dry and lighter in color. It was extracted once with ether and warmed with a very small amount of decolorizing charcoal, when practically the entire quantity was recovered as pure ω-bromomethyl-furfuraldehyde; m. p. 60°.

Fructose

This ketose showed much more reactivity toward hydrobromic acid at room temperature than the other materials, the chloroform solution becoming quite dark. In view of this initial reactivity it is quite possible that the conditions employed may have been too drastic, as shown by the somewhat lower yield obtained when compared with that found by Fenton and Gostling. The crude crystals weighed 1.2 g. and were very dark, but on purification yielded bromomethyl-furfuraldehyde; m. p. 60°.

Summary

Experimental evidence is submitted showing that the formation of ω-bromomethyl-furfuraldehyde by the action of dry hydrogen bromide on carbohydrates and polysaccharides is not alone characteristic of ketoses and ketose derivatives, but also takes place with aldoses and related compounds. Its formation from cellulose is thus no criterion as to the presence of ketone groupings in this product.

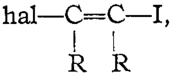
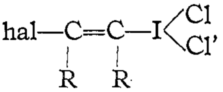
New Haven, Connecticut

[Contribution from the Chemical Laboratory of the Rice Institute]

THE SPONTANEOUS DECOMPOSITION OF UNSATURATED ALIPHATIC IODOCHLORIDES[1]

By Lloyd B. Howell

Received October 2, 1922

Some years ago it was shown by P. Thiele[2] that when an unsaturated iodine compound of the type,  $\text{hal—}\underset{R}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}\text{—I}$, is chlorinated in a solvent the chlorine does not add to the double union but to the iodine to give an unsaturated iodochloride,  $\text{hal—}\underset{R}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}\text{—I}\langle\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$, that is, the double bond is so highly "inactivated" by the adjacent halogen atoms that chlorine adds more readily to the iodine than to the unsaturated carbon. Thiele showed that these aliphatic iodochlorides are similar in all respects to the long-known aryl iodochlorides, although not nearly so stable. A second method of preparation of this type of compound by the addition of iodine

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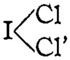
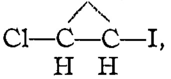
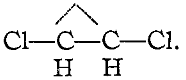
[1] A digest of the essentials of this paper was presented before the Organic Division of The American Chemical Society at the meeting in Pittsburgh, Sept. 6, 1922.

[2] Thiele, *Ann.*, **369**, 135 (1909).

trichloride to acetylene hydrocarbons was indicated in work with W. A. Noyes,[3] and a preliminary study of their decomposition and the nature of the products formed was undertaken.

This paper deals with the decomposition products of the two compounds, iodochloride-2-chloro-ethylene and iodochloride-1,2-dichloro-2-iodo-ethylene. The former was prepared by the action of iodine trichloride in dilute hydrochloric acid upon acetylene:[3] $\mathrm{H{-}C{\equiv}C{-}H + ICl_3 \longrightarrow Cl{-}CH{=}CH.ICl_2}$. The latter compound was made by the direct chlorination of di-iodo-acetylene in an inactive solvent (best ethyl chloride or carbon tetrachloride) in a freezing mixture:[4] $\mathrm{I{-}C{\equiv}C{-}I + 2\ Cl_2 \longrightarrow I{-}CCl{=}CCl.ICl_2}$. This compound may also be prepared by the chlorination of dichloro-diiodo-ethylene under the same conditions.

In the preliminary reports upon these compounds it was shown that they are very unstable and decompose spontaneously and violently in a relatively short time to give liquid products. The change is accompanied by no increase in gaseous volume. This fact, meaning that no chlorine is evolved during the highly exothermic decomposition, seems rather remarkable since phenyl-iodochloride and its homologs break down to give the original aryl iodide with loss of chlorine.[5] The supposition that would first occur to us is that the 2 chlorine atoms of the iodochloride group,  $\mathrm{I}{<}\genfrac{}{}{0pt}{}{\mathrm{Cl}}{\mathrm{Cl}}$, would rearrange during the "decomposition" and add to the double linkage to give the corresponding saturated polychloro-iodo compound. However, the investigation of the products of the decomposition of the 2 iodochlorides dealt with indicates that this alone does not occur. When iodochloride-2-chloro-ethylene decomposes, the compounds formed are iodine monochloride, trichloro-iodo-ethane,[6] *sym*-tetrachloro-ethane, and a dichloro-di-iodo-ethane. Of these, the first 2 are formed in much larger amounts than are the last 2. No simple reaction can be written to explain the formation of these products, but a very probable explanation may be stated as follows.

Iodochloride-2-chloro-ethylene in splitting off 2 chlorine atoms would leave the residue,  $\mathrm{Cl{-}}\overset{\wedge}{\mathrm{\underset{H}{C}{-}\underset{H}{C}}}\mathrm{{-}I}$, and in splitting off a mole of iodine monochloride would leave the residue,  $\mathrm{Cl{-}}\overset{\wedge}{\mathrm{\underset{H}{C}{-}\underset{H}{C}}}\mathrm{{-}Cl}$. These 2 unsaturated residues may then be converted to saturated halogen compounds by the four possible reactions.

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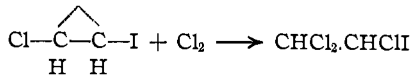
[3] Noyes, THIS JOURNAL, **42,** 991 (1920).

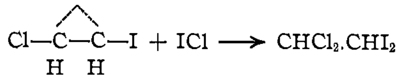
[4] *Ibid.*, **42,** 1002 (1920).

[5] *J. prakt. Chem.*, [2] **33,** 154–64.

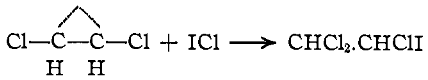
[6] Ref. 3, p. 1007.



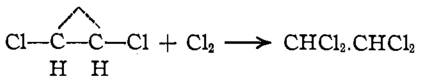
(1)



(2)



(3)

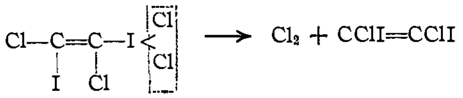


(4)

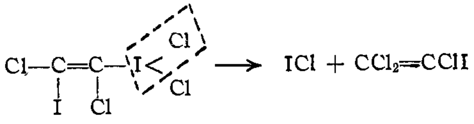
Since the first and third reactions give rise to the same product, 1,2,2-trichloro-1-iodo-ethane would be expected to form in larger amounts than either acetylene tetrachloride or the dichloro-di-iodo-ethane. As stated, this is in agreement with the experimental facts. The yields of trichloro-iodo-ethane are approximately 40%, whereas but 15–20% of acetylene tetrachloride and less than 10% of the dichloro-di-iodo-ethane are formed.

The structures of the new chloro-iodo derivatives of ethane are doubtless as represented above in the reactions given, although in the case of di-chloro-di-iodo-ethane, the 1-2-dichloro-1-2-di-iodo compound might be formed if we consider the feebly positive nature of the iodine atoms involved. Neither of these isomers has ever been reported so that no comparison of properties with those of known compounds is possible.

The decomposition of iodochloride-1-2-dichloro-2-iodo-ethylene appears to follow a different course. Aside from hexachloro-ethane it yields no saturated compounds. The products formed are iodine and iodine monochloride and the organic compounds, 1,2,dichloro-1,2-di-iodo-ethylene, 1-chloro-1,2,2-tri-iodo-ethylene, and a constant-boiling mixture of approximately 80% of trichloro-iodo-ethylene and 20% of hexachloro-ethane. As already reported[7] iodine monochloride and dichloro-di-iodo-ethylene form in by far the greatest amounts. The latter is the expected product of the reaction.



By the loss of iodine monochloride in a similar manner, trichloro-iodo-ethylene should be formed.



If we are to account for the formation of chloro-tri-iodo-ethylene and

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[7] Ref. 3, p. 1005.

hexachloro-ethane we must postulate the replacement of chlorine by iodine in one case and of iodine by chlorine in the other. The absence of any saturated mixed perhalogen derivatives such as $C_2Cl_5I_7$, $C_2Cl_4I_2$, $C_2Cl_3I_3$ etc., among the rearrangement products must be due to the extreme inactivity of the double bond in the two primary products, $CClI{=}CClI$ and $CCl_2{=}CClI$.

Of the above chloro-iodo substitution products of ethylene only the chloro-tri-iodo-ethylene has been otherwise prepared. K. A. Hofmann and H. Kirmreuther[8] reported such a compound formed from the organomercuric complex, $Hg(C{\equiv}C{-}Cl)_2$, upon treatment with iodine in ether. The chloro-tri-iodo-ethylene formed from iodochloride-1,2-dichloro-2-iodo-ethylene answers physically the same description as the one which they obtained, but it gives no such explosive residue when heated above its melting point as Hofmann claimed. The possibility of contamination of such products by explosive unsaturated mercury compounds renders it doubtful whether explosive properties are to be assigned to chloro-tri-iodo-ethylene.

Throughout the progress of this work the writer has been impressed by our lack of better methods for the analysis of organic compounds, particularly iodides, of high and mixed halogen content and of such stable nature as the perhalogen-ethenes. A number of the more recent methods described in the literature involving decomposition with sodium in alcohol, or by potassium permanganate and nitric acid under a reflux condenser,[9] and by heating with chromic acid and silver nitrate[10] have been found inadequate for compounds of the type described. In a previous article[3] reference was also made to the inapplicability of methods employing decomposition by sodium peroxide or by lime. The only method of use at all was the time-honored Carius determination with its attendant low values for iodine and its limitations as to decomposition temperatures. As yet no reliable and ready method for determining mixed halogens in organic compounds of very high halogen content is at our disposal.

Experimental Part

Decomposition of the Iodochlorides.—The methods of preparation and decomposition were the same as those previously employed[3] except that in cases where the quantity decomposed was relatively large (20 to 40 g.), the mixture was gently stirred. After the decomposition the iodine monochloride (upper layer) was separated and the organic products washed in order with conc. hydrochloric acid, water, saturated sodium carbonate solution, 10% sodium thiosulfate solution, and water again.

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[8] Hofmann and Kirmreuther, *Ber.*, **42**, 4235 (1909); *C. A.*, **4**, 449 (1910).

[9] *Chem. News*, **103**, 61 (1911).

[10] *Chem.-Ztg.*, **27**, 555 (1903); **35**, 450 (1911).

The products were dried with anhydrous sodium sulfate and subjected to distillation in a vacuum.

Organic Products from the Decomposition of Iodochloride-2-chloro-ethylene.—Approximately 30 g. of purified products freed from iodine and iodine monochloride was fractionated thrice at 30–32 mm., a set of small Claisen flasks, 25 cc., 5 cc. and 3 cc., being employed in the order given. Three main fractions were obtained as follows:

	B. p. ° C.	Mm.	G.
I	52–53	31	2.65 (chiefly 55.5–56.5°)
II	96–105	31–32	13.17 (chiefly 101–102°)
III	145–147	31–32	5.95

The combined weight of all intermediate fractions was 4.1 g. In different preparations the proportions of these fractions varied but little from those given.

Fraction II contains the chief product 1,2,2-trichloro-2-iodo-ethane as previously shown.[3] It is a colorless oil of pleasant odor resembling that of the lower alkylene halides. It darkens slightly on standing, due to liberation of iodine, and decomposes above 130° at atmospheric pressure; d^{22}_{22}, 2.266; $n^{26°}_{D}$, 1.5884.

Fraction I was identified as acetylene tetrachloride by its boiling point, 147°, d^{25}_{25} 1.61, and analysis.

Analyses. Subs., 0.2189: AgCl, 0.7428. Calc. for $C_2H_2Cl_4$: Cl, 84.52. Found: 84.0.

Fraction III is dichloro-di-iodo-ethane. It may be decolorized by the addition of a globule of mercury, but becomes deeply colored by iodine due to decomposition, even on standing in the dark. It is a heavy oil of pleasant but slightly lachrymating odor; d^{25}_{25}, 2.861; b. p. 146–8° (28 mm.).

Analyses. Subs., 0.2205: AgCl + AgI, 0.4746; loss in stream of chlorine, 0.1145. Calc. for $C_2H_2Cl_2I_2$: AgCl + AgI, 0.4754; Cl, 20.2; I, 72.4. Found: Cl, 20.2; I, 72.2.

Organic Products from the Decomposition of Iodochloride-1,2-dichloro-2-iodo-ethylene.—The mixture of products after removal of iodine and iodine monochloride was a clear, pale yellow, fragrant oil. The fractionations in a vacuum were carried out as before but at lower pressures. Approximately 20 g. gave, after the third fractionation, 3 main fractions.

	B. p. ° C.	Mm.	G.
I	60–65	10	6.50
II	109–111	12	10.00 (chiefly 110.2–110.4°)
III	Residue above 140°	10–11	1.42

The intermediate fractions were of negligible amount.

Fraction II is 1,2-dichloro-1,2-di-iodo-ethylene as previously shown.[11] It is a fragrant, pale yellow and highly refractive oil comparable to methylene iodide in density; b. p., 243.4°; m. p., 2.5–3.0°; d^{30}_{30}, 2.934.

Fraction I remains colorless in the dark and after a few hours (or in a few minutes if suddenly cooled) shows a separation of large colorless plates which rise to the surface of the liquid. When these were removed and recrystallized thrice from a 2 to 1 mixture of ether and alcohol they melted sharply at 187° (thermometer stem immersed); examined qualitatively they showed only chlorine present. A mixed melting point determination with pure hexachloro-ethane gave the value 186–187°. It was at once suspected that a mixture of hexachloro-ethane and some iodine compound must be present. Accordingly, Fraction I was redistilled several times at different pressures (2–3 mm., 10–12 mm., 24 mm. and 30 mm.), and the index of refraction taken and analyses made. Although hexachloro-ethane often sublimed alone before any of the distillate,

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[11] Ref. 3, p. 1005.

in no case could a distillate be obtained free from hexachloro-ethane nor of different refractive index or analysis from that given below. Unlike most compounds giving constant-boiling mixtures, hexachloro-ethane and trichloro-iodo-ethylene must show a close correspondence in boiling points over the entire range of pressures, since determinations upon the first distillate at atmospheric pressure gave the boiling point 182.2° (corr.) which lies very close to that of hexachloro-ethane.

For the identification of trichloro-iodo-ethylene in Fraction I, the material was redistilled and, 3 samples boiling at 66–68° (10–12 mm.), 66–68° (10–12 mm.) and 40–41° (2–3 mm.), respectively, were taken for analysis.

Analyses. Subs., 0.2793, 0.3088, 0.2717: AgCl + AgI, 0.7812, 0.8571, 0.7518; loss in stream of chlorine, 0.0786, 0.0898, 0.0775. Calc. for 20% C_2Cl_6 in 80% C_2Cl_3I: Cl, 51.0; I, 39.5. Found: Cl, 51.3, 51.1, 50.3; I, 39.4, 40.3, 39.5.

From these results it seems probable that very nearly 80% of the mixture is the unknown compound C_2Cl_3I. Molecular-weight determinations gave variable results due to dissociation and freeing of iodine in the solvent used. The specific gravity (d^{30}_{30} 2.127) and the index of refraction (n^{25}_D 1.5805) were of no value in determining the composition, as neither constant for trichloro-iodo-ethylene is known.

The residue III (boiling above 140° at 10 mm.) solidified immediately upon cooling to a pale yellow, volatile, crystalline mass. This, dissolved in ether and recovered, dried on a clay plate, washed with cold alcohol and recrystallized thrice from hot alcohol gave large glittering greenish-yellow plates. These melted sharply at 77–78°, but decomposed unexplosively when heated to higher temperatures.[8] The odor of the compound resembles both that of di-iodo-acetylene and hexachloro-ethane. It can be kept for months unchanged in the dark but when exposed to light turns faintly pink and shows free iodine at once when exposed to direct sunlight.

Analyses. Subs., 0.1763: AgCl + AgI, 0.3392; loss in chlorine, 0.1099. Calc. for C_2ClI_3: Cl, 8.05; I, 86.49. Found: Cl, 7.99; I, 86.54.

Summary

1. The study of the decomposition products of iodochloride-2-chloro-ethylene and iodochloride-1,2-dichloro-2-iodo-ethylene indicates that the changes consist in several rearrangements involving (a) the splitting off of chlorine and of iodine monochloride from the iodochloride group, (b) the addition of 1 mole of iodine monochloride or of chlorine to the unsaturated residues resulting from this dissociation, and (c) the replacement of iodine by chlorine or *vice versa* in the products from either a or b.

2. If the carbon atoms of the double union in an unsaturated aliphatic α-iodochloride hold hydrogen atoms the products of its decomposition are saturated (ethane) halogen derivatives.

3. If the carbon atoms of the double union in an unsaturated aliphatic α-iodochloride hold only halogen atoms the decomposition leads to unsaturated products.

4. Certain mixed halogen derivatives of ethane and ethylene have been prepared and described: 1,2,2-trichloro-1-iodo-ethane, 1,2-dichloro-1,2-di-iodo-ethane, 1,2-dichloro-1,2-di-iodo-ethylene and 1-chloro-1,2,2-tri-iodo-ethylene.

HOUSTON, TEXAS