The Absence of Double Bond–No Bond Resonance in the Ionization of *p*-Trifluoromethylphenol

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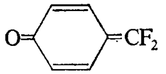
RECENTLY, several workers have criticized the concept of fluorine double bond–no bond resonance as a significant influence in rate and equilibrium processes. Streitwieser and his co-workers[1] have concluded from their studies that fluorine hyperconjugation is not significant in stabilizing fluoroalkyl anions. Sheppard[2] has reported that the original work by Roberts *et al.*[3] concerning the pK_a of *p*-trifluoromethylanilinium ion is in error and that the σ_p value needed to place the *p*-CF_3 group on a linear free energy plot with other *m*- and *p*-substituted anilinium ions in $+0{\cdot}65$ rather than $+0{\cdot}74$. Stock and his co-workers[4] have pointed out that a σ_p/σ_m ratio of $1{\cdot}26 \pm 0{\cdot}01$ is obtained for the trifluoromethyl derivatives of benzoic acid, aniline, and dimethylaniline, and have concluded that there is nothing unusual about the polar contribution of the trifluoromethyl substitutent.[5] Stock, however, used the incorrect σ_p for the aniline system; σ_p/σ_m is actually 1·33, showing that there is a small enhancement of polar effect over that predicted from the corresponding benzoic acids.

It has been reported by Jones[6] that *p*-trifluoromethylphenol, when dissolved in aqueous base at room temperature, is readily hydrolysed with the loss of fluoride ion.† Roberts[3] has used this observation as evidence for charge delocalization in the anion *via* double bond–no bond resonance interaction. In order to determine if such interaction is operating in this system, we have determined the thermodynamic pK_a's of *m*- and *p*-trifluoromethylphenol in water at 25° and have compared them with the thermodynamic pK_a's of other *m*- and *p*-substituted phenols by means of a Hammett correlation.

Since the *para*-isomer is known to react at room temperature with aqueous base,‡ measurements of pH of 50% neutralized solutions were determined with respect to time using a Beckman Model 1019 pH meter and 50% neutralized *p*-nitrophenol as the calibration standard. In all cases linear plots were obtained, which when extrapolated to $t = 0$, gave the pK_a of the acid. The pK_a of *p*-trifluoromethylphenol was determined in this manner at 18—32°. A plot of pK_a against temperature produced a smooth curve from which the pK_a of

(I)



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† Sheppard[2] has indicated that *p*-trifluoromethylaniline also appears to decompose in aqueous solution upon standing.

‡ The initial product of reaction is believed to be (I), which subsequently reacts with other phenol molecules to form telomeric species.

p-trifluoromethylphenol at 25° was determined by interpolation (pK_a = 8·675). The ionic strength of the solutions were kept low (0·0017 M) and it was assumed that the use of 50% neutralized *p*-nitrophenol as the calibration standard (a compound very similar in structure to *p*-trifluoromethylphenol), also at the same low ionic strength (0·0017 M), would result in a cancellation of activity coefficients.[7,8] The pK_a of the *meta*-isomer was determined by a method described previously[7] (pK_a = 8·950).

Comparison of the pK_a values determined in this study with the thermodynamic pK_a values of a variety of *m*- and *p*-substituted phenols[9] produces the following substitutent parameters: $\sigma(p\text{-CF}_3) = +\ 0{\cdot}56$ and $\sigma(m\text{-CF}_3) = +\ 0{\cdot}45$, the ratio $\sigma(p\text{-CF})/\sigma(m\text{-CF}_3)$ being equal to 1·25 which is essentially identical to the ratio of the corresponding benzoic acids (1·26). One may conclude, therefore, that the electrical effects of the trifluoromethyl group operating in the benzoic acid system are the same as those operating in the corresponding phenolic system. Consequently, double bond—no bond resonance interaction appears to be unimportant in the ionization of *p*-trifluoromethylphenol.

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[1] (a) A. Streitwieser, jun., and D. Holtz, *J. Amer. Chem. Soc.*, 1967, **89**, 692; (b) A. Streitwieser, jun., A. P. Marchant, and A. H. Pudjaatmaka, *ibid.*, p. 693.

[2] (a) W. A. Sheppard, *J. Amer. Chem. Soc.*, 1965, **87**, 2410; (b) W. A. Sheppard, *ibid.*, 1962, **84**, 3072.

[3] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408.

[4] F. W. Baker, R. C. Parish, and L. M. Stock, *J. Amer. Chem. Soc.*, 1967, **89**, 5677.

[5] Dewar has indicated that, in general, substituent effects are more efficiently propagated from the *para*-position than from the *meta*-position: σ_p/σ_m = 1·2. (M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, 1962, p. 159, 172; M. J. S. Dewar and A. P. Marchand, *J. Amer. Chem. Soc.*, 1966, **88**, 354.)

[6] R. G. Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346.

[7] C. L. Liotta, K. H. Leavell, and D. F. Smith, jun., *J. Phys. Chem.*, 1967, **71**, 3091.

[8] W. F. O'Hara, T. Hu, and L. G. Hepler, *J. Phys. Chem.*, 1963, **67**, 1933.

[9] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York and London, 1963, p. 373.