POSITIVE REACTIONS OF HALOGENS ATTACHED TO CARBON

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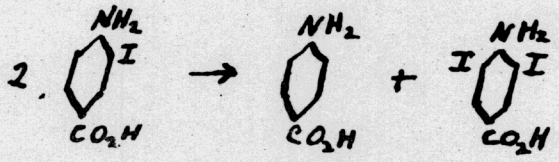
When the halogen atoms of an organic halogen compound can be removed by hydrolysis, they are usually replaced by hydroxyl, and appear in the solution as halide ions. This is often expressed by calling these halogens negative. In a number of cases, however, the hydrolysis of halogen compounds takes a different course, resulting in the replacement of halogen by hydrogen, and the appearance of the halogen liberated as HOX or an equivalent form. This behavior is well described by calling such halogens "positive". In neither case is there any intention of implying that, in the original compound, the halogen was necessarily either negative or positive to a degree sufficient to produce measurable ionization[1].

In most, if not in all, of the cases in which the halogen is attached to an amino or imino nitrogen, or to oxygen, the halogen is positive; this has long been recognized, and even made the basis of quantitative determinations of such compounds. Positive halogen attached to carbon has been recognized in certain aliphatic compounds[2].

In the aromatic series, a considerable number of the iodo and bromo-compounds show evidence of containing positive halogen, and it is in general possible to predict which will show this behavior[3]. A striking example is 3-iodo-4-aminobenzoic acid, which, as observed by Wheeler and Liddle[4], undergoes the following reaction when heated "for a few minutes" with hydrochloric acid.



[1] Cf., for the use of this idea of polar valence in organic compounds, Stieglitz, J. Am. Chem. Soc. *44*, 1293 (1922), and earlier papers; and Lewis, Valence and the Structure of atoms and Molecules (1923), particularly pp. 83 and 132.

[2] Nef, Ann. *308*, 329 (1899); Howell with Noyes, J. Am. Chem. Soc. *4*, 991 (1920); Macbeth and others, J. Chem. Soc. *119*, 1356 (1921); *121*, 892, 904, 1109, 1116, (1922).

[3] Nicolet, J. Am. Chem. Soc. *43*, 2081 (1921).

[4] Am. Chem. J. *42*, 453 (1909).

One notes that (a) an iodine has been removed, and replaced by hydrogen; and (b) the iodine thus removed retains the power of resubstituting in the bezene ring, a power which negative iodine does not have. A considerable amount of evidence collected since 1921 has confirmed the idea suggested at that time, that a somewhat similar behavior was to be expected on the part of any substance containing iodine in a position ortho- or para- to an amino- or to an hydroxyl-group, these two groups being among the most strongly negative known.

The rates at which iodine is removed under the conditions used (boiling with 10% hydrochloric acid, unless otherwise specified) vary greatly with the constitution of the substance examined. In many cases, too, resubstitution takes place less readily, and the iodine which then accumulates often oxidizes a portion of the substance. It is therefore often convenient, particularly when carrying out approximate quantitative measurements, to prevent both resubstitution and oxidation by the addition of a mild reducing agent. For this purpose stannous chloride has been used, and it may be emphasized that this has never as yet been found to act on any halogen which could not also be removed by acid alone.

From the relative stabilities of their inorganic compounds with oxygen and with hydrogen, it is obvious that iodine should show positive reactions more readily than bromine, and this in turn more readily than chlorine. This is found to be the case. When bromine occupies positions such as those specified for positive iodine, it is also removable under the same conditions, though some eight or ten times more slowly. The evidence for a similar reaction of chlorine, in the aromatic series, is indirect, though probably sufficiently definite, and for a single case only, namely, 2, 4, 6-triaminochlorobenzene.

More recent work has concerned itself with substances containing two amina- or hydroxyl-groups, and halogen ortho- or para- to at least one of them. Such halogens (bromine or iodine) are removed much more rapidly when the two negative groups are meta with respect to each other, and more slowly when these are otherwise

located. For instance, iodi-p-phenylenediamine lost iodine less rapidly than o-iodoaniline, while 2, 4-diamino-iodobenzene reacted more rapidly than either, as did also the corresponding iodoresorcinol.

It might be well to emphasize the fact that halogens not in favored positions show no sign of reacting under any of the conditions used. This is shown, for instance, by the fact that 2, 4, 5, 6-tetrabromo-m-dinitrobenzene, warmed with a stannous chloride and acid, loses three of its four bromines quantitatively, giving 1, 3-diamino-5-bromobenzene. One might choose an even more decisive case; 2-iodi-3,5-dibromo-4-aminotoluene, after refluxing for 8-10 hours with the same reagents, loses all of its bromine, without the formation of a detectible amount of iodide ion. The product, 2-iodo-4-aminotoluene, should not lose iodine if the considerations already advanced are correct.