In conclusion, it is a duty to state that the cost of this investigation has been defrayed out of a grant from the Rumford Fund of the American Academy, for which we express our thanks to the Rumford Committee.

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SUBSTITUTION IN THE BENZENE NUCLEUS.

By A. F. Holleman.

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A few years ago, I showed[1] that none of the hypotheses proposed to explain the phenomena of substitution in benzene nucleus are able to give a satisfactory explanation of the facts. Since then, H. S. Fry, in a series of papers,[2] published a new hypothesis and was able to explain some of the phenomena observed by means of it, *e. g.*, the fact that, in the rearrangement of phenyl acetyl nitrogen chloride $C_6H_5NCl.COCH_3$ and similar compounds, the halogen enters only in positions ortho or para to the nitrogen atom.

However, on studying this hypothesis more closely it seems to me that there are so many objections against it, that it cannot be accepted. I venture to present the most important ones in the following lines:

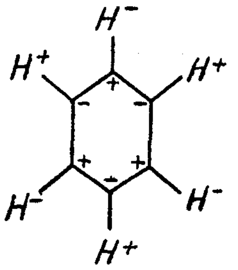

Fig. 1.

1. Fry admits that benzene has the structure of Fig. 1, based on Thomson's electronic theory of linking of the atoms. As he observes, this formula indicates the possibility of two isomeric compounds C_6H_5X, whereas no such isomers have been found thus far. In order to explain this, he assumes either that one of the two isomers ("electromers"), *e. g.*, of chlorobenzene is unstable under ordinary physical conditions, or that monochlorobenzene is an equilibrium mixture of two tautomeric electromers. It seems to me that serious objections may be made against both of these auxiliary hypotheses. With regard to the first one; admitting $C_6H_5\overset{-}{Cl}$ to be stable, $C_6H_5\overset{+}{Cl}$ would be unstable. But in o-$C_6H_4Cl_2$ and p-$C_6H_4Cl_2$, where one Cl-atom is negative and the other positive, we have perfectly stable compounds. On the other hand, if monochlorobenzene is a mixture of $C_6H_5\overset{-}{Cl}$ and $C_6H_5\overset{+}{Cl}$, the nitration of such a mixture ought to give a mixture of *o*- and *p*-chloronitrobenzene (derived from $C_6H_5\overset{-}{Cl}$) and of *m*-chloronitrobenzene (derived from $C_6H_5\overset{+}{Cl}$), since—according to Fry—"substituents of the same sign occupy positions which

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[1] "Die direkte Einführung von Substituenten in den Benzolkern," p. 203.

[2] This Journal, 34, 664 (1912); 36, 248, 262 (1914); see also *Z. physik. Chem.*, 76, 385 (1910).

are meta to each other, and substituents of opposite sign will occupy positions either ortho or para to each other." Now, I have been able to prove that in the nitration of chlorobenzene no trace of *m*-compound is formed, since the eutectic point of an artificial mixture of *p*- and *o*-chloronitrobenzene coincides with the eutectic point of the nitration product of chlorobenzene.

2. It can be proven in still another way that Fry's rule, just mentioned, with regard to the position taken by a new substituent, cannot be correct. Fry maintains that the iodine is positive in iodobenzene, since it is formed from sodium benzoate and iodine chloride, the latter having the formula $\overset{-}{Cl}—\overset{+}{I}$. But iodobenzene also yields *p*- and *o*-compounds on nitration, just as the other halogen-benzenes, though in these the halogen is admitted to have a negative charge. For the rest, it is somewhat striking, that Fry admits on p. 252, *l. c.*, that chlorobenzene has the formula $C_6H_5\overset{-}{Cl}$, whereas he declares on p. 264, that "it has been impossible so far to prove directly, whether the chlorine atom in monochlorobenzene is positive or negative."

3. According to Fry, "the radical SO_3H in phenylsulfonic acid may function either positively or negatively." He deduces this from the fact that this acid yields benzene on heating with water, but phenol on melting with alkali. But, since in *o*- and *p*-phenylene disulfonic acid one SO_3H should be positive when the other is negative, these acids should yield phenol exclusively on melting with alkali. In reality they yield pyrocatechol and hydroquinol.

4. The formula of *p*-chlorotoluene and *p*-chlorobromobenzene must be as is indicated in Fig. 2, according to the hypothesis of Fry.

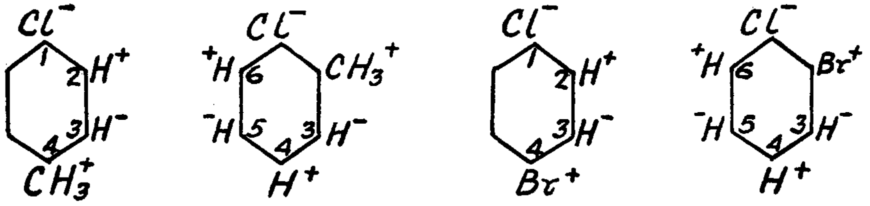

Fig. 2.

If his rule were correct, we should expect that in the nitration of the two *p*-compounds the group $nitro^+$ (because nitric acid must be $\overset{-}{HO}.\overset{+}{NO_2}$) should only take position **2**, because the H-atom placed there, must be positive. However, by researches executed in my laboratory by Wibaut[1] and by Heineken,[2] it is proved, that in both cases considerable

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[1] *Recueil*, 32, 244 (1913).

[2] Not yet published.

quantities of both of the isomers 2 and 3 are obtained. In the case of *o*-chlorotoluene and *o*-chlorobromobenzene, Wibaut[1] proved for the first substance, that the nitration yields all the four possible mononitro compounds in considerable quantity, and for the second substance, I have proved that the nitration product contains almost equal quantities of the nitro products 4 and 5,[2] though Fry's rule predicts the formation of only the isomers 4 and 6. It is evident, that these objections would undergo no change, if all the signs admitted here for the substituents were the reverse.

5. Fry's explanation of the fact that the chlorination of nitrobenzene yields *m*-nitrochlorobenzene, can neither be accepted. He supposes that $\overset{-}{HO}.\overset{+}{Cl}$ is the chlorinating agent "since absolutely anhydrous chlorine does not react with anhydrous reagents." However, this introduction of chlorine is only possible, when a large quantity of $SbCl_3$ is added ($^1/_5$ of the weight of the nitrobenzene). All traces of water must be taken away by it. The only plausible explanation is, that $SbCl_5$ is formed, which transports the chlorine to the nitrobenzene. As there can be little doubt that $SbCl_5$ is $\overset{-}{Sb}\overset{+}{Cl_5}$ (always according to the views of Fry), chlorine ought to replace an *o*- or *p*-H-atom in $C_6H_5NO_2$, when NO_2 in it is positive.

6. The substitution of chlorine in *o*- and *p*-chloronitrobenzene by OH is explained very well by Fry's hypothesis, admitting for the formulas of these compounds $\overset{-}{Cl}.C_6H_4.\overset{+}{NO_2}(p\text{-}o)$; for the negative OH is now able to change places with the negative Cl. The fact that chlorine in *m*-chloronitrobenzene cannot be replaced is also explained in this way, since it has the formula $\overset{+}{Cl}.C_6H_4.\overset{+}{NO_2}(m)$. Admitting this explanation, one Cl should also be replaceable by OCH_3 in *o*- and *p*-dichlorobenzene, $\overset{-}{Cl}.C_6H_4.\overset{+}{Cl}$, but not in *m*-dichlorobenzene, $\overset{-}{Cl}.C_6H_4.\overset{-}{Cl}$ (or $\overset{+}{Cl}.C_6H_4.\overset{+}{Cl}$). However, de Mooy[2] has proved in my laboratory, that the latter also reacts with sodium methylate, and that the velocity of this reaction is even greater than for the *p*- and *o*-isomers, one Cl-atom being replaced in all three compounds.

I wish, finally, to call attention to two further points. In the first place, it would probably be very difficult to designate what charge a given substituent has. In most cases it might as well be positive as negative. This naturally causes a great uncertainty in the explanation of the reactions. In the second place, I might direct the attention on the consequences of the hypothesis in the case of open carbon chains. For these, it leads to the formula $\underset{1}{\overset{+}{C}}—\underset{2}{\overset{-+}{C}}—\underset{3}{\overset{-+}{C}}—\underset{4}{\overset{-}{C}}\ldots$, for the linking of the

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[1] *Loc. cit.*

[2] Not yet published.

C-atoms comes about by C-atom 1 giving off an electron to C-atom 2, this sending off an electron in its turn to C-atom 2, and so on. This must cause the C-atoms at both ends of an open chain to have opposite signs. This would involve the consequence that the Br-atoms, *e. g.*, in a polymethylene dibromide, ought to show a different behavior, which is also in contradiction with the experimental facts.

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[CONTRIBUTIONS OF THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, No. 1241.]

THE ADDITION COMPOUNDS OF ORGANIC SUBSTANCES WITH SULFURIC ACID.

BY JAMES KENDALL AND CLIFFORD D. CARPENTER.[1]

Received October 26, 1914.

The treatment of aromatic organic substances with sulfuric acid, resulting in the formation of condensation products (sulfonic acids), is a well-known and widely-applied reaction. In a recent communication[2] the opinion was expressed that, in such condensations, the formation of addition compounds between the reacting substances may represent an intermediate stage of the process. The same view has been repeatedly advanced in the past, notably by Kekulé,[3] van't Hoff,[4] Michael,[5] and Guye.[6] Very little *systematic* evidence, however, has been brought forward in its support, save in the work of Menschutkin,[7] on the addition compounds of organic substances with inorganic salts, illustrating an intermediate phase of Friedel and Craft's reaction. The recent papers of Baume[8] and his pupils, on systems containing substances of very low freezing point, are also of importance.

Sulfonation is a vigorous reaction, induced by the application of heat. Of the mechanism of the process we know practically nothing, except that it is complex and probably consists of several distinct stages. Since, at the high temperatures employed, the reaction is rushed through all of these without a stop, no information has been obtained regarding possible intermediate products. Hoogewerff and van Dorp[9] have iso-

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[1] The work presented in this paper forms the basis of a dissertation submitted by Clifford D. Carpenter to the University of Chicago in part fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Kendall, THIS JOURNAL, **36**, 1722 (1914).

[3] Kekulé, *Ann.*, **106**, 129 (1858).

[4] Van't Hoff, *Ansichten über organische Chemie*, I, 225, 244.

[5] Michael, THIS JOURNAL, **32**, 1001 (1910).

[6] Guye, *J. chim. phys.*, **8**, 119 (1910).

[7] Menschutkin, *J. chim. phys.*, **9**, 538 (1911).

[8] Baume, *J. chim. phys.*, **12**, 212 (1914).

[9] Hoogewerff and van Dorp, *Rec. trav. chim. Pays-Bas*, **18**, 211 (1899); **21**, 353 (1902).