

INDUCTIVE AND MESOMERIC EFFECTS IN BENZENE DERIVATIVES

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THE terms of inductive (I) and mesomeric (M) effects form still the basis of recent qualitative and quantitative studies on substituent effects, benzene derivatives being a classical model. In practically all of these studies the difference in the influence of a certain substituent on the para and meta position is taken as a measure of its M-effect, tacitly being assumed that the I-effect is transmitted to both of these positions with the same intensity. These already familiar ideas have been expressed quantitatively by Taft<sup>1</sup>:

$$\sigma_p = \sigma_I + \sigma_R \quad (1a)$$

$$\sigma_m = \sigma_I + 0.33 \sigma_R \quad (1b)$$

where the constant  $\sigma_R$  is defined as a measure of the M-effect by means of the inductive constant<sup>2</sup>  $\sigma_I$  and the Hammett constants  $\sigma_{m,p}$ , the latter expressing the total substituent effect on the meta and para position, respectively. In addition to the equal intensity of the I-effect in both of these positions it

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<sup>1</sup> R.W.Taft J.Amer.Chem.Soc. 79, 1045 (1957); R.W.Taft, I.C. Lewis J.Amer.Chem.Soc. 80, 2436 (1958).

<sup>2</sup> R.W.Taft J.Amer.Chem.Soc. 74, 3120 (1952); 75, 4231 (1953).

was supposed in the derivation of eq.(1a,b) that both of the constants  $\sigma_{m,p}$  and  $\sigma_I$  are expressed in the same scale<sup>1</sup>.

To prove experimentally these suppositions we studied two series (meta and para) of benzoic acid derivatives with substituents for which solely the I-effect can be anticipated, especially with substituents of the type  $\text{CH}_2\text{X}$ . From the relative dissociation constants of these two series of acids plotted one against another on Fig.1 (upper line in 50% ethanol<sup>3,6,7</sup>, lower line in 80% methyl cellosolve<sup>3-5</sup>) the following conclusions can be drawn :

- (i) The relatively exact linearity and the fitting of the points for substituents H and  $\text{CH}_3$  prove that the so-called hyperconjugation is not operative in the case of substituent of the  $\text{CH}_2\text{X}$  type.
- (ii) From the slopes of the lines (expressed as  $\lambda = 1.15 \pm 0.05$ ) it follows that the influence of the I-effect is stronger on the para than on the meta position.
- (iii) The fitting of the points for some common substituents of the -M class ( $\text{NO}_2$ , CN, COOH etc.) on the lines shows that their M-effects are negligible in the compounds studied.

Results of kinetic measurements on Fig.2 (upper line for

<sup>3</sup> O.Exner, J.Jonáš Collection Czech.Chem.Comm. 27, 2296 (1962).

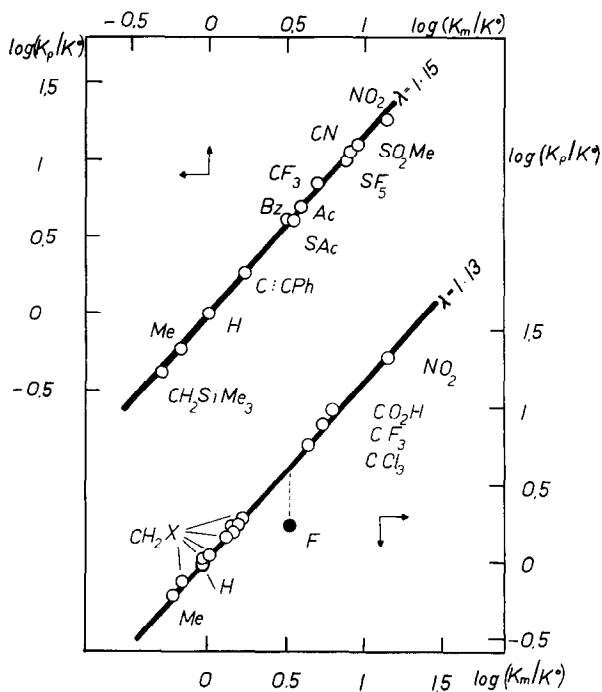
<sup>4</sup> O.Exner, W.Simon, not yet published.

<sup>5</sup> W.Simon, G.H.Lyssy, A.Mörkofer, E.Heilbronner Zusammenstellung von scheinbaren Dissoziationskonstanten im Lösungsmittelsystem Methylcellosolve/Wasser. Juris-Verlag, Zürich 1959.

<sup>6</sup> D.H.McDaniel, H.C.Brown J.Org.Chem. 23, 420 (1958).

<sup>7</sup> W.N.White, R.Schlitt, D.Gwynn J.Org.Chem. 26, 3613 (1961); W.A.Sheppard J.Amer.Chem.Soc. 84, 3072 (1962); J.K.Kochi, G.S.Hammond J.Amer.Chem.Soc. 75, 3452 (1953).

Fig. 1



the reaction of benzoic acids with diphenyldiazomethane <sup>8</sup>, lower line for the solvolysis of t-cumyl chlorides <sup>9</sup>) support these conclusions. Our finding (iii) is in contrast with the hitherto usual interpretation but is supported by roentgenographic investigation on nitrobenzene <sup>10</sup> and by some quantum

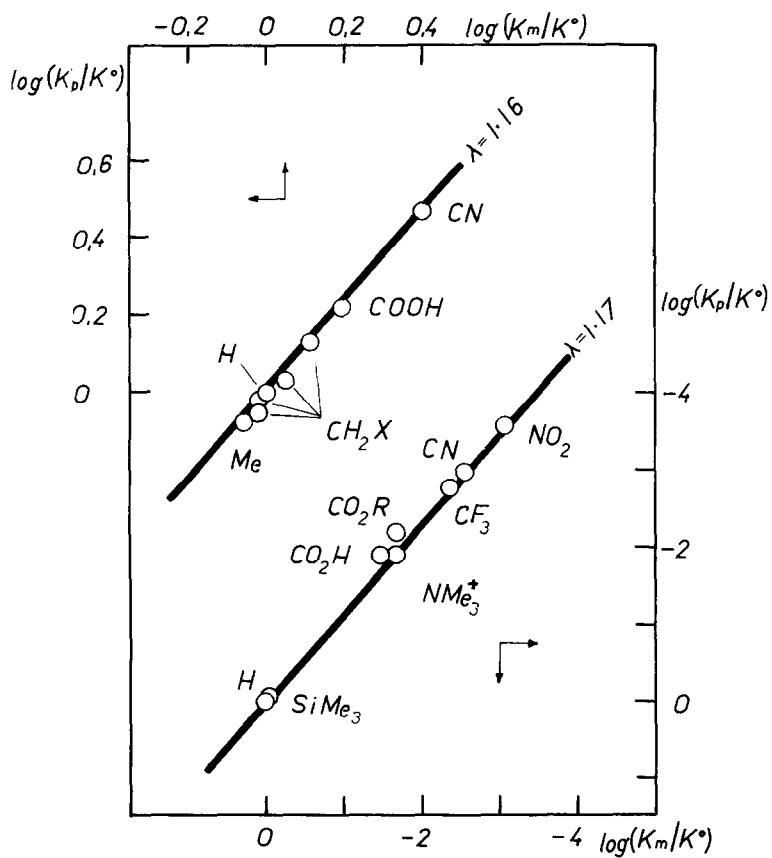
<sup>8</sup> A.Talvik, P.Zuman, O.Exner Collection Czech.Chem.Comm., in press.

<sup>9</sup> H.C.Brown, Y.Okamoto J.Amer.Chem.Soc. **80**, 4979 (1958).

<sup>10</sup> J.Trotter Tetrahedron **8**, 13 (1960).

chemical considerations <sup>11</sup>. We wish to emphasize that our result (iii) does not concern molecules where the conjugation with a present substituent of the opposite (+M) type is possible (e.g. p-nitraniline).

Fig. 2



<sup>11</sup> D. Peters J. Chem. Soc. 2654 (1957).

Our result (ii) can only be explained by the participation of  $\pi$ -electrons in transmitting the I-effect, called <sup>12</sup> the non-classical inductive effect. The integral I-effect between the  $C_1$  and  $C_r$  atoms of the benzene nucleus has been expressed <sup>11</sup> as

$$\sigma_r = \text{const.} \sum_s \pi_{rs} (\epsilon^{s-1} + \epsilon^{7-s}) \quad (2a)$$

where  $\pi_{rs}$  denotes the mutual polarizability between the atoms  $C_r$  and the variable  $C_s$ ; the constant  $\epsilon$  is named transmission factor. Starting with assumption (not confirmed by this work) that  $\lambda \equiv \sigma_p^I / \sigma_m^I = 1$  letters <sup>11</sup> evaluated from the eq.(2a) a reasonable value of  $\epsilon = 0.53$ , he did not allow, however, for higher terms. Therefore we propose as a better approach the equation

$$\sigma_r = \text{const.} (\epsilon^{r-1} + \epsilon^{7-r} - \pi_{1r}) \quad (2b)$$

where the first and second terms express the classical and the third term the non-classical I-effect. Using empirical values <sup>4</sup>  $\lambda = 1.15$ ,  $\epsilon = 0.46$  and an approximation  $\pi_{13} \approx 0$  we have calculated  $\pi_{14} = -0.100$  in fair agreement with the values <sup>11</sup>  $\pi_{13} = 1/108$ ,  $\pi_{14} = -11/108$ .

From our conclusions it follows that the simple difference of the reactivity in the para and meta position cannot be taken as a measure of the M-effect as it is usual and as is explicitly expressed by the eq.(1a,b). The mesomeric constants  $\sigma_R$  derived by means of this equation need unimportant corrections in the case of +M substituents but they are completely erroneous for -M substituents. If a correction by the factor 1.15 in eq.(1a) is applied it is possible to show that the

<sup>12</sup> K.B.Everard, L.E.Sutton J.Chem.Soc. 2821 (1951).

scale of the  $\sigma_I$  constants does not correspond accurately to that of  $\sigma_{m,p}$  and the former constants are to be multiplied by the factor of cca 1.12. A redetermining of the  $\sigma_I$  and  $\sigma_R$  constants will be published when more experimental data are available; it is evident that for the evaluation of the  $\sigma_R$  constants of -M substituents the substituted benzoic acids cannot be used and a new model reaction has to be found.

Finally, our data make it possible to clear some problems in the theory of Hine<sup>13</sup> who postulated a linear dependence between the  $\sigma_m$  and  $\sigma_p$  constants of corresponding substituents; this dependence has been later limited<sup>14</sup> to individual classes of substituents with a common first atom. According to Fig.1 and 2 where  $\log (K/K^0)$  is proportional to  $\sigma$ , the only condition of validity is the absence of M-effects, Hine's relation<sup>13</sup> is thus valid in the same range as the original unmodified Hammett equation.

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<sup>13</sup> J.Kine J.Amer.Chem.Soc. 81, 1126 (1959).

<sup>14</sup> D.H.McDaniel J.Org.Chem. 26, 4692 (1961).