at low concentrations. The general conclusions of the paper are not affected.

The most general expression for the first differential coefficient is

$$\frac{d\Lambda}{d(C\Lambda)} = \frac{\Lambda^2}{\Lambda_0{}^2K'}\left[\frac{C\Lambda}{K'}\,\frac{dK'}{d(C\Lambda)} - 1\right].$$

At low concentrations the $\Lambda, C\Lambda$-curve will cut the Λ-axis at an angle whose tangent is equal to $-\frac{1}{K'}$. At higher concentrations the tangent to the curve will decrease because of the increase in the value of K', as well as the increase in the value of the term involving $\frac{dK'}{d(C\Lambda)}$. The curve will, therefore, be convex toward the C-axis in dilute solutions. It is not possible to follow up the form of this curve readily at higher concentrations without introducing the equation for the conductance function. If the function XIV is introduced, we have the equation

$$\frac{d\Lambda}{d(C\Lambda)} = \frac{\Lambda^2}{\Lambda_0{}^2K'}\left[m - 1 - \frac{mK}{K'}\right].$$

So long as $m < 1$. $\frac{d\Lambda}{d(C\Lambda)}$ will always have a negative value which decreases with increasing concentration. When $m > 1$, $\frac{d\Lambda}{d(C\Lambda)}$ will pass through zero and thereafter become positive at higher concentrations, which corresponds with the form of conductance curves such as we have them in solvents of low dielectric constant. C. A. Kraus.

Worcester, Mass.

[Contribution from the Chemical Laboratory of the University of Illinois.]

POSITIVE HALOGEN IN ORGANIC COMPOUNDS. IODINE IN DI-IODOACETYLENE AND CHLORO-IODO-ETHYLENE.[1]

By Lloyd B. Howell, with William A. Noyes.

Received February 3, 1920.

For a number of years chemists have recognized the fact that certain organic halogen compounds, *e. g.*, those in which a halogen has replaced a hydrogen atom of any of the groups: —NH_2, >NH, or —OH, exhibit extraordinary activity. Unlike the halogen of the ordinary types of alkyl and acyl halide linkage, which are reduced with more or less difficulty, the halogen of the above-mentioned types shows actual oxidizing power in the presence of such reducing agents as aqueous solutions of ferrous

---

[1] An abstract of a thesis submitted by Mr. Howell in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

salts or metallic iodides. In addition to this exceptional property such compounds as a rule are unstable when isolated and many decompose with explosive violence. These peculiar properties have so far not been satisfactorily explained.

Inorganic halogen compounds which are similarly unstable and of oxidizing properties are the halogenated ammonias, nitrogen trichloride and nitrogen iodide. The work of Chattaway,[1] Orton, W. A. Noyes,[2] and others with these compounds has led to a satisfactory explanation of their behavior by the assumption that the halogen is combined as a positive atom and not negatively as in ordinary chlorides, bromides and iodides. Certainly no more reasonable explanation has so far been advanced.

It was our purpose in this investigation to determine whether or not a similar explanation might be made for the behavior of certain halogen derivatives of acetylene. In addition to the types of linkage mentioned above we have the $\equiv C — X$ linkage which gives relative instability to the molecule and, it will be shown, possesses oxidizing properties. Just as for many cases in the groups $—NH_2$, $>NH$, and $—OH$ the hydrogen atom may be replaced by either metals or halogen, so in acetylene or the monosubstituted acetylenes we have hydrogen replaceable by either metals or halogen. And since both the original hydrogen atom of acetylene and the metal of the acetylides or carbides are undoubtedly positive, it would seem a reasonable inference that the chlorine of chloro-acetylene and dichloro-acetylene, the bromine of bromo-acetylene and dibromo-acetylene, and the iodine of iodo-acetylene and di-iodo-acetylene are likewise of a positive nature.

Since it is relatively the most stable of the 6 known halogen substituted acetylenes and the easiest of preparation, di-iodo-acetylene has been investigated first for those properties which might indicate the nature of the $\equiv$C-hal. linkage. Certain of the properties of this compound attributed by Nef[3] to the existence of bivalent carbon in the molecule are better explained by the assumption that the iodine atoms are positive in nature and the carbon quadrivalent.

Di-iodo-acetylene when warmed with a neutral or faintly acid solution of potassium iodide or simply allowed to remain suspended in such a solution for a short time liberates free iodine and acetylene is regenerated. The rate of the reaction is very slow unless an excess of potassium iodide is present and a trace of acid added to neutralize the alkali formed in the reaction

$$I — C \equiv C — I + 2HOH + 2KI \rightleftarrows H — C \equiv C — H + 2KOH + 2I_2.$$

If the iodine be taken up by titration with sodium thiosulfate it is es-

---

[1] *J. Chem. Soc.*, **70**, 1572 (1896); *Am. Chem. J.*, **23**, 363 (1900); **24**, 139 (1900).

[2] THIS JOURNAL, **22**, 460 (1901); **35**, 767 (1913); **39**, 905 (1917).

[3] *Ann.*, **298**, 343 (1897).

pecially noticeable that the end-point of the titration is very indistinct, more iodine being liberated almost instantly as the equilibrium is displaced. It is difficult to adopt any explanation for this reaction other than that both iodine atoms of di-iodo-acetylene are strongly electropositive and capable of taking up 2 electrons each. That dibromo-acetylene and dichloro-acetylene recently prepared and described by Böeseken and Carriere[1] would show the same reaction even more markedly would be predicted from their relatively more unstable character. Experiments to test out these predictions are now in progress.

As a further indication of the positive character of the iodine atoms of di-iodo-acetylene, attempts have been made, first, to prepare it by means of iodine monochloride and, second, to prepare nitrogen iodide from di-iodo-acetylene by the action of ammonia. Since iodine monochloride and nitrogen iodide are both compounds containing positive iodine these reactions would furnish considerable evidence in the matter.

Iodine monochloride, however, as is well known, reacts by addition upon acetylene itself and this has been found to occur both in and out of solvents. The product always obtained is 1-chloro-2-iodo-ethylene as first shown by Plimpton.[2] The action of iodine monochloride upon metallo derivatives of acetylene however yields better results. Iodine monochloride with calcium carbide and with copper acetylide forms di-iodo-acetylene.

$$2ICl + CaC_2 \longrightarrow CI \equiv CI + CaCl_2$$

$$2ICl + Cu_2C_2 \longrightarrow CI \equiv CI + Cu_2Cl_2.$$

The reduction of di-iodo-acetylene by ammonia has not been accomplished. The reaction has been tried out in aqueous and in ether solution and in the absence of any solvent, employing liquid ammonia itself (in which di-iodo-acetylene is readily soluble). The conditions of temperature and of pressure were likewise varied but in no case could nitrogen iodide be isolated as a product, although the formation of traces of acetylene could be shown. This result might be predicted, however, since it has recently been shown by Datta and Prosad[3] that nitrogen iodide is an excellent iodinating agent for acetylene and gives practically quantitative yields of tetra-iodo-ethylene. This reaction would thus seem to be only slightly reversible.

In his well-known article on "Die Chemie des Methylens," Nef[4] has drawn the conclusion that di-iodo-acetylene and iodo-acetylene and the

---

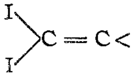
[1] *Verslag Akad. Wetenschappen, Amsterdam,* **22,** 1186–88 (1914); *C. A.* **8,** 3296 (1914).

[2] *J. Chem. Soc.,* **41,** 392 (1882)

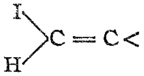
[3] THIS JOURNAL, **39,** 451 (191).

[4] *Loc. cit.*

other halogen substituted acetylenes must possess the acetylidene structures:

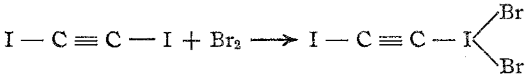


Di-iodo-acetylene.

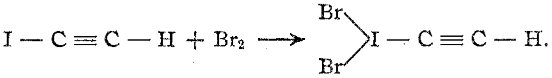


Iodo-acetylene.

He based this conclusion in part upon the ease with which these compounds add bromine and hydrobromic acid and with which the products decompose again to give the original iodo- or di-iodo-acetylene. The possibility that these additions might be on the iodine seems not to have occurred to Professor Nef. The reactions with halogen in molecular proportions could be expressed without assuming bivalent carbon by the equations

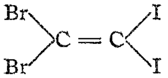


$$I - C \equiv C - I + Br_2 \longrightarrow I - C \equiv C - I\left\langle\begin{matrix}Br\\Br\end{matrix}\right.$$

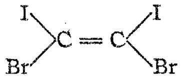


$$\text{and} \quad I - C \equiv C - H + Br_2 \longrightarrow \left.\begin{matrix}Br\\Br\end{matrix}\right\rangle I - C \equiv C - H.$$

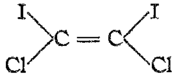
That is, the positive nature of the halogen atom as shown by its tendency to become trivalent might account for the formation of iodobromides as well as for the production of an iodochloride. In fact it is not entirely improbable that the compound $C_2I_2Br_2$, assumed by Professor Nef to be unsymmetrical,



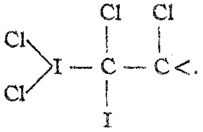
is in fact the compound,



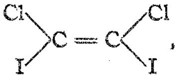
formed as a secondary or rearrangement product of the first reaction given above. The explanation for the formation of



as a secondary or rearrangement product in the chlorination of di-iodo-acetylene as given below is an analogous case. The poisonous character, disagreeable odor and irritating effects of the vapor of di-iodo-acetylene attributed by Nef to the presence of dyad carbon may possibly be due to positive or unsaturated iodine. The markedly poisonous character of the compounds nitrogen trichloride and nitrogen tri-iodide ammonia is well known. Moreover if we were to admit the compound C_2I_2 to be di-iodo-acetylidene, the structure of the iodochloride (described below) formed by the action of chlorine must be

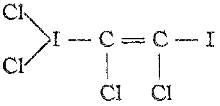


This is highly improbable since we must assume *5 halogen atoms connected to one carbon atom adjacent to a bivalent and, therefore, very reactive carbon.* Moreover the decomposition of this iodochloride to give 1,2-dichloro-1,2-di-iodo-ethylene,



would be very difficult to explain.

Although it cannot yet be considered as established that the more strongly electropositive an iodine atom is, the more readily it adds chlorine to give an iodochloride, yet some evidence as to this point might be found in the fact that di-iodo-acetylene reacts with chlorine giving iodochloride-1-chloro-2,2-chloro-iodo-ethylene, Biltz[1] has reported that the product of the reaction of chlorine upon di-iodo-acetylene is hexachloro-ethane. It has been found, however, that the primary product of this reaction is the iodochloride:



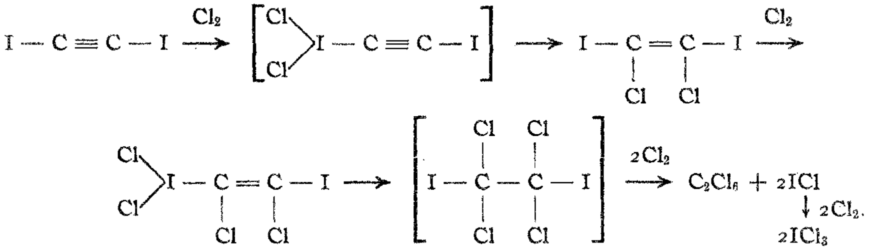
This compound is formed even at ordinary temperatures in any of the solvents; ethyl chloride, ethyl bromide, chloroform or petroleum ether, and, although with much difficulty, can be isolated and analyzed. It is relatively quite unstable and decomposes in a short time with the evolution of heat. The conclusion of Biltz[2] that hexachloro-ethane is the product of the action of chlorine upon di-iodo-acetylene was based upon his observation of the final result of the reaction. Both iodine atoms are ultimately replaced and the bonds between the carbon atoms saturated by chlorine if the latter be allowed to react indefinitely. Hexachloro-ethane, however, is formed not by direct replacement of the iodine but by an addition to iodine first and probably the subsequent splitting out of iodine monochloride. In repeating Biltz's experiment, passing chlorine into a chloroform solution of di-iodo-acetylene (at room temperature) the iodochloride was observed to form instantly and in quantity as long, yellow needles, but in a short while these disappeared entirely and the solution became a deep brown color due to iodine monochloride. On continuing the current of chlorine deposition of crystals of iodine trichlo-

---

[1] *Ber.*, 30, 1202 (1897).

[2] *Loc. cit.*

ride occurred and the filtrate when evaporated gave an excellent yield of hexachloro-ethane. The course of the chlorination is probably



$$I-C\equiv C-I \xrightarrow{Cl_2} \left[\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!I-C\equiv C-I\right] \longrightarrow I-\underset{Cl}{\underset{|}{C}}=\underset{Cl}{\underset{|}{C}}-I \xrightarrow{Cl_2}$$

$$\begin{matrix}Cl\\Cl\end{matrix}\!\!>\!I-\underset{Cl}{\underset{|}{C}}=\underset{Cl}{\underset{|}{C}}-I \longrightarrow \left[I-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-I\right] \xrightarrow{2Cl_2} C_2Cl_6 + 2ICl \xrightarrow{2Cl_2} 2ICl_3$$

However, it was not found possible to isolate the first iodochloride represented in these reactions nor to obtain the symmetrical tetrachloro-di-iodo-ethane.

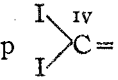
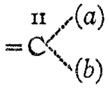
The very unstable character of iodochloride-1-chloro-2,2-chloro-iodo-ethylene makes it impossible to keep it, even in the dark and at temperatures obtainable with ice and salt, for more than a few minutes. Its analysis, necessarily difficult in itself, is also further complicated by the possibility of hexachloro-ethane and iodine trichloride being present. Satisfactory results are obtained when the compound is prepared from an excess of di-iodo-acetylene in ethyl chloride at —15° to —10° in the dark, freed from unchanged di-iodo-acetylene by washing with ethyl chloride and titrated in the presence of carbon tetrachloride by the iodometric method.[1]

This gives the percentage of chlorine which combines with the iodine. The total percentage of chlorine taken up may be determined on small weighed samples in a glass-stoppered side-neck test-tube. Analysis of the compound by the usual method of Carius is not satisfactory, while the method of decomposition with lime or with sodium peroxide fails to convert all of the iodine to iodide. The latter result, also the fact that iodochloride-1-chloro-2,2-chloro-iodo-ethylene, treated with sodium in alcohol yields di-iodo-acetylene again and is not completely decomposed, indicates that the iodine in the compound is abnormally unreactive toward those reagents which are generally efficient in breaking the linkage between carbon and halogen. Such "inactivity" may denote or be due to the positive character of the iodine. In the usual case of carbon halogen linkages iodine is more easily removed than chlorine (or bromine). In iodochloride-1-chloro-2,2-chloro-iodo-ethylene and in 1,2-dichloro-1,2-di-iodo-ethylene the reverse is true. Nef[2] noted this same result in the case of practically all of the compounds which he derived by addition from di-iodoacetylene. Sodium alcoholate, sodium in alcohol, and al-

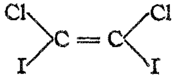
---

[1] *J. prakt. Chem.*, [2] 33, 158 (1886).

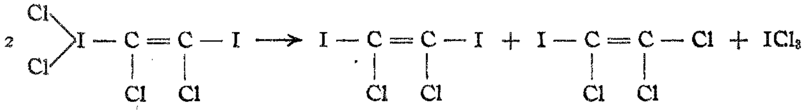
[2] *Loc. cit.*

coholic potash each reacted to give di-iodo-acetylene in the case of all such compounds. Nef naturally attributed it to the comparative stability of the group  as compared with  . It seems more reasonable to regard it as being due to the inherent positive (or basic) nature of the 2 iodine atoms. A very similar case in inorganic compounds is azoic iodide, N_3I. Abegg[1] is authority for the statement that the failure of this iodide to react with N_3Ag is the result of the positive nature of the iodine.

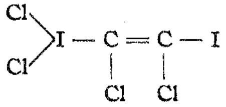
The chief product of the decomposition of iodochloride-1-chloro-2,2-chloro-iodo-ethylene is 1,2-dichloro-1,2-di-iodo-ethylene:



not previously prepared nor reported in the literature. Much iodine monochloride is liberated and traces of a second compound, an iodo-trichloro-ethylene appear to be formed. The exact nature of the decomposition is being studied further. The reaction can be shown to take place without any evolution of chlorine and indications are that its course is in part probably



1,2-dichloro-1,2-di-iodo-ethylene when treated with chlorine in ethyl chloride or petroleum ether gives also the same iodochloride,



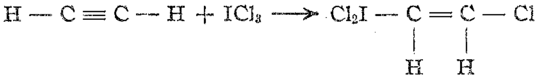
as was obtained from di-iodo-acetylene. It is always noted that decomposition of the iodochloride to give these products occurs only when the substance is either enclosed in a tube or left in a mass. Strangely enough, if some of the freshly prepared compound be spread out at once in a thin layer on a well-cooled porous plate, no darkening occurs and no liquid products form. The bright yellow color of the mass gradually fades and after about 1½ to 2 hours a nearly white solid remains. This no longer smells of chlorine but of di-iodo-acetylene and does not liberate iodine from potassium iodide. Recrystallization and qualitative analysis show only iodine compounds present, and the m. p. is that of a mixture (72–180°). The nature of this decomposition was not studied; it must be complex,

---

[1] "Handbuch der anorg. Chemie," Abt. 3, Bd. 3, S. 213.

involving that of di-iodo-acetylene into tetra-iodo-ethylene noted by V. Meyer.[1]

While investigating the action of iodine monochloride in hydrochloric acid as a solvent upon acetylene, occasion was had to employ crude iodine monochloride containing some iodine trichloride. This, in hydrochloric acid (1 : 2) solution was found to yield a small crop of fine, yellow needles of what at first seemed a stable substance. When these were removed and purification attempted they were found to decompose with the formation of liquid products deeply colored by iodine monochloride. Pure iodine trichloride was then prepared in hydrochloric acid solution and its action on acetylene tried out. The result was a very good yield of the compound, which in this case was purer and stable enough to permit its being washed, dried and analyzed. Titration by the iodometric method showed it to be an iodochloride and analysis by combustion and the method of Carius established the compound as iodochloride-2-chloro-ethylene, $Cl_2I-CH=CHCl$. As prepared by this reaction

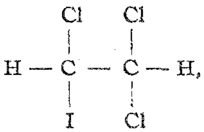


$$H-C\equiv C-H + ICl_3 \longrightarrow Cl_2I-\underset{\underset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-Cl$$

iodochloride-chloro-ethylene is much purer and far more stable than when prepared by the method of Thiele and Haakh[2] from chlorine and 1-chloro-2-iodo-ethylene.

It is of theoretical interest to note here that since iodine in iodine trichloride is positive and the group $-ICl_2$ which adds to one carbon atom in acetylene is the positive group, it is very probable that the iodine atom of 1-chloro-2-iodo-ethylene is also positive. Otherwise chlorination of chloro-iodo-ethylene would, perhaps, give a different product.

It is stated by Thiele and Haakh[3] that this iodochloride decomposes giving chlorine and 1,2-chloro-iodo-ethylene. The observation has been made, however, that here too, as in the case of iodochloride-1-chloro-2,2-chloro-iodo-ethylene, the decomposition occurs without any increase in volume and hence with rearrangement. A number of liquid halogen compounds appear to be formed and a large amount of iodine monochloride and free iodine liberated. However, the chief product of the decomposition has been shown to be 1,2,2-trichloro-1-iodo-ethane,



$$H-\underset{\underset{I}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-H,$$

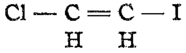
and no trace of

---

[1] *Ber.*, 29, 1411 (1896).

[2] *Ann.*, 369, 135 (1909); *Chem. Zentr.*, 1909, II, p. 2071.

[3] *Ibid.*, 369, 150 (1909).



$$\underset{}{Cl}-\underset{H}{C}=\underset{H}{C}-\underset{}{I}$$

has been found. A further study of the minor decomposition products of iodochloride-2-chloro-ethylene is being made.

The addition of iodine trichloride to unsaturated hydrocarbons appears to be an excellent method for the production of aliphatic iodochlorides having chlorine on the β-carbon and its possibilities are to be investigated further.

Experimental Part.

Oxidation of Hydriodic Acid by Di-iodo-acetylene.—Di-iodo-acetylene prepared according to the method of Dehn[1] was used in all experiments. This method of preparation is to be recommended most highly over those of the older workers Berend,[2] Biltz[3] and Nef.[3] The product is practically pure and of sharp m. p. as prepared and the method is so simple and the yields so good that it leaves nothing to be desired.

In a soft, glass bomb-tube 5 millimoles (1.39 g.) of di-iodo-acetylene was covered with 10 cc. of *N* sulfuric acid (*i. e.*, 10.0 millimoles) and 10 millimoles (1.66 g.) of C. P. potassium iodide, added. The pressure was reduced to 102 mm. and the bomb sealed off at the blast lamp. The tube was placed in a bomb case and immersed in a gently boiling water bath for from 8 to 10 hours. After cooling the bomb was opened by breaking the capillary within a rubber connection leading to a U-tube holding some ammoniacal cuprous chloride solution. The tube was still under reduced pressure as evidenced by bubbles of air being drawn back through the U-tube. A long glass tube reaching nearly to the liquid was introduced through a short length of rubber tubing and the connection made to the U-tube at once. On gently aspirating the gases from the bomb a fine, red precipitate of cuprous acetylide was produced in the U-tube. The test was repeated employing ammoniacal silver nitrate. The pale yellow precipitate of silver acetylide produced was partly dried and exploded in the characteristic manner on scraping with a glass rod.

The solid contents of the bomb after heating had changed over partly to a very dark brown mass of oily texture smelling strongly of unchanged di-iodo-acetylene, but consisting largely of a gray crystalline mass insoluble in water, in potassium iodide solution and in petroleum ether. This was exactly similar in all respects to the product obtained by V. Meyer and Pemsel[3] by heating di-iodo-acetylene with water in a bomb. The liquid above the solid showed the presence of some free iodine in solution.

The experiment was repeated and the contents of the bomb after heating were washed out into an Erlenmeyer flask. Titration of the iodine

---

[1] THIS JOURNAL, 33, 1598 (1911).

[2] *Ann.*, 135, 257 (1865).

[3] *Loc. cit.*

freed showed that the reaction had not proceeded far, only 1.00 cc. of 0.1 *N* sodium thiosulfate solution being taken up. The Erlenmeyer flask was connected by a stopper and glass tube to a small U-tube holding some acetone in the bend and having its outer arm closed by a Bunsen valve. The contents of the flask were now titrated for iodine at intervals for the next 11 days. Only a small fraction of a cc. of 0.1 *N* thiosulfate solution was required at any one time except in one case where the interval was 6 days, 1.51 cc. being required. The end-point was followed each time in a few minutes by the color of free iodine. At the end of 11 days when the experiment was discontinued a total of 5.62 cc. of 0.1 *N* thiosulfate solution had been added. This corresponds to 0.14 millimole of di-iodo-acetylene, assuming that all of the iodine formed came from the reaction

$$C_2I_2 + 2HOH + 2KI \longrightarrow 2KOH + 2I_2 + C_2H_2.$$

The acetone in the bend of the tube was found to give a positive test for acetylene within 72 hours from the time the tube was connected to the flask.

Action of Iodine Monochloride upon Metallo-acetylenes. (*a*) *Upon Copper Acetylide.*—Pure iodine monochloride was prepared by bubbling chlorine into iodine in a side-neck test-tube kept at 50–60° above a steam bath. When no further absorption occurred the tube was warmed by immersing in steam to decompose any iodine trichloride that had formed, and the product was then distilled under diminished pressure.

Copper acetylide was precipitated by treating ammoniacal cuprous chloride solution with acetylene washed by passing in the order given through (*a*) 1:2 nitric acid, (*b*) alkaline lead solution, (*c*) sodium hydroxide solution, (*d*) copper sulfate solution. The precipitate was filtered into a Gooch crucible, washed thoroughly with water and dried with alcohol and ether.

Iodine monochloride was added slowly a few drops at a time to the copper acetylide in the crucible and the mass allowed to stand a few minutes. No evidence of a violent reaction was observed. When the excess of iodine monochloride had been taken off by water and suction the odor of di-iodo-acetylene was very evident. The gray mass was now leached out thoroughly with ether, the ether extract decolorized by shaking with sodium thiosulfate solution and dried over anhydrous sodium sulfate. The ether was allowed to evaporate and a muddy white residue of characteristic odor was obtained. When taken up in alcohol (warmed to about 50–60°) and then diluted with water and cooled, very fine white needles of di-iodo-acetylene were precipitated.

(*b*) *Upon Calcium Carbide.*—Ordinary commercial crystalline calcium carbide was ground to a fine powder and treated with redistilled iodine monochloride a few drops at a time. The reaction was instantaneous but not violent and much iodine was freed. Ether (or petroleum ether, b. p. 25–40°) was added and the mass thoroughly extracted. The ether extract when decolorized by sodium thiosulfate solution, washed with water and dried over anhydrous sodium sulfate, gave nearly white crystals of di-iodo-acetylene when evaporated. The characteristic odor of the product even while in solution in the ether was quite noticeable.

Action of Ammonia upon Di-iodo-acetylene. (*a*) *In Aqueous Solution.*—A small sample of di-iodo-acetylene was introduced into a bomb tube and covered with about 2 cc. of conc. ammonium hydroxide (sp. gr. 0.90). The bomb was then sealed off, leaving a one-inch capillary. No change was apparent in the contents left at room temperature for 15 days. At the end of that time the bomb was placed in a bomb case and immersed in a steam bath for from 8 to 10 hours. As a result of this treatment the di-iodo-acetylene had disappeared and been replaced by a dark-brown mass. The liquid showed some brown color as of free iodine.

The bomb was cooled down slowly to about —10° and was opened by breaking the capillary within a rubber connection leading to a U-tube holding ammoniacal cuprous chloride solution. No test for acetylene resulted and the tube was under decidedly reduced pressure.

When the contents of the bomb were removed some of the dark solid (smelling strongly of unchanged di-iodo-acetylene) was transferred to a clay plate and dried. It was not explosive by concussion. No nitrogen iodide apparently had been formed.

(*b*) *In Ether Solution.*—About 0.5 g. of di-iodo-acetylene, dried over calcium chloride, was put into solution in 5 cc. of ether in a small U-tube and cooled to —8° with a freezing mixture. Dry ammonia was passed through the solution and the gas beyond allowed to bubble through a capillary U-tube containing a few drops of ammoniacal cuprous chloride solution.

In a short time an unmistakable dark-red precipitate of copper acetylide was produced in the outer tube. After a few hours of treatment with ammonia a mere trace of a brick-red solid had formed in the ether solution. When the ether had been decanted and the tube allowed to warm up the red solid decomposed rapidly but without explosion. Evaporation of the ether solution showed a brown-yellow color imparted to the large excess of di-iodo-acetylene which remained. As to the nature of the compound formed in the ether nothing can be said; acetylene was undoubtedly formed in small amounts by the reaction.

In another experiment dry ammonia was passed into a saturated solution of di-iodo-acetylene in anhydrous ether under gentle reflux. For about $^1/_2$ hour the only apparent change was the yellowing of those crystals of di-iodo-acetylene which were deposited about the inside of the delivery tube as the rapid stream of ammonia passed in. In the next few minutes, however, a very violent decomposition occurred almost explosive in nature filling the flask and connections with a dark, gray-brown deposit. This was removed and found to be largely iodine, carbon, and unchanged di-iodo-acetylene. The mass was entirely inert to concussion. The decomposition had given rise to no acetylene as shown by a U-tube holding ammoniacal cuprous chloride which had been connected to the top of the condenser.

Action of Chlorine upon Di-iodo-acetylene. Iodochloride-1,2-dichloro-2-iodo-ethylene, $Cl_2ICCl = CICl$.—Although other solvents such as ethyl bromide, chloroform, petroleum ether and liquid chlorine itself are found to serve, by far the best solvent in which to chlorinate di-iodo-acetylene is ethyl chloride. It is not only unacted upon by chlorine under the conditions of the experiment but its low, boiling point and the cooling effect produced by its evaporation are of much advantage.

Because of the ease with which the product decomposes it was rarely found advisable to attempt to chlorinate more than a few g. of di-iodo-acetylene at a time. In a typical preparation, where the material was *not* to be used for analysis from 3 to 8 g. of di-iodo-acetylene in from 10 to 20 cc. of ethyl chloride was employed. If the product was to be used in an analysis only a few tenths of a gram of di-iodo-acetylene in 1 to 2 cc. of solvent was used.

The solution of di-iodo-acetylene in ethyl chloride was poured into a test-tube 5 × 20 cm., provided with a 2-hole stopper and delivery tube (funnel-shaped end) and exit tube for the chlorine. The apparatus was cooled down to from —15° to —10° by ice and conc. hydrochloric acid and then chlorine (washed with water and conc. sulfuric acid) was passed in quite rapidly. A fleeting violet or blue coloration was at first produced, which gave way almost at once to a yellow color. In from 5 to 20 minutes bright yellow needles began to encrust the inside of the delivery tube. These increased rapidly in amount and soon formed a heavy precipitate on the sides and bottom of the tube. It was usually found best to discontinue the chlorination at the first signs of any darkening of the precipitate in the delivery tube. Otherwise both precipitate and solution rapidly turned brown indicating the replacement of iodine and the formation of iodine monochloride. In all cases where the reaction was allowed to continue to completion the crystalline precipitate slowly darkened and disappeared and was ultimately replaced by a more granular orange precipitate of iodine trichloride.

To free the crystals from any unchanged di-iodo-acetylene, iodine monochloride or hexachloro-ethane, they were washed several times by decantation with a small amount of well-cooled ethyl chloride. Material thus prepared could be kept in the dark at —15° to —10° for from 15 to 30 minutes. Exposure to light or to warmer air or reduction of the pressure (lower than 50 mm.) for more than 4 or 5 minutes brought about sudden decomposition and liquefaction. The compound gives an apparent m. p. of 42–43°, probably rather a decomposition point, but spontaneous decomposition was found to occur, seemingly unprovoked by external conditions, at lower temperatures. The crystals were rather soluble in ether and alcohol (with some decomposition) but relatively insoluble in the solvents: chloroform, carbon tetrachloride, petroleum ether (b. p. 25–40°, also of b. p. 45–65°), ethyl bromide and ethyl chloride.

For the titrations the material as prepared above was used. A well-cooled tared glass spatula was employed to remove a small sample in a thin layer. It was held for from 30 to 40 seconds in the air (and dark) to permit any ethyl chloride to evaporate and then the sample and spatula were immersed in a weighed Erlenmeyer flask or large test-tube containing a small amount of carbon tetrachloride under potassium iodide solution which had been cooled to 0°. The gain in weight was taken as soon as the solution was at room temperature again and the iodine freed was titrated with 0.1 *N* sodium thiosulfate. Results:

	Wt. sample taken. G.	Cc. of 0.1 *N* $Na_2S_2O_3$ required.	Calc. cc., 0.1 *N* $Na_2S_2O_3$ for $Cl_2I.CCl = CClI$.	% oxidizing chlorine found.	Theoretical % oxidizing chlorine.
I......	0.5677	25.92	27.04	16.2	16.88
II......	0.2039	9.45	9.71	16.43	16.88

Unless great care was taken to have the compound mixed thoroughly with the potassium iodide and carbon tetrachloride at once, the available chlorine found was always lower than the theoretical. Rearrangements as already discussed evidently occurred.

For determining the total chlorine and the iodine many analyses by the methods of Carius, of decomposition with lime, and by sodium peroxide fusion were carried out. All were found to be unsatisfactory on account of the difficulty in weighing the sample without decomposition or the failure to convert all of the iodine to iodide as already discussed in the theoretical part. In the cases where decomposition with lime was attempted the tube showed free iodine when cooled after ignition even above the fusion point of the Pyrex tubing employed (700°–800°). In instances where decomposition with sodium peroxide in a Parr sulfur bomb was resorted to, the odor of di-iodo-acetylene could be noted on opening the bomb. Mixtures of magnesium filings and magnesium oxide were tested out as decomposition agents, also sodium in absolute alcohol. Both failed to decompose all of the compound, and merely converted much of it to di-iodo-acetylene.

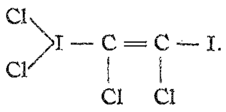
The percentage of chlorine was best determined by obtaining the ratio Cl_2/C_2I_2 in the case where only a small amount of the compound was prepared. The procedure was as follows: A glass-stoppered test-tube

100 mm. long with a side neck opening through the stopper was made. This together with a small funnel-end delivery tube about 80 mm. long was tared and the latter tube removed and the sample of from 0.1 to 0.3 g. of di-iodo-acetylene introduced and weighed. About one cc. of well cooled ethyl chloride was used as solvent and a slow current of chlorine was passed in (at —15° to —10° in the dark) employing the weighed delivery tube. This weight of di-iodo-acetylene treated with chlorine for from 25 to 40 minutes gave a fine light-yellow product without any darkening. At the end of this time the delivery tube was disconnected and left in the tube and the latter connected by the side neck to a filter pump so that cold (—5° to —10°) dry air could be drawn through a rather large capillary extending above the liquid to remove the ethyl chloride. In from 5 to 10 minutes the crystals could thus be freed from the solvent and excess of chlorine. Frequently sudden decomposition set in at this point, however, and ruined the experiment entirely. Where all went well the capillary was now removed and the tube closed by the glass stopper. After warming the outside by water at room temperature and opening the side neck momentarily the gain in weight was taken. This method of weighing the compound after decomposing it was, of course, based upon observations (see below) that no change of gaseous volume occurred during the transformation to the liquid.

Subs., 0.3188; 0.4719 g. iodochloride obtained. Hence, 0.1531 g. of chlorine was taken up. Ratio: $\frac{\text{moles of } Cl_2}{\text{moles of } C_2I_2} = \frac{2.155}{1.108}$ or 1.945.

Calc. for C_2I_2: Cl equiv., 33.8. Found: Cl, 32.44.

From the results of the titration and the per cent. of chlorine absorbed, also the fact that the compound gives di-iodo-acetylene again with alcoholic potash, we may conclude that di-iodo-acetylene under the conditions given combines with 4 atoms of chlorine, only two of which are combined to iodine and may be given up readily. This gives the structure



Spontaneous Decomposition of Iodochloride-1-chloro-2,2-chloro-iodo-ethylene. Symmetrical Chloro-iodo-ethylene.—That the spontaneous decomposition of iodochloride-1-chloro-2,2-chloro-iodo-ethylene was a rearrangement was shown by the fact that no increase or decrease of gaseous volume accompanied it. This was easily demonstrated by allowing a considerable sample of the iodochloride to decompose in a long, narrow test-tube immersed in a large graduate and closed by a one-hole stopper through which a connection was made to a small graduated (Mohr's) pipet immersed vertically beside the test-tube. The level of the water in the latter remained practically constant as the liquefaction took place, except for a slight, temporary depression due to the sudden liberation of heat.

The first indication that decomposition had begun in a sample of iodochloride-1-chloro-2,2-chloro-iodo-ethylene was a slight darkening of the crystals. This was followed immediately by an appearance of sintering and the formation of crystals of iodine trichloride, then strikingly sudden liquefaction and darkening of the mass with a sharp rise in temperature.

On standing a few hours in the tube in which the change had taken place the dark brown liquid separated into 2 layers, the upper one reddish brown and transparent, and the lower one very dark violet. The upper layer was removed and found to be miscible with water and when treated with alkali gave a precipitate of iodine; sodium thiosulfate caused iodine to precipitate at first and then to dissolve in excess. These reactions indicated iodine monochloride.

It was found best not to decolorize the lower layer of the products but to subject it at once to vacuum distillation. The yield from several decompositions was combined and fractionated 3 times; once at 42–45 mm. in a 15 cc. Claisen bulb and twice at 25–26 mm. using a 5 cc. Claisen bulb. Some iodine monochloride and much free iodine came over at first and the fraction boiling at 80–90° (25 mm.) was deeply violet colored. The intermediate fractions 90–115° and 115–125° were also violet but the highest boiling and largest fraction (125–132°) distilled nearly colorless but darkened to a reddish brown color in the receiver. After a third fractionation, over 80% of the material came over at 125–132° (25–26 mm.), the bulk of it at 127.5–128.5°. Refractionation of the 3 lower fractions gave only a few drops of dark liquid, b. p. 80–84° under 32 mm. pressure.

The chief product obtained at 127.5–128.5° (25–26 mm.) was analyzed at once by the method of Carius.

Subs., 0.2381; AgCl + AgI, 0.5109; loss on heating in a stream of chlorine, 0.1241.
Calc. for $C_2Cl_2I_2$: Cl, 20.34; I, 72.94. Found: Cl, 19.98.; I, 72.32.

The compound under atmospheric pressure boils with decomposition at 243.5° (corr.) and solidifies slightly below 0°. When pure it is odorless and of pale yellow color. The halogen is precipitated with difficulty by hot alcoholic silver nitrate solution. Alcoholic potash reacts upon it to give di-iodo-acetylene.

The lower boiling liquid, of which only a small percentage was obtained, at 80–84° (32 mm.), appeared to be trichloro-iodo-ethylene. Because of the small amount and its ease of decomposition even at 26 mm. pressure, it could not be purified further. Analysis of a crude sample of 0.2176 g. gave 0.4806 g. of silver halide which in a current of chlorine lost 0.0615 g. The ratio Cl:I was thus 3.3:1.

Action of Chlorine upon Symmetrical Dichloro-di-iodo-ethylene.—A weighed sample of 1,2-dichloro-1,2-di-iodo-ethylene was introduced into the glass-stoppered side-neck tube used above. Employing the same method as before, the weight of chlorine taken up at —15 to —10° in ethyl chloride as a solvent was determined.

Subs., 0.1410; yellow compound, 0.1704. (Hence the ratio $Cl_2/CICl:CICl$ = 1.025/1.0.)

Calc. for $C_2Cl_2I_2$: Cl taken up, 16.88. Found: 17.26.

That the mole of chlorine had combined to iodine to give the iodochloride: $Cl_2I.CCl=CClI$ and not to the carbon was shown by the reaction of the product with potassium iodide to give up one mole of chlorine again: 0.1106 g. acting on potassium iodide solution liberated iodine equivalent to 5.02 cc. of 0.1 *N* sodium thiosulfate.

Calc. for $Cl_2I.CCl = CClI$: 0.1 *N* $Na_2S_2O_3$, 5.27 cc. oxidizing Cl. Found: 16.1%.
Calc. for iodochloride-1-chloro-2,2-chloro-iodo-ethylene: 16.88%.

Addition of Iodine Trichloride to Acetylene. 1-Iodochloride-2-chloro-ethylene, $Cl_2ICH:CHCl$.—From 20 to 30 cc. of a solution of iodine trichloride in conc. hydrochloric acid, prepared preferably by the method given below, was diluted with 2 volumes of ice-water. This solution was then divided among each of 3 U-tubes (Peligot type) connected in series to an acetylene generator. The tubes were immersed in water containing large pieces of ice. Acetylene (purified by washing with nitric acid (1:2), alkaline lead solution, sodium hydroxide (20%) and copper sulfate solution in the order named) was allowed to bubble through the tubes in a rapid current. After occasional shaking of the tubes the first indication of a reaction followed in from 30 to 45 minutes, fine, yellow needles of the product beginning to separate out. The current of gas was usually allowed to continue for another hour and then the product was filtered out and the filtrate returned to the tubes for the formation of a second crop of crystals. Usually the latter yield was as large as the first.

Care had to be exercised not to allow the crystals to remain in the tubes too long after forming as they were apt to become pasty or sticky and incapable of being washed. This result was evidently due to the formation of traces of chloro-iodo-ethylene by the action of some iodine monochloride present. Attempts to filter again and get out a third crop of the crystals from the filtrate always resulted in the production of chloro-iodo-ethylene instead. The latter was proven by both b. p. (119–120°) and analysis. The iodochloride from the 2 crops of crystals was combined on the filter and washed quickly with ice-water 3 times and then dried by pressing well between hardened filters. If spread out at once in a thin layer it was possible to keep the product for several days, although much of it gradually disappeared and the residue became of a dirty, white color and its analysis showed a loss of chlorine. If the product was left in a compact mass or enclosed in a tube it darkened soon and decomposed to give liquid products as discussed below. To obtain a true melting point was difficult. The temperature 61–62° was the point of decomposition of the crystals when prepared from crude iodine trichloride (containing iodine monochloride) made by direct union of the elements. The same decomposition point was given for their crude product by Thiele and Haakh[1] and 75° as the true melting point for their recrystallized product. A melting point taken upon crystals freshly prepared and (recrystallized from methyl alcohol) was found to be 66° with decomposition. In other trials, however, the compound after standing for several hours showed a melting point of 80°. The compound is soluble in ether, benzene and methyl alcohol with but little decomposition for 24 hours or more but cannot be safely recrystallized from any of these except methyl alcohol.

Analyses for their product were not given by Thiele and Haakh, iodometric titrations alone being relied upon. In the case of the present preparation it was found possible, although difficult, to analyze the crystals both by combustion and by the method of Carius. The combustion was carried out in a long 100 mm. boat and the front end of the tube was filled by a silver, spiral gauze beyond 2 boats (length 80 mm.) of molecular silver. Imperfect absorption of the halogens was otherwise found to occur. The method of Dennstedt[2] was tried out but was found to give incomplete absorption of the halogens even using several boats of molecular silver ahead of the sample and burning the substance very slowly. It is scarcely to be recommended for aliphatic compounds of high halogen content.

Subs. (I) 0.2260, (II) 0.1984, (III) 0.2529; H_2O (I) 0.0194, (II) 0.0147; CO_2 (I), 0.0792, (II) 0.0663; AgI + AgCl (Carius) (III) 0.6409. with loss in a stream of chlorine, 0.0877.

Calc. for C_2HCl_3I: C, 9.25; H, 0.77; Cl, 41.0; I, 48.9 Found: C (I) 9.32, (II) 9.12; H (I) 0.95; (II) 0.82; Cl (III) 40.7; I, (III) 48.1.

Spontaneous Decomposition of Iodochloride-2-chloro-ethylene. 1,2,2-trichloro-1-iodoethane.—In several cases when samples of iodochloride-2-chloro-ethylene were being weighed in small open weighing tubes exothermic decomposition took place and it was noted that there was no increase in the rate at which the crystals had been losing weight. For example, a sample, freshly prepared and dried as stated, was placed on the balance and weighed 0.0367 g. Gradual loss of weight occurred. After about 10 or 15 minutes sudden darkening and liquefaction took place. The same rate of decrease of weight prevailed throughout the change. After the decomposition the loss became less rapid and the total loss for the entire time was less than one mg. or 2.7%. This led to the conclusion

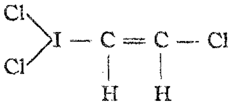
---

[1] *Loc. cit.*

[2] *Z. anal. Chem.*, 41, 525 (1902); *Ber.*, 41, 600 (1908).

that the change was, perhaps, a rearrangement and not a decomposition into chlorine and chloro-iodo-ethylene as reported by Thiele and Haakh. To confirm this, samples were allowed to "decompose" in a closed tube over water (method as above with iodochloride-1,2-dichloro-2-iodo-ethylene). No increase in volume accompanied the change.

A number of samples of iodochloride-2-chloro-ethylene were prepared, carefully washed and dried between hard filters and allowed to decompose in stoppered tubes immersed in water at room temperature. Within a short time after the change had occurred the liquid in each tube had separated into two layers. The upper layer proved to be iodine monochloride as shown by miscibility with water and the typical reactions with alkali and with sodium thiosulfate. The iodine monochloride represented nearly $^1/_4$ the volume of the products, approximately 12.8% of the weight of the original material or practically 1 mole of iodine monochloride to 5 moles of



taken. Boiling-point determinations made on the lower layer after its decolorization by sodium thiosulfate showed it to be a mixture. When distilled under a pressure of 23–24 mm. the boiling point rose from 40 to 120°, at which temperature decomposition occurred.

Twelve and two tenths g. of the decomposition products (lower layer) prepared as stated, was fractionated at 30–31 mm. in a long-necked Claisen flask of 5 cc. capacity. Much free iodine was evolved in the first fractionation. After 3 fractionations had been made, over 42% (5.2 g.) of the products came over at 96–103° (30 mm.) and of this 2.5 to 3.0 g. boiled at 99–101.5° (30 mm.). The other fractions of consequence, 2 in number, each held approximately 15–20% of the original material but neither was large enough nor of small enough range to permit of further concentration and subsequent analysis. The low boiling material came over at 56–96° and the highest fraction at 130–145°. The latter tended to decompose to give free iodine.

Whereas, it appeared that at least 3 compounds in addition to iodine monochloride had been formed, the chief product was that of b. p. 99–101.5° (30 mm.). It was analyzed by Carius determination and proved to be 1,2,2-trichloro-1-iodo-ethane.

Subs., 0.2405; AgI + AgCl, 0.6161; loss in a stream of chlorine, 0.0842.
Calc. for $CHCl_2CHClI$: Cl, 41.0; I, 48.9. Found: Cl, 41.2; I, 48.6.

The boiling point of pure chloro-iodo-ethylene is 27–28° under 23 mm. pressure (proven experimentally), hence it is not one of the chief products even of the decomposition of iodochloride-2-chloro-ethylene.

A Method of Preparation of Iodine Trichloride.—Since the usual methods for preparing iodine trichloride gave so large a proportion of iodine monochloride as to render the reagent useless in the above experiments, a new method was sought by which to prepare iodine trichloride in purer form. As it was to be used in hydrochloric acid solution a very satisfactory procedure was found to be the following, based upon the reaction

$$3HIO_3 + I_2 + 15HCl \longrightarrow 5ICl_3 + 9H_2O.$$

Ten and fifty-six one hundredth g. of iodic acid (3 moles) and 5.08 g. of resublimedi odine (1 mole) were ground up finely and thoroughly mixed. About twice the theoretical volume of hydrochloric acid (sp. gr. 1.19), usually 46.6 cc., was cooled down and the powdered mixture of iodine and iodic acid added in small portions with shaking. Very little chlorine was evolved and the two solids appeared to be taken up at about equal rates. All was added and dissolved giving an orange yellow solution in about 20 minutes. By employing the volume stated each cc. of the solution is theoretically equivalent to 0.5 g. of iodine trichloride. We have found that iodine trichloride in high concentrations of hydrochloric acid may be kept indefinitely at temperatures up to even 30°.

Iodine Monochloride from Nitrogen Iodide.—As being of theoretical interest iodine monochloride was prepared in hydrochloric acid solution by the reaction of conc. hydrochloric acid upon nitrogen tri-iodide. Finely powdered iodine in a Gooch crucible was digested for several minutes with ammonium hydroxide (sp. gr. 0.90). The excess of ammonium hydroxide was then drawn off and the brown mixture of iodine and nitrogen iodide washed twice with water. On adding to the mixture several cc. of conc. hydrochloric acid a sharp crackling noise gave evidence of a somewhat violent reaction. Fumes of ammonium chloride and iodine came off along with hydrochloric acid. To carry the iodine monochloride into solution excess of hydrochloric acid was now added and the clear reddish brown liquid drawn into the receiver.

This solution (*a*) diluted largely with water gave abrupt deepening of color as free iodine was liberated, (*b*) treated with sodium thiosulfate, gave a copious precipitate of iodine which redissolved in excess and (*c*) treated with acetylene in a U-tube gave a few globules of a heavy liquid resembling chloro-iodo-ethylene in odor and appearance (although not enough for a b. p. determination was obtained). The solution undoubtedly contained considerable iodine monochloride. The reaction was tried out merely to show that the iodine of nitrogen tri-iodide and of iodine monochloride are both of positive nature. Since hydrochloric acid is not oxidized by iodine itself the iodine monochloride must have been formed by the reaction

$$NH_3.NI_3 + 5HCl \longrightarrow 3ICl + 2NH_4Cl.$$

Summary.

1. Di-iodo-acetylene liberates iodine from aqueous solutions of iodides and acetylene is regenerated.

2. Di-iodo-acetylene reacts with ammonia giving acetylene and probably nitrogen iodide, a compound in which the iodine is positive.

3. The conduct of both iodo-acetylene and di-iodo-acetylene is best explained by the assumption that these compounds contain positive iodine, and that the structures are, respectively, $H - C \equiv C - I$ and $I - C \equiv C - I$. These structures seem at present much more probable than the acetylidene structures, $IHC = C<$ and $I_2C = C<$.

4. Biltz has reported that chlorine acts upon di-iodo-acetylene giving hexachloro-ethane. It has been shown that the primary product formed by the action of chlorine upon di-iodo-acetylene is iodochloride-1-chloro-2,2-chloro-iodo-ethylene, $Cl_2I.CCl = CClI$.

5. Iodochloride-1-chloro-2,2-chloro-iodo-ethylene decomposes very easily giving chiefly symmetrical dichloro-di-iodo-ethylene, $CICl = CICl$ and iodine monochloride, also probably a trichloro-iodo-ethylene.

6. The action of iodine trichloride upon acetylene gives iodochloride-2-chloro-ethylene, a compound previously prepared by Thiele and Haakh by the action of chlorine upon 1,2-chloro-iodo-ethylene. This reaction indicates that the iodine atom of chloro-iodo-ethylene is positive in nature. The addition of iodine trichloride to unsaturated linkages should be a ready method for preparing aliphatic iodochlorides having chlorine on the β-carbon.

7. The chief products formed when iodochloride-2-chloro-ethylene decomposes are iodine monochloride and 1,2,2-trichloro-1-iodo-ethane. The observation of Thiele and Haakh that 1-chloro-2-iodo-ethylene and chlorine gas result when iodochloride-2-chloro-ethylene decomposes, appears to be an error.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE.]

THE MECHANISM OF THE REACTION BETWEEN KETENES AND THE GRIGNARD REAGENT.

BY HENRY GILMAN AND L. C. HECKERT.

Received February 6, 1920.

The characteristic grouping of the ketenes is $\overset{|}{\underset{|}{C}} = C = O$. Superficially they may be regarded as unsaturated ketones. However, practically all their reactions are satisfactorily explained as involving primary addition to the ethylenic linkage. A few isolated reactions have been explained by assuming addition to the carbonyl group. Staudinger and his co-workers who have given to chemistry almost all of our present