Solvent Independent Transition-state Structures. Part III.[1] Sulfonyl Transfer Reactions

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A kinetic spectrophotometric study has been performed on the reactions of *p*-nitrophenyl benzenesulfonate (PNPBS) with *m*-chlorophenoxide, *p*-chlorophenoxide, phenoxide, *p*-methylphenoxide and *p*-methoxyphenoxide ions in DMSO–H_2O mixtures at 25.0 °C. Systematic variation of the DMSO content showed that the second-order rate constants (k_2) changed only moderately upon addition of DMSO up to 20 mol% for reaction of *p*-chlorophenoxide, phenoxide and *p*-methylphenoxide. On the other hand, the rates of reaction for all of the phenoxide ions studied increased markedly in solvent compositions greater than 40 mol% DMSO. The nature of the transition state (TS) for these reactions was probed *via* Brønsted-type linear free energy relationships (LFERs). Traditional Brønsted-type plots (method 'A'), in which the remote substituent on the aryloxide was varied and the solvent composition was held constant, were constructed for the reactions of the phenoxides with PNPBS in each of the following solvent compositions: 40%, 50%, 70% and 90% DMSO by mole. Novel Brønsted-type plots (method 'B'), in which variation in phenoxide pK_a was imparted through solvent changes while the remote substituent was held constant, were also constructed for the reactions of each of the five phenoxide nucleophiles. Method A yielded a set of lines whose slopes (β_{nuc} values) decreased steadily from 0.75 in 40 mol% DMSO to 0.60 in 90 mol% DMSO. Method B yielded a single straight line, $\beta_{nuc} = 0.60$, with satisfactory linearity for all data points ($r^2 = 0.995$, 95% CI = ±0.021), although closer examination suggested slight curvature with β_{nuc} varying from 0.54 for *p*-CH_3O to 0.66 for *m*-Cl. These results point to a discrepancy in the traditional view that Brønsted-type LFERs can be directly translated into a TS structure. Considerations based on the Marcus equation suggest that linearity in a Brønsted-type plot may result for a set of reaction series with differing intrinsic barriers provided that $\Delta G^{\#}_0$ varies linearly with ΔG_0.

Determination of the structure and properties of the transition-state (TS), and prediction how these may vary with the nature of the solvent and with structural changes in the reactants *via* substituents, *etc.*, remains one of the challenges in physical organic chemistry, in view of the elusive nature of this species.[2] Linear free energy relationships (LFERs) of various kinds have in the past been the most common probe of TS structure.[3] However, recently, the validity of using the slope of LFERs as a direct measure of TS structure has been seriously questioned.[4,5]

A variation of the Brønsted equation relating rates of proton transfer with basicity,[6] but in which the log *k* term [eqn. (1)] represents the rate of nucleophilic attack rather than proton-transfer has been among the most widely used of LFERs, particularly with respect to the study of the biologically significant transesterification and transamidation reactions as well as the common methyl-transfer process.[7]

$$\log k = (\beta_{nuc})\mathrm{p}K_a + C \qquad (1)$$

Traditionally, the reactivity and pK_a terms in eqn. (1) have been varied by altering a remote substituent on the nucleophile while maintaining all other reaction conditions constant (method A). We recently showed that an alternative Brønsted-type correlation could be obtained by varying the pK_a of the nucleophile through changing the solvent composition of the reaction medium while holding the remote substituent constant.[1,8] This novel method (method B) was applied to the reaction of substituted phenoxide ions with *p*-nitrophenyl acetate (PNPA) in aqueous dimethyl sulfoxide (DMSO) mixtures (40–90 mol%) and was found to yield a statistically better correlation for the individual plots, log *k vs.* pK_a, for the different solvent compositions than method A.[8] However, when this method was applied to the reaction of substituted phenoxide ions with the phosphinate ester, *p*-nitrophenyl diphenylphosphinate (PNPDPP),[1] in aqueous DMSO mixtures, one obtained a qualitatively different type of LFER information on using the two methods of analysis. When the data was analysed using traditional Brønsted-type plots, one for each solvent composition, the plots were seen to become increasingly curved with increasing DMSO content in the solvent. On the other hand, when the novel Brønsted-type plots were constructed for each respective phenoxide anion, the individual plots were found to be linear, with β_{nuc} decreasing with increasing basicity of the nucleophile.

To probe further the general applicability of this novel method, we have extended our studies to include the reaction of the same series of substituted phenoxide anions with *p*-nitrophenyl benzenesulfonate (PNPBS)[9] in aqueous DMSO mixtures [eqn. (2)] and report herein the results.

$$\mathrm{X{-}C_6H_4{-}O^-} + \mathrm{Ph{-}SO_2{-}O{-}C_6H_4{-}NO_2(p)} \longrightarrow \mathrm{(p)NO_2{-}C_6H_4{-}O^-} + \mathrm{Ph{-}SO_2{-}O{-}C_6H_4{-}X} \qquad (2)$$

Results

pK_a *Values in* DMSO–H_2O *Mixtures.*—The pK_a values for 4-chlorophenol and phenol in the aqueous DMSO mixtures were interpolated from values available in the literature.[10] The pK_a values of 4-methylphenol and 3-chlorophenol are known in water and in 100% DMSO, and since the other pK_a–mol%

DMSO curves are smooth functions with no extrema, parallel curves were constructed for both 4-methylphenol and 3-chlorophenol, from which the relevant pK_a values were obtained. The pK_a values of 4-methoxyphenol were similarly determined by extrapolation of a curve drawn using this method. It was previously found that the error introduced in determination of the pK_a values by the interpolation procedure could be estimated to be less than 0.1 pK_a units,[8] which is insignificant given that the pK_a range for the nucleophiles used in this study extends over more than 6 pK_a units. The accuracy of this method was confirmed by comparison with the pK_a values predicted by a mathematical treatment, in which an expression based on Hammett-type plots was found to predict the pK_a values of phenols in DMSO–H_2O mixtures to within 0.15 pK_a units, given only the pK value of the phenol in H_2O.[11] The derived pK_a values of the nucleophiles are given in Table 1.

Kinetic Data.—The rates of reaction in the DMSO–H_2O mixtures (40%, 50%, 70% and 90% DMSO by mole), of PNPBS with *m*-chlorophenoxide, *p*-chlorophenoxide, phenoxide, *p*-methylphenoxide and *p*-methoxyphenoxide ions, respectively, were determined at 25.0 °C. The rates of reaction of *p*-chlorophenoxide, phenoxide and *p*-methylphenoxide with PNPBS in various H_2O-rich mixtures (DMSO $\leqslant$ 30 mol%) were also determined.

All reactions were studied under pseudo-first-order conditions with the nucleophile being the reagent in excess by at least a factor of 20. The appearance of the leaving group, 4-nitrophenoxide ion, was followed by UV–VIS spectrophotometric techniques at the appropriate wavelength.[12]

First-order rate constants k_{obs} were obtained from plots of log $(A_\infty - A_t)$ *vs.* time which were linear over three half-lives or more, or from non-linear least-squares analysis of the absorbance *vs.* time plots. Second-order rate constants (k_2) were then obtained from linear plots of log k_{obs} *vs.* [Nu] which had negligible intercept showing that reaction due to solvent was negligible. All of the second-order plots were satisfactorily linear indicating that homoconjugation between the phenol and the phenoxide ion components of the buffering system was not a factor affecting the reaction kinetics. Pseudo-first-order rate constants are given as supplementary material in Supplementary Tables 1–38.*

Table 1 pK_a Values of substituted phenols (XC_6H_4OH) in DMSO–H_2O mixtures at 25.0 °C

	pK_a				
mol% DMSO	4-CH_3O	4-CH_3	H	4-Cl	3-Cl
0	10.20[a]	10.07[b]	9.86[c]	9.38[d]	9.08[a]
40	13.1[g]	12.9[g]	12.6[g]	12.0[g]	11.5[g]
50	14.1[g]	14.0[e]	13.5[e]	12.8[g]	12.3[g]
70	15.9[g]	15.5[e]	15.0[e]	14.4[g]	13.8[g]
90	17.7[g]	17.2[e]	16.6[e]	16.0[g]	15.4[g]
100	—	18.86[f]	18.03[f]	16.74[f]	15.83[f]

[a] Ref. 10(*a*). [b] Ref. 10(*b*). [c] Refs. 10(*b*), 10(*c*). [d] Ref. 10(*d*). [e] pK_a values were obtained by interpolation of literature pK_a data at specific solvent compositions, see ref. 8. [f] Ref. 10(*e*). [g] Values calculated from the following equation[11] (x = mole fraction of DMSO):

$$pK_a(\text{DMSO–H}_2\text{O}) = [1.43x + 0.840][pK_a(\text{H}_2\text{O})] - 5.35x + 0.866$$

The k_2 values are presented in Table 2, while a plot of the logarithm of the rate constants *vs.* solvent composition is presented in Fig. 1. The plots are essentially linear in the DMSO-rich region whereas they are curved in the water-rich region.

In the discussion that follows only the kinetic data obtained in solvent compositions with $\geqslant$40 mol% DMSO, with monotonic increases in reaction rate, are considered for purposes of analysis of linear free energy relationships. The

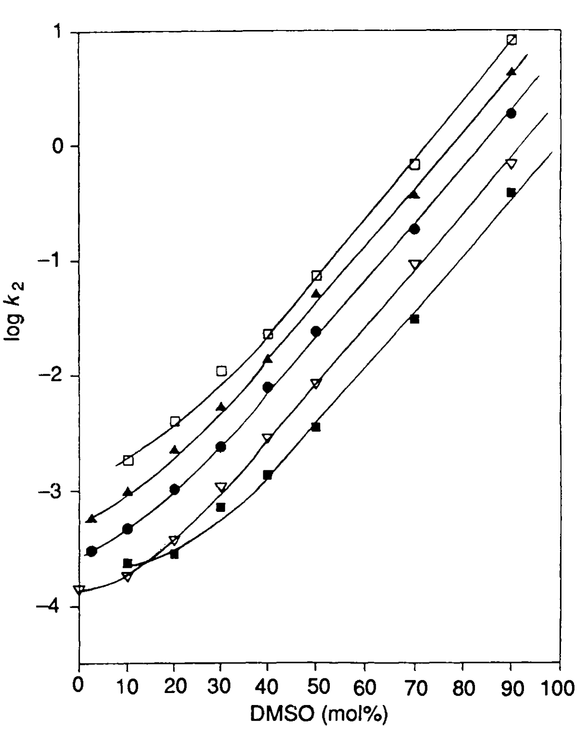

Fig. 1 Plots of log k_2 *vs.* mol% DMSO for the reaction of *m*-chlorophenoxide (■), *p*-chlorophenoxide (▽), phenoxide (●), *p*-methylphenoxide (▲), and *p*-methoxyphenoxide (□) with PNPBS in DMSO–H_2O mixtures at 25.0 °C

Table 2 Second-order rate constants, k_2/dm^3 mol^{-1} s^{-1}, for the reaction of substituted phenoxides with PNPBS in aqueous DMSO–H_2O mixtures at 25.0 °C

Solvent	k_2/dm^3 mol^{-1} s^{-1}				
mol% DMSO	4-$CH_3OC_6H_4O^-$	4-$CH_3C_6H_4O^-$	PhO^-	4-$ClC_6H_4O^-$	3-$ClC_6H_4O^-$
0	—	—	—	1.41×10^{-4}	—
2.5	—	5.76×10^{-4}	2.99×10^{-4}	—	—
10	1.82×10^{-3}	9.75×10^{-4}	4.66×10^{-4}	1.81×10^{-4}	2.33×10^{-4}
20	4.02×10^{-3}	2.25×10^{-3}	1.03×10^{-3}	3.71×10^{-4}	2.85×10^{-4}
30	1.06×10^{-2}	5.20×10^{-3}	2.37×10^{-3}	1.06×10^{-3}	7.01×10^{-4}
40	2.25×10^{-2}	1.36×10^{-2}	7.69×10^{-3}	2.79×10^{-3}	1.36×10^{-3}
50	7.29×10^{-2}	5.45×10^{-2}	2.36×10^{-2}	8.34×10^{-3}	3.47×10^{-3}
70	6.65×10^{-1}	3.66×10^{-1}	1.85×10^{-1}	9.08×10^{-2}	3.03×10^{-2}
90	8.14	4.28	1.85	6.74×10^{-1}	3.81×10^{-1}

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* Supplementary Tables 1–38 have been deposited at the British Library Sup. No. 57036 (14 pp.). For details of the supplementary publication scheme see 'Instructions for Authors (1994)', *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

'capricious'[13] behaviour in the water-rich zone ($\leqslant$30 mol% DMSO) is now well established. As has been discussed previously[8] a variety of physical evidence points to solvent–solvent aggregation phenomena in the H_2O-rich DMSO–H_2O media and these structural effects manifest themselves in anomalous rate behaviour for a number of nucleophilic reactions.[14]

Discussion

In the ensuing discussion we attempt to address the question as to what kind of information can one glean from the kinetic data that we have obtained for nucleophilic sulfonyl transfer in the reaction of *p*-nitrophenyl benzenesulfonate (PNPBS) with aryloxides, as a function of solvent (H_2O–DMSO) composition and substituent changes [eqn. (2)]. Scrutiny of linear free energy relationships obtained from application of Brønsted-type plots is a common approach, but does this lead to unequivocal answers concerning TS structure? We show in fact that the kind of answer one is led to depends largely on how the data is analysed, according to the traditional or the novel method for construction of Brønsted plots, and whether these are considered to be linear or curved.

Brønsted Coefficients.—A Brønsted-type plot for nucleophilic reactions is constructed by plotting log *k* *vs.* the pK_a of the nucleophile. In the traditional manner (method A) the pK_a parameter is varied by appropriate substitution on the nucleophile. Recently we have devised a novel strategy (method B) in which the pK_a of the nucleophiles is varied by changing the solvent composition of the reaction medium.[8] For example, variation of the mol% DMSO in aqueous media from 40% to 90% changes the pK_a of PhOH from 12.8 to 16.6.

Two types of behaviour have been observed in using method B in contrast with method A. In the first type, which was found for nucleophilic attack on PNPA, a single straight line was obtained when all the log *k* and pK_a data points obtained for a series of nucleophiles at different solvent compositions (40–90 mol% DMSO) were combined.[8] This line extends over nearly 6 pK_a units. In comparison, the traditional method A gave, for each solvent composition over this range, a similar β_{nuc} value (0.64 ± 0.04), yet over a much smaller pK_a range. The second type of behaviour was found for nucleophilic attack on phosphinate esters, where the traditional method A plots were found to be markedly curved. In the novel method B, this deviation from linearity manifested itself in the fanning out of the individual log *k* *vs.* pK_a plots, yielding a set of straight lines each belonging to a different nucleophile.[1]

The behaviour of the PNPBS + ArO^- system currently investigated resembles that of PNPA since, as is shown in Fig. 2, the combined data according to method B is nicely accommodated by a single straight line. Application of method A yields a set of straight lines with β_{nuc} values decreasing from 0.75 in 40 mol% DMSO to 0.60 in 90 mol% DMSO (Table 3).

Linearity vs. *Curvature.*—One of the major problems facing one in differentiating between linearity and curvature in Brønsted-type plots is the lack of a good statistical criterion. As was noted above, for the PNPBS + ArO^- system the combined log *k* and pK_a data show a satisfactory correlation coefficient when analysed as a straight line (r^2 = 0.995, Fig. 2). Moreover, the 95% confidence interval (CI) for its slope (0.60) is rather small (±0.02) especially when compared with the confidence intervals of some of the individual plots obtained by method A (Table 3).

However, close examination of the data (Table 4) reveals that, in fact, the data points for each of the nucleophiles fall on a separate straight line, with slope (β_{nuc}) varying gradually from 0.56 for *p*-MeO to 0.63 for *m*-Cl (Table 4). This is best illustrated in Fig. 3 which shows that although all the CI largely overlap, the individual centres of these intervals are slightly shifted. Moreover, reexamination of the data for PNPA shows the same phenomenon of slightly varying slopes for the individual phenols (Table 5).

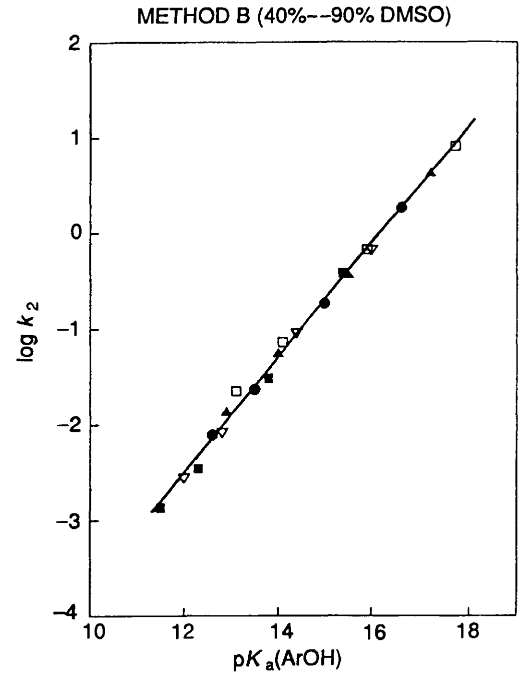

Fig. 2 Novel (method 'B') Brønsted-type plots of log k_2 *vs.* pK_a for the reactions of *m*-chlorophenoxide (■), *p*-chlorophenoxide (▽), phenoxide (●), *p*-methylphenoxide (▲) and *p*-methoxyphenoxide (□) with PNPBS in DMSO–H_2O mixtures at 25.0 °C

Table 3 Brønsted β_{nuc} values derived by varying the remote substituent while maintaining a constant solvent composition (method A) for the reaction of the substituted phenoxides with PNPBS. 95% confidence intervals and correlation coefficients (r^2) are shown

Method	Solvent mol% DMSO	β_{nuc}	r^2	95% CI
A	40	0.745	0.995	±0.095
A	50	0.714	0.998	±0.060
A	70	0.622	0.994	±0.086
A	90	0.597	0.994	±0.083

The small number of data points for each of the inividual phenols reduces the statistical significance of the slope for each phenoxide. Yet the trends, both in the present case as well as in that of PNPA, seem to indicate some curvature. One obtains a slightly larger β_{nuc} value for the acidic phenols and a slightly smaller β_{nuc} for the basic ones.

Transition-state Structure.—We begin the discussion of the TS structure assuming that the aforementioned curvature is real.

An essential question at this point is: what is a reaction series? In terms of linear free energy relationships a reaction series is defined as a family of reactions for which the TS structure remains essentially constant (in spite of small variations in reaction parameters). Relevant to the case at hand are two LFERs: one is based upon variation of substituents on the nucleophile (method A) while the other is based on solvent variation (method B). It should be pointed out that for the latter LFER, in selecting the 40–90 mol% DMSO range only, special care was taken to avoid the erratic non-monotonic behaviour of solvent variations which is typical of lower DMSO content solutions.[8,13,14] Thus, according to the traditional approach

Table 4 Brønsted β_{nuc} values for different aryloxides as a function of solvent composition for reaction with PNPBS. 95% confidence intervals and correlation coefficients (r^2) are shown. The composite plot for all the aryloxides (method B) is shown in Fig. 2.

Method	Solvent mol% DMSO	Nucleophile	β_{nuc}	r^2	95% CI
B	40–90	$3\text{-}ClC_6H_4O^-$	0.632	0.998	±0.095
B	40–90	$4\text{-}ClC_6H_4O^-$	0.601	0.999	±0.069
B	40–90	PhO^-	0.597	0.999	±0.052
B	40–90	$4\text{-}CH_3C_6H_4O^-$	0.580	0.999	±0.060
B	40–90	$4\text{-}CH_3OC_6H_4O^-$	0.556	0.999	±0.065
B	40–90	Composite	0.603	0.995	±0.021

Table 5 Brønsted β_{nuc} values for different aryloxides as a function of solvent composition for reaction with PNPA. 95% confidence intervals and correlation coefficients (r^2) are shown. The composite plot for all the aryloxides (method B) is given as Fig. 5 in ref. 8.

Method	Solvent mol% DMSO	Nucleophile	β_{nuc}	r^2	95% CI
B	40–90	$4\text{-}CNC_6H_4O^-$	0.645	1.000	±0.043
B	40–90	$4\text{-}ClC_6H_4O^-$	0.582	0.998	±0.077
B	40–90	PhO^-	0.567	0.996	±0.11
B	40–90	$4\text{-}CH_3C_6H_4O^-$	0.543	0.997	±0.086
B	40–90	Composite	0.605	0.993	±0.030

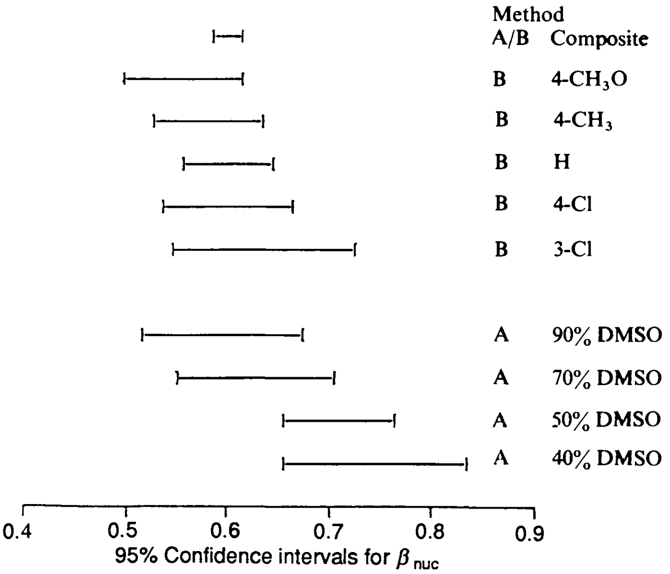

Fig. 3 Bar graph comparing β_{nuc} values, including 95% confidence intervals, for the traditional method 'A' (constant solvent, varying substituent) Brønsted-type plots, the novel method 'B' (constant substituent, changing solvent) Brønsted-type plot, and a composite Brønsted-type plot.

and in light of the modest variations made in the solvent and the substituents, the TS structure in the sulfonyl-transfer reaction should remain essentially constant.

Another traditional assumption is that β_{nuc} can be directly translated into a TS structure.[3] The present study seems to indicate that the two paradigms (hypotheses) are mutually exclusive. If the TS structure is believed to remain constant over the series and if the solvent-based LFERs provide a measure for the TS structure, then β_{nuc} values derived from solvent variations should be of constant value regardless of the identity of the substituent. Yet, as one sees in Table 4, these values vary from 0.56 for *p*-MeO to 0.63 for *m*-Cl. Conversely, if the TS is believed to be constant over the whole solvent range, application of the substituent-based LFER method as a probe for TS structure at each solvent composition should give the same β_{nuc} value. However, the results (Table 3) show that β_{nuc} varies from 0.75 at 40 mol% DMSO to 0.60 at 90 mol% DMSO, and therefore the TS structure is not constant. It would seem therefore, once again,[5] that LFER parameters cannot be directly translated into TS structures.

One can take the alternative approach and assume that the line obtained *via* method B is indeed linear and hence, the variations in the individual slopes is merely an artefact. If one chooses to assume that β_{nuc} values are a direct measure of TS structure, it follows then that the latter remains constant over the whole range of substituents and solvent compositions employed. This conclusion supports recent notions regarding the robustness of TS structures. The implasticity of the TS was demonstrated computationally for S_N2 reactions[15] and was suggested for metal-ion-catalysed transphosphorylation reactions by Jencks *et al.*[16] on the basis of experimental studies.*

Marcus Equation.—It is interesting to examine the situation in light of the Marcus equation,[17] eqn. (3). From this equation,

$$\Delta G^{\#} = \Delta G_0^{\#} + \tfrac{1}{2}\Delta G^{\circ} + (\Delta G^{\circ})^2/16\Delta G_0^{\#} \qquad (3)$$

β_{nuc} can be obtained by derivitisation with respect to ΔG_0, eqn. (4). Thus, since ΔG_0 (pK_a in our case) is varied along the

$$\beta_{nuc} = \tfrac{1}{2} + \Delta G_0/8\Delta G_0^{\#} \qquad (4)$$

series then β_{nuc} must also vary and therefore, curvature is inherent to this equation. Yet, as will be shown below, in the present case, the Marcus equation may result in a linear plot.

As we have mentioned before, the definition of a reaction series is of crucial importance. Within the framework of the traditional approach a series is defined as a group of reactions whose TS structure is constant. In terms of the Marcus equation, which does not relate to the structure of the TS, a reaction series must have a single intrinsic barrier. If each of the

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* A referee has pointed out, also contrary to the traditional interpretation, that in general, linearity of FER can be obtained if the TS structure is varied along the reaction series (and therefore the energy as well) in a way which parallels the variations due to perturbations made in reactants, solvent, *etc.*

substituted phenoxides forms a four-membered reaction series (reactions in 40, 50, 70 and 90 mol% DMSO) and these series differ from each other in their intrinsic barriers, then a linear plot may be obtained even according to the Marcus equation and even over a large ΔG_0 range. For that to occur, the intrinsic barrier $\Delta G_0^\ddagger$ must vary linearly with ΔG_0. In this case, the second term in eqn. (4) will be constant along the series and as a result β_{nuc} itself will also be rendered constant.

Conclusions

In this work we have analysed the kinetic data for the PNPBS + ArO^- reaction in different H_2O–DMSO mixtures (40–90 mol% DMSO) according to two methods for construction of Brønsted-type plots. The traditional method A (varying the substituent on ArO^-) yields a set of lines of different slopes on varying the solvent composition. Thus, according to the traditional interpretation, the changing β_{nuc} values are indicative of changing transition-state structure which can be interpreted on the basis of the Hammond postulate.

Application of the novel method B (pK_a changes effected by solvent changes) gives statistically acceptable linearity for all substituents and all solvent compositions, in accord with invariant β_{nuc} and transition-state structure. However, the same data points in method B can also be fitted on separate lines where β_{nuc} varies slightly as the substituent is changed.

Application of the Marcus equation shows that if the condition of constant intrinsic barrier, as implied for a single reaction series, does not hold but $\Delta G_0^\ddagger$ varies linearly with ΔG° (for each of the substituted phenoxides at the various solvent compositions being considered as separate reaction series), this will be manifested in a constant β_{nuc} value, that is, a linear plot regardless of the inherent curvature in the Marcus equation.

Finally, it should be pointed out that the doubt cast on the validity of using the slopes of LFERS as *direct* measures of TS structure does not imply that these slopes are of little or no value. Quite the contrary, it is clear that information regarding the TS structure is indeed hidden in the LFER coefficients. The missing link seems to be the algorithm which should be used in order to translate these LFER coefficients into an actual TS structure. In the absence of an appropriate key, a comparative phenomenological study of the LFER coefficients such as the one described above is of considerable significance since it may provide an important clue for the formulation of the much sought-after algorithm.

Experimental

p-Nitrophenyl benzenesulfonate (PNPBS) was prepared by the general procedure of Davy *et al.*[18] To benzene sulfonyl chloride (Aldrich, 5.01 g, 0.028 mol) dissolved in 100 cm^3 of dry diethyl ether was added Et_3N (6 cm^3, 0.043 mol) followed by *p*-nitrophenol (2.8 g, 0.023 mol). The solution was stirred at ambient temperature for 2 days, after which it was filtered to remove precipitated Et_3NHCl. The filtrate was washed with 5% aqueous HCl (4 × 50 cm^3) and then distilled water until the washings were neutral. The ether solution was dried (Na_2SO_4) and concentrated under reduced pressure to give a crude product which was recrystallized from ethyl acetate–light petroleum. The product, m.p. 84–86 °C, was characterized by IR and ^1H NMR spectroscopy.

The phenols used were of the highest quality available and were recrystallized prior to use and stored under argon in a glove box. Doubly distilled deionized water was boiled and cooled under nitrogen prior to use. DMSO was refluxed over CaH_2 at reduced pressure (64–66 °C/6–7 mmHg) for 16 h and distilled; the middle fraction was collected and stored under nitrogen. DMSO–water mixtures of various compositions were prepared by weight prior to use.

Nucleophilic stock solutions of *ca.* 0.2 mol dm^{-3} were prepared in 25.0 cm^3 volumetric flasks in a glovebox under an argon atmosphere by addition of 2 equiv. of the appropriate phenol to 1 equiv. of $Me_4NOH \cdot 5H_2O$. One equivalent each of the phenol and the corresponding phenoxide resulted, ensuring a self-buffering solution which suppressed attack by hydroxide ion on the substrate during the kinetic run. Six equivalents of H_2O were also formed and thus the appropriate quantity of pure DMSO was added to the flask as a correction for this H_2O, after which the flask was cut to the mark with the appropriate freshly prepared DMSO–H_2O binary solvent.

Reactions were initiated by injecting with a syringe 5 cm^3 of 0.02 mol dm^{-3} PNPBS in dry dioxane into a 10 mm quartz UV cell containing 2.5 cm^3 of solvent and an aliquot of the nucleophile stock solution. The cell was placed in the thermostatted cell holder of the spectrophotometer (Perkin-Elmer Lambda 5 for reactions with $t_{\frac{1}{2}} > 3$ h, or Hewlett-Packard 8452A Diode Array for reactions with $t_{\frac{1}{2}} < 3$ h). The reactions were followed spectrophotometrically by monitoring the appearance of *p*-nitrophenoxide ion at the appropriate wavelength (λ_{max} = 400 nm in H_2O and 2.5% DMSO, 410 nm in 10% DMSO, 414 nm in 20% and 30% DMSO, 420 nm in 50% DMSO, 426 nm in 70% DMSO, and 432 nm in 90% DMSO). First-order (k_{obs}) rate contants were calculated from at least 20 points spanning three half-lives, the infinity value being taken after at least 10 half-lives. All reactions were carried out under pseudo-first-order conditions with the concentration of phenoxide ion in at least 25-fold excess over the substrate. The concentration of nucleophile was in the range 1–25 × 10^{-3} mol dm^{-3} while the substrate concentration was generally 2 × 10^{-5} mol dm^{-3}.

Rate constants (k_{obs}) from data obtained on the Perkin-Elmer spectrophotometer were derived using the standard linear least-squares method of obtaining the slope of a plot of $\ln(A_\infty - A_t)$ *vs.* time, while those derived from the Hewlett-Packard spectrophotometer were obtained by a non-linear least-squares fit to the experimental data. It is estimated from replicate runs that the error in any particular measured rate constant is not greater than ± 3%. Second-order rate constants were obtained from the slope of a plot of k_{obs} *vs.* nucleophile concentration, which had negligible intercepts showing that the reaction with solvent did not occur to an appreciable extent. All plots of k_{obs} *vs.* nucleophile concentration were satisfactorily linear. Homoconjugation effects, which would have led to downward curvature in the plots of k_{obs} *vs.* nucleophile concentration, were not observed.

Acknowledgements

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. Discussions with Prof. C. F. Bernasconi are also acknowledged.

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Paper 4/03184I
Received 1*st June* 1994
Accepted 27*th July* 1994