on the assumption that the reaction is of the first order, are given in Table II.

Table II

Rate of Iodine Removal

Time, min.	2-Iodo-aniline Reaction, %	K	2,5-Di-iodo-4-aminotoluene[a] Reaction, %	K
5	7.82	0.0165	6.72	0.0137
15	25.18	.0194	23.13	.0169
30	49.18	.0226	36.22	.0150
60	75.19	.0232	61.46	.0161
120	93.23	.0225	83.50	.0150

[a] Only one iodine is reactive.

Summary

1. A number of new halogen derivatives of 2-iodo-4-aminotoluene have been prepared.

2. A study of the selectivity and rate of halogen removal in these compounds offers striking confirmation of predictions based on a consideration of the removable halogens as positive.

Chicago, Illinois

[Contribution from the Kent Chemical Laboratory, University of Chicago]

POSITIVE HALOGENS ATTACHED TO CARBON IN THE AROMATIC SERIES. V. ANALOGY BETWEEN POSITIVE AND NEGATIVE HALOGENS

By Ben H. Nicolet

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The pronounced reactivity toward all alkaline reagents of the halogens in 2,4- and 2,6-dinitrophenyl halides is well known. The halogens are removed as halide ion and replaced by —OH, —NH_2, etc. Very few chemists have hesitated to attribute this increase in reactivity to an increase in the negative character of the halogen in question by the nitro groups, which in turn are usually conceded, in recent years at least,[1] to be positive in character. The fact that no case was known in which a halogen attached to carbon in a benzene ring was given a conspicuously negative character by substituents occupying only positions *meta* to it, appears to have caused little apprehension.

Recent papers[2] from this Laboratory have discussed as positive certain halogens (bromine and, more conspicuously, iodine) which, when occupying positions *ortho* or *para* to one or more amino or hydroxyl groups, were

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[1] Fry, "Electronic Conception of Valence," Longmans, Green and Co., **1921,** p. 122. Stieglitz, This Journal, **44,** 1305 (1922). Shoesmith, Hetherington and Slater, *J. Chem. Soc.,* **125,** 1314 (1924).

[2] (a) Nicolet, This Journal, **43,** 2081 (1921). (b) Nicolet and Sampey, *ibid.,* **49,** 1796 (1927). (c) Nicolet and Ray, *ibid.,* **49,** 1801 (1927). (d) Nicolet and Sandin, *ibid.,* **49,** 1806 (1927).

hydrolyzed (usually in acid solution) in such a way that the halogen was replaced by hydrogen, while the solution acquired oxidizing properties, as shown by the liberation of halogen, the formation of more highly substituted products, or the oxidation of suitable[3] reducing agents. This interpretation appears to have been less widely accepted, perhaps because of its relative novelty, although reactions seeming to justify it have been found in all the suitable cases investigated.

The present paper records an unsuccessful attempt to demonstrate positive halogen in what is perhaps the ideal case of those subject to the limitation that only *meta* substituents should be present. 3,5-Dinitroiodobenzene has been prepared, and shown to have no appreciable tendency to split off iodine when heated at 100° in acid solution.

In this connection, however, it was decided to test also the ease of hydrolysis of 3,5-diaminochlorobenzene by alkalies. This compound contains its chlorine (the most negative of the halogens, with the exception of fluorine) *meta* to two amino groups. It was boiled for two hours with an alcoholic solution of sodium ethylate, and allowed to stand two days longer, without the slightest observable liberation of chloride ion. One is thus faced with the following paradox: two amino groups, suitably located, suffice to give to iodine (or even to bromine)[4] a pronounced positive character; two nitro groups, suitably located, give to chlorine (or even to bromine or iodine) a pronounced negative character; but neither two nitro groups, both *meta* to halogen (even iodine), nor two amino groups, both *meta* to halogen (even chlorine) suffice to give a character which is definitely positive or negative, respectively.

One conclusion appears to be that the negativity and positivity, respectively, of halogens attached to carbon in the benzene ring, rest on approximately the same basis. A further conclusion might well be that if one is to assume polarity at all (and this seems necessary, to explain the great difference in character of the two types of reaction discussed), one must further assume that the character of the reaction is such that the latter is definitely conditioned by the presence of suitable groups in the *ortho* or *para* positions. The logical interpretation of this assumption would be that the reactions in each case are due to the possibility of the formation of intermediate products of a special (presumably quinoidal) type. A possible interpretation of this sort for the reactions of compounds assumed to contain positive halogens will be given below.

Extension of the reasoning outlined leads to another consequence. For those chemists who wish to attribute polar structures (or structures at least partially polar) to organic compounds in general, it may be nec-

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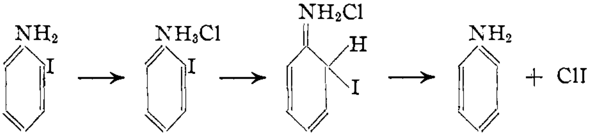
[3] Usually stannous chloride; as to its "suitability," see Ref. 2.

[4] But not to chlorine which, however, shows similar properties in 2,4,6-triaminochlorobenzene.

essary to recognize as a fact that non-reactivity, under given conditions, of a certain atom or radical has no bearing whatever on the structure to be attributed; or, to state it differently, altogether aside from the polar (or partially polar) structure which a given molecule may possess, demonstration of the structure in question by a given diagnostic reaction depends also on other conditions, which may or may not permit the expected reaction to take place.

The considerations discussed above suggest most strongly that both the types of hydrolysis mentioned take place through the formation of a quinoidal intermediate. In view of the discussions given by Robinson[5] of 1,3 addition to α,β-unsaturated amino compounds, as a case of addition to a special type of conjugated system, it seems especially tempting to assume that the elimination of halogens in the positive form from amino derivatives[6] of the type discussed, may take place by 1,3 elimination from an analogous system in the way pictured below.



It is an experimental fact that halogen is liberated in positive form when compounds of the type indicated are heated in acid solution. It is also an experimental fact, although the data have not yet been published, that in analogous cases a quantitative study of the reaction involved when analogous compounds are heated with acid and stannous chloride has shown that the reaction rate is not proportional to the concentration of the stannous chloride. It would seem to follow that the reaction in the presence of stannous chloride (which is the one more generally studied) is really a succession of reactions of which the first is simply one of hydrolysis (or at least one independent of the presence of the reducing agent), followed by the reduction of the positive halogen as it appears in the initial reaction. The mechanism may prove, on further study, to be other than that outlined above, but it is not believed likely that the principles stated will require serious modification.

Experimental Part

3,5-Diaminochlorobenzene.—This substance has been made by Cohn,[7] by the reduction of 3,5-dinitrochlorobenzene. A method analogous to that by which Jackson and Calvert[8] obtained the corresponding bromo compound was preferred.

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[5] (a) Hamilton and Robinson, *J. Chem. Soc.*, **109**, 1029 (1916). (b) Robinson, *ibid.*, **109**, 1038 (1916).

[6] The possible extension of this type of reaction to phenolic derivatives is obvious.

[7] Cohn, *Monatsh.*, **22**, 119 (1901).

[8] Jackson and Calvert, *Am. Chem. J.*, **18**, 487 (1896).

2,4,6-Tribromo-3,5-dinitrochlorobenzene[9] was reduced with tin and concd. hydrochloric acid; with the addition of some glacial acetic acid to increase the solubility of the dinitro compound, the reduction was completed in two hours on the water-bath. The product was further identified by the preparation of its diacetyl and dibenzoyl derivatives.[7]

ATTEMPTED HYDROLYSIS.—Jackson and Calvert[8] say of 3,5-diaminobromobenzene, "Sodic hydrate seems to have no action even when warmed with it several minutes on the water-bath." One g. of 3,5-diacetylaminochlorobenzene was added to a solution of 2 g. of sodium in 50 cc. of alcohol; the mixture was refluxed for two hours, and allowed to stand for two days. The solution contained only a trace of chloride ion, and a control showed an equal trace in the sodium ethylate so prepared. It was shown that the acetyl derivative was completely hydrolyzed under the conditions present; on reacetylation, more than 90% of the original material was recovered as the diacetyl derivative. There was thus no evidence of hydrolysis.

3,5-Dinitro-aniline.[10]—Flürscheim,[11] reviewing the work of Bader[12] and de Kock,[13] described a method for obtaining this substance in 62% yield. A 74% yield was obtained as follows.

Hydrogen sulfide was passed into a mixture of 100 cc. of 95% alcohol and 60 cc. of concd. ammonium hydroxide until the weight increased 5.5 g. This solution was added drop by drop to a refluxing solution of 6 g. of 1,3,5-trinitrobenzene in 150 cc. of alcohol, and heating continued for one hour after addition was complete. The mixture was then collected, filtered to remove sulfur, and the alcohol distilled off. The residue was extracted thoroughly with hot water, and the extract concentrated till crystallization began, and then cooled in ice water. The product, recrystallized from hot water, melted at 155–156°.

3,5-Dinitro-iodobenzene.—The amino group was replaced by iodine in the usual way, and the product recrystallized from 60% alcohol. It formed golden plates; m. p., 99°.

Anal. (Carius). Calcd. for $C_6H_4O_3N_2I$: I, 43.26. Found: 43.14.

ATTEMPTED HYDROLYSIS.—Dinitro-iodobenzene (0.2 g.) was dissolved in 15 cc. of acetic acid and 15 cc. of 10% sulfuric acid added, and the mixture refluxed for one hour. No iodine color appeared, and the solution gave no test for inorganic iodine. Most of the material was recovered unaltered.

3,5-Diacetylamino-iodobenzene.—The dinitro-compound was reduced with tin and hydrochloric acid, and the tin removed with hydrogen sulfide. Excess of sodium acetate was added, and then an excess of acetic anhydride. The acetyl derivative which separated melted after recrystallization at 291°.

Anal. (Carius). Calcd. for $C_{10}H_{11}O_2N_2I$: I, 39.94. Found: 40.22.

Summary

1. 2,4-Dinitrochlorobenzene and 2,4-diamino-iodobenzene are known to behave on hydrolysis as though their halogens were negative and positive, respectively. 3,5-Diaminochlorobenzene and 3,5-dinitro-iodo-

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[9] Jackson and Carlton, *Am. Chem. J.*, **31**, 375 (1904).

[10] The remainder of the experimental work described was carried out by Mr. Ben Wilbur Goldman.

[11] Flürscheim, *J. prakt. Chem.*, [2] **71**, 537 (1905).

[12] Bader, *Ber.*, **24**, 1655 (1891).

[13] de Kock, *Rec. trav. chim.*, **20**, 112 (1900)

benzene (both ideal cases, in terms of the theory discussed) have been prepared, and show no indications of polar characteristics for the halogens present.

2. A possible mechanism for the elimination of positive halogen from amino derivatives, involving the formation of a quinoidal intermediate compound and subsequent 1,3 elimination, has been suggested.

3. It is pointed out that failure to react under given conditions is no adequate indication of polar structure.

4. The assumption of negativity and positivity, respectively, for certain halogens attached to carbon in the benzene ring, is shown to rest on essentially the same basis.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY, No. 303]

ADDITION COMPOUNDS OF ALLYLTHIO-UREA WITH SILVER HALIDES[1]

BY S. E. SHEPPARD AND H. HUDSON

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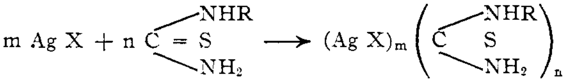
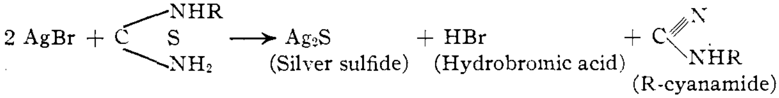
In an investigation on photographic gelatin[2] it was found that the photographic activity of certain gelatins depends upon the presence of traces of mustard oil, or allyl isothiocyanate, and the thio-urea (allyl thiocarbamide, thiosinamine) derived therefrom. Further, it was shown that this photographic sensitizing power was a general property of thioureas and a number of cognate bodies,[2] being due to the formation of small traces of silver sulfide in the silver halide grains. These traces of silver sulfide were considered to constitute the so-called "sensitivity centers" of photographic theory.

The chemical reactions in this sensitizing process are essentially



$$m\,\mathrm{Ag\,X} + n\,\mathrm{C}\begin{matrix}\nearrow \mathrm{NHR}\\ = \mathrm{S}\\ \searrow \mathrm{NH_2}\end{matrix} \longrightarrow (\mathrm{Ag\,X})_m\left(\mathrm{C}\begin{matrix}\nearrow \mathrm{NHR}\\ \mathrm{S}\\ \searrow \mathrm{NH_2}\end{matrix}\right)_n \quad (1)$$

(where m and n are simple integers)



$$2\,\mathrm{AgBr} + \mathrm{C}\begin{matrix}\nearrow \mathrm{NHR}\\ \mathrm{S}\\ \searrow \mathrm{NH_2}\end{matrix} \longrightarrow \underset{\text{(Silver sulfide)}}{\mathrm{Ag_2S}} + \underset{\text{(Hydrobromic acid)}}{\mathrm{HBr}} + \underset{\text{(R-cyanamide)}}{\mathrm{C}\begin{matrix}\nearrow\!\!\!\nearrow\!\!\!\nearrow \mathrm{N}\\ \searrow \mathrm{NHR}\end{matrix}} \quad (2)$$

In Reaction 2 sufficient alkalinity is necessary to neutralize the hydrobromic acid and the cyanamide.

The present investigation is concerned with the formation and properties of the intermediate double compounds of silver halide and thio-

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[1] Read in part at the Regional Meeting of the American Chemical Society, January, 1926.

[2] Sheppard, *Phot. J.*, **65**, 380 (1925).