Tetrahedron Letters No. 9, pp 753 - 756, 1972. Pergamon Press. Printed in Great Britain.

ON THE INTERPRETATION OF DEVIATIONS FROM LINEARITY IN FREE ENERGY PLOTS

M. Godfrey

Department of Chemistry, University of Southampton, Southampton SO9 5NH

(Received in UK 14 January 1972; accepted for publication 27 January 1972)

Two pieces of experimental work cast serious doubt on the validity of those theories of the origin of Hammett σ constants which involve a combination of the following two types of substituent effect: (a) field effects which strongly depend on the distance between the substituent and the reaction site, and (b) resonance effects which depend on the effectiveness of conjugation between the sites. First, Ceska and Grunwald[1] have observed that the equilibrium constants for ion-pair formation from substituted anilines in glacial acetic acid correlate very well ($r=0.996$) with the Hammett σ constants, but that the equilibrium constants for the dissociation of the ion-pairs correlate poorly ($r=0.78$) with the same parameters. Secondly, Eaborn, Eastmond, and Walton[2] have found that the rates of base-catalysed cleavage of substituted $C_6H_5(C{\equiv}C)_3SiEt_3$ compounds correlate very well ($r=0.994$) with the σ constants. In this reaction series the separation between the substituent and the reaction site is very much greater than in the reaction series which defines the Hammett constants (the dissociation of benzoic acids in water).

We now report how these results can be explained in terms of the recently proposed field and charge-transfer (FCT) treatment of σ constants.[3] The explanations involve a new interpretation of the significance of deviations from linearity in free energy plots. We also indicate why our method of treatment might be especially useful when applied to photoreactions.

A Summary of the FCT Treatment of the Transmission of Substituent Effects.[3] The direct interactions between a hydrocarbon and a substituent group are divided into three types, namely, field, exchange, and charge-transfer. The rate constant or equilibrium constant for a chemical reaction occuring within a complex of a functional substituent and a reactant (hereafter called a functional complex) depends on changes in the interactions between the functional complex (Z) and the hydrocarbon. The change in each type of interaction is affected by the interactions between the hydrocarbon and a non-functional substituent (Y). Thus the non-functional substituent affects the reactivity of the functional complex.

It is predominantly the field and exchange effects of the Y substituents on changes in charge-transfer interactions between Z and benzene that determines the value of the Hammett σ constants. The values of σ should be almost independent of the nature of the functional complex provided that the transition state or the final state for each reaction can be regarded as a perturbation of the initial state.[4] However, Hammett σ and ρ scales should not be good measures of the field and exchange effects on changes in charge-transfer interactions with benzene in an excited electronic state, or with any other hydrocarbon even in the ground state. The introduction of one or more methylene groups (or other saturated species) between the hydrocarbon and the functional complex should attenuate but not eliminate the charge-transfer interactions.

The effects of Y substituents on changes in the combined field and exchange interactions between a Z substituent and the hydrocarbon are summarised by the expression (1) in which Z and Z' are the final and initial forms of the functional complex, t are known charge-transfer functions, f are known field and exchange functions, and ζ_i are parameters with values which are characteristic of the electronic structure of the hydrocarbon and of the sites of the substituents.

$$\frac{t_1(Y)f_1(Z-Z')}{[t_2(Y) + f_2(Z)][t_2(Y) + f_2(Z')]} + \zeta_i f_3(Y)f_3(Z-Z') \qquad (1)$$

The two terms in expression (1) tend to cancel out when the effects on the dissociation of benzoic acid are being considered. However, in the general case, the effects of Y substituents on changes in the combined field and exchange interactions between a functional complex and benzene should cause significant deviations from $\rho\sigma$ behaviour. The deviations for different functional complexes should not in general parallel one another.

A New Interpretation of Deviations from Linearity in Free Energy Plots. Our interpretation of the experimental observations mentioned above is based on the following hypothesis concerning changes in the interactions between the functional complex and the hydrocarbon during a reaction. Changes in the charge-transfer interactions are invariably dominant in the early stages of covalent bond rupture (or the late stages of covalent bond formation) within the functional complex, but changes in the field interactions may be significant in other situations provided that there is a net flow of electronic charge within the functional complex during the reaction.

In terms of our treatment, for any pair of reactions involving the same parent hydrocarbon, if the log-log plot of substituent effects on the rate constants or equilibrium constants is not linear, then the movement of charge within at least one of the functional complexes is mainly responsible for the non-linearity. Neither the formation of ion-pairs from substituted anilines nor the cleavage of the substituted $C_6H_5(C{\equiv}C)_3SiEt_3$ compounds is likely to involve a large movement of charge within that region of the functional complex which is close to the benzene ring. Hence, there is no reason why either reaction series should not correlate well with Hammett σ constants. However, the separation of the anilinium and acetate ions, which does not involve rupture of a covalent bond, should be influenced mainly by the charge separation within the functional complex. Hence, the poor correlation with Hammett σ constants. We have shown[3] that the observed deviations from linearity can be interpreted in terms of expression (1).

Our treatment yields new interpretations of some commonly used parameters such as the Taft σ^0 scale, the σ^+ and σ^- scales, and the Brønsted coefficients. Consider, for example, the Taft σ^0 scale. The log-log plot for the rates of deprotonation by base of substituted $C_6H_5CH_2CHMeNO_2$ and of substituted $C_6H_5CHMeNO_2$ gives an excellent straight line ($r=0.998$; slope$=0.46$).[5] This suggests that the changes in the field interactions between the functional complex and the benzene ring are extremely small compared with the changes in the corresponding charge-transfer interactions. Each reaction series correlates better with Taft σ^0 values than with Hammett σ values, suggesting that the Taft constants are dominated by field and exchange effects on changes in charge-transfer interactions to an even greater extent than the Hammett constants. This argument is supported by the result that ion-pair formation from benzoic acids in benzene correlates better with σ^0 than with σ.[6]

Our treatment could be of especial importance in the study of photochemical reactions as the following example shows. We have calculated that the amount of charge-transfer in the fluorescent state (perturbed $^1B_{2u}$) of a typical substituted benzene need not be very much greater than in the ground state. We have also calculated that the ζ parameters are several times as great in the fluorescent state as in the ground state. These results suggest that deviations from linearity in free energy plots for fluorescent state reactions could be very pronounced. In those fluorescent state reactions in which changes in the field reactions between the functional complex and the hydrocarbon are small, the relative effects of corresponding meta and para substituents should be qualitatively the reverse of those expected in similar ground state reactions. However, in those reactions in which changes in the field interactions are dominant, we predict that such reversals will not be found. Experimentally reversals are observed among the rates of solvolysis of certain substituted benzenes,[7] but they are not observed among the equilibrium constants for the dissociation of phenols.[8]

REFERENCES

1. G.W. Ceska and E. Grunwald, J. Amer. Chem. Soc., 1967, 89, 1371.
2. C. Eaborn, R. Eastmond, and D.R.M. Walton, J. Chem. Soc. B, 1971, 127.
3. M. Godfrey, J. Chem. Soc. B, 1971, 1534, 1540.
4. The equilibria between certain nitroalkanes and their conjugate bases are examples of reactions in which the final states are probably not perturbed initial states. The transition states for the deprotonations probably are perturbed initial states. Hence the unusual values of the Brønsted coefficients.[5]
5. F.G. Bordwell, W.J. Boyle, and K.C. Yee, J. Amer. Chem. Soc., 1970, 92, 5926.
6. R.W. Taft, J. Phys. Chem., 1960, 64, 1805.
7. H.E. Zimmerman and V.R. Sandel, J. Amer. Chem. Soc., 1963, 85, 915.
8. E.L. Wehry and L.B. Rogers, J. Amer. Chem. Soc., 1965, 87, 4234.