249. *The Dissociation Constants of the Isomeric Halogeno- and Nitro-anilines and -phenols.*

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The dissociation constants of the halogeno- and nitro-anilines and -phenols have been correlated with the electrostatic potential at the carbon atom to which the amino- or hydroxyl group is attached. Linear relations have been discovered. A proof is offered of the proportionality, as between one nuclear position and another, of the mesomeric effect to the inductive in such systems. No ortho-effect exists in either the anilines or the phenols.

A PREVIOUS paper (this vol., p. 640) dealt with the dissociation constants of the halogeno- and nitro-benzoic acids. These have been correlated with the change in the electrostatic potential taking place at the carbon atom to which the carboxyl group is attached, when a substituent dipole is introduced and moved from the *p*- to the *m*- or *o*-position. A direct result has been proof of the normality of the dissociation constants of *o*-halogeno- and nitro-benzoic acids. The present paper extends the work to similarly substituted anilines and phenols.

Anilines.—A selection of relevant data for the monosubstituted anilines is given in Table I and plotted in Fig. 1. The dissociation constants for all the halogenoanilines

TABLE I.

Substituent.	$10^{12} K$.	$\log K$.	$\psi = \mu \cos \theta/r^2$.	Substituent.	$10^{12} K$.	$\log K$.	$\psi = \mu \cos \theta/r^2$.
	In 30% aqueous C_2H_5OH at 25°.				In 30% aqueous C_2H_5OH at 25°.		
H	126	$\bar{1}0\cdot1004$	$\pm0\cdot000$	*o*-I	0·36	$\bar{1}3\cdot5563$	$-0\cdot279$
o-Br	1·00	$\bar{1}2\cdot0000$	$-0\cdot344$	*m*-I	7·59	$\bar{1}2\cdot8802$	$-0\cdot125$
m-Br	7·94	$\bar{1}2\cdot8998$	$-0\cdot1480$	*p*-I	15·1	$\bar{1}1\cdot1790$	$-0\cdot1030$
p-Br	21·9	$\bar{1}1\cdot3404$	$-0\cdot1220$				
	In water at 25°.				In water at 25°.		
H	530	$\bar{1}0\cdot7243$	$\pm0\cdot000$	*m*-NO₂	4·0	$\bar{1}2\cdot6021$	$-0\cdot408$
o-NO₂	0·0056	$\bar{1}5\cdot7482$	$-0\cdot919$	*p*-NO₂	0·124	$\bar{1}3\cdot0934$	$-0\cdot339$

have been taken from Bennett, Brooks, and Glasstone's potentiometric glass-electrode titrations (J., 1935, 1821) in 30% aqueous ethyl alcohol at 25°. The nitroanilines in water at 25° were measured by Farmer and Warth (J., 1904, **85**, 1726), using a distribution method. These authors' value for aniline (530 × 10⁻¹²) has been taken in preference to more recent values in order to make a just comparison of the basicities of the isomerides based on the results of one investigator.

Each series of anilines gives a straight line going through the points for the *o-*, *p-*, and unsubstituted compounds, but in each halogeno-series the *m-*aniline, and in the nitroaniline series the *p-*aniline, deviates from the linear relationship. The lines can be represented by equations of the form, $\ln K_s = \ln K_u + \gamma\psi$, after conversion to Napierian logarithms, and γ has the following values :

Substituent	F	Cl	Br	I	NO₂
γ	10·6	12·6	14·7	21·3	12·6

FIG. 1.
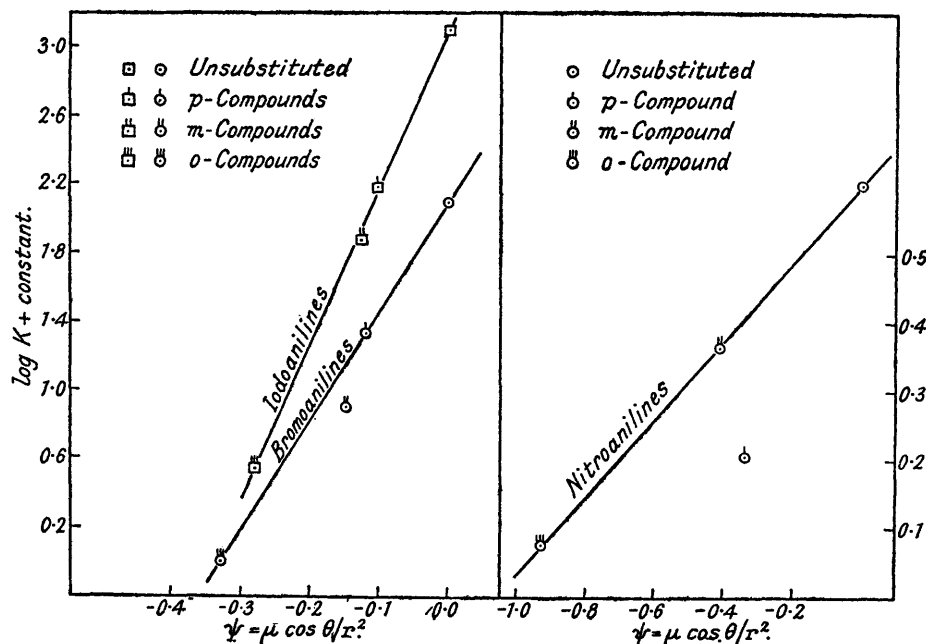
The slopes increase systematically and, as in the case of the acids, approximate to $N\epsilon/RT$, since the absolute value of a slope when electric moments are expressed in e.s.u. and distances in cm. is obtained by multiplying each of the above figures by 10^2.

The *o-*substituted anilines will now be considered. It is often stated that their strengths are abnormally low, but no explanation of this statement is available. When Victor Meyer's conception of steric hindrance, as applied by Flürscheim (J., 1909, **95**, 708) to acids, was extended to the equilibrium, $R \cdot NH_2 + H_2O \rightleftharpoons R \cdot \overset{+}{N}H_3 + \overset{-}{O}H$, it became evident that any extra steric effect would operate in the wrong direction. Far from producing abnormally low strengths in *o-*substituted bases, it would rather tend to shift the equilibrium to the right and increase the basic strengths. Again, it was realised that chelation as an explanation offered difficulties in some cases. In *o-*chloroaniline, for example, if the nitrogen atom of the amino-group, with its lone pair of electrons, is to act as donor, a four-membered ring will result and this is certainly improbable. However, since the hydrogen atoms of the amino-group can act as acceptors, a five-membered ring structure can be at least visualised. The present calculations clearly show that neither explanation is needed. No particular effect exists

here characteristic of the o-substituted compounds which is not to be found in the p-derivatives.

Phenols.—A selection of data is given in Table II and plotted in Fig. 2. The data in

TABLE II.

Substituent.	$10^{10} K$.	log K.	ψ.	Substituent.	$10^{10} K$.	log K.	ψ.
In 30% aqueous $C_2H_5 \cdot OH$ at 25°.				In 30% aqueous $C_2H_5 \cdot OH$ at 25°.			
H	0·32	$\bar{1}1$·5051	±0·000	o-Cl	10·20	$\bar{9}$·0086	−0·355
o-F	4·27	$\bar{1}0$·6304	−0·363	m-Cl	4·90	$\bar{1}0$·6902	−0·158
m-F	1·51	$\bar{1}0$·1790	−0·161	p-Cl	1·32	$\bar{1}0$·1206	−0·130
p-F	0·76	$\bar{1}1$·8808	−0·134				
In 50% aqueous $CH_3 \cdot OH$ at 20°.				In 50% aqueous $CH_3 \cdot OH$ at 20°.			
H	0·125	$\bar{1}1$·0899	−0·000	m-Cl	1·95	$\bar{1}0$·2900	−0·158
o-Cl	3·2	$\bar{1}0$·5051	−0·355	p-Cl	0·47	$\bar{1}1$·6721	−0·130

FIG. 2.
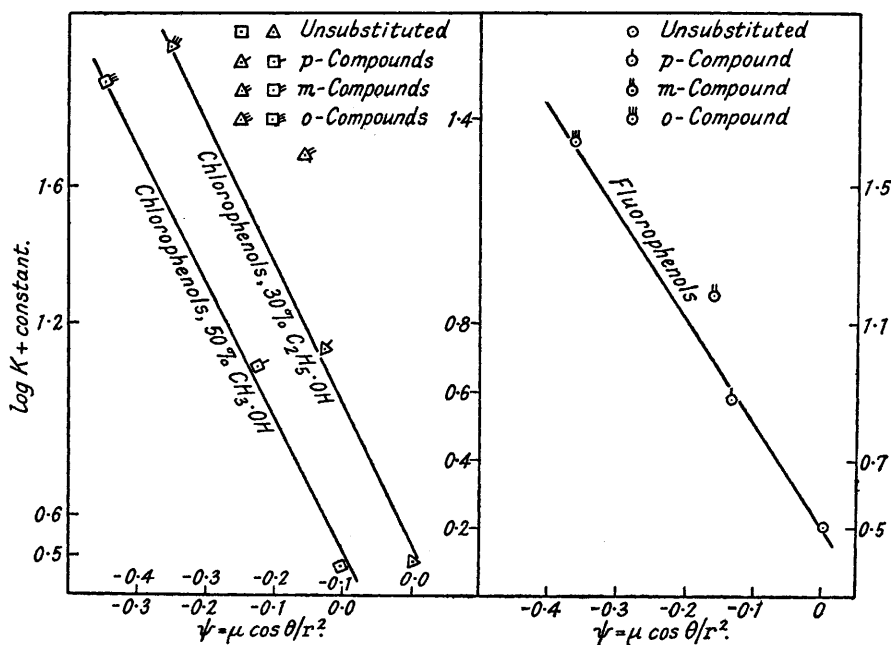
30% aqueous ethyl alcohol have been taken from Bennett, Brooks, and Glasstone (*loc. cit.*), and those for the chlorophenols in 50% aqueous methyl alcohol from Kuhn and Wassermann (*Helv. Chim. Acta*, 1926, **11**, 31). As in the case of the anilines, a linear relation exists between the points for unsubstituted p- and o-halogenophenols. The m-halogenophenols deviate from linearity, but in the opposite direction to that found in the substituted anilines. Each straight line can be represented by an equation of the form $\ln K_s = \ln K_u - \gamma'\psi$ after conversion to Napierian logarithms, and γ' has the following values :

Substituent	F	Cl	Br	I	NO₂
γ'	7·0	9·3, 9·0*	10·4	12·0	7

* In 50% aqueous $CH_3 \cdot OH$.

No ortho-effect exists in the o-halogenophenols. Dippy, Evans, Gordon, Lewis, and Watson (*J.*, 1937, 1422) have pointed out that o-phenols are not appreciably less reactive than their isomerides. Clearly also, very little chelate ring formation can take place in these compounds. Inspection of the data of Holleman and Herwig (*Rec. Trav. chim.*,

1902, **21**, 444) for the nitrophenols shows that *o*-nitrophenol has an abnormally low dissociation constant, and the chelate ring hypothesis accounts for this. An approximate value of γ' is included in the table.

The Mesomeric Effect.—The *m*-halogeno-anilines and -phenols (and also the *p*-nitro-compounds) deviate from the linear relationship, but in opposite directions to one another (see Figs. 1 and 2). For example, *m*-bromoaniline has an abnormally low, and *m*-fluorophenol an abnormally high, dissociation constant, the linear relation being used as the criterion. Also the deviations are systematic. This is illustrated by Table III for the halogeno-anilines, in which K' is a theoretical dissociation constant which would be obtained if the linear relation held.

TABLE III.

Substituent.	$12 + \log K$.	$12 + \log K'$.	Diff.	Substituent.	$12 + \log K$.	$12 + \log K'$.	Diff.
m-F	1·02	1·35	0·33	*m*-Br	0·90	1·12	0·22
m-Cl	0·93	1·22	0·29	*m*-I	0·88	0·95	0·07

Inspection of Fig. 1 reveals that the linear relation is almost obeyed by *m*-iodoaniline, and that there is a bigger deviation for *m*-bromo-aniline, and so on through the halogeno-series. A similar table can be constructed for the *m*-phenols. These facts give the clue to the cause of the divergence, since Baddeley and Bennett (J., 1933, **261**, 1112) state that the mesomeric effect of the halogens $(+ M)$ diminishes in the order $F > Cl > Br > I$. This is supported by the calculations of Groves and Sugden (J., 1937, 1922). We have two possibilities. (i) There may be some extra effect in the *m*-substituted anilines and phenols in the same direction as the simple dipole inductive effect, the extra effect diminishing from fluoro- to iodo-. (ii) However, a far more probable explanation is the following. Only the *m*-compounds exhibit the simple inductive effect, and both *o*- and *p*-compounds exhibit a mesomeric effect opposite in direction to the inductive effect. Again, it is stressed that in these systems such mesomeric effects would have to be proportional to the inductive effects so as to preserve the observed linearity (see Fig. 3, where

FIG. 3.
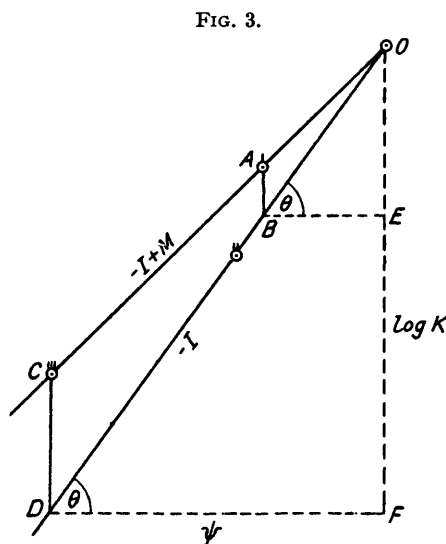
consideration of the geometry of similar triangles gives $AB/CD = OB/OD = OE$ cosec θ/OF cosec $\theta = OE/OF)$; *i.e.*, the ratio of the mesomeric effect in the *p*-compound to that in the *o*-compound is the same as the ratio of the inductive effect in the *p*- to that in the *o*-compound. This complicating effect seems very small in the acids. In the light of the above, we now regard the strengths of *o*-substituted anilines as being high rather than low.

Change of Solvent.—Inspection of Table II and Fig. 2 reveals that the slope of ψ plotted against log K for the chlorophenols in two solvents (and this is supported by data for the fluoroanilines in 30% ethyl alcohol and in water) is approximately the same. This does not seem to bear out the speculations of Wynne-Jones (*Chem. and Ind.*, 1933, **52**, 273) on the relative strengths of acids and bases in different solvents.