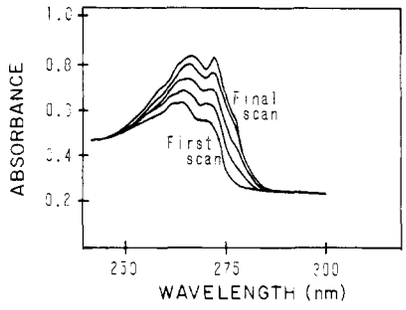


Figure 3. Spectral scans in kinetic run of reaction between methyl *p*-methylphenyl sulfate and methanolic sodium methoxide at 25 °C.

result of the fact that the absorption maxima of the reactant and product occur in close proximity in this system. As previously, confirmation of the above interpretation could be found by acidification of the solutions at the completion of the methoxide ion reactions, which resulted in characteristic spectral changes in accord with the acid-catalyzed conversion of the aryl sulfates to the respective phenols.

Thus it is found that all the aryl methyl sulfates in this series react with MeONa/MeOH at the methyl carbon, i.e., by alkyl–oxygen scission.[30] The kinetic data for the latter set of aryl methyl sulfates could be readily analyzed. For an individual kinetic run, k_{obsd} was obtained from the linear plot of log ($A_\infty - A_t$) vs. time, selecting a wavelength where changes in absorbance were maximal. A series of kinetic runs performed at different MeO⁻ concentrations yielded the data in Table I. Plots of k_{obsd} vs. [MeO⁻] were analogous in each case to the graph shown in Figure 2, yielding k_{MeO^-} from the slope and k_{sol} from the intercept. These results are included in Table I.

Phenoxide Ion Reactivity. The reactivity of phenoxide ion with the series of aryl methyl sulfates was evaluated by using the following experimental design. In methanol solution, the solvolytic equilibrium PhO^- + MeOH ⇌ PhOH + MeO^- is established with the result that the nucleophilic species present in this system will be PhO^- and MeO^- in addition to MeOH. However, by setting a constant ratio of phenoxide ion–phenol, i.e., [PhO^-]/[PhOH] = 1, one can then prepare solutions of varying [PhO^-] while [MeO^-] is maintained constant and, of course, [MeOH] is also effectively constant. These reaction solutions are conveniently prepared by partial neutralization of phenol with methanolic sodium methoxide as described in the Experimental Section. The rate coefficient k_{PhO^-} can then be derived as the slope of a linear plot of k_{obsd} vs. [PhO^-].

(37) J. L. Kice and J. M. Anderson, *J. Am. Chem. Soc.*, 88, 5242 (1966).
(38) S. J. Benkovic and P. A. Benkovic, *J. Am. Chem. Soc.*, 88, 5504 (1966).
(39) E. J. Fendler and J. H. Fendler, *J. Org. Chem.*, 33, 3852 (1968).
(40) K. T. Douglas, *Prog. Bioorg. Chem.*, 4, 193 (1976).
(41) (a) E. Buncel, A. Raoult, and J. F. Wiltshire, *J. Chem. Educ.*, 51, 814 (1974); (b) C. Chuaqui, Ph.D. Thesis, Queen's University, 1977.

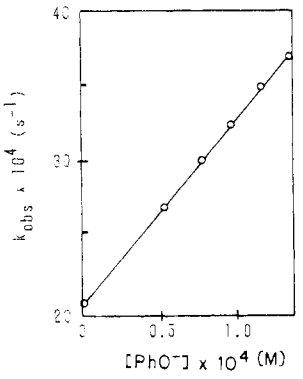


Figure 4. Plot of k_{obsd} vs. [PhO⁻] for reaction of methyl *p*-nitrophenyl sulfate with phenoxide ion in methanol at 25 °C.

The spectral changes observed for the reaction of PhO⁻ (actually PhO⁻/PhOH/MeO⁻/MeOH) with the aryl methyl sulfates are somewhat similar to Figure 1, though only a single isosbestic point is exhibited, and are characteristic of the formation of the aryl sulfate *p*-NPS which has λ_{max} at 282 nm. The absorptions due to PhOH (271 nm) and PhO⁻ (279, 286 nm) do not interfere appreciably since the corresponding extinction coefficients are considerably smaller than that of *p*-NPS. In the other reactions, the absorption of the aryl sulfate produced is superimposed on the PhO⁻/PhOH absorptions. Thus the mode of reaction with phenoxide ion throughout this series is shown to be attack at the methyl carbon with $ArOSO_3^-$ as the leaving group, i.e., alkyl–oxygen scission, as in the case of the reactions with MeO⁻/MeOH.

The data obtained in the phenoxide ion reactions could be analyzed in a straightforward manner. For each run k_{obsd} was obtained from a linear plot of log $(A_\infty - A_t)$ vs. time, selecting a wavelength at which the changes in absorbance were largest. Runs were performed at varying [PhO⁻] values, including at [PhO⁻] = 0, which defines the MeO⁻/MeOH reactivity for each substrate and reaction system. Plots of k_{obsd} vs. [PhO⁻] were then constructed, as illustrated in Figure 4 for the case of *p*-NPMS, the slopes of these plots yielding k_{PhO^-} for each substrate. The results are summarized in Table II.

Reactivity Relationships. It has been shown in the previous sections that methanol, methoxide ion, and phenoxide ion react with the series of alkyl aryl sulfates by alkyl–oxygen scission, i.e., nucleophilic attack on the methyl carbon with $ArOSO_3^-$ as the leaving group. Reactivity in these processes, as given by the rate constant data in Tables I and II, can be compared by means of the log *k* vs. σ correlations shown in Figure 5, where σ are the Hammett substituent constants.[42] The slopes of these plots yield the Hammett ρ parameters, which are obtained as 1.39, 0.92, and 0.74 for MeOH, MeO⁻, and PhO⁻[43] as nucleophiles. Hence, provided that ρ can be taken as a valid selectivity parameter, it follows that selectivity in this reaction series bears an inverse relationship to reactivity, which is in accord with the RSP.

It is noted that caution must be exercised in ascertaining that ρ values should indeed be valid measures of transition-state character and selectivity for the reaction series under investigation. For example, it has been pointed out[29] that a simple direct comparison of ρ values for the alkaline hydrolysis of ethyl benzoates ($ArCO_2Et$, ρ = 2.54) and aryl acetates ($ArCH_2CO_2Et$, ρ = 0.824) would be misleading as an assessment of transition-state character for the two systems since the transmission of charge in the latter case is dampened by the intervening methylene group. Methods to allow for variable transmission factors by correcting the apparent ρ (or σ) values have been proposed.[29] However, the present reaction series is clearly free from this type of interpretation and it can be taken that the ρ values

Table II. Kinetic Data for Reaction of Aryl Methyl Sulfates with Phenoxide Ion in Methanol at 25 °C[a]

substituent (substrate)	$10^4 \times$ [PhO⁻], M	$10^4 \times k_{obsd}$,[b] s^{-1}	k_{PhO^-},[c] $M^{-1}\,s^{-1}$
p-NO_2 (*p*-NPMS)	0	21.8	10.9
	0.56	27.4	
	0.80	30.4	
	1.00	32.8	
	1.19	35.1	
	1.39	36.5	
m-NO_2 (*m*-NPMS)	0	18.7	6.70
	0.63	22.4	
	0.96	25.7	
	1.30	26.7	
	1.49	28.0	
p-Br (*p*-BPMS)	0	6.02	2.89
	1.23	9.55	
	1.94	11.6	
p-Me (*p*-MPMS)	0	14.8	1.50
	1.48	17.2	
	2.28	18.0	
	3.00	19.2	

[a] See Experimental Section for constitution of reaction solutions which contain, in addition to phenoxide ion, also phenol and methoxide ion. [b] Overall pseudo-first-order rate constant for conversion to the respective aryl sulfate ion. [c] Obtained from slope of plot of k_{obsd} vs. [PhO⁻].

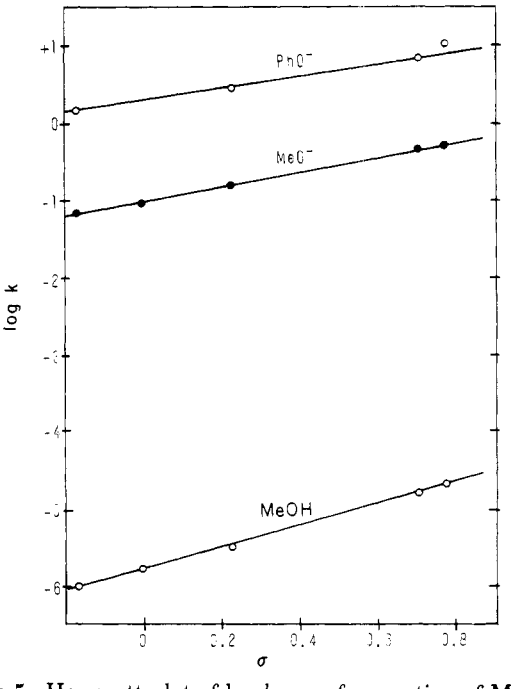


Figure 5. Hammett plot of log *k* vs. σ for reaction of MeOH, MeO⁻, and PhO⁻ with the series of substituted aryl methyl sulfates in methanol at 25 °C.

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

(43) The point for the PhO⁻ reaction corresponding to PNPMS has been omitted in calculating the ρ value of 0.74 as this compound reacts the fastest in this series and is associated with the largest experimental error. If, however, all the data points for the PhO⁻ reaction are given equal weight in Figure 5, one obtains a least-squares ρ value of 0.84 ± 0.05. Including the error limits (standard deviation) for the set of ρ values given in the text, one obtains 1.39 ± 0.02, 0.92 ± 0.02, and 0.74 ± 0.05, respectively.

as obtained provide valid measures of transition-state character.

It is thus concluded that the RSP does in fact hold for the processes under investigation. In view of the previous discussion and the ongoing controversy in the literature regarding this topic, it is deemed proper to emphasize that when the reaction system has been carefully chosen then transition-state character does indeed follow predicted trends in accord with reactivity–selectivity relationships, at least in the present case. It remains to be seen whether this will hold also in other designed systems.

An aspect of the results which can be commented upon is the greater nucleophilic reactivity of phenoxide ion than of methoxide ion. Several other systems have been observed to follow this reactivity order,[44,45] although in the majority of cases known to us the opposite order has been found to hold.[46-50] The order $k_{MeO^-} > k_{PhO^-}$ is the expected one if nucleophilicity bears a direct relationship to basicity. Among other factors known to contribute to nucleophilicity[51,52] is the polarizability factor (cf. Edwards' equation, $\log k/k_0 = AP + BH$),[53] which would favor PhO^- over MeO^-. Additionally, desolvation of MeO^- will be energetically more costly than of PhO^- in which charge is delocalized into the ring. The solvation factor could be especially important in the present system in that the electronegative oxygens on the aryl sulfate moiety could bring about considerable structuring of solvent molecules which would be enhanced by methoxide ion as the reagent relative to phenoxide ion.

The low sensitivity of the reaction rate to reagent basicity and the greater sensitivity to polarizability suggest that the transition state occurs early along the reaction coordinate. For substitution at saturated carbon, a small dependence of rate on nucleophile basicity is in accord with the unavailability of low-lying unoccupied orbitals on the electrophilic center for bond formation.[54] Since an early transition is thus implied for the reaction of these nucleophiles with the methyl phenyl sulfates, the extent of bond rupture to the oxygen of the leaving group will also be small, provided that the total bond order to the central carbon remains constant during the reaction. This is a reasonable assumption in this system although some other systems show "anomalous" behavior in this respect.[14,15] The conclusion reached is thus one of a transition state having a small degree of bond formation to the nucleophile and a small degree of bond rupture to the leaving group. This is also in accord with the already noted facile nucleofugality of the $ArOSO_3^-$ moiety.

Experimental Section

The preparation and characterization of the series of aryl methyl sulfates have been given previously.[1] *p*-Nitrophenyl sulfate was procured as the potassium salt (Sigma Chemicals) while the other aryl sulfates were synthesized by standard methods and samples were provided by the courtesy of Professor D. J. Phelps (St. Mary's University). Sodium methoxide solutions were prepared by dissolving sodium metal in anhydrous methanol. Phenol was used as reagent-grade quality.

Kinetic measurements were performed by using the spectrophotometric method described previously.[30,55,56] For example, in a typical methanolysis run using *m*-NPMS, 0.50 mL of 1.020×10^{-2} M MeONa/MeOH solution and 2.50 mL of MeOH were placed into a 10-mm quartz cuvette in the thermostatted cell compartment of the spectrophotometer and after temperature equilibration the reaction was initiated by adding 50 μL of a stock solution of the aryl methyl sulfate in ether, yielding a final methoxide concentration of 1.67×10^{-3} M and a substrate concentration of 5.90×10^{-5} M. The reaction was monitored by repeated scanning over the range 200–370 nm. In the reactions with phenoxide ion as nucleophile, the reaction solutions contained a constant ratio of phenoxide ion–phenol, i.e., $[PhO^-]/[PhOH] = 1$, while varying $[PhO^-]$. The solutions were prepared by partial neutralization of phenol with standard MeONa/MeOH, such that a constant value of $[MeO^-]$ could be maintained. For this purpose, a stock solution containing $[PhOH]_0 = 4.86 \times 10^{-3}$ M and $[MeONa]_0 = 5.59 \times 10^{-3}$ M was prepared and since[57] $pK_a(PhOH) = 14.2$ it follows that after neutralization equilibrium is established when $[PhO^-] = [PhOH] = 2.43 \times 10^{-3}$ M and $[MeO^-] = 3.16 \times 10^{-3}$ M. This stock solution was then diluted in various proportions with 3.16×10^{-3} M MeONa/MeOH solution to 3.00 mL in the cuvette and the reaction was initiated as previously by addition of 50 μL of the aryl methyl sulfate solution.

Registry No. *p*-NPMS, 38319-17-4; *m*-NPMS, 66735-53-3; *p*-BPMS, 66735-54-4; PMS, 66735-55-5; *p*-MPMS, 46231-81-6.

(44) C. F. Bernasconi and M. C. Muller, *J. Am. Chem. Soc.*, **100**, 5530 (1978).
(45) (a) J. J. Ryan and A. A. Humffray, *J. Chem. Soc. B.*, 1300 (1967); (b) L. H. Gan and A. R. Norris, *Can. J. Chem.*, **52**, 18 (1974).
(46) J. F. Bunnett and G. T. Davis, *J. Am. Chem. Soc.*, **76**, 3011 (1954).
(47) C. W. L. Bevan and J. Hirst, *J. Chem. Soc.*, 254 (1956).
(48) G. D. Leahy, M. Liveris, J. Miller, and A. J. Parker, *Aust. J. Chem.*, **9**, 382 (1956).
(49) D. Cook, I. P. Evans, E. C. F. Ko, and A. J. Parker, *J. Chem. Soc. B*, 404 (1966).
(50) D. J. Hupe and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 451 (1977).
(51) J. F. Bunnett, *Annu. Rev. Phys. Chem.*, **14**, 271 (1963).
(52) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms and Structure", 2nd ed., McGraw Hill, New York.
(53) J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 1819 (1956).
(54) A. R. Fersht and W. P. Jencks, *J. Am. Chem. Soc.*, **92**, 5442 (1970); ref 9, p 87.
(55) E. Buncel and A. Raoult, *Can. J. Chem.*, **50**, 1907 (1972).
(56) E. Buncel, A. Raoult, and L. I. Lancaster, *J. Chem. Soc., Perkin Trans. 2*, 691 (1972).
(57) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966).