

A Correlation of Hammett Reaction Constants ρ with Infrared Frequencies

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A number of correlations of substituent constants in the Hammett equation¹ with physical properties of the molecules has been reported in the literature,² but such correlations for reaction constants are far fewer, and these constants are generally less well understood. The form of dependence of reaction constants on molecular structure and reaction conditions has already been suggested by Hammett.³ Factors determining ρ constants have been discussed by Jaffé,⁴ who has also attempted to correlate the values of ρ observed in a series of apparently similar acid dissociations with the refractivity (*i.e.* polarisability) of the atoms transmitting the substituent effects. The example chosen by Jaffé, however, is not a valid one, because the Lewis-acid character of phenylboronic acids has been neglected. Interest in factors determining the reaction constants has been growing in recent years, and trends and correlations between ρ of certain reactions and σ of the groups transmitting the substituent effects have been found.^{5,6} Zuman⁶ has also correlated ρ constants obtained in polarographic reductions of a number of organic compounds with polarographic half-wave potentials for the unsubstituted compounds. A correlation of ρ constants in a

series of acid-base reactions with infrared frequencies is reported here.

Data recently obtained for the basicity of substituted benzoyl chlorides in 100% sulphuric acid ($\rho = 0.25$),⁷ together with existing data for the basicities of acetophenones ($\rho = 2.47$),^{8a} benzaldehydes ($\rho = 2.34$),^{8b} and benzoic acids ($\rho = 1.30$)^{8c} in sulphuric acid-water mixtures (the ρ values quoted are corrected to the new acidity function scale of Jorgenson and Hartter⁹ and refer to plots of pK_{BH^+} against σ^+) provide a series of values of ρ , showing almost purely the effect of structure of the transmitting group on the effectiveness of transmission. This is so, because all other factors known to influence ρ are practically the same in these reactions (*i.e.* the electronic requirements at the reaction site, the length of the side chain, and the temperature (25°) are the same, and the reaction medium is closely comparable and of high dielectric constant throughout). A plot of these ρ values against the infrared frequency of the carbonyl bond¹⁰ proves to be linear (Figure). This means that the differences in ρ are determined here by the same factors as the differences in the infrared frequency of the C=O bond. Since this is a "mass-insensitive"

¹ L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, 1940, p. 184.

² P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

³ L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

⁴ H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

⁵ J. Hine, *J. Amer. Chem. Soc.*, 1959, **81**, 1126.

⁶ P. Zuman, *Coll. Czech. Chem. Comm.*, 1960, **25**, 3225.

⁷ M. Liler, in preparation.

⁸ R. Stewart and K. Yates, (a) *J. Amer. Chem. Soc.*, 1958, **80**, 6355, (b) *Canad. J. Chem.*, 1959, **37**, 664, (c) *J. Amer. Chem. Soc.*, 1960, **82**, 4059.

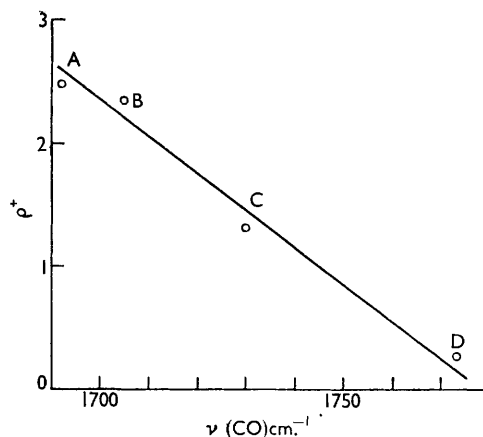
⁹ M. J. Jorgenson and D. H. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

¹⁰ L. J. Bellamy, *J. Chem. Soc.*, 1955, 4221.

vibration, the primary factor is the electron density on the carbon atom,¹⁰ and ρ is seen to increase with increasing electron density. The results are, therefore, a confirmation of Hammett's suggestion that ρ should depend on the "displaceability of electrons on the reacting group,"³ *i.e.* on the polarisability of the side chain. It should also be mentioned that the low ρ value for benzoic acids as compared with the values for acetophenones and benzaldehydes has previously been ascribed to the resonance in the protonated carboxyl group.^{9c} The correlation found here shows that resonance does not play an important part in determining ρ in these compounds.

These ρ values were also found to vary linearly with the primary σ_m constants² of the groups attached to the carbonyl carbon. This is consistent both with the claim that primary σ_m values measure purely inductive effects and that ρ values are dependent upon electron density along the path of transmission. (The two linear plots, of course, imply a linear correlation between the infrared frequencies of the carbonyl bond and the primary σ_m constants of the groups attached to the carbonyl carbon, a correlation which has not been pointed out before). A similar correlation of ρ with σ has been found by Yeh and Jaffé,¹¹

in a study of the basicities of disubstituted azobenzenes.



A, acetophenones; B, benzaldehydes; C, benzoic acids; D, benzoyl chlorides. ρ^+ indicates that σ^+ constants were used in obtaining the ρ values.

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¹¹ Si-Jung Yeh and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1959, **81**, 3279.