Conflicting evidence regarding the mechanism of the sulfonyl transfer reaction

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Application of the novel solvent-dependent pK_a method for the construction of Brønsted-type plots to the sulfonyl transfer reaction with phenoxide nucleophiles, finds the pK_a's of aryloxides lower than those of the *p*-nitrophenoxide leaving group on separate lines, whereas nucleophiles of greater pK_a fall on a common line, contrasting with the observed behaviour when using the traditional method.

Several years ago we introduced a novel method for the construction of Brønsted-type (log *k vs.* pK_a) plots.[1] Whereas in the traditional method pK_a changes are effected through structural or substituent changes in the nucleophile moiety,[2] the novel method utilizes variation of the solvent composition to effect pK_a changes.[1] Special care was taken to insure that the effect of solvent variation on rate will be monotonic. Thus, for DMSO–water mixtures, only data for 40 mol% Me_2SO and greater was used.[3] The novel method was successfully employed for the reaction of *p*-nitrophenyl acetate (PNPA) with phenoxide ions in Me_2SO–water mixtures.[1] The combined plot over the whole range of solvent compositions and substituents on the phenoxide ring ranged over *ca.* 9 pK_a units whereas for the traditional plots the pK_a range extended between 3.5 to 6 pK_a units.

Interestingly, different behaviour was found for the reaction of *p*-nitrophenyl diphenylphosphinate with aryloxide nucleophiles in Me_2SO–water mixtures on applying the two methods. Here the traditional approach yielded a curved Brønsted relationship, while the novel method likewise did not result in straight Brønsted plot but instead yielded a set of non-overlapping individual lines.[4] Thus, the two-step mechanism for the reaction of *p*-nitrophenyl diphenylphosphinate was evidenced by both methods, although in characteristically different ways.

The present study continues with the series, from nucleophilic substitution at C(O) and P(O), to $S(O_2)$ centres. Application of the novel method to the reaction of *p*-nitrophenyl benzenesulfonate (PNPBS) [eqn.(1)] with aryloxide nucleophiles with pK_a's higher than those of the *p*-nitrophenoxide leaving group ($X{-}C_6H_4O^-$ where X = 4-MeO, 4-Me, H, 4-Cl, 3-Cl) yielded a linear plot[5] as in the case of PNPA.[1] This work has now been extended to phenolate nucleophiles with pK_a values lower than that of $p\text{-}NO_2{-}C_6H_4{-}O^-$ [eqn. (1), X = 2,4,5-Cl_3, 2,3,5-Cl_3, 2,3,5,6-F_4] in 50, 70 and 90% aqueous Me_2SO solutions, and also 4-cyanophenoxide [eqn. (1), X = 4-CN] with a pK_a only slightly greater than that of the leaving group. Analysis of the data in the traditional manner yields a linear plot for each of the three solvent compositions with slope of 0.63,r^2 = 0.985; 0.58, r^2 = 0.997; and 0.56, r^2 = 0.997, for the 50, 70 and 90% Me_2SO media, respectively (*e.g.* Fig. 1 for 70 mol% Me_2SO). These plots using substituent changes are in accord with the observations of Williams[6] who studied this reaction in 10% aqueous dioxane and employed a series of nucleophiles having both higher and lower pK_a's than *p*-nitrophenoxide. The linear Brønsted plot which was obtained led the authors to conclude that the displacement reaction is a concerted rather than an addition–elimination one.[6]

$$XC_6H_4O^- + PhSO_3C_6H_4\text{-}p\text{-}NO_2 \longrightarrow p\text{-}NO_2C_6H_4O^- + PhSO_3C_6H_4X \qquad (1)$$

Surprisingly, applying the novel method to the PNPBS–aryloxide reaction did not result in a linear plot as expected. Instead, the data points for nucleophiles with pK_a's higher than *p*-nitrophenoxide[5] were all grouped nicely on a single straight line (with the possible exception of one data point) which

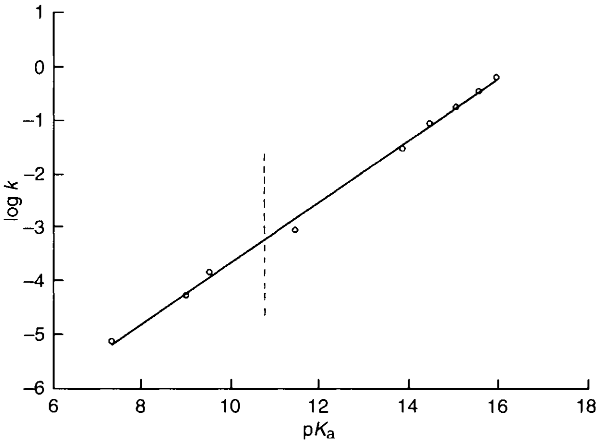

Fig. 1 Brønsted-type plot for the reaction of *p*-nitrophenyl benzenesulfonate with a series of substituted phenolate nucleophiles in 70 mol% Me_2SO at 25 °C. The line is calculated from the equation log k = (0.580 ± 0.01) pK_a − (9.46 ± 0.10), (r^2 = 0.997, n = 9). The dashed line indicates the expected break point for the addition–elimination stepwise mechanism (*i.e.* pK_a of *p*-nitrophenol in this medium).

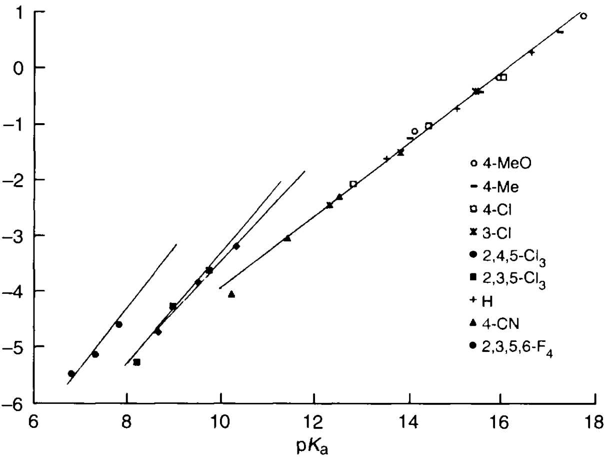

Fig. 2 Novel Brønsted-type plot[1,5] for the reaction of *p*-nitrophenyl benzenesulfonate with phenolate nucleophilies in Me_2SO–H_2O mixtures at 25 °C

extended over *ca.* 7 pK_a units with a slope of 0.62 and r^2 = 0.997 (Fig. 2, excluding the deviant point for 4-cyanophenoxide). However, the data for nucleophiles having pK_a values lower than that of *p*-nitrophenoxide gave a set of non-overlapping lines, of different slopes (Fig. 2).

The results reported in this paper are thus unique in that conflicting evidence is obtained from application of the two diagnostic tools. The traditionally constructed linear Brønsted-type plots seem to indicate that the reaction is concerted,[2b,6] whereas the novel method which yields a set of non-overlapping straight lines at the lower pK_a range clearly suggests that the nature of the reaction varies as the nucleophiles become more acidic than the leaving group. It is thus possible that in the present study, curvature begins only at lower pK_a values and that the novel method is sensitive enough to sense the change.

It should be pointed out that the traditional approach to extracting information regarding the transition state (TS) of a reaction from linear free energy relationships (LFER) has been under criticism in recent years.[2,7–20] It is clear though that LFERs do accommodate information regarding the TS and what is missing is a proper algorithm for their interpretation. This is even more applicable to the novel method for which limited experience has been gathered so far and it is therefore too early to assign mechanistic interpretation to the phenomenological outcome of that method. Yet one wonders if it might be suggesting that mechanistic changes do occur at the lower pK_a region, and that these changes are not discerned by the traditional method.

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