

mercuric sulfate in sulfuric acid solution is the cheapest and most efficient for the purpose. It was found that the chief difficulties in its use lie in the impossibility of separating acetaldehyde from the more concentrated acid solution and in the rapid reduction of the mercury compounds in the dilute acid which is now commercially employed. The reduction of mercury compounds by acetylene and aldehyde is greatest where the conditions are the most favorable for hydrolysis, and the catalytic mercury compounds being organic are probably more readily hydrolyzed than the inorganic salts of mercury. No reduction takes place in a suitable dry mixture where there is no hydrolysis but this method is too slow for commercial use. Attention was therefore turned to methods of utilizing acetaldehyde in rather concentrated solutions of sulfuric acid or the acid sulfates.

A new method for the synthesis of quinaldine and related products has been worked out. A new paraldehyde process has been developed which is capable of being used as a substitute for the method of acetaldehyde production now in use and which has the following advantages: (1) the ratio of aldehyde to reduced mercury is much higher; (2) the apparatus is simpler and the catalyst less bulky; (3) no distillation or separation process is necessary; (4) there are no by-products and no waste products; (5) there is no excess acetylene to be recovered.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE EXISTENCE AND REACTIONS OF POSITIVE HALOGEN ATTACHED TO CARBON IN AROMATIC COMPOUNDS.

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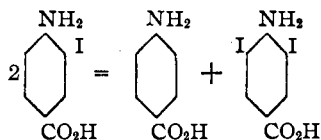
The halogen atoms in certain organic compounds have the property of being replaced by hydrogen, and appearing combined with the hydroxyl group as hypohalous acids, on hydrolysis. This behavior is frequently expressed by referring to such atoms as positive halogen atoms. Most, if not all, of the compounds in which halogen replaces the hydrogen of an hydroxyl, amino, or imino group, have this halogen in the positive form.

Without doubt, halogen attached to carbon is usually negative. Nevertheless, Howell and Noyes¹ have recently offered excellent evidence that iodine is positive in the compound C_2I_2 . Fry² had previously assigned a structure involving positive chlorine and bromine, to certain aromatic compounds, but primarily on the ground of the extreme difficulty of hydrolyzing such compounds. The negative test of non-reaction is necessarily an uncertain basis for the assignment of electronic structures.

¹ Howell and Noyes, *THIS JOURNAL*, **42**, 991 (1920).

² Fry, *ibid.*, **38**, 1327, 1333 (1916).

It is the object of the present paper to call attention to certain aromatic halogen compounds whose reactions are such as would be expected if the halogens were in the positive form. Typical of all these cases so far examined, is the reaction observed by Wheeler and Liddle,³ which takes place when 3-iodo-4-aminobenzoic acid is boiled for a "few minutes" with hydrochloric acid.



Obviously, iodine is here removed in such a manner as to be replaced by hydrogen; and yet the first stage of the reaction can scarcely involve a reduction, since the iodine thus removed is capable of resubstitution in the benzene ring. The latter reaction is only given by positive iodine. The formation of the di-iodo derivative is thus fairly good evidence of the intermediate formation of some product such as represented by the formulas HOI or CII, and confirms the positive nature of the original halogen.

Similar reactions have been observed by Limpricht⁴ on several amino-bromo-benzene sulfonic acids, and by Fittig⁵ on *p*-bromo-aniline. In both cases, however, temperatures of 150° or higher were necessary.

It has now been found that 3-iodo-4-aminotoluene, 4-iodo-aniline, 3-bromo-4-acetamino-toluene, and 3-iodo-4-hydroxybenzoic acid, when boiled with 10% hydrochloric acid, are hydrolyzed with a readiness decreasing in the order named, in such a way that the halogen is removed and replaced by hydrogen; and further that the halogen is in each case resubstituted in the benzene ring to give di-(or tri-) halogen substitution products. This is considered to be the best evidence yet offered for the existence of "positive" halogen attached to carbon in the benzene nucleus. It will be noticed that in all the cases mentioned the halogen in question is *ortho* or *para* to a strongly negative group.

It has also been found that alkali is incomparably less effective than acid in removing such "positive" halogens, as was to be anticipated. This is true even when sodium arsenite is added to the alkaline solution; but this is not particularly surprising, since in acid solution also, the product of hydrolysis, HOX, is effectively removed, either by resubstitution or by conversion to HX and HXO₃.

In the presence of stannous chloride, naturally, the same hydrolysis takes place; but here resubstitution is prevented, and the halogen is simply removed from the molecule. This reaction, involving as it does the

³ Wheeler and Liddle, *Am. Chem. J.*, **42**, 453-7 (1909).

⁴ Limpricht, *Ber.*, **10**, 1541 (1877).

⁵ Fittig, *Ann.*, **188**, 20, 24, 28 (1877).

use of a reducing agent, is valueless for the proof of electronic structure, but in the few cases investigated it runs so definitely parallel to the action of acid alone, that it may yet prove valuable as a preliminary test for positive halogens in aromatic compounds.

The present paper is purely preliminary, and further work is contemplated on all the questions raised, particularly as regards aromatic derivatives.

Experimental Part.

3-Iodo-4-aminotoluene.—The base was prepared according to Wheeler and Liddle.³ Boiled with 10% hydrochloric acid, the color of iodine vapor was visible almost at once and at the end of 10 minutes, di-iodo-toluidine could be isolated. An hour's boiling was sufficient (perhaps more than sufficient) to give complete conversion to toluidine and 3,5-di-iodo-toluidine, both of which were identified.

3-Bromo-4-acetamino-toluene.—On boiling for an hour with 10% hydrochloric acid, noticeable amounts of 3,5-dibromo-toluidine had sublimed into the condenser. The reaction is however much slower than that of the iodine compound, as even after boiling for 5 hours, only 6-7% of the theoretical amount of the dibromo-derivative had been formed, and on re-acetylation, most of the original material was recovered unaltered. Toluidine was identified only by the color reaction with sodium hypochlorite.

4-Iodo-aniline.—Boiling with 10% hydrochloric acid seemed to cause liberation of iodine readily (as judged by the color), but after an hour the transformation was far from complete. The solution contained aniline, and a mixture of iodoanilines.

3-Iodo-4-hydroxybenzoic Acid.—After an hour's boiling, an appreciable amount of the di-iodo acid had separated from the originally clear solution. At the end of 6 hours, the yield of 3,5-di-iodo-4-hydroxybenzoic acid was only 6.7% of that theoretically possible, and much unaltered product was isolated.

Action of Alkalies.—Mono-iodo-toluidine was recovered quantitatively unaltered after heating for 3 hours with an excess of alkaline sodium arsenite solution in dil. alcohol. The solution gave no test for iodide. Refluxing for 3 hours with 10% alcoholic potash was also without effect, and did not produce an odor of isocyanide. (Alcohol reacts much more readily than do aromatic amines, with alkaline hypo-iodites; when iodine is added to an alkaline alcoholic solution of aniline, for instance, the isocyanide odor appears promptly and unmistakably.)

Action of Mild Reducing Agents in Acid Solution; SnCl₂.—The various substances were boiled under reflux with 10% hydrochloric acid containing an excess (2 mols.) of stannous chloride.

4-Bromo-aniline, after one hour, scarcely gave a color test for aniline. After 5 hours the test was very distinct; but at the end of 8 hours most of the original bromo-aniline was recovered unchanged.

3-Iodo-4-aminotoluene, heated for one hour, gave practically pure *p*-toluidine, m. p. 42°, which liquified on mixing with the original base.

3,5-Di-iodo-4-aminotoluene, after 8 hours, had gone into solution almost completely. Steam distillation of the alkaline solution gave *p*-toluidine, recognized by its color reaction with hypochlorite, and by its acetyl derivative, m. p. 152°.

4-Iodo-aniline, heated for one hour, gave tests for aniline and for iodide. After 4 hours, the reaction was somewhere near complete, as steam distillation gave a liquid base, whose crude acetyl derivative, melted at 113°.

3-Bromo-4-acetamino-toluene gave qualitative indications of reaction after one hour. After 8 hours, debromination was slightly more than 75% complete.

3-Iodo-4-hydroxybenzoic acid, after one hour, showed little sign of reaction. After 5 hours, the solution contained considerable iodide, but the reaction was very incomplete.

Iodobenzene, treated as above and boiled for 5 hours, showed no evidence whatever of reaction. The same result was obtained when alcohol was added to render the substance more soluble. In both cases the test for iodides was negative.

Summary.

1. It has been shown that certain compounds containing iodine or bromine *ortho* or *para* to an amino or anhydroxyl group, when boiled with hydrochloric acid in part replace their halogen by hydrogen and in part give di- (or tri-) substitution products. Together, these reactions are considered to characterize these derivatives as containing positive halogen.

2. In similar compounds, iodine is more positive than bromine, and *ortho* than *para* compounds.

3. Compounds which, by the above standards, contain positive halogen, are abnormally readily dehalogenated by stannous chloride, in acid solution.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

NITROMALIC ACID.

By ARTHUR LACHMAN.

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The abnormal action of alkalis upon organic nitrates, whereby varying and at times considerable amounts of nitrous acid are produced, has been accounted for in two quite different manners. Nef¹ assumed what he called "methylene dissociation" to take place, and definitely ascribed this dissociation to the alkali. Klason and Carlson,² holding the view that nitric acid is a peroxide, looked upon the formation of nitrous acid as a direct hydrolysis of the nitric ester into nitrous acid and an organic peroxide. They also regarded the alkaline reagent as an essential factor.

The recently noted behavior of nitrotartaric acid,³ hydrolyzing normally and almost quantitatively as a true nitric ester in strongly acid media, and equally quantitatively as a nitrous ester in weaker acid, did not accord with either of the above interpretations. The suggestion was made that nitrotartaric acid goes over into a pseudo form, $\text{COOH}.\text{CH}(\text{ONO}_2).-\text{CH}(\text{ONO}_2).\text{COOH} \rightarrow \text{COOH}.\text{C}(\text{OH})(\text{ONO}).\text{C}(\text{OH})(\text{ONO}).\text{COOH}$. Nitrotartaric acid, being soluble both in water and organic solvents, seemed to offer a better opportunity for the investigation of what really happens in these intramolecular oxidations, than the esters studied by Nef and by Klason and Carlson. At the same time, Michael's view that

¹ Nef, *Ann.*, 309, 176 (1899).

² Klason and Carlson, *Ber.*, 40, 4183 (1907).

³ Lachman, *THIS JOURNAL*, 43, 577 (1921).