POSITIVE HALOGEN IN ORGANIC COMPOUNDS. IODINE IN DIODOACETYLENE AND CHLORO-IODOETHYLENE

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A. B. Wabash College, 1909
M. S. University of Illinois, 1918

THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

UNIVERSITY OF ILLINOIS

1919
UNIVERSITY OF ILLINOIS
THE GRADUATE SCHOOL

May 17, 1919

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Lloyd Brelsford Howell

ENTITLED Positive Halogen in Organic Compounds. Iodine in Diiodoacetylene and Chloro-Iodoethylene

BE ACCEPTED AS FULFILLING THIS Part OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy

[Signatures]

Recommendation concurred in*

[Signatures]

*Required for doctor's degree but not for master's
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I. Introduction.

For a number of years chemists have recognized the fact that certain organic halogen compounds e.g. those in which the halogen atom has replaced hydrogen of any of the groups \( \cdot \text{NH}_2 \), \( >\text{NH} \), \( -\text{OH} \) exhibit extraordinary activity. Unlike the halogen of the ordinary types of alkyl and acyl halide linkage, \( C-x \) and \( O-x \), 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 solution of ferrous 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 been unsatisfactorily explained.

Inorganic halogen compounds similarly unstable and of oxidizing properties are the substituted ammonias; nitrogen trichloride, nitrogen tri-iodide. The work of Chattaway\(^1\), Orton, W.A. Noyes\(^2\) and others with these compounds has of recent years led to satisfactory explanation of the behavior of these compounds by the assumption that the halogen is combined as a positive atom and not negatively as in the case of ordinary chlorides, bromides and iodides. Certainly no more reasonable explanation has so far been advanced.

It is the purpose of this investigation to determine whether or not a similar explanation might not be made for the behavior of certain organic halogen compounds. In addition to the types of linkage mentioned above we have the \( \equiv C - \text{hal} \) linkage which gives relative instability to the molecule and, it will be shown, shows
oxidizing properties. Just as for the cases $\equiv \text{NH}_2$, $\equiv \text{NH}$, and $\equiv \text{OH}$, the hydrogen atom may be replaced by either metals or halogen so in acetylene or the mono substituted acetylenes we have hydrogen replaceable by either metals or halogen. And since both the original H atom of acetylene and the metal of the acetylides or carbides are undoubtedly positive, it would seem a reasonable inference that the chlorine of chloroacetylene and dichloroacetylene, the bromine of bromoacetylene and dibromoacetylene, and the iodine of iodoacetylene and diiodoacetylene are likewise of positive nature. Since it is relatively the most stable of the six known halogen substituted acetylenes and the easiest of preparation, diiodoacetylene has been investigated for those properties which might indicate the nature of the $\equiv \text{C}$-hal. linkage. Certain of the properties of this compound attributed by Nef\textsuperscript{10} 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.

As a result of the work a new example of aliphatic iodochloride has been prepared and characterized and a new method of preparation of iodochlorides from triple bonded compounds has been devised. Also the investigation has been extended to the decomposition products of iodochloride-1-chloro 2-2-chloro-iodo ethylene and iodochloride 2-chloro ethylene. A new method for preparing iodine monochloride and for iodine trichloride has been employed.

II. Theoretical.

Diiodoacetylene 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 is added to neutralize the alkali formed in the reaction:

\[ \text{I}_2\text{C}=\text{C}-\text{I} + 2 \text{HOH} + 2 \text{KI} \rightarrow \text{H}-\text{C}=\text{C}-\text{H} + 2 \text{KOH} + 2 \text{I}_2 \]

If the iodine be taken up by titration with sodium thiosulphate it is especially 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 diiodoacetylene are strongly electropositive and capable of taking up two electrons each. That dibromo acetylene, and dichloroacetylene recently prepared and described by Boëseken and Carriere would show the same reaction even more markedly would be predicted from their relatively more unstable character.

Since the oxidizing action of diiodoacetylene must depend upon the hydrolysis of the compound to hypoiodous acid and acetylene in the first stage, experiments have been made to show that acetylene is slowly generated by the reaction of water alone upon the compound.

To attempt hydrolysis by means of alkali would not appear feasible since the reverse reaction:

\[ 2 \text{NaOI} + \text{H}-\text{C}=\text{C}-\text{H} \rightarrow 2 \text{NaOH} + \text{Cl}=\text{Cl} \]

by which diiodoacetylene is formed runs so smoothly to completion. Tubes containing diiodoacetylene under water after standing at room temperature for even a few weeks show the presence of acetylene.

The mechanism of the hydrolysis might be variously explained, viz:
If the suspension of diiodoacetylene in water be warmed up in a bomb the reaction is hastened, but if heated to the temperature of the steam bath the compound undergoes sudden partial decomposition as mentioned by Nef and gives the dark mass of undetermined composition reported by V. Meyer.

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

Iodine monochloride however reacts by addition upon acetylene itself as do the halogens, and this has been found to occur both in
and in the absence of solvents. The product always obtained was 1-chloro 2-iodo ethylene as first shown by Plimpton. The action of iodine monochloride upon metallo derivatives of acetylene however yields better results. Iodine monochloride with calcium carbide and with copper acetylide forms diiodoacetylene.

\[ 2 \text{ICl} + \text{CaC}_2 \rightarrow \text{Cl}=\text{Cl} + \text{CaCl}_2 \]

\[ 2 \text{ICl} + \text{CuC}_2 \rightarrow \text{Cl}=\text{Cl} + \text{Cu}_2\text{Cl}_2 \]

The reduction of diiodoacetylene by ammonia has not been accomplished. The reaction has been tried out in aqueous and ether solution and in the absence of any solvent employing liquid ammonia itself (in which diiodoacetylene 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 that nitrogen iodide is an excellent iodinating agent for acetylene and gives practically quantitative yields of tetraiodoethylene. This reaction would thus seem to be only slightly reversible.

In his well known article on "Die Chemie des Methylens", Nef has drawn the conclusion that diiodoacetylene and iodoacetylene and the other halogen substituted acetylenes must possess the acetylidene structures:

\[ \text{II} \searrow \text{C} = \text{C} \quad \text{I} \searrow \text{C} = \text{C} \]

diiodoacetylene iodoacetylene
He based this conclusion chiefly upon the ease with which these compounds added bromine and hydrobromic acid and with which the products decomposed again to give the original iodo- or diiodo-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 better without assuming bivalent carbon by the equations:

\[
\text{I-C=I} + \text{Br}_2 \rightarrow \text{I-C=I} - \text{Br}
\]

and

\[
\text{I-C=H} + \text{Br}_2 \rightarrow \text{I-C=H} - \text{Br}
\]

That is, the positive nature of the iodine atom as shown by its tendancy 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 \( \text{C}_2\text{I}_2\text{Br}_2 \) 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 diiodoacetylene as given below is an exactly analogous case. The poisonous character, disagreeable odor and irritating effects of the vapor of diiodoacetylene attributed by Nef to the presence of diad carbon might instead be due to positive or unsaturated iodine. Other compounds containing iodine on a carbon next to a double or triple bond exhibit similar physical prop-
erties. Also the poisonous character of the compounds, NCl₃ and NH₃NI₃ is well known. Moreover if we were to assume the compound C₂I₂ to be diiodoacetylidene, the structure of the iodochloride described below must be:

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{I} \\
\text{I} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{I} \\
\text{I} \\
\end{array}
\]

This is highly improbable since we must assume five halogen atoms connected to one carbon atom adjacent to a divalent and therefore very reactive carbon. Moreover the decomposition of the iodochloride to give 1-2 dichloro 1-2 diiodoethylene would be very difficult to explain.

Although it can not yet be considered as established that the more strongly electropositive an atom is, the more readily it adds chlorine to give an iodide chloride, yet some evidence as to this point might be found in the fact that diiodoacetylene reacts with chlorine giving iodochloride-1-chloro-2-2-chloro-iiodoethylene. Biltz⁷ has reported that the product of the reaction of chlorine upon diiodoacetylene is hexachloroethane. It has been found however that the primary product of this reaction is the iodochloride:

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{I} \\
\end{array}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

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 was isolated and analyzed. It is relatively quite unstable and decomposes in a short time with
the evolution of heat. The conclusion of Biltz\(^7\) that hexachloroethane is the product of the action of chlorine upon diiodoacetylene 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. Hexachloroethane 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 diiodoacetylene (at room temperature) the iodidechloride 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 ICl. On continuing the current of chlorine a second deposition of crystals of an orange color occurred. These were removed and proved to be iodine trichloride. The filtrate when slowly evaporated gave an excellent yield of hexachloroethane. The course of the chlorination is probably:

\[
\begin{align*}
n & \text{I-C=CI} \quad \text{Cl}_2 \rightarrow \left[ \text{Cl} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{I-C=CI} \right] \rightarrow \text{I-C=C-I} \quad \text{Cl}_2 \\
\text{Cl} \quad \text{I-C=C-I} \quad \text{Cl}_2 \rightarrow \left[ \text{Cl} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \text{I-C=C-I} \right] \rightarrow \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6 + \text{ICl} \quad \text{Cl}_2 \rightarrow \text{ICl}_3
\end{align*}
\]

However it was not found possible to cause diiodoacetylene to take up less than two moles of chlorine.

The very unstable character of iodochloride -1-chloro-2-2-chloro-
iodoethylene makes it impossible to keep it even in the dark and at the 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 hexachloroethane and iodine trichloride being present. Satisfactory results are obtained when the compound is prepared from an excess of diodoacetylene in ethyl chloride at \(-15^\circ\) to \(-10^\circ\) in the dark, freed from unchanged diodoacetylene by washing with ethyl chloride and titrated in the presence of carbon tetrachloride by the iodometric method.

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 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-iodoethylene treated with sodium in alcohol yields diiodoacetylene 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-iodoethylene and in 1-2 dichloro 1-2 diiodoethylene the reverse is true. Nef\textsuperscript{10} noted this same result in the case of practically all of the compounds which he derived by addition from diiodoacetylene. Sodium alcolholate, sodium in alcohol and alcoholic potash reacted to give diiodoacetylene in the case of all such compounds. Nef naturally attributed it to the
comparative stability of the group \( \text{I} \stackrel{\text{C=}}{\text{I}} \) as compared with
\( \text{C} \). It seems much more reasonable to regard it as being due to the inherent positive (or even basic) nature of the two iodine atoms. A very similar case in inorganic compounds is azoic iodide \( \text{N}_2\text{I} \). Abegg\textsuperscript{13} is authority for the statement that the failure of this iodide to react with \( \text{N}_3\text{Ag} \) is the result of the positive nature of the iodine.

The chief product of the decomposition of iodochloride-1-chloro-2-2-chloro-iodoethylene is 1-2 dichloro 1-2 diiodoethylene:
\[
\text{Cl} \quad \text{I} \quad \text{C} = \text{C} \quad \text{Cl} \quad \text{I}
\]
not previously prepared nor reported in the literature. Much iodine monochloride is liberated and traces of a second compound 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 increase in volume and indications are that its course is in part probably:

\[
2 \quad \text{Cl} \quad \text{I} \quad \text{C} = \text{C} \quad \text{I} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

1-2 dichloro 1-2 diiodoethylene when treated with chlorine in ethyl chloride or petroleum ether gives also the same iodochloride,
\[
\text{Cl} \quad \text{I} \quad \text{C} = \text{C} \quad \text{I} \quad \text{Cl} \quad \text{Cl}
\]
as was obtained from diiodoacetylene. It is always noted that decomposition of the iodide chloride 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 cool-
ed porous plate, no darkening occurs and no liquid products form. The bright yellow color of the mass gradually fades and after about 1 1/2 to 2 hrs. a nearly white solid remains. This no longer smells of chlorine but of diiodoacetylene and does not liberate iodine from potassium iodide except on long standing. Recrystallization and qualitative analysis shows only iodine compounds present, the m.p. (72 - 180°) indicating a mixture of C₂I₂ (m.p. 80°) and C₂I₄ (m.p. 185°). The nature of this decomposition was not studied; it must be complex, involving that of diiodoacetylene into tetraiodoethylene noted by V. Meyer⁴.

While investigating the action of iodine monochloride in hydrochloric acid as a solvent upon acetylene, occasion was had to employ accidently, crude iodine monochloride containing some iodine trichloride. Such 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 and dried and analysed. Titration by iodometric method showed it to be an iodidechloride and analysis by combustion and the method of Carius established the compound as iodochloride-2-chloroethylene, Cl₂I-CH=CHCl. As prepared by this reaction:

\[
\text{H-} \overset{\text{H}}{\text{C=}} \overset{\text{H}}{\text{C}} \overset{\text{H}}{\text{H}} + \overset{\text{H}}{\text{I}} \overset{\text{H}}{\text{C}} \overset{\text{H}}{\text{H}} \rightarrow \overset{\text{H}}{\text{C}} \overset{\text{H}}{\text{I}} \overset{\text{H}}{\text{C}} \overset{\text{H}}{\text{H}} \overset{\text{H}}{\text{H}} \]

iodochloride chloroethylene is much purer and far more stable than when prepared by the method of Thiele and Haakh³ from chlorine and
12.

1-chloro-2-iodoethylene.

It is of theoretical interest to note here that since iodine in iodine trichloride is positive and the group -ICl₂ which adds to one carbon atom in acetylene is the positive group, it is very probable that the iodine atom of 1-chloro-2-iodoethylene is also positive. Otherwise chlorination of chloro-iodoethylene would perhaps give a different product.

It is stated by Thiele and Haakh⁹ that this iodidechloride decomposes giving chlorine and 1-2-chloro-iodoethylene. The observation has been made however that here too as in the case of iodochloride-1-chloro-2-2-chloro-iodoethylene the decomposition occurs without any increase in volume and hence with rearrangements. The decomposition products of iodochloride 2-chloroethylene should be investigated. The addition of iodine trichloride to unsaturated linkages 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.
13.

III. Experimental.

1. Oxidation of Potassium Iodide by Diiodoacetylene.

Diiodoacetylene prepared according to Dehn's\(^1\)\(^2\) method was used in all experiments. This method of preparation is to be recommended most highly over those of the older workers Berend\(^1\)\(^1\), Biltz\(^7\) and Nef\(^1\)\(^0\). The product is practically pure white 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 gm.) of diiodoacetylene were covered with 10 c.c. of N sulphuric acid (i.e. 10.0 millimoles) and 10 millimoles (1.66 gm.) of c.p. potassium iodide, added. The pressure was then 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 8-10 hrs. 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 the rubber connection and the connection to the U-tube at once made. On gently aspirating the gases from the bomb a fine dark red precipitate of cuprous acetylide was produced in the U-tube. It was removed and replaced by a tube containing ammoniacal silver nitrate. On again withdrawing gases from the bomb by means of the pump a pale yellow precipitate of silver acetylide was produced. The latter precipitate was partly dried and exploded in the characteristic manner on scraping it by 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 diiodoacetylene, but largely consisting of a gray crystalline mass insoluble in water, potassium iodide solution and in petroleum ether. This was exactly similar in all respects to the product obtained by V. Meyer and Pemsel by heating diiodoacetylene 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 freed showed that the reaction had not proceeded far, only 1.00 c.c. of N/10 Na₂S₂O₃ 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 was now titrated for iodine at intervals for the next eleven days. Only a small fraction of a c.c. of N/10 Na₂S₂O₃ was required at any one time except in one case where the interval was six days, 1.51 c.c. being required. The end point was followed each time in a few minutes by the color of free iodine. At the end of eleven days when the experiment was discontinued a total of 5.62 c.c. of N/10 Na₂S₂O₃ had been added. This corresponds to 0.14 millimoles of diiodoacetylene, assuming that all of the iodine formed came from the reaction:

\[
\text{C}_2\text{I}_2 + 2 \text{HOH} + 2 \text{KI} \rightarrow 2 \text{KOH} + 2 \text{I}_2 + \text{C}_2\text{H}_2
\]

The acetone in the bend of the tube was found to give a positive test for acetylene within 72 hrs. from the time the tube was connected to the flask.
2. Hydrolysis of Diiodoacetylene to Acetylene.

A few 0.1 gms. of diiodoacetylene were placed under 2 to 3 c.c. of distilled water (a) in a stoppered weighing tube (b) in a bomb and sealed. The tube in the first case was allowed to stand at room temperature for 10 weeks, and the bomb tube for 3 1/2 weeks before opening. In the case of (a) employing a longer time for the reaction the tube opened with slight pressure and tests with both ammoniacal cuprous chloride and ammoniacal silver nitrate showed the presence of acetylene (red and yellow precipitates respectively of the acetylides soluble in dilute acids).

The contents of the tubes when tested with litmus showed a faint acid reaction and though without apparent action upon potassium iodide solution showed the presence of iodide ion on treating with dilute acid and sodium nitrite in the presence of a globule of carbon disulphide (violet coloration).

3. Reaction 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 about 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 sulphate 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. The excess of iodine monochloride being washed off with water and suction the odor of diiodoacetylene was very evident. The gray mass was now leached out thoroughly with ether, the ether extract decolorized by shaking with sodium thiosulphate solution and dried over anhydrous sodium sulphate. The ether was allowed to evaporate and a muddy white residue of characteristic odor obtained. When taken up in alcohol (warmed to about 50°- 60°) and then diluted with water and cooled, very fine white needles of diiodoacetylene 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 petro ether, b.p. 25°-40°) was added and the mass thoroughly extracted. The ether extract when decolorized by sodium thiosulphate solution, washed with water and dried over anhydrous sodium sulphate, gave nearly pure white crystals of diiodoacetylene when evaporated. The odor of the product even while in solution in the ether was quite noticeable.

4. Reaction of Ammonia upon Diiodoacetylene.

(a) In Aqueous Solution.

A 0.1 gm. sample of diiodoacetylene was introduced into a bomb tube and covered with about 2 c.c. of concentrated 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 8-10 hours. As a result of this treatment the diiodoacetylene 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°C 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 diiodoacetylene) was removed to a clay plate and dried. It was not explosive by concussion. No nitrogen iodide had apparently been formed.

(b) In Ether Solution.

About 0.5 gm. of diiodoacetylene, dried over calcium chloride, was put into solution in 5 c.c. of ether in a small U-tube and cooled to -8°C 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 tube was raised from the freezing mixture and warmed up by the hand it was noted that bubbles would arise slowly from the particles of this solid. 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 diiodoacetylene 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 diiodoacetylene in anhydrous ether under gentle reflux. For about 1/2 hour the only apparent change was the yellowing of those crystals of diiodoacetylene 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 diiodoacetylene. 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.

In still another experiment where an ether solution of diiodoacetylene saturated with dry ammonia at -8°C had been sealed in a bomb into which a test tube holding some acetone had been placed, a still different result was obtained. Nothing occurred apparently for about 10 days, the bomb being at room temperature. At about 12 days free iodine appeared to be dissolved in the ether and a brown precipitate forming. After three weeks however the precipitate was obscured by a reddish-brown viscous liquid beneath the now nearly colorless ether layer. No further change being apparent the bomb was cooled and opened with the precautions mentioned above.
The acetone solution in the test tube was diluted and tested directly for acetylene. Heavy precipitates of both Cu₂C₂ and Ag₂C₂ soluble in dilute acid were obtained by the use of ammoniacal cuprous chloride and silver nitrate respectively. Yet the examination of the brown liquid and the solid in suspension in it failed to give any explosive substance such as NH₃·N₂."}

5. Action of Chlorine upon Diiodoacetylene.

Although other solvents such as ethyl bromide, chloroform, petroleum ether and liquid chlorine itself were all found to serve, by far the best solvent in which to chlorinate diiodoacetylene was 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 decomposed it was rarely found advisable to attempt to chlorinate more than a few grams of diiodoacetylene at a time. In a typical preparation, where the material was not to be used for analysis from 3 to 8 gm. of diiodoacetylene in from 10 to 20 c.c. of ethyl chloride was employed. If the product was to be used in an analysis only a few 0.1 gms. of diiodoacetylene in 1 to 2 c.c. of solvent were used.

The solution of diiodoacetylene in ethyl chloride was poured into a large test tube provided with a two hole stopper and delivery tube (funnel-shaped end) and exit tube for the chlorine. The apparatus was cooled down to from -15° to -10° in either ice and hydrochloric acid or in a salt freezing mixture and then chlorine (washed with water and bubbled through concentrated sulphuric acid) 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 five to twenty 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 diiodoacetylene, iodine monochloride or hexachlorethane, 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 minutes to one half hour. 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 the 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 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
21. 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 N/10 sodium thiosulphate. Results:

<table>
<thead>
<tr>
<th>Wgt. Sample taken</th>
<th>c.c. of N/10 Na₂S₂O₃ required</th>
<th>Theory, c.c., % oxidizing chlorine for Cl₂I, CCl=CCl</th>
<th>N/10 Na₂S₂O₃</th>
<th>% oxidizing chlorine found</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. 0.5677 gm.</td>
<td>25.92</td>
<td>27.04</td>
<td>16.2</td>
<td>16.88</td>
</tr>
<tr>
<td>II 0.2039 gm.</td>
<td>9.45</td>
<td>9.71</td>
<td>16.43</td>
<td>16.88</td>
</tr>
</tbody>
</table>

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 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 bomb was resorted to, the odor of diiodoacetylene 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 diiodoacetylene. In all twelve analyses were attempted.

The percentage of chlorine was best determined by obtaining the ratio Cl₂: C₂I₂ in the case where a small amount only 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 gm. of diiodoacetylene introduced and weighed. About one c.c. 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 diiodoacetylene 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 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 part 6, experimental) that no change of volume occurred during the
change to the liquid.

0.3188 gm. of C₂I₂ gave 0.4719 gm. of the iodochloride. Hence, moles of C₂I₂ = moles of Cl₂

\[
\frac{0.3188}{0.4719} = \frac{0.1531}{0.3150} \quad \text{or} \quad 1:1.945.
\]

Total chlorine found = 32.44%; theory 33.8%.

From the results of the titration and the percent of chlorine absorbed, also the fact that the compound gives diiodoacetylene again with alcoholic potash, we may conclude that diiodoacetylene under the conditions given combines with four atoms of chlorine, only two of which are combined to iodine and may be given up readily. This gives the structure:

\[ \text{Cl} \quad \overset{\text{I}}{\text{C}} = \overset{\text{C}}{\text{I}} \quad \text{Cl} \quad \text{Cl} \]

This was partly confirmed also by the results in the case of one Carius analysis: - 0.1267 gm. gave 0.3147 gm. of silver halide; theory, 0.3150 gm.


That the spontaneous decomposition of iodochloride-1-chloro-2-2-chloro-iodoethylene was a rearrangement was shown by the fact that no increase or decrease of 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) pipette 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-iodoethylene 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 two 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 thiosulphate caused iodine to precipitate at first and then 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 product of several decompositions was combined and fractionated three times; once at 42-45 mm. in a 15 c.c. Claisen bulb and twice at 25-26 mm. using a 5 c.c. Claisen. Some iodine monochloride and much free iodine came over at first and the fraction boiling at 80°-90° (25mm) 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 the 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 three lower fractions gave only a few drops of dark liquid, b.p. 80°-84° under 32 mm.

The chief product obtained at 127.5°-128.5° (25-26 mm.) was
analysed at once by the method of Carius: 0.2381 gm. gave 0.5109 gm
AgCl - AgI which heated in a stream of chlorine lost 0.1241 gm.

<table>
<thead>
<tr>
<th>Found:</th>
<th>Theory for C₂I₂Cl₂:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine 72.32%</td>
<td>72.94%</td>
</tr>
<tr>
<td>Chlorine 19.98%</td>
<td>20.34%</td>
</tr>
</tbody>
</table>

The compound under atmospheric pressure boils with decomposition at 243.5° (cor.) 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 diiodoacetylene.

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

7. Reaction of Chlorine upon Symmetrical Dichloro-diiodoethylene.

In a preliminary trial 1-2 dichloro-1-2 diiodoethylene, dissolved in a little petroleum ether was found to give with chlorine pale yellow needles of a compound to all appearances the same iodoiodochloride as was prepared from diiodoacetylene. It was too unstable to weigh and reacted with potassium iodide solution liberating iodine. A sample of 1-2 dichloro-1-2 diiodoethylene was introduced into the glass-stoppered tube used in experiment #5.Employing the same method as before, the weight of chlorine taken up at -15° to -10° in ethyl chloride as a solvent was determined:
0.1410 gm. of 1-2-dichloro-1-2-diiodoethylene gave 0.1704 gm. of the yellow compound. Hence ratio Cl₂:ClI=ClCl = 1.025:1.0 or chlorine taken up = 17.26%; theory = 16.88%.

That the mole of chlorine had combined to iodine to give the iodochloride: Cl₂I.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 gm. acting on potassium iodide solution liberated iodine equivalent to 5.02 c.c. of N/10 sodium thiosulphate. Theory for Cl₂I.CCl = CClI = 5.27 c.c. Hence oxidizing chlorine, found: 16.1%, theory for iodochloride-1-chloro-iodoethylene: 16.88%.

8. Addition of Iodine Trichloride to Acetylene.

From 20 to 30 c.c. of a solution of iodine trichloride in concentrated hydrochloric acid, prepared preferably by the method given in experiment #9, were diluted with two volumes of ice-water. This solution was then divided among each of three 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 sulphate 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 crop.
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-iodoethylene by the action of the iodine monochloride being produced.

\[
\text{ICl}_3 \rightarrow \text{ICl} + \text{Cl}_2
\]

\[
\text{HClO} + \text{Cl}_2 \rightarrow \text{HClO}_2 + \text{HCl}
\]

Attempts to filter again and get out a third crop of the crystals always resulted in the production of chloro-iodoethylene instead. The latter was proven by both b.p. (119° - 120°) and analysis. The iodidechloride from the two crops of crystals was combined on the filter and washed quickly with ice water three 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 chlorino. 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 ICl₃ (containing ICl) made by direct union of the elements. The same decomposition point was given for their crude product by Thiele and Haakh, and 75° as the true melting point for their recrystallized product. A melting point taken upon freshly prepared crystals was found to be 80° without decomposition. But in another trial where crystals (prepared 48 hrs. previously) were used they were found not to melt but to sublime with decompo-
sition at 93.5° to 94°. The compound was soluble in ether, benzene and methyl alcohol with but little decomposition for 24 hrs. or more but could not be 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 analyse the crystals both by combustion and by the method of Carrius. 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 two boats of molecular silver. Imperfect absorption of the halogens was otherwise found to occur. The method of Dennstedt 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.

Combustion: (I) 0.2260 gm. gave 0.0194 gm. of water and 0.0792 gm. of carbon dioxide. (II) 0.1984 gm. gave 0.0147 gm. water and 0.0663 gm. carbon dioxide. Hence:

\[
\begin{align*}
\text{C:} & \quad \text{H:} \\
\text{Found, I} & \quad 9.32 \quad 0.952 \\
\text{" II} & \quad 9.12 \quad 0.82 \\
\text{Calculated,} & \quad 9.25 \quad 0.77
\end{align*}
\]

Carius determination: 0.2529 gm. gave 0.6409 gm. AgI + AgCl, which in a stream of chlorine lost 0.0877 gm. Hence:

\[
\begin{align*}
\text{I:} & \quad \text{Cl.} \\
\text{Found,} & \quad 48.1\% \quad 40.7\% \\
\text{Calculated} & \quad 49.0\% \quad 41.1\%
\end{align*}
\]
In several cases when samples of iodochloride-2-chloroethylene were being weighed in small weighing tubes 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 gm. Gradual loss of weight kept occurring. 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 1 milligram or only 0.27%. This led to the conclusion that the change was a rearrangement and not a decomposition into chlorine and chloro-iodoethylene as reported by Thiele and Haakh. To confirm this, samples were allowed to "decompose" in a closed tube over water (method as above in experiment #6). No increase in volume accompanied the change.

A number of samples of iodochloride-chloroethylene were prepared, carefully washed and dried between filters and allowed to decompose in tubes immersed in cold water. 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 the typical reactions with alkali and sodium thiosulphate. The iodine monochloride represented nearly one-fourth the volume of the products. Boiling point determinations made on the lower layer after its decolorization by sodium thiosulphate 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 decomposition occurred. Refractionation showed two liquid products present, one of sharp odor and lachrymating properties boiling about 51°-55° (25 mm.)
and one boiling at 94°-95° (25 mm.) of pleasant odor resembling that of the lower alkyl halides. In addition to these traces of a volatile solid coming off as long white needles at room temperature were found. Analyses of these products were not conclusive. The boiling point of pure chloro-iodoethylene is 27°-28° under 23 mm. pressure, hence it is not one of the chief products even of the decomposition of iodochloride-chloroethylene.


Since the usual methods of preparing iodine trichloride gave so large a proportion of iodine monochloride as to render the reagent useless in the above experiment, 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:

\[ 3 \text{HIO}_3 + \text{I}_2 + 15 \text{HCl} \rightarrow 5 \text{ICl}_3 + 9 \text{H}_2\text{O} \]

10.56 gm. of iodic acid (3 moles) and 5.08 gm. of resublimed iodine (1 mole) were ground up finely and thoroughly mixed. About twice the theoretical volume of C.P. hydrochloric acid (sp. gr., 1.19), usually 46.6 c.c., 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 c.c. of the solution is theoretically equivalent to 0.5 gm. of ICl3. Iodine trichloride in high concentrations of hydrochloric acid may be kept indefinitely.
31.

10. Iodine Monochloride from Nitrogen Iodide.

As being of theoretical interest iodine monochloride was prepared in hydrochloric acid solution by the reaction of concentrated hydrochloric acid upon nitrogen triiodide. Finely powdered iodine (1.27 gm.) in a Gooch crucible was digested for several minutes with ammonium hydroxide (sp.gr., 0.90). The excess 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 c.c. of concentrated hydrochloric acid a sharp crackling noise gave evidence of a somewhat violent reaction. Ammonium chloride and iodine came off along with the fumes of hydrogen chloride. 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 thiosulphate, 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-iodoethylene in odor and appearance (although not enough for a b.p. was obtained). The solution undoubtedly contained considerable iodine monochloride. The reaction was tried out merely to show that the iodine of nitrogen triiodide 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:

\[ \text{NH}_3\text{.NI}_3 + 5 \text{HCl} \longrightarrow 3 \text{ICl} + 2 \text{NH}_4\text{Cl} \]
IV. Summary.

1. Diiodoacetylene liberates iodine from aqueous solutions of iodides and acetylene is regenerated.

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

3. The conduct of both iodoacetylene and diiodoacetylene is best explained by the assumption that these compounds contain positive iodine, and that the structures are respectively H-C≡C-I and I-C≡C-I. These structures seem at present much more probable than the acetylidene structures, IHC=O and I₂C=O.

4. Biltz has reported that chlorine acts upon diiodoacetylene giving hexachloroethane. It has been shown that the primary product formed by the action of chlorine upon diiodoacetylene is iodochloride-1-chloro-2-2-chloro-iodoethylene, Cl₂ICCl=CClI.

5. Iodochloride-1-chloro-2-2-chloro-iodoethylene decomposes very easily giving chiefly symmetrical dichloro-diiodoethylene, CICl=ClICl and iodine monochloride, also probably trichloro-iodoethylene.

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

   Am. Chem. Jr. (1900) Vols. 23,24
   " " " " (1913), 767
   " " " " (1917), 905
4. V. Meyer and Pemsel: Ber. 29, 1411 (1896)
5. Plimpton; Jr. Chem. Soc. 41, 392 (1882)
7. Biltz: Ber. 30, 1202 (1897)
8. Thiele and Haakh: Ann. 369, 135 (1909); Centr. (1909)II, 2071
9. Thiele and Haakh: loc. cit., page 150
10. Nef: Ann. 298, 343
11. Berend: Ann. 135, 266
Acknowledgment.

The writer desires to express his appreciation to Professor W.A. Noyes for the constant aid and many helpful suggestions which have been accorded him in the direction of this work. No results of the work itself can compare in value to the writer with the memory of the hours spent in the laboratory with so renowned yet so kindly an investigator.
Vita.

The writer was born in Miami County, Ohio, Aug. 29, 1887. He attended the public schools of Piqua, Ohio, Cleveland, Ohio, and Crawfordsville, Indiana, and received his A.B. degree at Wabash College in June 1909. He was a graduate student in Chemistry at Ohio State University in the Summer of 1912 and at the University of Illinois from June 1914 to June 1919. The degree of M.S. was conferred upon him by the University of Illinois in February, 1918. He has had six years of experience as a teacher in secondary schools and served as Instructor in General and Analytical Chemistry at Wabash College in 1912-13 and as Assistant in Organic Chemistry at the University of Illinois in 1916-17 and 1917-18 and the Summer Session of 1918. During the past year, 1918-19 he has held a Fellowship in Chemistry at the University of Illinois. The writer has the honor of being a member of the honorary chemical fraternity, Phi Lambda Upsilon, and of election to membership in Sigma Xi.