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.

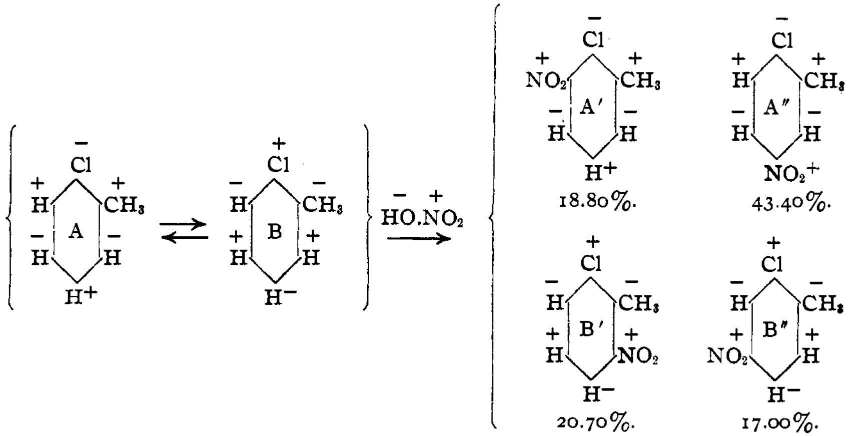
By Harry Shipley Fry.

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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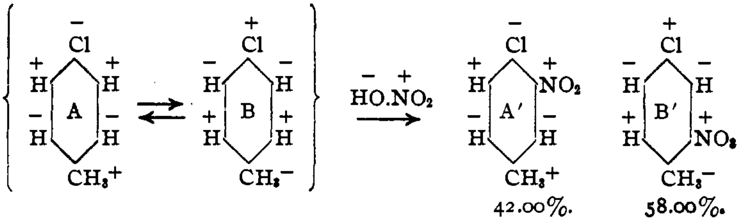
[1] Fry, This Journal, **37**, 863 (1915).

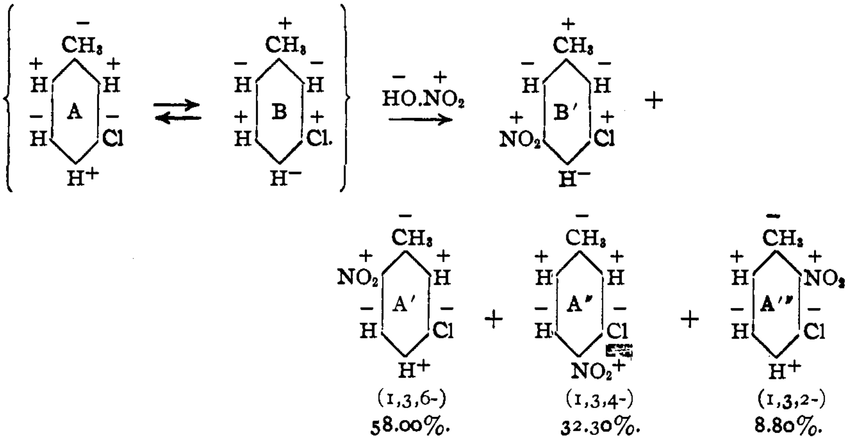
[2] Fry, *Z. physik. Chem.*, **76**, 390 (1911); This Journal, **37**, 864 (1915).

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

Scheme 2.—The nitration of *p*-chlorotoluene.



Scheme 3.—The nitration of *m*-chlorotoluene.



The above schemes were the bases of the interpretations of the nitration reactions of Wibaut,[1] Holleman[2] and Wibaut,[3] respectively, who determined the percentage yields of the several isomers of each nitration by physical methods—processes of fractional crystallization and comparisons of curves of fusion of mixtures of unknown composition with those of known composition.

In each of these schemes it will be observed that the nitration products (A′, A″, etc.) of the electromer A embody negative chlorine while those (B′, B″, etc.) of electromer B embody positive chlorine. Now, if it be possible to show by quantitative chemical methods that the yields of the isomers (chloronitrotoluenes) which contain negative chlorine are commensurate with the yields of the same isomers ascertained by Holleman and Wibaut by physical methods, then the conception of the electronic tautomerism of the chlorotoluenes as indicated in Schemes 1, 2, and 3, is, in a measure, substantiated.

The chemical method for the determination of the yields of the isomers containing negative chlorine depends, first, upon the completeness of

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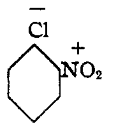
[1] *Recueil*, 32, 244 (1913).

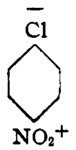
[2] *Ibid.*, 28, 408 (1909).

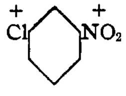
[3] *Ibid.*, 32, 244 (1913).

their interaction with sodium methylate and, second, the noninteraction of the isomers containing positive chlorine. In order to test the applicability of these two points, the action of sodium methylate in methyl alcohol solution upon *o*-, *p*-, and *m*-chloronitrobenzenes was investigated. These isomers were chosen because it is commonly recorded that the *o*- and *p*-isomers exchange their halogen atom for OH, $O(CH_3)$ or NH_2, while the *m*-isomer is nonreactive.

An interpretation of these reactions has been given[1] from the standpoint of the electronic formula of benzene and the substitution rule. The abbreviated electronic formulas of the chloronitrobenzenes are as follows:







Only those isomers containing negative halogen (*o*- and *p*-) should interact with sodium methylate, thus,

$$\overset{+}{NO_2}.C_6H_4.\overset{-}{Cl} + \overset{+}{Na}.\overset{-}{OCH_3} \longrightarrow \overset{+}{NO_2}.C_6H_4.\overset{-}{OCH_3} + \overset{+}{Na}.\overset{-}{Cl},$$

and the *m*-isomer, containing positive chlorine, should be nonreactive under the same conditions.

The extent of the replacement of negative chlorine can be found by determining the quantity of sodium chloride liberated. After repeated experiments, designed to secure the conditions noted, the following method was found to yield theoretical results: About 0.2 g. of the chloronitrobenzene was dissolved in 15 cc. of a normal solution of sodium methylate in absolute methyl alcohol. The solution was heated in a sealed glass tube for 5 hours at 100°. The contents of the tubes were then diluted to a volume of 200 cc., acidified with nitric acid, boiled to expel the methyl alcohol, cooled, and filtered. The quantity of sodium chloride in the respective filtrates was determined by titration with standard solution of silver nitrate. The following results were obtained:

Substance.	(Grams.)	No. cc. 0.9957 *N* $AgNO_3$ solution.	% negative Cl. Found.	% negative Cl. Theor.
o-$\overset{-}{Cl}.C_6H_4.\overset{+}{NO_2}$	0.2005	12.81	22.56	22.51
p-$\overset{-}{Cl}.C_6H_4.\overset{+}{NO_2}$	0.2007	12.78	22.48	22.51
m-$\overset{+}{Cl}.C_6H_4.\overset{+}{NO_2}$	0.1992	00.00	00.00	00.00

These results show that isomers containing negative chlorine may be estimated quantitatively, provided conditions are secured for their complete interaction with sodium methylate, while under the same conditions the isomer containing positive chlorine is nonreactive.

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[1] Fry, *Z. physik. Chem.*, 76, 395 (1911); THIS JOURNAL, 36, 253 (1914).

The chief problem of the present investigation was to secure conditions under which the negative halogen atoms of the nitration products of *o*-, *p*-, and *m*-chlorotoluenes would completely interact with sodium methylate and thus afford a chemical method for determining the percentage yields of the isomers of chloronitrotoluene which contain negative chlorine. A comparison of the chemically determined and the physically determined yields could then be made. With this end in view, *o*-, *p*-, and *m*-chlorotoluenes were each separately nitrated (at 0°) according to the specific directions given by Wibaut, Holleman and Wibaut, respectively.[1] The methods were originally designed to yield only mononitro substitution products. The respective products of nitration of each of the chlorotoluenes, which consisted of mixtures of the different isomers (nitrochlorotoluenes), as indicated in the preceding Schemes 1, 2, and 3, were treated with sodium methylate solutions of varying concentrations—0.5 *N*, *N*, 2 *N* and 3 *N*. Samples, 0.2 to 0.4 g., of the nitration products were heated, each with 15 cc. of the sodium methylate solution in sealed tubes, for 10 hours at 100°. The contents of the tubes were then analyzed, as previously described, for the negative chlorine, liberated as $\overset{+}{\mathrm{Na}}.\overset{-}{\mathrm{Cl}}$, precipitated and weighed as silver chloride. The percentage yield of the combined isomers containing negative chlorine was calculated from the ratio $\overset{+}{\mathrm{Ag}}.\overset{-}{\mathrm{Cl}} : \overset{-}{\mathrm{Cl}}.\overset{+}{\mathrm{NO_2}}.\overset{+}{\mathrm{CH_3}}.\mathrm{C_6H_3}$. The results of these experiments are recorded in three sections (I, II and III) to correspond with Schemes 1, 2, and 3 for the nitration of *o*-, *p*-, and *m*-chlorotoluenes, respectively. All reactions were conducted in duplicate.

TABLE I.

I. Action of Sodium Methylate upon the Isomers Derived from *o*-Chlorotoluene. (See Scheme 1.)

Mixture of isomers (gram).	Normality $NaOCH_3$.	AgCl (gram).	% yield of isomers A' + A". 1,2,6- and 1,2,4-$\overset{-}{\mathrm{Cl}}.\ \overset{+}{\mathrm{CH_3}},\ \overset{+}{\mathrm{NO_2}},\ \mathrm{C_6H_3}$.	Average.
0.2625	0.5 *N*	0.1163	53.01	
0.2434	0.5 *N*	0.1084	53.29	53.15
0.2835	*N*	0.1388	58.58	
0.2938	*N*	0.1446	58.89	58.73
0.3283	2 *N*	0.1362	49.64	
0.2994	2 *N*	0.1254	50.12	49.83
0.2772	3 *N*	0.0884	38.16	
0.2940	3 *N*	0.0941	39.30	38.23

These results indicate that the extent of the reaction with sodium methylate is greatest in the normal solution. A 58.73% yield of the combined isomers containing negative chlorine was obtained. The yields of these isomers determined by the physical methods of Wibaut[1] totals 62.20%.

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[1] *Loc. cit.*

The yields obtained by the two methods, while not identical, approximate closely. Variations will be considered later.

TABLE II.

II. Action of Sodium Methylate upon the Isomers Derived from *p*-Chlorotoluene. (See Scheme 2.)

Mixture of isomers (gram).	Normality $NaOCH_3$	AgCl (gram).	% yield of isomer A'. 1,2,4-$\overset{-}{Cl}$, $\overset{+}{NO_2}$, $\overset{+}{CH_3}$, C_6H_5.	Average.
0.2707	0.5 *N*	0.0799	35.33	
0.2868	0.5 *N*	0.0842	35.13	35.23
0.3068	*N*	0.0946	36.89	
0.2608	*N*	0.0773	35.47	36.18
0.2854	2 *N*	0.0750	31.44	
0.3068	2 *N*	0.0780	30.42	30.93
0.3297	3 *N*	0.0814	29.54	
0.3037	3 *N*	0.0769	30.30	29.92

Here also the extent of the reaction with sodium methylate was greatest in the normal solution, which indicated a yield of 36.18% of the isomer containing negative chlorine. The yield of the same isomer determined by Holleman (fusion curve method) was 42.00%.

TABLE III.

III. Action of Sodium Methylate upon the Isomers Derived from *m*-Chlorotoluene. (See Scheme 3.)

Mixture of isomers (gram).	Normality $NaOCH_3$.	AgCl (gram).	% yield of isomers A' + A" + A"', 1,3,6- + 1,3,4- + 1,3,2-$\overset{-}{CH_3}$, $\overset{-}{Cl}$, $\overset{+}{NO_2}$, C_6H_5.	Average.
0.2257	0.5 *N*	0.1652	87.59	
0.2510	0.5 *N*	0.1843	87.86	87.77
0.2672	*N*	0.1987	88.99	
0.2520	*N*	0.1853	87.99	88.49
0.2670	2 *N*	0.1898	85.06	
0.3212	2 *N*	0.2308	85.98	85.52
0.2809	3 *N*	0.1923	81.92	
0.2808	3 *N*	0.1888	80.46	81.19

Again the extent of the reaction was greatest in the normal solution indicating a yield of 88.49% of the three isomers containing negative chlorine. Wibaut (fractional crystallization and fusion curve methods) obtained a 100% yield of these isomers.

The yields of the isomers containing negative chlorine determined by physical methods and the maximum yields of the same isomers determined by chemical methods are summarized in the following table:

TABLE IV.

Scheme.	Isomers.	Physical.	Chemical.	% Ratio.
1...........	(A' + A")	62.20 (Wibaut)	58.73 (Fry)	94.42
2...........	(A')	42.00 (Holleman)	36.18 (Fry)	86.14
3...........	(A' + A" + A"')	100.00 (Wibaut)	88.49 (Fry)	88.49

The extreme care with which Holleman and Wibaut conducted their physical determinations leads one to accept their results as practically final. Accordingly, in the last column above, the chemically determined yields are recorded as percentages of the physically determined yields. If each of the values in the last column was 100% then it might be assumed without question that the conception of the electronic tautomerism of the *o*-, *p*-, and *m*-chlorotoluenes given in Schemes 1, 2, and 3, respectively, is completely substantiated. Without making this assumption or claim it may, nevertheless, be maintained that in so far as the values in the last column do approach the theoretical, so far do they substantiate the electronic tautomerism of the chlorotoluenes. Moreover, it may be said that the electronic tautomerism of *o*-, *p*-, and *m*-chlorotoluenes is the only hypothesis that has accounted for the replaceability of certain halogen atoms in some of the isomeric nitrochlorotoluenes and the nonreplaceability of certain halogen atoms in others. The data presented in this paper substantiate the hypothesis.

The fact that the chemically determined quantities of the isomers containing negative chlorine were less than the quantities determined by physical methods may have been due to two causes. First, the interaction with sodium methylate of one or more of these isomers in the mixtures may have been incomplete. This is not likely, since the results of the experiments with the analagous chloronitrobenzenes gave results in perfect agreement with the theory. Furthermore, a survey of the quantitative data given in connection with Schemes 1, 2, and 3 shows a maximum replacement in every reaction in which the uninormal solutions of sodium methylate were used. Concentrations below or above normal gave lower yields.

In the second place, the low yields of the isomers containing negative chlorine may be due to the fact that the relative quantities of the isomers obtained on nitration of the chlorotoluenes in Holleman's laboratories may not have been identical with the relative quantities of the same isomers obtained in this laboratory, even though the original directions given by Holleman and Wibaut were carried out precisely. The variations are most likely due to lack of standardization in certain details of manipulation, such as the rate of the addition of the nitric acid, methods of stirring, cooling, etc. While the temperature variations were kept within the prescribed limits, primarily to avoid the formation of polynitro derivatives, it is quite likely that the local temperature effects in the reaction mixture may have altered the relative quantities of the isomers formed. In fact, when nitrations were conducted separately, but under identical conditions, variations in the fusion points of the resulting mixtures were noted. This signifies corresponding variations in the relative quantities of the isomers in these mixtures.

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.]

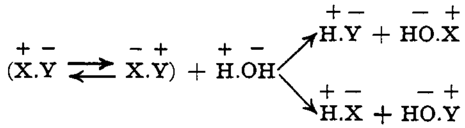
VIII. FURTHER EVIDENCE FOR THE ELECTRONIC TAUTOMERISM OF BENZENE DERIVATIVES.[1]

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:



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

If the compound in question, XY, on hydrolysis yields only H.Y and HO.X, then XY is qualified by the electronic formula $\overset{+}{X}$——$\overset{-}{Y}$, 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

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[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).