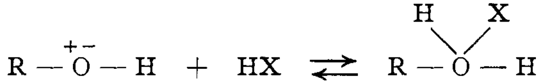
isolated and described. Systems containing components of not so widely divergent acidic strengths give no compound formation.

The reaction is assumed to be similar in its nature to those studied in previous papers, *i. e.*, the compounds are regarded as true oxonium salts. The equation may be written as follows:



$$R-\overset{+-}{O}-H + HX \rightleftharpoons R-\overset{H\quad X}{O}-H$$

This reaction probably represents the first stage in the formation of phenolic esters of organic acids. The further study of the mechanism of the esterification process will be the subject of a subsequent paper.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

VI. FURTHER EVIDENCE FOR THE ELECTRONIC FORMULA OF BENZENE AND THE SUBSTITUTION RULE.[1]

BY HARRY SHIPLEY FRY.

Received April 13, 1916.

In previous papers of this series[2] numerous facts have been presented and interpreted by means of the electronic formula of benzene (abbreviated formula, Fig. 1). A substitution rule was indicated maintaining that when substituents are of the same sign or polarity they will occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy either ortho or para positions to each other. This follows from the fact that the electronic formula of benzene is the only formula presenting conjointly a structural basis and an electronic interpretation of the relations between the ortho and para positions and substituents in contradistinction to the meta positions and substituents.

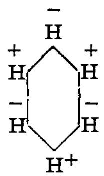

Fig. 1.

The purpose of the present paper is to present briefly additional experimental facts which further substantiate the electronic formula of benzene and the substitution rule. The facts here offered seem particularly significant since they involve polysubstituted derivatives of benzene.

Phenol, when directly nitrated, yields ortho- and para-nitrophenols. Further nitration yields the two isomeric 1,2,4- and 1,2,6-dinitrophenols.

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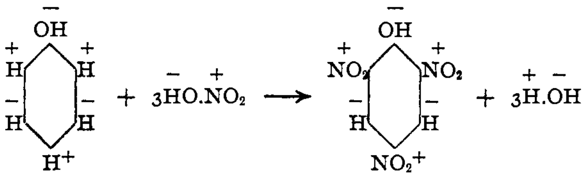
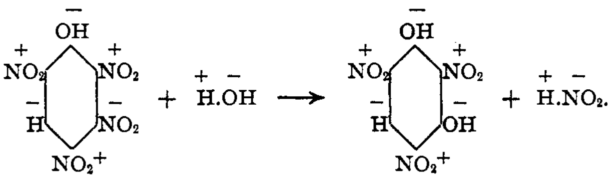
[1] This and the two following papers constitute Parts VI, VII, and VIII of the series, "Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences." Parts VI and VIII were read before the Cincinnati Section of the American Chemical Society, May 12, 1915.

[2] Fry, THIS JOURNAL, **36**, 248, 262, 1035 (1914); *Ibid.*, **37**, 855, 863, 883, 2368 (1915); see also Fry, *Z. physik. Chem.*, **76**, 385, 398, 591 (1911); *Ibid.*, 80, 29 (1912); *Ibid.*, **82**, 665 (1913); *Ibid.*. **90**, 458 (1915).

Finally, nitration of either of these products gives the symmetrical trinitro derivative, picric acid. These reactions are summarized in the following electronic equation:[1]



In trinitrophenol each of the nitro groups is positive but the electronic formula indicates that in tetranitrophenol a fourth nitro group in position 3 or 5 would be negative. Now if some nitro groups are positive and others are negative there should be some marked difference in their behavior toward certain reagents. These conclusions are substantiated by the fact that "the nitro group in nitrobenzene is extremely stable compared with the fourth nitro group in tetranitrophenol, which water will remove in the form of nitrous acid."[2] These facts are in perfect agreement with the electronic formula of tetranitrophenol, the hydrolysis of which yields nitrous acid ($\overset{+}{\text{H}}.\overset{-}{\text{NO}_2}$ or $\overset{+}{\text{H}}.\overset{-}{\text{ONO}}$)[3] according to the electronic equation



Since direct nitration with nitric acid results in the substitution of positive nitro groups and since in tetranitrophenol the negative nitro group may occupy either of the equivalent positions 3 or 5, with negative hydroxyl in position 1, it follows that substituents in positions 1, 3, and 5 are negative while those in positions 2, 4, and 6 are positive. This is a confirmation of the electronic formula of benzene and the substitution rule stated above.

In previous papers it has been shown that hydrogen-,[4] halogen-, hydroxyl-sulfonic-,[5] and carboxyl-radicals[6] may function either positively or negatively, depending principally upon the relative positions they may occupy in the benzene nucleus. Now with reference to the existence of positive

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[1] For detailed description of the mechanism of substitution, see Fry, This Journal, 37, 875 (1915).

[2] Cohen, "Organic Chemistry," Vol. II, p. 90.

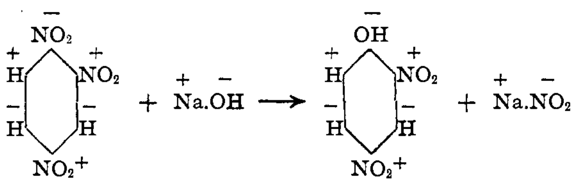
[3] For tautomeric and electronic formulas of nitrous acid see Fry, This Journal, 37, 875 (1915) and *Z. physik. Chem.*, 90, 464 (1915).

[4] Fry, This Journal, 36, 262 (1914).

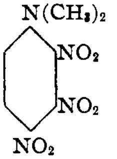
[5] *Ibid.*, 37, 864 (1915).

[6] *Ibid.*, 36, 256 (1914).

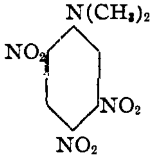
and negative nitro groups, it may be noted that when the nitro groups occupy positions ortho- or para- to each other, one of them functions positively while the other functions negatively. This is shown by the replacement of only one of the nitro groups by negative hydroxyl or oxymethyl on interaction with $\overset{+}{Na}.\overset{-}{OH}$ or $\overset{+}{Na}.\overset{-}{OCH_3}$, and the liberation of $\overset{+}{Na}.\overset{-}{NO_2}$. In addition to the hydrolysis of tetranitrophenol given above, 1,2-dinitro- and 1,2,4-trinitrobenzenes interact readily with solutions of sodium hydroxide or sodium methylate. The nitro group in position 1 is replaced by $\overset{-}{OH}$ or $\overset{-}{OCH_3}$ and $\overset{+}{Na}.\overset{-}{NO_2}$ is formed. These reactions find an interpretation in the electronic formula of benzene and may be summarized in the following equation:



Other facts which not only indicate the existence of negative nitro groups but also further substantiate the electronic formula of benzene are recorded in the recent work of P. van Romburgh and I. W. Wensink[1] who found that the nitro group in position 3 of either 2,3,4- or 3,4,6-trinitrodimethylaniline is readily replaced either by an NH_2- or $NH(CH_3)$-group on interaction with alcoholic solutions of ammonia or methylamine, respectively. Ordinarily, the hydrogen atoms of ammonia are positive and the three valences of the nitrogen atom are negative. Hence the abbreviated electronic formulas of ammonia and methylamine are $\overset{+}{H}.\overset{-}{NH_2}$ and $\overset{+}{CH_3}.\overset{-}{NH_2}$. Accordingly, the replacement of only one of the three nitro groups (that in position 3) by $\overset{-}{NH_2}$ is perfectly analogous to the replacement of $\overset{-}{NO_2}$ by $\overset{-}{OH}$ in the reactions given above. Furthermore, the nitro groups in positions 2 and 4 in the 2,3,4-compound are regarded as positive since they are not replaceable by $\overset{-}{NH_2}$. They also occupy positions ortho- to the replaceable negative nitro group of position 3. Again,



(2,3,4-)



(3,4,6-)

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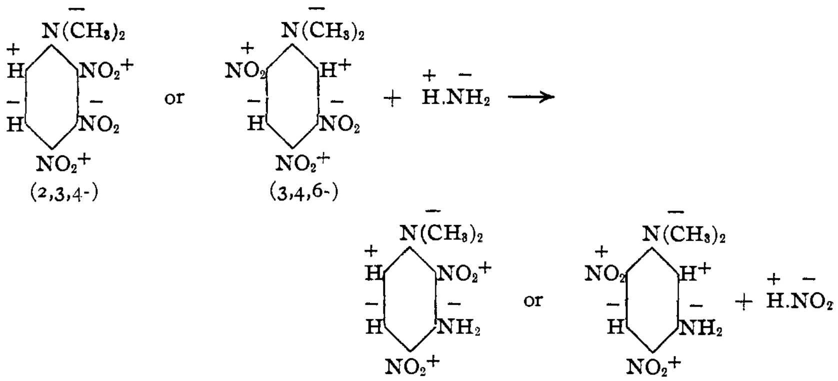
[1] *Verslag K. Akad. Wetenschappen*, **23**, 966 (1914).

in the 2,4,6-compound the nitro groups in positions 4 and 6 are also regarded as positive since they are not replaced by $\overline{NH_2}$. They occupy positions ortho- and para-, respectively, to the negative nitro group of position 3. All of these facts and conclusions are embodied in and interpreted by the following electronic formulas and equations:



In all benzene formulas positions 2 and 6 are equivalent as are also positions 3 and 5. Accordingly, the 2,3,4- and 3,4,6-trinitrodimethylanilines (and their products of interaction with ammonia) coincidently show that when the substituents in positions 1, 3, and 5 are negative, the substituents in positions 2, 4, and 6 are positive. This also constitutes a further substantiation both of the electronic formula of benzene and the substitution rule.

Additional evidence leading to the above conclusions might be described in detail but brief mention may suffice. Michele Giua[1] and A. Contardi[2] have described a number of polynitro derivatives of benzene which suffer replacement of a nitro group by OH, $O(CH_3)$, NH_2 and $NH(CH_3)$ with the liberation of nitrites. In some instances hydrolysis with water yields nitrous acid anhydride. In these various instances two nitro groups are adjacent, *i. e.*, occupy positions ortho- to each other, and only one of them suffers replacement. Giua maintains that this behavior substantiates the rule on the reactivity of the nitro groups in the benzene ring proposed by Körner and Laubenheimer who attribute the facility of reaction of the one nitro group to the adjacence of the two nitro groups and the consequent "*loosening*" action of one group upon the other. This interpretation is not only vague but it fails to take into account the highly significant facts that the nitro group is replaced by a substituent of *negative polarity* and that the group thus replaced is liberated as a *nitrite* in which *the nitro radical is also negative*. The electronic conception of positive and

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[1] *Atti accad. Lincei*, **23**, 484 (1914); *Gazz. chim. ital.*, **45**, 339, 352 (1915).

[2] *Ibid.*, **23**, 464 (1914).

negative valences and the existence of positive and negative nitro groups affords a more satisfactory interpretation, since all of the facts noted are indicated and correlated by the electronic formula of benzene and the substitution rule. Conversely, *the facts verify the electronic formula of benzene and the substitution rule.*

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

VII. THE ACTION OF SODIUM METHYLATE UPON THE PRODUCTS OF NITRATION OF ORTHO-, PARA- AND META-CHLOROTOLUENES.

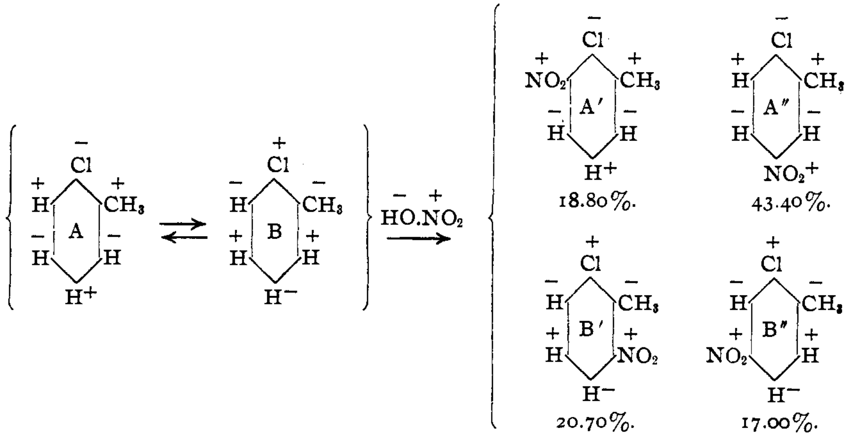
BY HARRY SHIPLEY FRY.

Received April 13, 1916.

Part IV[1] of this series considered in detail the simultaneous formation of *o*-, *p*-, and *m*-substituted derivatives of benzene from the standpoint of the electronic tautomerism of benzene derivatives.[2] The present paper (VII) is a continuation of Part IV and embodies the results of a quantitative study of the action of sodium methylate solutions of various concentrations upon the products of nitration of *o*-, *p*-, and *m*-chlorotoluenes. The results of these experiments, in addition to the facts given in Part IV, are offered as further evidence for the electronic tautomerism[3] of certain substituted derivatives of benzene.

In order to follow the experimental part of this work it will be necessary to indicate briefly, from the standpoint of the conception of electronic tautomerism, the electronic equations for the nitrations of *o*-, *p*-, and *m*-chlorotoluenes according to the following Schemes 1, 2, and 3, respectively.

Scheme 1.—The nitration of *o*-chlorotoluene.



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[1] Fry, THIS JOURNAL, **37**, 863 (1915).

[2] Fry, *Z. physik. Chem.*, **76**, 390 (1911); THIS JOURNAL, **37**, 864 (1915).

[3] For a detailed account of the mechanism of the electronic tautomerism of benzene derivatives see Fry, THIS JOURNAL, **37**, 873 (1915).