Quantitative Evaluation of Polar *ortho*-Substituent Effects

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ATTEMPTS to describe quantitatively the polar effects of *ortho*-substituents on rates and equilibria have been complicated by the superimposition of steric and solvation phenomena. Taft's[1] endeavours to separate polar and steric effects are well known ($\sigma_o^{\bullet}$) but the basic assumptions of his approach are somewhat tenuous. This communication reports *ortho*-substituent parameters which appear to be free from the influence of steric and solvation effects.

Davis and Hetzer[2] have measured the extent of ion-pair formation ("apparent acidities") of a series of *ortho*-, *meta*-, and *para*-substituted benzoic acids toward 1,3-diphenylguanidine in benzene at 25°. During the course of another investigation it became obvious that a graphical comparison of their results for the *ortho*- and *para*-isomers would be of interest. A plot of log K_o against log K_p is shown in the Figure. An excellent linear correlation is obtained. Points representing substituents of widely varying steric bulk fall directly on the line, an observation which is unprecedented.[3] It may be concluded that both primary and secondary steric effects appear to be absent in this system and that only polar effects are responsible for the extent of ion-pair formation. The following equation quantitatively describes the correlation in the Figure:

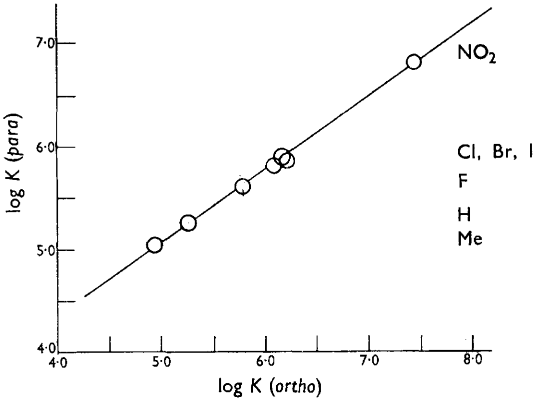
$$\left[\log\left(\frac{K_{\mathrm{X}}}{K_{\mathrm{H}}}\right)_o = 1{\cdot}41 \log\left(\frac{K_{\mathrm{X}}}{K_{\mathrm{H}}}\right)_p\right] = \sigma_o^0$$

where $(K_{\mathrm{X}}/K_{\mathrm{H}})_o$ and $(K_{\mathrm{X}}/K_{\mathrm{H}})_p$ are the ratios of the equilibrium constants for the *ortho*- and *para*-substituted benzoic acids, respectively, and σ_o^0 is defined as the parameter which measures the relative polar effects of *ortho*-substituents.[4] The Table summarizes the σ_o^0 parameters derived from the above equation. It should be emphasized that σ_o^0 parameters may be determined by this approach only if the substituent obeys the bracketed portion of the equation. Substituents such as hydroxy and methoxy, which are known to be hydrogen bonded to the reaction centre when substituted in the *ortho*-position, would not be applicable.

TABLE

Substituent	H	F	Cl	Br	I	Me	NO_2
σ_o^0	0·00	0·51	0·82	0·91	0·96	−0·32	2·18

As anticipated, Taft's σ_o^* parameters are not a linear function of the σ_o^0 parameters in the Table—an observation which indicates that σ_o^* parameters are not completely free of steric effects. That this is so is not surprising since Taft's approach depended on the exact cancellation of steric effects by the comparison of two processes which supposedly had the same steric requirements—the basic and acidic hydrolysis of esters. It is believed, therefore, that the new σ_o^0 parameters better represent the true polar effect of *ortho*-substituents.



FIGURE

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[1] R. W. Taft, jun., in M. S. Newman, "Steric Effects in Organic Chemistry", Wiley, New York, 1956, p. 587. R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 4231.

[2] M. M. Davis and H. B. Hetzer, *J. Res. Nat. Bur. Stand. U.S.A.*, 1958, **60**, 569.

[3] Traynham and Tribble have recently reported a plot of the relative hydroxy chemical shift dependence of *ortho*- and *para*-substituted phenols in dimethyl-sulphoxide, however, the correlation had a rather large degree of scatter (J. G. Traynham and M. T. Tribble, presented at the 154th Meeting of the American Chemical Society, Chicago, 1967; also private communication.)

[4] Jones and Smith, *J. Org. Chem.*, 1964, **29**, 3531, have derived a series of σ_o^0 parameters from the rates of pyrolysis of *ortho*-substituted isopropyl benzoates for the substituents Me, H, F, Cl, and NO_2. A reasonable linear relationship exists between the *ortho*-substituent parameters reported in this communication $(\sigma_o)^0$ and those of Jones and Smith (σ_{JS}): $\sigma_o^0 = 2{\cdot}38\sigma_{\mathrm{JS}}$.