in (2) it turned orange; and in (3) it turned red. In (2) and (3) a film of purple colored material was observed in the necks of the flask. In (3) red fumes were given off immediately in abundance, and (3) was the first to quiet down. Experiments 1 and 2 evolved red fumes more gradually, in such fashion that it was perfectly apparent that the rate and vigor of the oxidation was greater the greater the amount of sulfuric acid which was present. Nitrobenzene was obtained in each case, 13.8, 13.8 and 9.0 g., respectively; and m-dinitrobenzene was identified in the solid product in each case. No picric acid was isolated, but there was distinct yellow color in the product of each experiment, and the yellow color was most intense in the case where the least sulfuric acid had been used. The results indicate that sulfuric acid either hinders the formation of picric acid by the action of mercuric nitrate or provokes the destructive oxidation of the aromatic material, and indicate that an investigation of the action of sulfuric acid on aromatic compounds in the presence of mercury salts might lead to results of considerable theoretical interest.

Investigations will be continued of the action of naphthalene with nitric acid in the presence of mercuric nitrate, of the action with naphthalene, benzene, etc., of sulfuric acid in the presence of mercuric sulfate, and of the black intermediate compound which we have found to be formed in the reaction which leads to the production of picric acid.

CAMBRIDGE 39, MASSACHUSETTS.

MERCURI-ORGANIC DERIVATIVES: II. NITROBENZENE MERCURY COMPOUNDS; AN INDIRECT METHOD OF MERCURIZING ORGANIC COMPOUNDS.

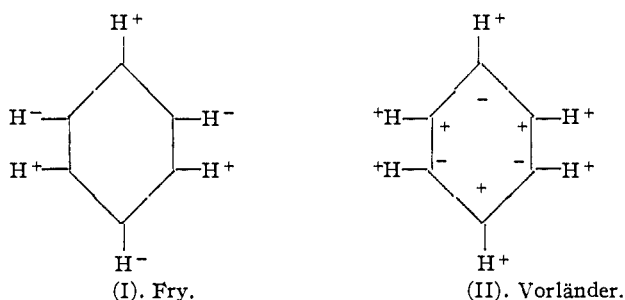BY MORRIS S. KHARASCH[1] AND LYMAN CHALKLEY, JR.
Received November 19, 1920.

Theoretical Part.

Some time ago, one of us became interested in the study of the mercurization of aromatic compounds and its relation to the various theories of substitution in the benzene nucleus. It is well known that at the present time no theory explains satisfactorily all the known facts about substitution. The Crum Brown and Gibson rule of substitution is merely an empirical generalization which is not rigidly correct, and does not suggest the mechanism of the reaction. In the last few years, some theories have been advanced to explain orientation in the benzene nucleus from an electronic point of view. Of the latter the structure formulas of benzene proposed by Fry[2] and by Vorländer[3] deserve most consideration. The two differ in the following respects. Fry assumes the existence in benzene of hydrogen atoms alternately positive and negative, as in Formula I,
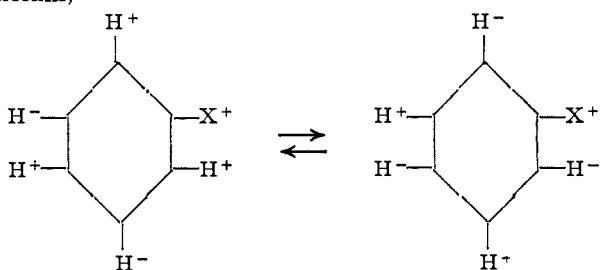
$$
\begin{array}{c}
\text{H}^+ \\
\text{H}^- \quad\quad \text{H}^- \\
\text{H}^+ \quad\quad \text{H}^+ \\
\text{H}^-
\end{array}
$$

(I). Fry.

$$
\begin{array}{c}
\text{H}^+ \\
{}^+\text{H} \quad + \quad - \quad + \quad \text{H}^+ \\
{}^+\text{H} \quad - \quad + \quad - \quad \text{H}^+ \\
\text{H}^+
\end{array}
$$

(II). Vorländer.

and, for monosubstituted derivatives, the existence of electromers in tautomeric equilibrium,

$$
\begin{array}{c}
\text{H}^+ \\
\text{H}^- \quad\quad \text{X}^+ \\
\text{H}^+ \quad\quad \text{H}^+ \\
\text{H}^-
\end{array}
\quad\rightleftarrows\quad
\begin{array}{c}
\text{H}^- \\
\text{H}^+ \quad\quad \text{X}^+ \\
\text{H}^- \quad\quad \text{H}^- \\
\text{H}^+
\end{array}
$$

in which the group or element X determines whether the equilibrium is more to the right or the left as indicated by the arrows. Furthermore, it appears that Fry assumes that orientation takes place by a direct exchange of radicals,

$$
\begin{array}{c}
\text{X}^- \\
\text{H}^+ \quad\quad \boxed{\text{H}^+ \ \text{Br}^-}\text{—Br}^+ \\
\text{H}^- \quad\quad \text{H}^- \\
\text{H}^+
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
\text{X}^- \\
\text{H}^+ \quad\quad \text{Br}^+ \quad + \quad \text{H}^+\,\text{Br}^- \\
\text{H}^- \quad\quad \text{H}^- \\
\text{H}^+
\end{array}
$$
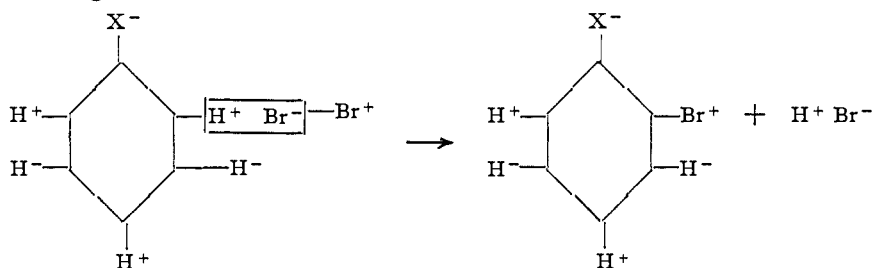
Vorländer, on the other hand, assumes that all of the hydrogen atoms function postively, and that absorption precedes substitution. His structure formula of benzene, therefore, becomes that of Formula II.[1]

While either of the 2 formulas can be made to fit some of the facts fairly satisfactorily, the one of Fry, with the additional postulate of the existence of electromers in tautomeric equilibrium, explains the facts better, since with its aid one can explain, for instance, the formation of o- and p-dinitrobenzene in the nitration of nitrobenzene; while according

[1] An electronic structure for benzene similar to Vorländer's non-electronic one has been advocated by Professor Julius Stieglitz for the last 5 years. His views are based on the following considerations: (1) Tendency for identical valences (all positive or

to Vorländer *m*-dinitrobenzene should be the sole product. However, this postulate of Fry removes the basis for critical experimental tests.

Inasmuch as we have cases in which a group supposedly enters the benzene nucelus as a positive group, but upon hydrolysis is removed as a negative group, *e. g.*, in the case of tetranitrophenol (1–OH; 2,3,4,6-NO₂) where the nitro group in the *meta* position to the hydroxyl group is removed as potassium nitrite upon boiling the compound with potassium hydroxide solution, we must assume that intramolecular oxidation and reduction has taken place. And since this is always supposed to be the case whenever we have a positive group enter *ortho* or *para* to a positive group already present in the nucleus, a postulate which, according to Fry, is a very strong point in favor of his theory, it appears desirable to consider this reaction more in detail.

A very significant observation was made by Dimroth[1] that, on mercurizing nitrobenzene, the mercury enters a position *ortho* to the nitro group. As a matter of fact, no organic mercury derivatives have ever been prepared by direct mercurization of a monosubstituted aromatic compound in which the mercury occupies a position *meta* to a positive group. While mercurization of a monosubstituted compound containing a negative group is not difficult; the reaction takes place in a relatively short time and at a relatively low temperature, seldom exceeding 70°. Furthermore, the position taken by the mercury is quite in agreement with the Crum Brown and Gibson rule of substitution and the theories of the electronic structure of benzene based on it.

It appeared to the writers that it would be much simpler to study the effect of the influence of one group upon the entrance of another by using the salt of an element which we know to be positive under all condi-

all negative) at ends of double bonds; (2) phenol tautomeric-proving positive end of bond
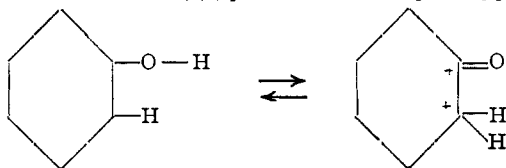
(3) for series with positive substituting groups a start is made from nitrophenol and its tautomerism,
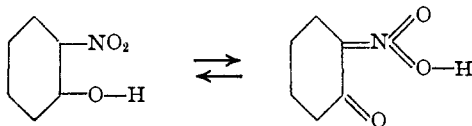
proving negative character, etc. Reference to this may be obtained by consulting Ray R. McClure's dissertation (1917) on the "Electronic Structure of Benzene," University of Chicago Libraries.

[1] Dimroth, *Ber.*, **35**, 2036 (1902).

tions, namely mercury. Should intramolecular oxidation and reduction take place between the mercury and the carbon, the former is immediately thrown out as metallic mercury. This serves as a safeguard in interpreting our results.

As the first step, therefore, in elucidating the structure of benzene, we had to determine whether a positive group would orient an entering mercury group *meta*. As previously stated, Dimroth in mercurizing nitrobenzene and upon heating mercury benzoate obtained *ortho* substituted mercury compounds.[1] The position taken by the mercury was proved by isolating o-bromonitrobenzene and o-bromobenzoic acid, respectively, by treatment of these compounds with a water solution of potassium perbromide. While the validity of this method as a proof of the constitution of mercury compounds has never been questioned, it appeared desirable to place the method beyond any shadow of doubt.

We have, therefore, attempted to prepare mercury compounds in which we would be certain of the position of the mercury, even before replacing it by bromine. To accomplish this result, we made use of the observation recorded by Walter Peters[2] that, upon heating a 50% alcoholic solution of benzene sulfinic acid with mercuric chloride, phenyl mercury chloride was obtained. Similarly, p-tolyl sulfinic acid, when treated with the same reagent, gave p-tolyl mercury chloride. Peters, however, interested only in the isolation of the structural isomers of the metal and

the sulfinic acid, $R-S\overset{\displaystyle/\!\!/ O}{\underset{\displaystyle \backslash O-Hg/_2}{}}$ and $R-S\overset{\displaystyle/\!\!/ O}{\underset{\displaystyle \backslash Hg/_2}{=\!O}}$, did not realize the full

significance of his accidental discovery, since he did not try to find out whether the method is applicable to the *ortho* and to the *meta* derivatives as well as to the *para*.[3]

The method was found to apply also to *ortho* and *meta* derivatives, and the 3 nitrobenzene mercury compounds have been prepared by it from the nitrobenzene sulfinic acid. The o-nitrobenzene mercuric chloride prepared by this method was found to correspond with the compound prepared by Dimroth by mercurizing nitrobenzene. Upon treatment of it with potassium perbromide it gave o-bromonitrobenzene. When the p- and m-nitrobenzene mercuric chlorides were treated with potassium perbromide they yielded p-bromonitrobenzene and m-bromonitrobenzene, respectively.

    [1] *Ber.*, **35**, 2870 (1902).

    [2] W. Peters, *Ber.*, **38**, 2567 (1905).

    [3] As a matter of fact, this reaction is the only one known to the writers which can be used for placing mercury in any desired position. One of us (K.) has already applied this method, with a fair degree of success, also to the preparation of arsenic derivatives. We also intend to expand this method to the preparation of other organometallic derivatives, and we should like to have this field reserved for us.

The 3 nitrobenzene mercury compounds behave similarly when treated with hydrochloric acid, the mercury is replaced by hydrogen.
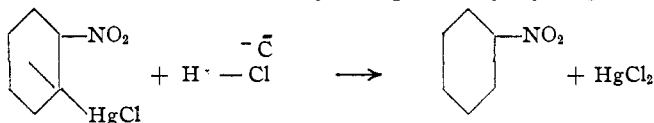
This indicates that mercury remains positive when attached to the carbon atom of the nucleus. According to Fry's structure formula of benzene, it would, therefore, be necessary, in the case of o- and p-nitrobenzene mercuric chlorides, that the nitro group change its polarity, $i.\ e.$, upon hydrolysis with sodium hydroxide, it should be removed as sodium nitrite. However, not a trace of nitrite can be detected after o-nitrobenzene mercuric chloride has been boiled with sodium hydroxide.

Moreover, it has been shown that benzene and mercuric acetate, when heated at 115°, give p-phenylene dimercury acetate, and that both mercury atoms can be removed from the nucleus by hydrochloric acid,[1]
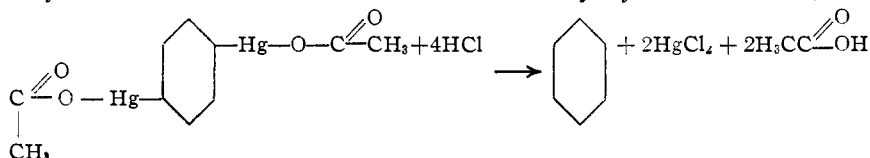
Also, picric acid can be mercurized.[2] These facts taken in conjunction with the work described in this paper, constitute, in our estimation, quite important limitations to Fry's electronic structure of benzene.[3]

Experimental Part.

Preparation of *Ortho* **Nitrobenzene-Mercuric Chloride,** $o\text{-}NO_2C_6H_4HgCl$.—The o-nitrobenzene sulfinic acid was prepared from o-nitroaniline by the method of Gattermann.[4] A solution of 2 g. of o-nitrobenzene sulfinic acid in 20 cc. of alcohol was added to a solution of 6 g. of mercuric chloride in a mixture of 20 cc. of alcohol and 20 cc. of water, and the resulting solution was boiled for 45 minutes. The precipitate which formed was extracted with boiling acetone and the extract evaporated to dryness on the water-bath. The residue was crystallized from 95% alcohol. The o-nitrobenzene mercuric chloride separated in well formed, faintly yellow crystals that melted at 185° (corr.). The yield was 3 g. or 78%.

Analyses.—Subs., 0.4253; 15.20 cc. dry N_2 (24.5° and 726.6 mm.). Calc. for $C_6H_4O_2NClHg$: N, 3.91. Found: 3.91.

This substance is very soluble in acetone; it is soluble in hot alcohol, but very little soluble in cold alcohol. It does not give mercuric sulfide with ammonium sulfide, but it gives a test for inorganic mercury after it is boiled with hydrochloric acid or chlorine water. When the o-nitrobenzene mercuric chloride is boiled with hydrochloric

[1] Dimroth, *Ber.*, **32**, 760 (1899).

[2] Hantzsch and Auld, *ibid.*, **39**, 1105 (1906).

[3] The limitations to Vorländer's conceptions of the orientation of aromatic compounds and a new theory as to o- and p-substitution will appear in the next paper by Kharasch and Jacobsohn.

[4] Gattermann, *Ber.*, **32**, 1136 (1899).

acid an oil heavier than water and having the odor of nitrobenzene may be distilled with steam. The presence of nitrobenzene was confirmed by reduction of this oil and the identification of aniline by a test with bleaching powder. Apparently, none of the compound goes into solution when it is boiled for several hours with twice the calculated amount of a 5% water solution of sodium hydroxide; furthermore, the resulting mixture does not give a Griess-Ilvosay test for nitrite. When the compound is shaken with the calculated amount of bromine dissolved in potassium bromide, the mixture rendered alkaline with sodium hydroxide and extracted with ether and the ether evaporated, a compound is obtained which melts at 43°. This melting point is not lowered by mixing the compound with o-bromonitrobenzene prepared by nitrating bromobenzene.

m-Nitrobenzene Mercuric Chloride, m-$NO_2C_6H_4HgCl$.—The sodium salt of *m*-nitrobenzene sulfinic acid was prepared from the sulfon chloride by the method of Limpricht.[1] Eight g. of the sodium salt of *m*-nitrobenzene sulfinic acid was dissolved in 40 cc. of water and added to a solution of 21 g. of mercuric chloride in 100 cc. of alcohol. Glacial acetic acid, slightly more than enough to liberate the sulfinic acid (2.3 cc.), was added, and the resulting solution boiled for 20 hours. The *m*-nitrobenzene mercuric chloride is extracted with acetone from the precipitate that forms, and recrystallized from absolute alcohol. The yield is 5.7 g., 42% of the calculated amount. The substance forms white crystals that melt at 236–237° (corr.).

Analyses.—Subs., 0.5796: 20.42 cc. dry N_2 (25.3° and 724 mm.). Subs., 0.3857: HgS, 0.2506. Calc. for $C_6H_4O_2NClHg$: N, 3.91; Hg, 56.01. Found: N, 3.83; Hg, 55.99.

This substance is less soluble in acetone or in alcohol than the *ortho* compound. However, a relatively large amount remains in an alcohol solution even after it is cooled to —20°; this remainder is precipitated by addition of water. The mercury is not as easily removed by hydrochloric acid as it is from the *ortho* or the *para* compounds. If the compound is shaken with a solution of the calculated amount of bromine, a compound is formed which melts at 52° and whose melting point is not lowered by mixing it with *meta* bromo-nitrobenzene prepared by brominating nitrobenzene.

p-Nitrobenzene Mercuric Chloride, p-$NO_2C_6H_4HgCl$.—A small amount of the *p*-nitrobenzene-sulfinic acid was prepared from *p*-nitro-aniline by Gattermann's method. The yield was very poor; only a very little of the pure acid melting at 120° was obtained. The substance used for preparing the mercury compound was not the pure sulfinic acid, but was a product containing an impurity that was composed largely, if not entirely, of *p*-nitrobenzene-*p*-nitrophenyl-sulfazide, $NO_2C_6H_4NHNHSO_2C_6H_4NO_2$. However, the mercury compound was not formed from the latter substance as no *p*-nitrobenzene mercuric chloride could be prepared by boiling a solution of the *p*-nitrobenzene-*p*-nitrophenyl sulfazide made by Limpricht's method,[2] with mercuric chloride. One g. of somewhat impure sulfinic acid in 10 cc. of alcohol was added to a solution of 3 g. of mercuric chloride in 10 cc. of alcohol and 10 cc. of water, and the solution boiled for 15 hours. The substance was isolated and purified by the same method as given for the o-nitrobenzene mercuric chloride. It crystallizes from alcohol in colorless crystals and melted at 265–266° (corr.), with decomposition. The yield was 0.7 g.

Analyses.—Subs., 0.4458: 15.80 cc. dry N_2 (23° and 732.4 mm.). Calc. for $C_6H_4O_2NClHg$: N, 3.91. Found: 3.93.

p-Nitrobenzene mercuric chloride is similar to the *ortho* compound in its solubilities and reactions. If it is shaken with bromine water, it gives a compound that melts at 125°; this melting point is not changed by mixing the substance with Kahlbaum's *p*-bromonitrobenzene.

CHICAGO, ILL.

[1] Limpricht, *Ber.*, 25, 75 (1892); see also p. 3477.

[2] Limpricht, *ibid.*, 20, 1238 (1887).