A STUDY OF THE REACTION
OF HYDROGEN IODIDE WITH SILICON

THESIS

by

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# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I  Previous Work on the Preparation of the Iodides of Silicon</td>
<td>1</td>
</tr>
<tr>
<td>II Introduction</td>
<td>3</td>
</tr>
<tr>
<td>III Preparation of Hydrogen Iodide</td>
<td>4</td>
</tr>
<tr>
<td>IV Figure I. Apparatus Used in the Reaction between Silicon and HI</td>
<td>6</td>
</tr>
<tr>
<td>V  The Reaction of Silicon with HI</td>
<td>7</td>
</tr>
<tr>
<td>VI Figure II. Revised Apparatus for the Reaction of Silicon with HI</td>
<td>10</td>
</tr>
<tr>
<td>VII General Conclusions from the Reaction between Silicon and HI</td>
<td>13</td>
</tr>
<tr>
<td>VIII Reaction of Calcium Silicide with HI</td>
<td>14</td>
</tr>
<tr>
<td>IX Figure III. Apparatus Used for the Reaction of Calcium Silicide with HI</td>
<td>15</td>
</tr>
<tr>
<td>X  Figure IV. Apparatus for Distillation of the Crude Product of the Reaction</td>
<td>19</td>
</tr>
<tr>
<td>XI The Purification of Silicon Tetra-iodide</td>
<td>21</td>
</tr>
<tr>
<td>XII Figure V. Apparatus for Fractionation of Crude Silicon Tetra-iodide</td>
<td>22</td>
</tr>
<tr>
<td>XIII Figure VI. Apparatus for Purification of SiI₄</td>
<td>23</td>
</tr>
<tr>
<td>XIV Summary</td>
<td>28</td>
</tr>
<tr>
<td>XV Bibliography</td>
<td>29</td>
</tr>
</tbody>
</table>
Previous Work on the Preparation of the Iodides of Silicon

The first attempt to prepare an iodide of silicon was made by J. J. Berzelius, in 1824. He ignited silicon in iodine vapor, and reported that there was no action. In 1857 H. Buff and F. Wöhler studied the action of dry HI on red hot silicon, and they obtained a product which Friedel, in 1868, showed to be a mixture of silicon tetraiodide and tri-iodo silane (silico iodoform). The yield of silico iodoform was less than 8%, and was found by Friedel to be increased by passing a stream of hydrogen, along with the hydrogen iodide, over the heated silicon. Friedel fractionally distilled the product of this reaction, thus separating the iodoform from the tetraiodide. He isolated the tetra-iodide in pure condition, by passing iodine vapor, entrained in CO₂, over red hot silicon, and by purifying the sublimate by shaking it with carbon disulphide and mercury, and distilling the liquid in a stream of CO₂. His product was tinged slightly yellow. In 1869 R. Mahn obtained a mixture of SiI₄ and HSiI₃ by the reaction of silicon hydride with iodine vapor. In the same year C. Friedel and A. Ladenburg reported the preparation of Si₂I₆, by the heating of SiI₄ with finely divided silver, in a sealed tube at 300° for several hours. Upon heating Si₂I₆, they found that Si₂I₄ was formed. In 1889 L. Gattermann carried out the reaction between HI and Si, using crude silicon which he ob-
tained by reducing quartz sand with magnesium. He reported that the crystals of the tetra-iodide are at first colorless, but soon turn red, due to the deposition of iodine.

(13) A.J. Besson, in 1891, prepared SiI₄ by passing a mixture of silicon tetra-chloride and iodine vapor over heated silicon. In 1896 Combes tried the effect of substituting copper silicide for silicon, in the reaction with HI, and he reported that no silico-iodoform was formed. In 1907 M. Guichard prepared the tetra-iodide by passing iodine vapor over silicon at 500°C, under reduced pressure. In 1908 O. Ruff found that the solid product formed when HSiI₃ is heated to 300°C is mostly SiI₄. Ruff obtained his HSiI₃ by the action of HI on SiNH, in cold carbon disulphide solution, or by heating SiH(NH₃H₅)₃, in benzene solution, with HI.

In all of these preparations the yields were low, and no very precise details concerning the necessary conditions were given.
Introduction

Back in 1857 Buff and Wöhler, and a few years later Besson and Fournier, prepared a mixture of SiBr₄ and HSiBr₃ by passing HBr over red-hot silicon, and the latter workers found that less than 2% of the product consisted of HSiBr₃. No further experimentation on this method of preparing the bromides of silicon was tried until, in 1930, W. C. Schumb and R.C. Young studied the effect of temperature on this reaction, and, by carrying out the reaction at a lower temperature, they succeeded in increasing the yield of the bromoform to as high a value as 66%. With the similarity between this reaction, and that of HI on silicon in view, this research was initiated. The object was, at first, to try the effect of lowering the temperature on the products formed in the reaction.

With the use of HI in place of HBr, two differences will be noted at the offset. First, HI would be expected to require a higher temperature in its reaction with silicon than would HBr. Secondly, the rate of decomposition of HI increases rapidly with increased temperature, and this would tend to make the reaction more difficult to carry out. Another factor is the ease of decomposition of the products. The iodides of silicon are much more easily decomposed than are the corresponding bromides. These factors all had to be considered.
EXPERIMENTAL

Preparation of HI

The method which proved most satisfactory for the preparation of hydrogen iodide was by the hydrolysis of a mixture of red phosphorus and iodine. The apparatus used for this preparation is shown in the first part of figure I. It was necessary, at the start, to evacuate the system, and then to pass in hydrogen, since the iodides of silicon are all oxidized by air. A mixture of red phosphorus and iodine, in the proportions calculated for the formation of PI₅, or better with even a slight excess of iodine to inhibit the formation of phosphonium iodide, was introduced through the opening at A, which was then sealed. A stream of dry hydrogen was introduced at O, and passed out through the drying tube L, in order to prevent any back flow of air into the system. Flask B was cooled with ice-water, and water was dropped in through the dropping funnel C, at such a rate that as little gas as possible was formed. After the theoretical amount of water for the hydrolysis of PI₅ had been added, the flask was fanned with a bunsen burner, and the gas evolved slowly passed through the U-tube D, which was filled with glass wool, and cooled with alcohol-dry ice to -35°, thus serving to remove moisture and any other less volatile products than HI, which may have been formed in the reaction. The gas was then condensed in E, which was cooled to -78°C with dry ice-alcohol.
The HI solidified to a partially opaque colorless solid, and it was necessary to intermittently raise and lower the Dewar flask around E, to completely condense the gas without clogging the tube with the solid formed. After the gas had all been driven over, stopcock P was closed, and the HI generator was cut off from the rest of the system. This method of preparation of HI proved to be very satisfactory. Each preparation produced about 170 g of the pure compound, thus conforming with a yield of about 68%.
Apparatus Used in the First Attempt to
Prepare Silico-iodoform.

Fig. I
SILICON and HI

Hydrogen iodide, together with hydrogen gas, was swept through the P₂O₅ tube F, into the reaction tube, which contained small chunks of crystalline silicon (containing a small percentage of Fe). The tube was heated electrically to the temperature desired. The products of the reaction were condensed in containers H and K, and the hydrogen and the unused HI were vented through a CaCl₂ drying tube into the hood. In the first runs variations in the following conditions were tried: (a) the temperature, (b) the rate of flow of HI, (c) the rate of flow of hydrogen. It was found that fresh silicon was not perceptibly attacked below 500°. At this temperature a bright red solid was deposited in the tube just beyond the furnace. After a nine hour run, during which time about 100g of HI were passed over the silicon, it was noted that the temperature of the reaction tube could be lowered to 460° without an appreciable loss of HI. At this temperature, as before, the product appeared to be a red solid, and there was no perceptible sign of the formation of any liquid. Since HSiI₃ begins to decompose at as low a temperature as 150°, it was thought that any formed might have been decomposed in the hot tube. The speed of volatilization of the HI was increased, but this only caused the loss of HI, as shown by the fuming at the exit tube. The rate of flow of the hydrogen was increased, in the hope that
this would cause the products of the reaction to be swept out of the hot area more quickly. This, apparently had little effect.

Solidification of the tetraiodide in the tube caused difficulty by clogging. At first, as soon as a quick enough deposit was formed, it was melted down the tube with a luminous flame, but this method was not satisfactory because the temperature of the burner could not be regulated, and there was danger of causing further decomposition of any iodoform which may have been formed. Since the tetraiodide melts at 120.5°, and decomposition of the iodoform does not begin below 150°, it was thought that clogging could be prevented without danger of decomposing the iodoform, by winding a heating coil around the tube at N. By keeping this at 125° no solid product should remain in the tube. This proved to be unsatisfactory, since the tetraiodide packed around the tube K. It was thought advisable to revise the apparatus to eliminate this difficulty.

Although in this first run, fractionation of the product could not be carried out, it will be well to state briefly the purpose of the two sample tubes, and the magnetic breaker system. The apparatus was made with the idea of sealing off the tube, just beyond the furnace and melting all of the product into container K. Dry
carbon disulfide and mercury were to be admitted through the funnel M, and the contents of the flask shaken until, due to the removal of the iodine, the red color would disappear. Then by decanting the liquid into H, sealing the distillation apparatus on at J, and then breaking the inner seal, a fractionation of the product could be carried out. However, the glass had been so badly attacked by the silicon compounds that, in sealing off the tube, it cracked, and it was necessary to seal the tube in some other way. A tight cork stopper was sealed on with pycene, and carbon disulfide and mercury introduced. After this had stood for twenty-four hours, the stopper blew, and the contents of the tube were scattered. A cause for this was not known, since the tube was at no time above room temperature and was completely sealed from air and moisture.

The apparatus shown in Fig. 2 was designed for the purpose of preventing clogging by the use of tubing of a sufficiently large diameter. The flask H served for the collection of the product, and the unchanged gases passed up through the drying tube K into the hood. By means of the inner seal at L, the distillation apparatus could be sealed on without admitting air to the system. The silicon was kept at 400° for three hours, during which time an inappreciable amount of product was formed.
The Revised Apparatus for Studying the Reaction of Hydrogen Iodide with Silicon.
The temperature was raised to 430° and after a half hour a few drops of a pale lavender liquid condensed on the walls of the flask. The furnace temperature was lowered to 420° with little loss of HI, but the rate of flow of the HI had to be very slow. In spite of the wide tubing, the formation of the solid still caused difficulty. A thin packing of red crystals formed across the whole diameter of the tube, and it was necessary to melt these down at least every two hours to prevent clogging. The amount of liquid formed was very slight. As the emerging gases bubbled through water, the tube became coated with a white substance which must have been due to the hydrolysis of some silicon compound. Occasionally enough of this was formed to clog the tip of the tube. Just what the silicon compound causing this could have been is questionable, since it had to pass through the solid material in the drying tube. Possibly minute amounts of silane were formed.

The furnace temperature was gradually lowered to 400°, and although this necessitated slowing up the rate of flow of the HI still further, it caused no appreciable loss. The rate of flow of hydrogen was increased to about five bubbles a second (from a two mm. tube just under the surface of the water), so that any silico-iodoform formed could be swept out of the hot tube as quickly as possible.
By decreasing the rate of volatilization of HI, the temperature could be lowered to 380°, but at that temperature it required thirty-six hours to volatilize 170 g. of the HI. The color of the solid subliming from the furnace appeared much lighter than previously, and towards the end of the run a trace of almost colorless solid appeared.

The neck of the flask was sealed off close to the furnace, and mercury and dry carbon disulfide were introduced through the funnel at J, and the contents of the flask were shaken until the red color due to iodine was replaced by the greenish yellow color of the mercurous iodide formed. The apparatus for distillation showed in Fig. 2b, was then sealed on, evacuated, and the inner seal broken. The carbon disulfide was distilled in a high vacuum into the trap P, which was cooled with a dry ice alcohol mixture. The remaining contents of the flask were then heated with an oil bath, The first fraction, a colorless liquid, began to come over when the outer bath temperature was about 110°, and this fraction was collected in the tube M. As soon as the liquid fraction had all passed over, the distillation was interrupted and the system brought to atmospheric pressure by passing in dry CO₂. In sealing off this sample tube, a very feeble explosion occurred and the product was lost. Apparently
enough of the iodoform adhered to the walls of the tube, to be suddenly decomposed by the oxygen flame. All that remained in the tube was a coating of iodine covering the walls. About five cc. of the iodoform, amounting to some 16 g., had been prepared. The remainder of the product proved to be the tetraiodide. The apparatus was tilted and tube N was cooled with a Dewar. The flask was heated strongly with a burner and a mixture of the tetraiodide and some mercurous iodide was driven over. The solid at first appeared yellowish, and evidently contained most of the mercurous iodide. After this had passed over a pale red solid began to appear, and, by the end of the distillation, the solid appeared bright red. Evidently decomposition had again occurred, thus setting free iodine. Almost 300 g. of crude tetra-iodide were collected. This was put aside to be later purified.

General Conclusions from the Reaction between HI and Silicon

When HI, entrained in hydrogen, is passed over heated silicon, no reactions occur below 380°C, and at this minimum temperature the reaction is very slow. The product formed is almost entirely solid, but it is possible to isolate a small amount of liquid, HSiI₃, by a crude fractionation.
THE REACTION OF HYDROGEN IODIDE WITH CALCIUM SILICIDE

In order to obtain higher yields of the iodoform, a method which would enable a reaction at a lower temperature was sought. It has been known for some time that, in general, certain silicides may undergo reactions similar to those of silicon, but at a lower temperature. In 1896 Combes tried the effect of replacing silicon by copper silicide, which he then reacted with HI. He found, however, that in this case no iodoform was formed. No other record of the trial of silicides in this reaction was found in the literature. It was decided to make a trial run with commercial calcium silicide. Since clogging of the tube had caused difficulty in previous runs, a method was devised whereby the product was kept at a temperature just above the melting point of the tetra-iodide, but still below the initial decomposition point of the iodoform. For this purpose the apparatus shown in Fig. III was employed. The reaction tube A was placed vertically, in order that the heavy silicon compounds would drop down more quickly through the heated tube, and there would therefore be less opportunity for their decomposition. The flask C was surrounded by an oil bath at 125°C, and this extended almost up to the electric sleeve, so that solidification of the product would not occur at any point. The unchanged gases passed out through the drying tube E, into the hood. The purpose of the inner
The Reaction of Hydrogen Iodide with Calcium Silicide
seal at E was, as before, to enable the distillation apparatus to be sealed on without the admission of air. The calcium silicide was broken up into chunks about $\frac{1}{2}$ sq. cm. in cross section.

No reaction was found to occur until the temperature reached $340^\circ$. At this temperature almost colorless droplets appeared to condense on the walls of the tube, and the product (all liquid at that temperature), light red in color, ran down into the bottom of the flask. After a ten hour run the oil bath was allowed to cool, whereupon most of the product solidified to a light reddish solid. However droplets of an almost colorless liquid still appeared on the walls of the side tubes. The number of these droplets increased during the course of the run, and some passed through the stopcock up into D. After standing for some time the droplets appeared to be partially decomposed, as seen by the appearance of small globules of iodine. Calculations had been made in order to ascertain approximately how much HSiI$_3$ could be lost by using the hot oil-bath, and it was found that the amount lost would be negligible. However, by the number of droplets condensed up in D, some other factor must enter. During the remaining runs, a current of cold air was directed down on the tube just below the stopcock, to condense any vapor which might be carried up into the tube.

After the reaction had been run for about ten hours,
the temperature was gradually lowered to 300° without loss of HI. The rate of flow of hydrogen was decreased to about one-fifth that of the previous runs. The reasons for this were: (1) because of the upright position of the reaction tube a fast stream of hydrogen was not necessary to force the product through the tube more quickly, (2) on account of the hot bath the amount of product passing through uncondensed would be increased considerably with an increase in the rate of flow of hydrogen. As the reaction was continued the rate with which the HI could be passed without loss became much slower. About forty-eight hours were required to use up 170 g. of HI. This slowing up of the reaction was to be expected since the surface was being coated with calcium iodide, and this was decreasing the amount of active silicide.

The hydrogen was replaced by dry CO₂, and flask C was sealed off at the point B, which had been constricted to help the sealing. The stopcock below D was closed and the tube was cut off above the funnel. Droplets which were on the walls of the tube just cut off did not spontaneously burst into flame when exposed to the air, as did those of the bromoform, but upon gentle warming they ignited with a pop. Although it would be expected that silico-iodoform would be less stable than the corresponding bromine compound, it is
also less volatile, and this may account for the difference noted. Mercury and carbon disulfide were admitted as before through D, and the contents of the flask were shaken until iodine free.

The apparatus for distillation, which was sealed on at F, is shown in Fig. 4. The carbon disulfide distilled in a high vacuum, was condensed in trap H, which was then disconnected. The crude product was distilled at low pressure from an oil bath. Only a few drops of the liquid corresponding to the iodoform were collected. The main part of the product began to distil when the outside bath temperature was 180° and this consisted of a mixture of Hg₂I₂, SiI₄, and a trace of iodine, as shown by the red tinge which persisted. The temperature of the bath had to be raised to 250° before the volatile product had completely distilled. The material left in the flask consisted of mercury and a black deposit. It was thought that possibly a small amount of Si₂I₄ might be formed from heating the iodide with mercury. No evidence of this could be seen. A separation of the Hg₂I₂, SiI₄, and I₂, by distilling from one tube into the next, was only partially successful, and it was thought at the time that by increasing the number of distillations by the use of more tubes, the method might prove successful.
Distillation of the Crude Product from the Reaction of Hydrogen Iodide with Calcium Silicide
From the results of the reaction between HI and calcium silicide, it can be seen that the temperature of the reaction may be lower than that of HI on silicon itself. With silicon, the more attacked the element is, the greater is the ease of the reaction. In the case of the silicide the ease of the reaction increases for a short time at the start but soon begins rapidly to decline due to the coating of the calcium iodide formed. The use of calcium silicide for this reaction had not been previously reported in the literature. The proportion of the iodoform to the tetraiodide was found to be very small, even at the lowest temperatures which could be employed.
The Purification of Silicon Tetraiodide.

The apparatus shown in Fig. 5 was devised with the hope of effecting a separation of Hg₂I₂, SiI₄, and I₂, of the crude mixture previously obtained, by subliming the mixture from one tube into the next until separation was complete. Since there is an appreciable difference in boiling points and consequently in vapor pressures, it was expected that this method would serve, and consequently a dozen sample tubes were sealed on. The oblique tube A was for the introduction of the sample which was to be fractionated. It was found however that separation by this method could not be effected, and another had to be resorted to.

The apparatus which was used in a further attempt to obtain the tetraiodide in pure condition is shown in Fig. 6. At first, in place of the stopper with the thermometer there was inserted a thimble filter, as shown in Fig. 6a. Carbon dioxide was passed through the drying tube D, and out through the opening at A. While this current of gas was allowed to sweep through a sample of the crude tetraiodide was opened, shaken with mercury and carbon disulfide until iodine free, and then quickly poured through the filter into A. The mercurous iodide and excess mercury were thus removed and the solution in B appeared colorless. The filter
Fig. V

Purification of Silicon Tetraiodide

12 tubes in all
Purification of Silicon Tetrabromide

Fig. VI
was removed, and the stopper with the thermometer was introduced and made tight with shellac. The carbon disulfide was removed as before under a vacuum. The solid remaining was at first almost colorless, but during distillation into the sample tubes it again became colored a pale red orange, apparently due to slight decomposition. Purification by distillation thus did not prove satisfactory.

A sample of the crude tetraiodide was again freed of iodine, and the tube containing the clear filtrate was immersed in a dry ice alcohol bath. The whole solution immediately formed a colorless solid, so that it was impossible to decant the carbon disulfide from the solid iodide. This operation was carried out in the absence of air and moisture by the use of a large metal container through which was passed a continuous stream of dry oxygen-free carbon dioxide. No fuming occurred during the filtration. It was observed that the cooled sample originally a pure white began to color lavender when removed from the dry ice. Evidently decomposition was occurring. Since both air and moisture had been excluded from the sample, it was conceived that the tetraiodide might be photosensitive, and this was though not improbable, since this property is characteristic of many iodides. Although no mention
of this had been made in the literature, Gattermann reported that the colorless crystals soon turned red due to the deposition of iodine.

Another sample of the tetraiodide, frozen with carbon disulfide in a similar manner, was kept in dry ice in the dark for twelve hours. At the end of this time the sample still appeared to be colorless. It was then allowed to come to room temperature, still in the absence of light, and the end of an additional twelve hours showed no decomposition. When it was put into diffused light it soon began to color, and this occurred very rapidly in direct sunlight. The same effect would have been observed if a trace of moisture had been present, since the HI formed by the hydrolysis of the iodide would decompose in the presence of sunlight. However with the precautions taken to exclude air and moisture it would be impossible for sufficient moisture to have been admitted to allow the deposition of iodine to continue for an appreciable length of time. From the large amounts of iodine gradually formed from one of these sealed samples, it was evident that photochemical change was taking place.

The method whereby pure crystalline silicon tetraiodide was finally obtained consisted in removing the carbon disulfide from the colorless solution (pre-
pared as previously explained) at room temperature, in the absence of air, by the use of a high vacuum. The metal container used previously was again employed, and it was kept covered as much as possible of the time, thereby keeping out most of the light. The samples obtained were a very pale yellow,—almost colorless,—and well crystallized. When left in the dark these remained unchanged indefinitely (kept ten days thus far). One of these samples, well sealed, was exposed to the sunlight and immediately began to turn brown, with the separation of iodine. This continued to separate out until the solid appeared to be a dark brown. When half of a tube containing some tetraiodide was covered with a piece of black paper, and the tube then exposed to sunlight, decomposition in the exposed portion of the tube was evident, while that part which was covered remained practically unchanged.

Rough qualitative tests on the solubility of silicon tetraiodide in various organic solvents were made. The literature reports the solubility of the compound in carbon disulfide and benzene. As would be expected, the solubility in toluene and in xylene is about the same as that in benzene, and less than that in carbon disulfide. The iodide was found to be less soluble in carbon tetrachloride and in chloroform than in the disulfide, and to be only slightly soluble in
petroleum ether. It was found that the almost colorless solid obtained by the evaporation of carbon disulfide could be washed with carbon tetrachloride, and the liquid decanted from the crystalline solid, which was still tinged a very pale yellow.

An attempt was made to seal off a sample tube which had been constricted to facilitate this process. Although the walls of the tube appeared to be clean, a trace of the iodide must have coated them, since, as soon as a flame was applied, iodine vapors were evolved, and these colored the sample. For this reason the tubes were tightly corked and sealed with wax. The fact that sealing the tubes was not possible was noted by Friedel, who, in 1868, reported that in sealing his tubes decomposition had occurred.
Summary

A study of the reaction of hydrogen iodide with silicon was made. It was found that the lowest temperature at which a reaction would occur was 380°C. Silicon was replaced by calcium silicide, whereby the minimum reaction temperature was lowered to 300°C. The products formed in both cases consisted chiefly of silicon tetraiodide, with a very small amount of silicoiodoform.

Silicon tetraiodide was purified and formed almost colorless, well-defined crystals. It was observed that these crystals are decomposed by light with the liberation of iodine.
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