CCCXCVIII.—*The Effect of the Spatial Position of Substituent Groups on Acidic Strength.*

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SOME years ago (J., 1909, **95**, 718; 1910, **97**, 84), I attempted to show that the electrolytic equilibria of acids, bases, and salts depend on the same three internal (constitutional) factors *p*, *q*, and *s* which determine reactions in general. In so far as the steric factor (*s*) is concerned, I suggested that the rate of association of ions is retarded by spatial obstruction, whereas the reverse process of dissociation into ions remains unaffected, so that *ceteris paribus* steric hindrance must raise the dissociation constant. In support of this view, the relative steric effects on dissociation constants were shown to run parallel to the relative steric inhibitions of other reactions; the order for different substituents and positions being:

$$I > Br, C_6H_5 > Cl, O, N, C(CH_3, CO) > H;$$

o- > β- > α-; and γ-, δ-, *m*-, *p*-, side-chain in *o*- almost = 0. The evidence included a correlation of the dissociation constants of more than 100 acids and bases and of the dissociation constants and relative hydrolysis of certain organic salts by means of semi-quantitative evaluations of the steric and the other two effects. Later (*Trans. Faraday Soc.*, 1923, **19**, 531; *Phil. Mag.*, 1924, **47**, 569) I suggested that the remarkable extent to which the approach even of a hydrogen ion can be inhibited sterically by substituents in the anion is intelligible in view of Lapworth's proof that hydrogen ions are solvated.

Independent evidence for the steric effect in electrolytic equilibria was found by me (*Chem. and Ind.*, 1925, **44**, 249) in the dissociation constants of certain ethylenic isomerides. Since the ratio of these constants for α-bromo*allo*cinnamic acid/α-bromocinnamic acid = maleic acid/fumaric acid = 15 (approx.), and *iso*crotonic acid/crotonic acid > 1, and since *p* and *q* must be identical for the *cis*- and the *trans*-form of the same acid, the conclusion was drawn that the greater strength of each *cis*-form must be due to a pure steric effect in the above sense; if it were a *polar* effect across space, the ratio K_{cis}/K_{trans} would be smaller for the α-bromocinnamic acids (effect of phenyl) than for maleic and fumaric acids (effect of carboxyl), and would be less than 1 for the crotonic acids (effect of methyl).

A recent paper by D. H. Hey (this vol., p. 2321) deals wholly with this question of the steric effects on acidic strength. This author has evidently overlooked the papers mentioned above, for although he puts forward views on this question identical with those put forward by me, and his arguments are the same as those used by me, no reference is made to my work.

Contrary to the general assumption that ionic reactions are instantaneous, the introduction of a steric delay in association implied, of course, that association of ions is a time reaction, from which it follows that dissociation must also be a time reaction (governed, I suggest, by the internal factors p and q); if dissociation alone were instantaneous, it would always be practically complete. The principle of ionic time reactions has recently also been advocated by Brönsted and Pedersen (*Z. physikal. Chem.*, 1924, **108**, 230) and Brönsted (*Ber.*, 1928, **61**, 2050, footnote), who suggest that it is therefore "possible, but not very probable, that the same equilibrium (strength) might be determined by very different values of the absolute velocities of dissociation and association." The introduction of a steric factor, however, for association alone transforms such a remote contingency into a virtual certainty. Thus *o*-chloro- and *o*-iodo-benzoic acid have approximately the same dissociation constant; let k_1 and k_2, respectively, be the rates of dissociation and association in the chloro-acid, and $m \times k_1$ and $n \times k_2$ those in the iodo-acid, then we have (compare J., 1909, **95**, 731) $m < 1$ (since p for $I < Cl$) and $n < 1$ (since s for $I > Cl$); whenever $m = n$, the dissociation constants of the two acids are, of course, identical ($= k_1/k_2$), and this is what approximately applies in the present case.

Spiers and Thorpe (J., 1925, **127**, 538) introduced an "approach effect" brought about by altered valency direction. Where primary dissociation constants are concerned, this approach effect is obviously a special case of the steric effect postulated by me, for which these authors' observations supply further valuable evidence. In cases of secondary dissociation, however, the electrostatic effect of the first charge on the charges involved in the secondary dissociation (Ostwald, *Z. physikal. Chem.*, 1892, **9**, 558; Bjerrum, *ibid.*, 1925, **106**, 219) may, and usually will, outweigh all other factors (*e.g.*, in the classical example, secondary dissociation constant of maleic acid < fumaric acid). In view of what has been said above, Spiers and Thorpe's remark on my views—"no explanation is offered as to how this steric influence is produced"—can hardly be upheld.*

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* Quite recently (*Ber.*, 1928, **61**, 1524), the possibility of a steric inhibition of the association of ions has also been admitted by Hückel; and since the above was written, the steric effect on the tautomerism of kations (or "anionotropy" or "mobile anion tautomerism," to use recently coined expressions), *e.g.*, in the triphenylmethane, benzopyrilium, and acridinium series (Flürscheim, J., 1910, **97**, 90—94), has found support in an investigation by Cook (this vol., p. 2798) on a similar kationic tautomerism in the anthracene series.

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