

## The Phenomenology of Differently Constructed Brønsted-type Plots

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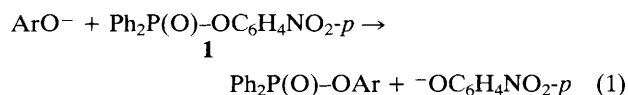
Two different methodologies for the construction of Brønsted-type plots are compared; curved plots using the traditional approach and linear plots by a novel approach are obtained for the reaction of phenoxides with *p*-nitrophenyl diphenylphosphinate in dimethyl sulfoxide–water media at 25 °C.

Brønsted-type relationships have been widely used to glean information on nucleophilic reactions but the validity of the information concerning transition state (TS) structure which can be derived from such free energy relationships (FER), and the coefficient ( $\beta_{\text{nuc}}$ ) values of the plots, have been increasingly questioned in recent years.<sup>1</sup>

We recently described a new method to construct a Brønsted-type plot, *i.e.* a correlation between the logarithm of the rate constants of nucleophilic reactions and the  $\text{p}K_{\text{a}}$  values of the nucleophiles. While in the traditional method the  $\text{p}K_{\text{a}}$  of the nucleophile was varied by varying the substituents, in the new method  $\text{p}K_{\text{a}}$  variations were imparted by a gradual variation of solvent composition while the identity of the nucleophile was retained. The method was first applied to the reaction of *p*-nitrophenyl acetate (PNPA) with phenoxides in dimethyl sulfoxide (DMSO)–H<sub>2</sub>O mixtures<sup>2a</sup> and, more recently, to the analogous reaction of *p*-nitrophenyl benzenesulfonate (PNPBS).<sup>2b</sup> In each case, the novel method yielded a single linear plot for all phenoxides with  $\text{p}K_{\text{a}}$  variation over *ca.* 8 pK units, from which  $\beta_{\text{nuc}}$  values of greater accuracy than afforded by the normal Brønsted-type plots could be obtained.

An important question which remained open was: how would curvature in the 'traditional' plots manifest itself in the new method for construction of Brønsted-type plots? Such a system is reported herein with some unexpected observations.

The reaction of phenoxides with *p*-nitrophenyl diphenylphosphinate **1** in DMSO–H<sub>2</sub>O media at 25 °C, resulting in displacement of *p*-nitrophenoxide [eqn. (1)], was studied



spectrophotometrically under pseudo-first-order conditions with the phenoxide in excess, as previously.<sup>3</sup> From the resulting  $k_{\text{obs}}$  values the second-order rate coefficients ( $k$ ) were obtained in the usual way. Plotting  $\log k$  vs.  $\text{p}K_{\text{a}}$  in the

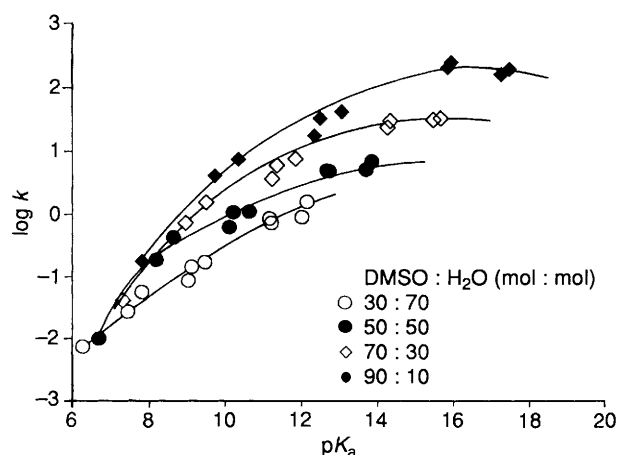


Fig. 1 Brønsted-type plot for the reaction of phenoxides with *p*-nitrophenyl diphenylphosphinate in DMSO–H<sub>2</sub>O media at 25 °C;  $\text{p}K_{\text{a}}$  variation effected by substituent changes in the phenoxides ('traditional' method)

traditional manner gave curved Brønsted-type plots for the various DMSO–H<sub>2</sub>O compositions (Fig. 1). However, applying the new method resulted this time, not in the formation of a single line as previously found for PNPA<sup>2a</sup> and PNPBS,<sup>2b</sup> but in a set of individual non-overlapping straight lines (Fig. 2).

The curvature observed in the traditional plots may reflect a change in the identity of the rate-determining step in a two-step addition–elimination mechanism. On the other hand, Williams<sup>4</sup> has shown that in pure water the reaction of **1** with phenoxides occurs by a concerted  $S_{\text{N}}2$  type mechanism. If it is assumed that this mechanism prevails in DMSO–H<sub>2</sub>O media as well, then the curvature in the Brønsted-type plot, Fig. 1, may most reasonably be assigned to progressively stronger desolvation of the nucleophile with increasing  $\text{p}K_{\text{a}}$ , following the reasoning advanced by Jencks<sup>1a,b</sup> and Bernasconi.<sup>5</sup>

Non-linear Brønsted plots can be analysed at three levels which differ in their intricacy. The one which probes most deeply into the intimate details of the reaction has to do with the (possible) correlation between the (local) slope and the transition state structure.<sup>6</sup> The second one is associated with the general nature of the reaction; for example, does the curvature indicate a stepwise mechanism with a change in the identity of the rate-determining step or does it stem from another reason such as low intrinsic barrier or progressive desolvation? At the third level, the curvature itself is questioned, that is, is the plot indeed curved or is it composed, for example, of two straight lines of different slopes? Vigorous debate is conducted on curved Brønsted relationships at all three levels. In many cases it was found to be extremely difficult to achieve irrefutable evidence in favour of one option or another. In the present case, we cannot unambiguously decipher the data at the two first aforementioned levels. However, one can justifiably question the curvature itself of each of the lines in Fig. 1, suggesting that the curves are in fact composed of two straight lines: one for phenols more acidic than the leaving group (*p*-nitrophenol) and one for those less acidic than the leaving group. Alternatively, most of the plots can be visualized as constructed from a straight line and a

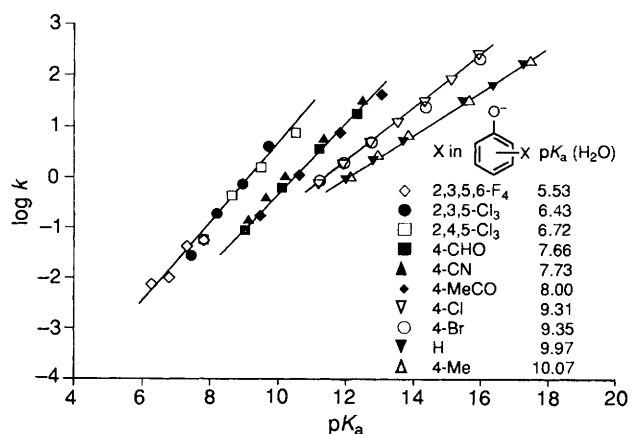


Fig. 2 Brønsted-type plot for same reaction as in Fig. 1 but  $\text{p}K_{\text{a}}$  variation imparted by changes in solvent composition ('novel' method)

single deviating point: that of the most acidic phenol. At least at this level the new method offers an unequivocal answer. The even spread of slopes of the lines in Fig. 2 cannot be accounted for either by singling out one phenol or by dividing the phenols into two groups according to their acidity relative to the leaving group. Thus we conclude that the lines in Fig. 1 are definitely curved in nature.

It is rather obvious today that although FER coefficients contain information regarding TS features, they cannot be directly translated into TS structure. Finding an algorithm for decoding of these coefficients has therefore become a major challenge. Thus the importance of the new method for the construction of Brønsted-type plots, besides its possible use as a diagnostic tool, is two-fold: (a) owing to its different nature it may provide an important clue for the development of the aforementioned algorithm, and (b) it may also provide a critical test for the generality of any new model which will be developed in the future.

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