

The Hammett σ -Value for the Formyl Group

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ALTHOUGH it has been established¹ that a continuous range of σ_p -values is required for correlating the reactivity of an aromatic substituent in the *para*-position, the continued success² of the Hammett equation,³ using a single σ_p -value, justifies its application to kinetic and equilibrium data. If a single σ_p -value is to be used, it should preferably be based on the thermodynamic acidity constant for a substituted benzoic acid in water at 25° c.⁴

When the *meta*- and *para*-substituent constants for the formyl group,⁵ CHO (σ_m 0.355, σ_p 0.216) are compared with those for the acetyl group⁵ (σ_m 0.306, σ_p 0.516), or for the ethoxycarbonyl

group⁵ (σ_m 0.398, σ_p 0.522) the σ_p -value for the formyl group appears to be too small. We have measured the pK_a values, in water at 25° c, for iso- and tere-phthalaldehydic acids, by the method of Albert and Phillips,⁶ with the following results:

Isophthalaldehydic acid pK_a 3.84 \pm 0.03

Terephthalaldehydic acid pK_a 3.77 \pm 0.03

Taking the pK_a -value of benzoic acid as 4.20,⁷ the substituent constants for the formyl group are σ_m 0.36 \pm 0.03, σ_p 0.43 \pm 0.03. The latter value was confirmed by conductance measurements on terephthalaldehydic acid solutions,

¹ H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

² H. H. Jaffé and H. L. Jones, *Adv. Heterocyclic Chem.*, 1964, **3**, 209.

³ L. P. Hammett, "Physical Organic Chemistry", McGraw-Hill Book Co., New York, 1940, p. 190.

⁴ D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

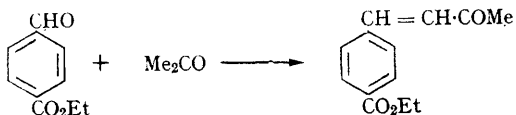
⁵ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

⁶ A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1956, 1294.

⁷ G. Kortüm, W. Vogel, and K. Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solution", Butterworths, London, 1961, pp. 352-353.

which gave, using the treatment of Ives,⁸ pK_a 3.75 ± 0.03 , σ_p 0.45 ± 0.03 .

The σ_m -value agrees well with the established value² which, in Hammett's original tabulation⁹ was derived from the acid hydrolysis of aryl-sulphuric acids.⁹ The low published σ -value² was derived from results of Tommila,¹⁰ on alkaline hydrolysis of substituted ethyl benzoates in 56% acetone; these results also give a σ_m -value for the formyl group of 0.21. When an attempt was made to repeat Tommila's measurements, the solutions rapidly became yellow in colour, undoubtedly due to the occurrence of a Claisen-Schmidt condensation between the solvent acetone and the aldehyde group,



Such a reaction should be favoured by the electron-attracting CO_2Et group, and hindered by a CO_2^- group, and hence should occur more readily before, than after, hydrolysis of the ester. Thus Tommila's results probably relate to the $-\text{CH}=\text{CH}\cdot\text{COMe}$ group, rather than to CHO . It is of interest to note that the group $-\text{CH}=\text{CH}\cdot\text{NO}_2$ has a σ_p -value of 0.26.¹¹

Further confirmation for the view that acetone reacts with the formyl group in alkaline solution was provided by kinetic measurements on the alkaline hydrolysis of the ethyl esters of iso- and tere-phthalaldehydic acids in 85% alcohol, under the conditions used by Evans, Gordon, and Watson.¹² No change occurred in colour of the solutions, and the substituent values obtained for the formyl group were σ_m 0.38, σ_p 0.43.

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⁸ D. J. G. Ives, *J. Chem. Soc.*, 1933, 731.

⁹ G. N. Burkhardt, C. Horrex, and D. I. Jenkins, *J. Chem. Soc.*, 1936, 1654.

¹⁰ E. Tommila, *Ann. Acad. Sci. Fennicae*, 1941, A, 57, No. 13, 3.

¹¹ R. Stewart and L. G. Walker, *Canad. J. Chem.*, 1957, 35, 1561.

¹² D. P. Evans, J. J. Gordon, and A. B. Watson, *J. Chem. Soc.*, 1937, 1430.