In conclusion, the variations between the chemically and the physically determined yields are not sufficient to invalidate the principle of the electronic tautomerism of the chlorotoluenes. The conception affords a consistent interpretation of the observed facts and is substantiated in a great measure by the quantitative data offered in this paper. In the following paper (Part VIII) the conception of electronic tautomerism is developed further and confirmed more completely.

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

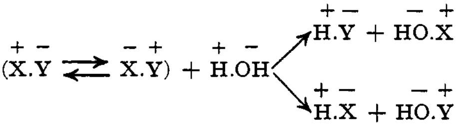
VIII. FURTHER EVIDENCE FOR THE ELECTRONIC TAUTOMERISM OF BENZENE DERIVATIVES.[1]

BY HARRY SHIPLEY FRY.

Received April 13, 1916.

The purpose of the present paper is to consider certain experimental facts, the interpretation of which fully warrants the assumption of the existence of electromers in dynamic equilibrium, *i. e.*, electronic tautomerism. Quantitative data will also be presented which conclusively confirm the principle of electronic tautomerism. A few underlying principles should be recalled.

Hydrolysis reactions commonly constitute an experimental method[2] for designating the polarity of the radicals of a compound under the particular conditions of hydrolysis. The following general scheme embodies the theoretical and the actual possibilities presented by hydrolysis reactions:



$$(\overset{+}{X}.\overset{-}{Y} \rightleftarrows \overset{-}{X}.\overset{+}{Y}) + \overset{+}{H}.\overset{-}{OH} \left\langle \begin{array}{l} \nearrow \overset{+}{H}.\overset{-}{Y} + \overset{-}{HO}.\overset{+}{X} \\ \searrow \overset{+}{H}.\overset{-}{X} + \overset{-}{HO}.\overset{+}{Y} \end{array} \right.$$

If the compound in question, XY, on hydrolysis yields only H.Y and HO.X, then XY is qualified by the electronic formula $\overset{+}{X}\text{——}\overset{-}{Y}$, or $\overset{+}{X}.\overset{-}{Y}$. If, on the other hand, conditions are such that hydrolysis yields only H.X and HO.Y, then XY is qualified by the formula $\overset{-}{X}.\overset{+}{Y}$. In some reactions the four possible products are obtained and, accordingly, the compound XY presents an illustration of electronic tautomerism, *i. e.*, the existence of both electromers $(\overset{+}{X}.\overset{-}{Y} \rightleftarrows \overset{-}{X}.\overset{+}{Y})$ in dynamic equilibrium. A number of instances[3] has been recorded in which reactions proceed

---

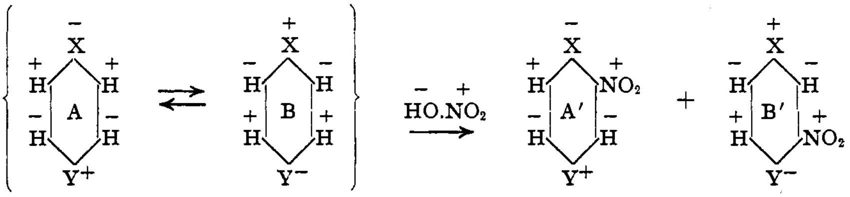
[1] Read before the Cincinnati Section of the American Chemical Society, May 12, 1915.

[2] Fry, *Z. physik. Chem.*, 76, 395 (1911); W. A. Noyes, THIS JOURNAL, 23, 460 (1901) and Stieglitz, THIS JOURNAL, 23, 796 (1901) were the first to employ hydrolysis reactions as a means of indicating the polarities of the radicals of substances.

[3] Fry, THIS JOURNAL, 37, 864 (1915); L. W. Jones, *Am. Chem. J.*, 50, 414 (1913).

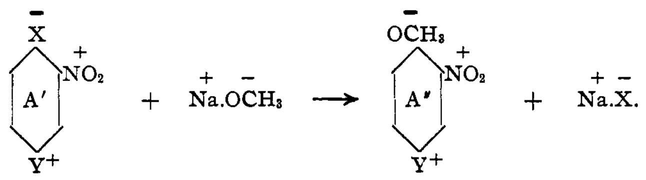
according to the above and analogous schemes, and therefore substantiate the existence of electromers and electronic tautomerism. Particularly significant, in this connection, are the nitrations of the mixed dihalogen benzenes and the subsequent hydrolyses of their nitration products with sodium methylate. Some remarkable consequences may now be predicted if we consider the mixed dihalogen benzenes from the standpoint of the electronic formula of benzene and the principle of electronic tautomerism.

When two substituents occupy positions either ortho or para to each other they are of opposite polarity. Hence in the electronic formula for a *p*-dihalogen benzene in which the halogen atoms X and Y are different chemically, it follows that if X is negative, Y is positive; or, if X is positive, Y is negative. Now, in the nitration of a *p*-disubstituted derivative of benzene only two mononitro substitution products are possible, and, from the standpoint of the principle of electronic tautomerism as applied to a *p*-dihalogen benzene, the nitration reaction should conform to the following general scheme:



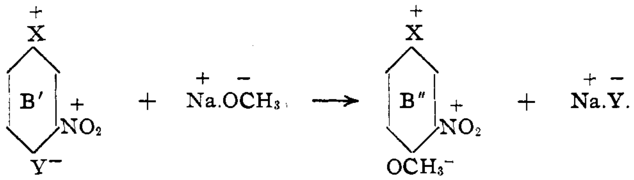
If the principles underlying this general scheme are correct, then certain definite consequences follow which should lend themselves to verification by experiment. What are some of these consequences? If the electromers of C_6H_4XY (designated as A and B) are in tautomeric equilibrium and if each electromer interacts with nitric acid, the respective isomers, A′ and B′, should be formed. Note particularly that in the isomer A′, X is negative and Y is positive, while in isomer B′, X is positive and Y is negative. In view of the facts presented in the preceding paper, notably the action of sodium methylate upon *o*-, *p*-, and *m*-chloronitrobenzenes, it follows that isomer A′ on interaction with sodium methylate ($\overset{+}{Na}.\overset{-}{OCH_3}$) should exchange $\overset{-}{X}$ for $\overset{-}{OCH_3}$ and liberate $\overset{+}{Na}.\overset{-}{X}$ according to Equation 1.

(1)



On the other hand, isomer B′ should exchange $\overset{-}{Y}$ for $\overset{-}{OCH_3}$ and liberate $\overset{+}{Na}.\overset{-}{Y}$ according to Equation 2:

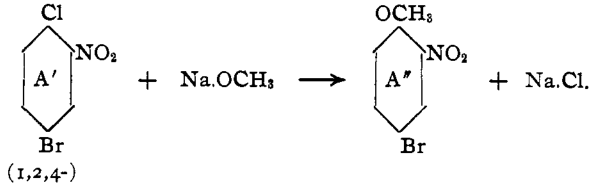
(2)



Furthermore, if electromers A and B are in tautomeric equilibrium and nitration yields a mixture of isomers A′ and B′ then the action of sodium methylate upon this mixture should yield not only the oxymethyl derivatives, A″ and B″, (Equations 1 and 2, respectively) but also *a mixture of the sodium halides,* $\overset{+}{Na}.\overset{-}{X}$ *and* $\overset{+}{Na}.\overset{-}{Y}$. An experimental verification of these predictions would lead to a very definite conclusion, namely, that *the para mixed dihalogen compound,* C_6H_4XY, *affords an example of electronic tautomerism.* Otherwise it would be difficult, if not impossible, to account for the simultaneous formation of the halides, $\overset{+}{Na}.\overset{-}{X}$ and $\overset{+}{Na}.\overset{-}{Y}$, when sodium methylate interacts with the products of nitration of the mixed dihalogen benzene.

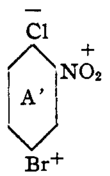
Experimental facts will now be considered which are completely in agreement with the principles and general reactions just postulated. Holleman[1] and Heineken have made a thorough study of the nitration (at 0°) of various mixed dihalogen benzenes. For the present, attention will be confined to the nitration of *p*-chlorobromobenzene, which gave a mixture of the isomers 1,2,4- and 1,3,4-chloronitrobromobenzenes. In developing a quantitative chemical method for determining the yields of these isomers in the nitration mixture, Holleman found that the *1,2,4-isomer* heated with 0.35 *N* sodium methylate solution in a sealed tube for five hours at 80° gave *practically complete displacement of chlorine as sodium chloride while the bromine remained intact.* The reaction proceeded quantitatively (98.40%) according to Equation 3.

(3)



Note that this reaction is perfectly analogous to Equation 1, given above, in which $\overset{-}{X}$ may now be $\overset{-}{Cl}$, and $\overset{+}{Y}$ may be $\overset{+}{Br}$. The liberated sodium halide is $\overset{+}{Na}.\overset{-}{Cl}$. In other words, the 1,2,4-isomer (A′) has the electronic formula

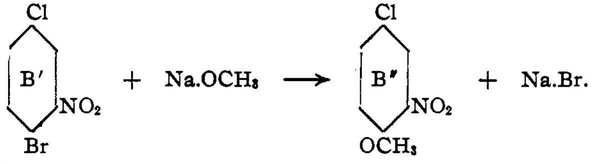
[1] *Recueil,* 34, 204 (1915).



otherwise the liberation of chlorine as $\overset{+}{Na}.\overset{-}{Cl}$ is inexplicable.

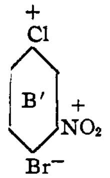
On the other hand, the 1,3,4-isomer on interaction with sodium methylate (under identical conditions) suffered *practically complete displacement of bromine as sodium bromide while the chlorine atom remained intact.* The reaction proceeded quantitatively (98.00%) according to Equation 4.

(4)



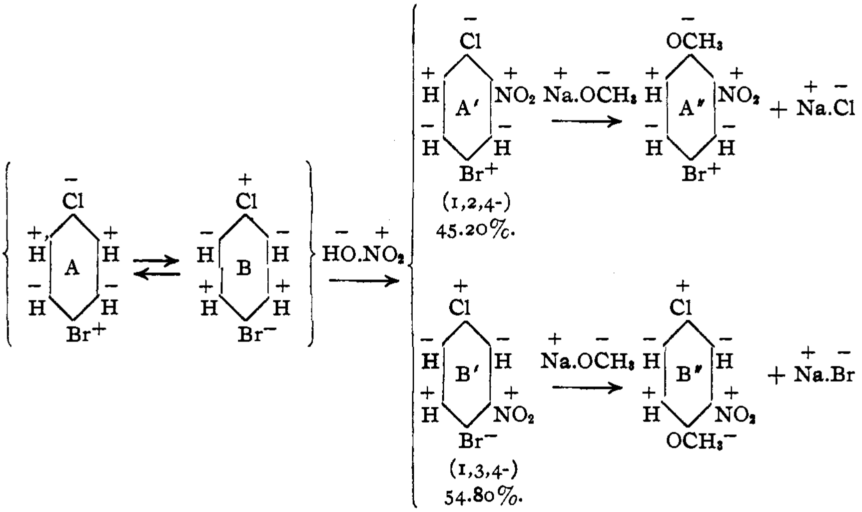
(1,3,4-)

Note that this reaction is perfectly analogous to Equation 2 above, in which $\overset{+}{X}$ may now be $\overset{+}{Cl}$, and $\overset{-}{Y}$ may be $\overset{-}{Br}$. The liberated sodium halide is $\overset{+}{Na}.\overset{-}{Br}$. In other words, the 1,3,4-isomer (B′) has the electronic formula



otherwise the liberation of bromine as $\overset{+}{Na}.\overset{-}{Br}$ is inexplicable.

The quantitative interaction of 1,2,4- and 1,3,4-chloronitrobromobenzene with sodium methylate enabled Holleman to determine the relative quantities of these isomers obtained on nitrating *p*-chlorobromobenzene. The sodium chloride and sodium bromide liberated were precipitated as silver chloride and bromide. An analysis of the mixed precipitates gave the percentage yields of the isomers calculated upon the ratios AgCl: 1,2,4-isomer, and AgBr : 1,3,4-isomer. These calculations were based upon Equations 3 and 4 which are perfectly analogous to the preceding electronic Equations 1 and 2, respectively. The yields of the isomers were 45.20% and 54.80%, respectively. The complete correlation of all of these reactions with the electronic formulas and the principle of electronic tautomerism is embodied in the following scheme:



Now a survey of the above scheme shows that those molecules of 1,4-chlorobromobenzene which interact with nitric acid to give the 1,2,4-isomer, which in turn exchanges its *chlorine* atom for OCH_3 and yields *sodium chloride*, cannot be identical with the molecules of 1,4-chlorobromobenzene which interact with nitric acid to give the 1,3,4-isomer, which in turn exchanges its *bromine* atom for OCH_3 and yields *sodium bromide*. In other words, the 1,2,4-isomer (A′), containing $\overset{-}{\text{Cl}}$ and $\overset{+}{\text{Br}}$, must be derived from molecules of 1,4-chlorobromobenzene which also contain $\overset{-}{\text{Cl}}$ and $\overset{+}{\text{Br}}$, *i. e.*, electromer A; and the 1,3,4-isomer (B′), containing $\overset{+}{\text{Cl}}$ and $\overset{-}{\text{Br}}$, must be derived from molecules of 1,4-chlorobromobenzene which also contain $\overset{+}{\text{Cl}}$ and $\overset{-}{\text{Br}}$, *i. e.*, electromer B. Thus *the existence of two types of molecules of 1,4-chlorobromobenzene, namely electromers A and B, is conclusively indicated. Their simultaneous interaction with nitric acid indicates tautomeric equilibrium.* The relative yields of the isomers A′ and B′ are functions of the speeds of interaction of nitric acid with the respective electromers A and B, and, as shown in a previous paper,[1] the speeds of interaction are intimately related to the concentrations of the respective electromers in the reaction mixture.

It will not be necessary to extend this paper by giving similarly detailed descriptions of the nitrations of other mixed dihalogen benzenes,[2] since each example conforms perfectly to the schemes and principles presented in this and preceding papers. In conclusion, it is maintained

[1] See Parts III and IV of this series (Fry, *Loc. cit.*).

[2] *p*-Flurochloro-, *p*-flurobromo-, *p*-chloroiodo-, *o*-chlorobromo-, *o*-chloroiodo-, and *o*-bromoiodo benzene.

that each of these cases further substantiates the principle of electronic tautomerism or the existence of electromers in dynamic equilibrium.[1]

CINCINNATI, O.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF IOWA.]

4-NITRO-5-METHYL-2-SULFOBENZOIC ACID AND SOME OF ITS DERIVATIVES.

BY WILLIAM J. KARSLAKE AND PERRY A. BOND.

Received March 29, 1916.

In an earlier paper[2] we have shown that when 6-nitro-1,3-dimethylbenzene-4-sulfonic acid is oxidized by potassium permanganate in very dilute potassium hydroxide solution, three main products are formed, to wit, 6-nitro-3-methyl-4-sulfobenzoic acid, 4-nitro-5-methyl-2-sulfobenzoic acid and 6-nitro-4-sulfoisophthalic acid. Sometime later, Karslake and Huston[3] made derivatives of 6-nitro-3-methyl-4-sulfobenzoic acid. The present work was undertaken to complete our knowledge of the second of these three acids.

In our previous work, 4-nitro-5-methyl-2-sulfobenzoic acid was obtained in the form of the neutral potassium salt as the first crop of crystals from the oxidized nitro-xylene sulfonic acid. Analyses of this salt were persistently low in potassium. Since then it has been found that this first crop of crystals is usually contaminated with unoxidized 6-nitro-1,3-dimethylbenzene-4-sulfonic acid in the form of the potassium salt. The separation was accomplished finally by systematic fractional crystallization, the crystals being filtered off first from the fairly concentrated solution at 50°, and then from the cold, somewhat diluted filtrate after stand-

---

[1] Any objection to the use of the conception of electronic tautomerism on the grounds that electronic isomers (electromers) have not as yet been isolated is unwarranted because the conception of tautomerism, both in its historical and practical aspects, neither involves nor demands the immediate possibility of the isolation of the tautomers. In 1885, Laar (*Ber.*, 18, 648 (1885)), in a paper "Ueber die Möglichkeit mehrerer Strukturformeln für dieselbe chemisch Verbindung," defined tautomerism as the phenomenon of one substance doing duty for two structural isomers, *but the isolation of dynamic isomers or desmotropes was not effected until 1893*, the earliest examples being acetyldibenzoylmethane, tribenzoylmethane, and mesityloxide-oxalic ester described by Claisen (*Ann.*, 277, 183 (1893); **291**, 25 (1896)). Strictly speaking, the term *tautomeric* is now applied to substances in which *only the equilibrium mixture of the structural isomers is known;* the term *desmotropic* is employed in cases where the isomers have been shown to be capable of independent existence. (Clarke, "Organic Chemistry," p. 251.) The existence of electromers in dynamic equilibrium has been conclusively indicated. Their isolation as *electronic desmotropes* has not as yet been effected. Further discussion of this phase of the subject is reserved for future papers.

[2] THIS JOURNAL, 31, 405 (1909).

[3] *Ibid.*, 31, 1057 (1909).