

## Letters to the Editor

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## Theory of Induced Polarities in Benzene

THE letter from Dr. E. and Prof. W. Hückel in these columns<sup>1</sup> explains that "H<sup>+</sup>" on page 326 of Dr. E. Hückel's original paper was a misprint for "H-atom". The misprint, occurring at a crucial point, was unfortunate, and in the light of this explanation we naturally withdraw all such criticism as was based on the misapprehension that Hückel postulated extrusion of proton during the ordinary "substitution of hydrogen" in the aromatic series.

Our objections to Hückel's theory as we now understand it are no less serious than when our first letter<sup>2</sup> was written. E. and H. Hückel now say that "the assumption in Hückel's theory is . . . only that for a definite reaction the heat of activation is smaller for a hydrogen atom bound more loosely and greater for a hydrogen atom bound more strongly. It cannot be denied that for all simple substitution reactions which have been investigated quantitatively up to the present time, this assumption—taking the charge density calculated by Hückel—leads to results which are in agreement with observation."

We may point out that the apparent agreement is real only if Hückel's additional assumption relating to the direct connexion between the strength of the bond in C-H and the Coulombic attractive force on the nucleus of the H-atom can be justified. Even if it could be justified, it has not been shown that the few data quoted by Hückel are inconsistent with the theory of aromatic substitution which we support. In contrast to this state of things, there is a vast body of data which fit in most satisfactorily with our own ideas but not with Hückel's, and no better illustration of this statement is needed than the statement made by Dr. E. and Prof. W. Hückel that "We cannot see what connexion there is between the dissociation of acids and bases and substitution reactions in benzene".

That there is, nevertheless, a very close connexion between these phenomena has, we believe, been widely recognised, in English-speaking countries perhaps more particularly, since the publication of the classical paper<sup>3</sup> of Flürscheim on the subject, and although organic chemical theory has undergone revolutionary changes during the interval and many of the examples, such as aliphatic acids, quoted by Flürscheim are now considered inappropriate, the paper embodied a discovery of first-rate importance, which is only emphasised by addition of new examples that are even more convincing than those given by the discoverer.

We would direct attention first to the mono-substituted phenols. Adequate data for use in the above connexion are available only in three cases: (a) the cresols (methylphenols), (b) the dihydroxybenzenes (hydroxyphenols), and (c) the nitrophenols. Of the three cresols, the meta-derivative is the most acidic.<sup>4</sup> Of the hydroxyphenols, the meta-derivative has a higher ionisation constant than the ortho-derivative,<sup>5</sup> and partition measurements made in the laboratories of the University of Manchester prove that the meta-derivative is also a more powerful acid than the para-derivative. Of the three nitro-phenols,

on the other hand, the meta-derivative is much the weakest acid.<sup>6</sup> These cases represent typical alternate effects as this expression is now most widely used, no reversals in sign being required or implied.

The significance of the data relating to the acidities of isomeric substituted phenols can best be appreciated by reference to a well-known generalisation illustrated by the following quotation from G. N. Lewis:<sup>7</sup> "If we consider corresponding hydroxides of nitrogen, phosphorus, arsenic, antimony, and bismuth, we see the effect of the diminishing pull of electrons by the central atom as we proceed from nitrogen to bismuth. The hydroxides become progressively weaker acids and stronger bases."

The application of this generalisation to the arrangement C-OH in isomeric phenols leads to the conclusion that, other things being equal, the acidity of the hydroxyl group will be most pronounced when the group is attached to that carbon atom in the neighbourhood of which the electrons are most under the control of the central system either of the carbon atom or of the aromatic ring as a whole—in other words, at the carbon atom where the negative charge density is least or the positive charge density is greatest. In the three trios of substituted phenols above mentioned, the data, combined with Lewis's generalisation, show that the distribution of the charge densities in E. Hückel's two pictures (*loc. cit.*, p. 301) must be incorrect.

Relationships between isomeric substituted benzoic acids are more complicated. Nevertheless, as was pointed out by Flürscheim, the ionisation constant of the meta-substituted acid is greater than that of the para-substituted acid when the substituent is of the 'o-p-directive' type, while the converse is true when the substituent is of the 'meta-directive' type. This generalisation holds good for the chloro- and nitro-benzoic acids<sup>8</sup> cited by Dr. E. and Prof. W. Hückel in evidence against our views, and is quite independent of whether the acids are weaker or stronger than benzoic acid, a question which depends mainly on the magnitude and orientation of the dipole moment associated with the introduction of the substituent into the aromatic system.

Our idea that attachment of the substituting agent to aromatic carbon precedes elimination of proton and is not simultaneous with the latter process is admittedly not proved, but it has served as a useful working hypothesis which has helped to correlate known data and to foresee others. Our fundamental thesis is that substituting agents of the electron-seeking type, such as halogens, sulphuric acid and sulphuric anhydride, nitric (or nitrous) acid, enter most readily into reaction with those carbon atoms of the aromatic ring at which there is an electronic excess, whilst agents such as alkalis, amines, metallic cyanides and sulphites, which act normally through their anions or by using their own electrons to form new covalencies, enter into reaction only with aromatic carbon atoms at which there is a decided electronic deficiency.

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<sup>1</sup> NATURE, 129, 937; June 25, 1932.

<sup>2</sup> *Ibid.*, 129, 278; 1932.

<sup>3</sup> *Trans. Chem. Soc.*, 95, 718; 1909.

<sup>4</sup> Boyd, *ibid.*, 107, 1533; 1915.

<sup>5</sup> Boeseken and van Rossem, *Rec. trav. Chim.*, 30, 392; 1911.

<sup>6</sup> "International Critical Tables," 6, 272; 1929.

<sup>7</sup> "Valence and the Structure of Atoms and Molecules." Amer. Chem. Soc. Monograph Series, 138; 1923.

<sup>8</sup> Ostwald, *Z. phys. Chemie*, 3, 369; 1889.