# 145. *The Dissociation Constants of the Isomeric Halogenobenzoic and Nitrobenzoic Acids.*

By H. O. Jenkins.

A linear relation has been found between the logarithm of the dissociation constant and the electric intensity due to the substituent dipole in each halogenobenzoic acid series and in the nitrobenzoic acids. The *o*-acids are now considered, in the light of the above relation, to have quite normal dissociation constants, and the co-ordinate-bond hypothesis is not needed in these equilibrium studies. The slope of the line connecting electric potential and logarithm of the dissociation constant has been evaluated, with good agreement between theory and experiment. An approximate equation has been suggested for the dissociation constant of a halogen- or nitro-substituted benzoic acid in terms of various constants and the variable potential.

The introduction of a substituent into an organic acid produces a change in the acidity as measured by the dissociation constant, and attempts have been made to correlate such changes with the polar properties of the substituted atom or group. For example, Dippy and Watson (*Chem. and Ind.*, 1935, **54**, 735; J., 1936, 436), following Nathan and Watson (J., 1933, 890), showed that for *m*-substituted benzoic and phenylacetic acids

$$\log K_s = \log K_u - x(\mu + a\mu^2)$$

where $K_s$ and $K_u$ are the dissociation constants of substituted and unsubstituted acids, $x$ and $a$ are constants for a series, and $\mu$ is the electric dipole moment in Debye units of the corresponding monosubstituted benzene. These relations apply to thermodynamic dissociation constants, *i.e.*, Ostwald constants corrected for activities and mobilities, and vapour values of dipole moments.

Another correlation has been suggested by Dippy (*Nature*, 1937, **139**, 591), *viz.*, that a linear relation exists between the dipole moments of the appropriate monosubstituted benzenes and the dissociation constants of *m*-substituted benzoic, phenylacetic, and β-phenylpropionic acids. *m*-Acids are used in these correlations to avoid complicating factors, if any exist, such as electromeric and steric effects.

Relations such as these have many advantages. It is conceivable that prediction of one property from another may be possible in cases where measurement presents difficulty. Again, a clue may be given to the underlying physical phenomena. This paper suggests further correlations.

From the method of plotting used by Watson and his co-workers it is clear that they did not intend their relation to include *o*- and *p*-derivatives with their *m*-isomers. On such graphs the abscissæ would be the same for the three isomers, unless some correction is made for distance and direction, and the ordinates vastly different. It is emphasised that no satisfactory relation is on record between the dissociation constants of unsubstituted and the three isomeric substituted acids with some function of the group moment of the substituent. That such a relation should be found is most important for many reasons, one being in connexion with the so-called ortho-effect. It is often stated that the strengths of *o*-substituted benzoic acids are abnormally high, and a chelation process has been suggested (Dippy, Evans, Gordon, Lewis, and Watson, J., **1937**, 1421) to account for the abnormality. However, the grounds upon which abnormality is ascribed are not clear. *o*-Toluic acid obviously has an abnormally high dissociation constant, since this is almost twice as great as that of the unsubstituted acid and the methyl group in the *m*- and *p*-positions normally depresses the acidity. Whether *o*-chlorobenzoic acid ($K_s/K_u = 18{\cdot}2$) has an abnormally high constant does not seem self-evident, since there are no means of predicting the normal value.

Some time ago Wynne-Jones (*Chem. and Ind.*, **1933**, **52**, 273) suggested that organic acids of the same type did not show the same order of strengths in all solvents. One criticism made was that *o*-substituted acids were compared with their *m*- and *p*-isomers, whereas they should be omitted in a general discussion. The validity of this objection is now examined.

Smallwood (*J. Amer. Chem. Soc.*, 1932, **54**, 3048) has elaborated an electrostatic theory in an attempt to account for dissociation-constant changes. However, his calculations require a knowledge of the extent to which free rotation of the acid group takes place with respect to the rest of the molecule in, say, *o*-nitrobenzoic acid. Restricting ourselves to the halogen- and nitro-substituted benzoic acids, a simpler method than that used by Smallwood is to consider the carbon atom to which the carboxyl group is attached as the important centre determining the free energy of ionisation. This is equivalent to regarding the $C{\cdot}CO_2H$ system as a more or less perfect conductor or equipotential surface, and our difficulties regarding free rotation in the benzoic series vanish.

Now the field intensity in a vacuum at this carbon atom due to a small dipole whose centre is $r$ cm. away and whose axis is inclined at an angle $\theta$ to $r$ is

$$F = \mu(1 + 3\cos^2\theta)^{\frac{1}{2}}/r^3$$

In a medium of dielectric constant $\varepsilon$ we should have to divide by $\varepsilon$, but this is not essential for the present purpose. This field, which varies with the nature and position of the substituent, will alter both the strength of the O–H bond and the internuclear distance (Badger's rule) and thus facilitate or inhibit ionisation. Now, for the groups considered, if no secondary influence is at work, or if the inductive effect of the dipole is predominant, some relation should exist between $F$ and the dissociation constant, which is, of course, related to the free energy of ionisation. To see whether this supposition is justified, values of $F$ have been calculated for the acids by using the latest vapour values of dipole moments, due to Groves and Sugden and others, and values of $r$ are taken from Pauling and Huggins's table of interatomic distances (*Z. Krist.*, 1934, **87**, 205) and from Brockway (*Ann. Reports*, 1937, **34**, 197); $\theta$ in each case has been calculated trigonometrically. The dipole has been assumed to be located half-way between the carbon atom of the ring and the first substituent atom. Table I gives the results of calculation for unsubstituted benzoic acid and the three bromo-substituted acids, and Fig. 1 shows them graphically. Similar results for the iodo- and nitro-acids are included in the figure. The C–Br internuclear distance has been taken as

1·88 A., and $\mu_{C_6H_5Br}$ as 1·71 D. The dissociation constants, which are thermodynamic, have been taken from a table prepared by Dr. J. F. J. Dippy, to be published shortly.

TABLE I.

| Substituent. | $10^5$ *K*. | log *K*. | *F*. | Substituent. | $10^5$ *K*. | log *K*. | *F*. |
|---|---|---|---|---|---|---|---|
| (H) | 6·27 | $\bar{5}$·7973 | ±0·000 | *m*-Br | 15·4 | $\bar{4}$·1875 | −0·092 |
| *o*-Br | 140 | $\bar{3}$·1461 | −0·344 | *p*-Br | 10·7 | $\bar{4}$·0294 | −0·065 |

For all the mono-halogeno- and -nitro-benzoic acids, good straight lines are obtained on plotting *F* against 5 + log *K*, and each line goes through the point for the *o*-acid, so the dissociation constant of any one of these *o*-acids can be calculated from the constants of its two isomers. Better linearity would be obtained if the dissociation constant of the *p*-fluoro-acid were a little higher and that for the *p*-nitro-acid a little lower. This may be correlated with their opposed mesomeric effects, but it is clear that in the cases studied, the *o*-effect is non-existent and the inductive effect of the dipole through space is the predominant factor. The equations to the lines, after conversion of common into Napierian logarithms, are given by ln $K_s$ = ln $K_u$ — β*F*, where β has the following values :

FIG. 1.

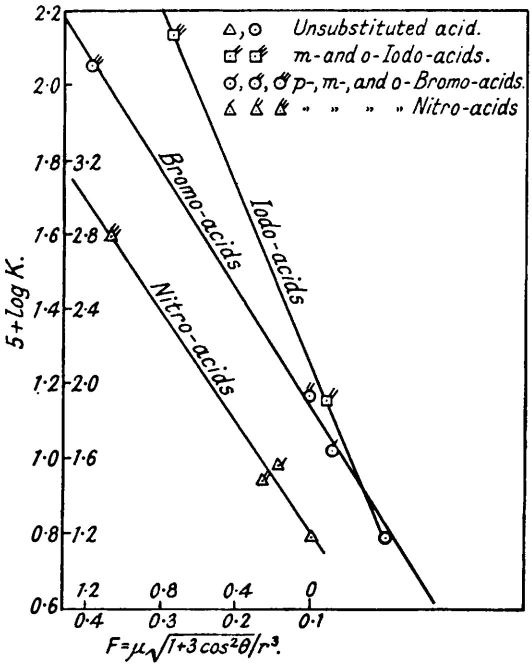
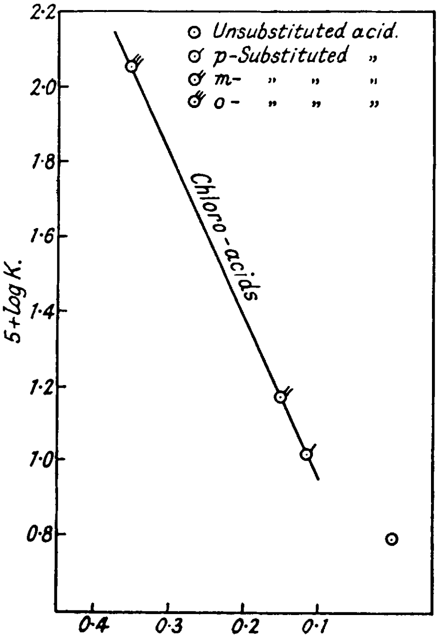


FIG. 2.



| Substituent | F | Cl | Br | I | $NO_2$ |
|---|---|---|---|---|---|
| β | 4·99 | 7·47 | 8·97 | 10·81 | 4·5 |

For the halogen acids, the slopes increase gradually from the fluoro- to the iodo-acid. Since distances have been expressed in A., and electric moments in D., the absolute value of the slope for, say, the iodobenzoic acids is 10·81 × $10^{-6}$. Because the ionisation constant varies with temperature, Hammett (*J. Chem. Physics*, 1936, **4**, 613) has suggested that entropy and heat-capacity changes may invalidate the comparison of dissociation constants of related acids at a fixed temperature. Wynne-Jones (*loc. cit.*) has argued similarly. There may be cases in which these objections have point, but the regularities now presented indicate that, in our examples, they are second-order effects. Since the *o*-acids are not now believed to be abnormally strong, the co-ordinate-bond hypothesis is not needed to account for these equilibrium data, and, of course, it cannot be used for *o*-fluorobenzoic acid, since fluorine cannot expand its valency group of electrons. This must not, however, be taken to prejudice the use of the chelation idea when applied to hydroxy-acids, or even to an activated complex to account for some anomalous reaction rates. In the case of the methyl-substituted benzoic acids, we are faced with a different situation. The dipole moment of the C–$CH_3$ link is very small, and the magnitude and sign of $F$ do not play the major part in determining the dissociation constant. Inclined groups such as O–H and O–$CH_3$ have been ignored in this investigation on account of difficulties in calculation.

Reaction velocity measurements have been made by Williams and Hinshelwood (J., 1934, 1079), Ingold and Nathan (J., 1936, 222), Evans, Gordon, and Watson (J., 1937, 1430) and others to throw light on the inductive effects of groups. Changes in velocity as a substituent is changed, say, in the alkaline hydrolysis of benzoic esters, are attributed to variations in $E$ or in $P$, or in both, in the equation $k = PZe^{-E/RT}$. If the preceding ideas are correct, we should expect a definite systematic variation of the energy of activation in any one reaction as $F$ alters owing to change of substituent or change of position of the same substituent. Ingold and Nathan (*loc. cit.*) find this when the substituent is changed. Evans, Gordon, and Watson (*loc. cit.*) find only slightly lower values for $E$ for *o*-substituted esters than for their *m*- and *p*-isomerides. The difference, however, is in the right direction, and until a quantitative theory is forthcoming further discussion is unprofitable.

There is another instructive method of plotting, for, instead of using the field intensity along $r$, we can plot the electrostatic potential $\psi = \mu \cos \theta / r^2$ at the same carbon atom due to the dipole in its various *o*-, *m*-, and *p*-positions. The relevant data for the chlorobenzoic acids are given in Table II, and are plotted in Fig. 2; C–Cl has been taken as 1·70 A., and $\mu_{C_6H_5Cl}$ as 1·73 D.

TABLE II.

| Substituent. | $10^5 K$. | log $K$. | $\psi$. | Substituent. | $10^5 K$. | log $K$. | $\psi$. |
|---|---|---|---|---|---|---|---|
| (H) | 6·27 | $\bar{5}$·7973 | 0·000 | *m*-Cl | 14·8 | $\bar{4}$·1703 | −0·158 |
| *o*-Cl | 114 | $\bar{3}$·0569 | −0·355 | *p*-Cl | 10·5 | $\bar{4}$·0232 | −0·130 |

This type of graph has the following characteristics. All the acids dealt with give good straight lines going through the points for *o*-, *m*-, and *p*-isomers, but each line does not go through the point for the unsubstituted compound. The line for the chlorobenzoic acids is represented by the equation

$$\ln K_s = \ln K_u - 6{\cdot}9 - 10{\cdot}12\,\psi$$

and the appearance of the constant is to be expected on account of the relation between $F$ and $\psi$, *viz.*, $\psi = -\int F . dr$. When electric moments are expressed in electrostatic units and distances in cm., the absolute value of the above slope is $10{\cdot}12 \times 10^2$. As in the graphs of intensity, no ortho-anomaly is found. It is to be specially noticed that for every acid the experimental slopes of the lines for potential plotted against Napierian logarithm of the dissociation constant are between $10^3$ and $10^4$. Now, since the electric potential is defined as the work done to bring up a hydrogen ion from infinity against the field of the dipole, and since, in going from one isomeric compound to another, we can assume entropy and work terms to cancel, we would expect the potential slope to approximate to $\boldsymbol{Ne}/\boldsymbol{R}T$, where $\boldsymbol{N}$ is the Avogadro number ($6{\cdot}06 \times 10^{23}$), $\boldsymbol{e}$ the electronic charge ($4{\cdot}77 \times 10^{-10}$ e.s.u.), $\boldsymbol{R}$ the gas constant ($83 \times 10^6$), and $T$ is the absolute temperature. Evaluation gives $\boldsymbol{Ne}/\boldsymbol{R}T = 1{\cdot}1 \times 10^4$ at 25°, and this agrees reasonably well with the experimental slopes. Approximately, then, we have for the acids

$$\ln K_s = \ln K_u - \alpha - \psi(\boldsymbol{Ne}/\boldsymbol{R}T)$$

or

$$\ln K_s = \ln K_u - \alpha - (\mu \cos \theta / r^2)(\boldsymbol{Ne}/\boldsymbol{R}T)$$

Dr. H. B. Watson and Dr. J. F. J. Dippy have both read this manuscript and made valuable suggestions.

THE TECHNICAL COLLEGE, CARDIFF. [*Received, February 22nd, 1939.*]