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THE RELATIONSHIP BETWEEN KINETIC HYDROGEN ISOTOPE EFFECTS AND TRANSITION STATE SYMMETRY IN ELECTROPHILIC AROMATIC SUBSTITUTION.

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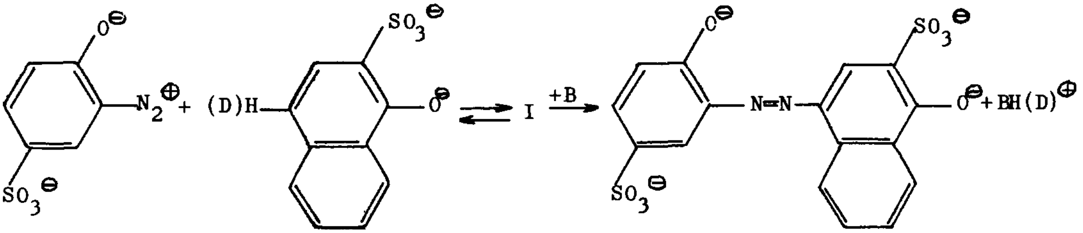
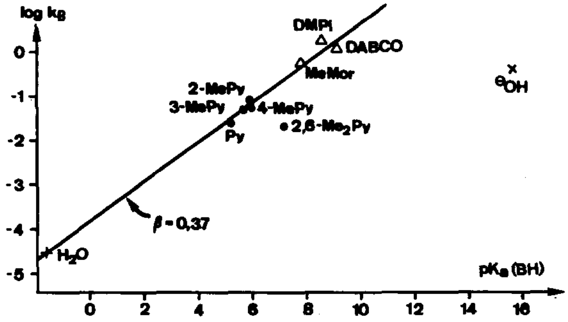
In an attempt to study the relationship between the magnitude of k_H/k_D and the parameter β of the Brönsted catalysis law, we have looked into the diazo coupling of 2-aminophenol-4-sulphonic acid with 1-naphthol-2-sulphonic acid in aqueous buffer solutions (pH 11.3):



The reaction proceeds with the formation of a ketone-like σ complex (I) from which proton transfer is rate limiting. The reaction is subject to general base catalysis, and a Brönsted plot (Fig. 1) covering a range of 10^{11} in basicity constants gives β = 0.37. The deviation of 2,6-lutidine is understandable for steric reasons (1). However, the pronounced deviation of $^{\ominus}$OH may be explained in terms of electrostatic repulsion between the σ complex, with 3 anionic charges, and the $^{\ominus}$OH ion. If the β value of 0.37 in this reaction is taken as a measure of the degree of proton transfer in the T.S. (2), one



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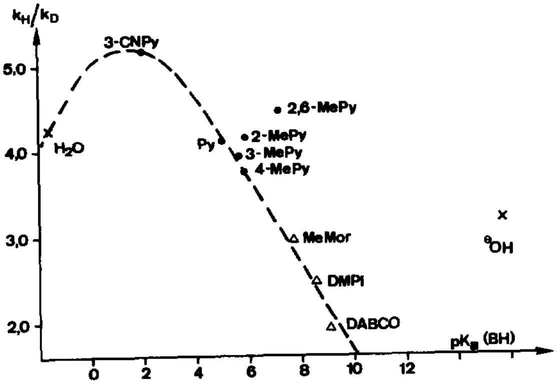
would have expected k_H/k_D to be about the same for the variety of bases used with the exception of $^{\ominus}OH$ and 2,6-lutidine. The measured k_H/k_D, at 0°C, are plotted in Fig. 2 against the pK_a values of the used bases. A maximum is quite evident at $pK_a \approx 1$. We believe this is the first such reported behaviour for an electrophilic aromatic substitution proper. This behaviour, however, has been observed for other reactions, in particular for aromatic hydrogen exchange (3), and is predicted from isotope effect theory (4). Our work suggests that the difference in basicity between the proton donor and proton acceptor (ΔpK_a) may be a far better measure than β of transition state symmetry.



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(4) See R.A. More O'Ferrall and J. Kouba, J. Chem. Soc., B, 985 (1967), for a recent review and references.