XXXVII.—*Researches on Silicon Compounds. Part VIII. The Preparation and Constitution of Silico-Oxalic Acids, and the Action of Methyl and Ethyl Alcohols on Trisilicon Octachloride.*

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SILICO-OXALIC acid, $(\text{SiO}_2\text{H})_x$, has hitherto been prepared by two methods only, by neither of which can it be obtained pure.

The first method is that described by Friedel and Ladenburg (*Annalen*, 1880, **203**, 250), and consists in decomposing disilicon hexaiodide, Si_2I_6 , with water, when the following change takes place:

However, the product contains, according to Gattermann and Weinlig (*Ber.*, 1894, **27**, 1943), only 86 per cent. of silico-oxalic acid.

The second method, discovered by Gattermann and Weinlig (*loc. cit.*) consists in decomposing disilicon hexachloride, Si_2Cl_6 , by means of atmospheric moisture at the temperature of melting ice:

Even under the most favourable conditions Gattermann and Weinlig did not succeed in obtaining a product of more than 96—97 per cent. purity.

The displacement of iodine or chlorine atoms (which are directly attached to the silicon atoms) by hydroxyl groups evidently causes such a shock to the unstable molecule that a certain amount of decomposition seems inevitable, no matter how carefully the displacement is carried out. It therefore occurred to the author that a considerably purer specimen of silico-oxalic acid would be obtainable if one proceeded from a derivative of disilicon hexachloride, Si_2Cl_6 , in which the oxygen atoms were already attached to the silicon atoms, as this would not involve such a deep-seated change as is represented by the displacement of a chlorine atom by hydroxyl.

When hexaethylsilicoethane, $\text{Si}_2(\text{OEt})_6$ (T., 1914, **105**, 2871), is treated with water, hydrolysis to pure silico-oxalic acid slowly proceeds in the cold. It is possible by this method to obtain silico-oxalic acid (99—100 per cent.), the action being represented by the equation $\text{Si}_2(\text{OEt})_6 + 4\text{H}_2\text{O} = \text{Si}_2\text{O}_4\text{H}_2 + 6\text{EtOH}$.

The production of silico-oxalic acid by this method also settles conclusively the question of its constitution. For this substance there have been proposed the two constitutional formulæ:

Both formulæ explain fairly well the chemical behaviour of the substance, and up to the present time no clear proof has been given as regards which formula is to be preferred. The subject has attained some importance recently, since in Abegg's "Handbuch der anorganischen Chemie," 1909, **3**, II., p. 351, the formula I is chosen as being the more probable, because it explains very naturally the tendency of the substance to decompose into silica, and it brings the constitution of silico-oxalic acid into line with that of the anhydride of silico-formic acid, which is usually supposed to be $\text{O}:\text{SiH}\cdot\text{O}\cdot\text{SiH}:\text{O}$.

However, formula I cannot be correct, because, as shown below, silico-oxalic acid can be produced quantitatively by the following series of reactions:

The hydrolysis of hexaethoxysilicoethane, $\text{Si}_2(\text{OEt})_6$, into silico-oxalic acid, $\text{Si}_2\text{O}_4\text{H}_2$, proceeds smoothly, without any violent action or the evolution of appreciable amounts of heat, so that it is out of the bounds of probability that any intramolecular rearrangement has taken place during the process of hydrolysis.

The above reasoning does not exclude the possibility that silico-oxalic acid is a cyclic silicon compound, a view which the author will develop in a later communication.

The success of the method of preparing silico-oxalic acid by the hydrolysis of hexaethoxysilicoethane, $\text{Si}_2(\text{OEt})_6$, by means of water led the author to attempt to obtain mesosilico-oxalic acid,

by preparing octaethoxysilicopropane, $\text{Si}_3(\text{OEt})_8$, and decomposing this with water. For this purpose trisilicon octachloride, Si_3Cl_8 , was treated with ethyl alcohol in a manner similar to that employed by the author in the preparation of hexaethoxysilicoethane (*loc. cit.*).

However, instead of obtaining the required substance, it was found that an almost complete decomposition of the molecule occurred, with the evolution of heat, and among the distillation products there was isolated tetraethoxysilicomethane, $\text{Si}(\text{OEt})_4$.

A similar attempt to prepare the methoxy-derivative, $\text{Si}_3(\text{OMe})_8$, by treating trisilicon octachloride, Si_3Cl_8 , with methyl alcohol led to a similar but not so extensive decomposition of the molecule. Evidently merely treating trisilicon octachloride with methyl or ethyl alcohol is sufficient to sever the chain of three directly linked silicon atoms, $\cdot\text{Si}\cdot\text{Si}\cdot\text{Si}\cdot$, in the molecule of trisilicon octachloride, producing decomposition products which do not contain more than two directly linked silicon atoms in the molecule, as was proved by estimating the amount of hydrogen evolved with potassium hydroxide.

This fact furnishes a striking illustration of the decrease in stability occasioned by an increase in the number of directly linked silicon atoms. This is obvious when it is recalled that hexaethoxysilicoethane, $\text{Si}_2(\text{OEt})_6$, containing only two directly united silicon atoms, can be produced directly from disilicon hexachloride, Si_2Cl_6 , merely by treating with alcohol, and that it will bear distillation under diminished pressure without decomposition, whereas the corresponding compounds, having the formulæ $\text{Si}_3(\text{OEt})_8$ and $\text{Si}_3(\text{OMe})_8$, are so unstable that they cannot be prepared by a similar method, and will not bear distillation.

The marked superiority of stability of disilicon hexachloride, Si_2Cl_6 , over trisilicon octachloride, Si_3Cl_8 , has already been commented upon in a previous paper (T., 1914, **105**, 2838), whilst specimens of mesosilico-oxalic acid, $\text{HO}_2\text{Si}\cdot\text{Si}(\text{OH})_2\cdot\text{SiO}_2\text{H}$, prepared by the author by decomposing trisilicon octachloride by atmospheric moisture, were certainly more explosive than similar specimens of silico-oxalic acid.

EXPERIMENTAL.

Action of Water on Hexaethoxysilicoethane, $\text{Si}_2(\text{OEt})_6$.

1.60 Grams (1 mol.) of hexaethoxysilicoethane were placed in a small weighing bottle, and 1.6 c.c. (18 mols.) of cold water were run in from a burette. The oil was slowly decomposed by the water, a white substance gradually separating out, and a very feeble development of heat was observed. After ten minutes the whole had set to a stiff paste. The mixture was kept for forty-eight hours, and was then collected and washed with a little water. The washings were tested for ethyl alcohol by means of the iodoform reaction, and the presence of a large amount was proved, showing that the action of water was a hydrolysing one. A white, amorphous solid was left on the filter, which, after washing with cold water and drying overnight in a vacuum over sulphuric acid, amounted to 0.595 gram, so that 1 gram of hexaethoxysilicoethane yielded 0.37 gram. Another experiment gave 0.372 gram. According to the equation:

1 gram of hexaethoxysilicoethane should yield 0.375 gram of silico-oxalic acid.

The silico-oxalic acid obtained in this way dissolved in aqueous potassium hydroxide to a clear solution, with the evolution of hydrogen. It exploded feebly when scratched, rubbed, or suddenly heated. The hydrolysis was complete in the cold, because on boiling the substance with water in a test-tube fitted with a reflux condenser, no alcohol could be detected in the filtrate. This result was confirmed by some other experiments.

Experiments were now carried out in order to see whether the same final product was obtained when hexaethoxysilicoethane was hydrolysed by means of hot water; 0.9086 gram of the substance was placed in a crucible, treated with a little water, allowed to remain overnight, then heated with water on the water-bath, and finally evaporated to dryness. The drying was completed in the steam-oven. The solid finally obtained weighed 0.3391 gram. Hence 1 gram of hexaethoxysilicoethane gave 0.373 gram. According to theory (see above equation) the yield should be 0.375 gram.

This experiment proved that heating with water does not noticeably affect the nature of the product. Also that the product can be dried in the steam-oven without a noticeable alteration in weight. However, as will be seen immediately, the silico-oxalic acid produced in the cold is considerably purer (as judged by the volume of hydrogen evolved by the action of potassium hydroxide) than the similar product produced by means of hot water.

This is only to be expected from the unstable nature of silico-oxalic acid.

Analysis of the Product of Hydrolysis.—The identity with silico-oxalic acid of the white solid produced by the hydrolysis of hexaethoxysilicoethane was proved by analysis and by measuring the hydrogen evolved with potassium hydroxide.

The silicon was determined as follows: First of all a specimen of silico-oxalic acid was prepared by treating hexaethoxysilicoethane with cold water, and drying in a vacuum over sulphuric acid.

Next the substance was placed in a platinum crucible and covered with ammonia solution. This decomposed the silico-oxalic acid, evolving hydrogen. The addition of ammonia was necessary because a direct heating of the solid may cause a mild explosion, with resulting loss of silica. When the hydrogen ceased to be evolved the whole was evaporated to dryness on the water-bath, and the white residue was ignited:

0.1012 gave 0.0994 SiO_2 . $\text{Si} = 46.12$.

$\text{Si}_2\text{O}_4\text{H}_2$ requires $\text{Si} = 46.15$ per cent.

A combustion with copper oxide showed that the substance contained no appreciable amount of carbon, proving that the displacement of the ethoxy-groups was complete.

The volume of hydrogen evolved with potassium hydroxide was determined in the usual way by means of a Lunge nitrometer, using 50 per cent. potassium hydroxide solution, and warming towards the end of the reaction, when a clear solution was effected:

0.1272 gave 24.8 c.c. H_2 (moist) at 19° and 770 mm., whence
1 gram gave 181.0 c.c. H_2 (dry) at N.T.P.

According to theory, 1 gram of pure silico-oxalic acid, $\text{Si}_2\text{O}_4\text{H}_2$, should evolve 182.7 c.c. H_2 (dry) at N.T.P.; hence the specimen of silico-oxalic acid thus obtained was of 99 per cent. purity.

The best specimens of silico-oxalic acid obtained by Gattermann and Weinlig's process of decomposing disilicon hexachloride with water never exceeded 96–97 per cent. purity.

Specimens of silico-oxalic acid, prepared by hydrolysing hexaethoxysilicoethane with hot water, or after being boiled for some time with water, evolved considerably less hydrogen—as is to be expected from the unstable nature of silico-oxalic acid. Even if the product be rubbed or pressed, a certain amount of decomposition may ensue; for example, two specimens of silico-oxalic acid, obtained by decomposing hexaethoxysilicoethane by hot water, evolved, when treated with potassium hydroxide, 175 c.c. and 167 c.c., respectively, of dry hydrogen per gram weight. These numbers correspond respectively with 96 and 91 per cent. of

silico-oxalic acid. The last specimen had actually been boiled with water before analysis.

The details given above show that by this method of preparation almost pure silico-oxalic acid can be obtained, provided that ordinary precautions are taken, and that the temperature is kept low.

Properties.—Pure silico-oxalic acid is a snow-white, amorphous powder, insoluble in the usual mineral acids, with the exception of hydrofluoric acid, which decomposes it. Alkalis and ammonia decompose it, causing the evolution of hydrogen. Pressure, friction, or sudden heating usually cause its explosive decomposition, and the purer the substance is the more liable is it to decompose. However, the explosion does not readily spread from particle to particle; for example, if some of the amorphous powder is spread thinly over the bottom of a glass dish and part touched with a hot glass rod, the particles touched will explode, but the explosion usually confines itself to the immediate neighbourhood of the hot glass.

When freshly prepared and dried in a vacuum over sulphuric acid it is very hygroscopic.

Action of Ethyl Alcohol on Trisilicon Octachloride.—The favourable results obtained by the above method of preparing silico-oxalic acid led the author to see whether mesosilico-oxalic acid, $\text{HO}_2\text{Si}\cdot\text{Si}(\text{OH})_2\cdot\text{SiO}_2\text{H}$, could be obtained of great purity by the similar method of first preparing octaethoxysilicopropane, $\text{Si}_3(\text{OEt})_8$, by acting on trisilicon octachloride with alcohol, and then hydrolysing the product with water.

In order to prepare octaethoxysilicopropane, 23 grams of trisilicon octachloride were placed in a flask fitted with a reflux condenser and a calcium chloride tube, and 50 c.c. of alcohol (99.8 per cent.) were gradually added. A vigorous action took place, much hydrogen chloride being evolved.

Seeing that great cold is produced when excess of alcohol is added to disilicon hexachloride (hoar frost actually collecting on the sides of the flask, compare T., 1914, **105**, 2861), it was expected that an even more pronounced degree of cold would be experienced by treating the more unstable trisilicon octachloride in the same way. To the author's surprise, however, although at first the mixture became moderately cold, yet the temperature soon began to rise as the action proceeded, and finally the contents of the flask became quite hot.

This, as will immediately be seen, was due to the decomposition of the chain of three directly linked silicon atoms in the trisilicon octachloride. From all grounds of analogy the production of a

compound of formula $\text{Si}_3(\text{OEt})_8$ should have been attended with the absorption of more heat than the formation of a compound of formula $\text{Si}_2(\text{OEt})_6$.

When the evolution of hydrogen chloride had almost ceased, the liquid was warmed on the water-bath and left overnight. Since in the case of the preparation of hexaethoxysilicoethane, $\text{Si}_2(\text{OEt})_6$, the complete displacement of the chlorine by ethoxy-groups proceeded only slowly, it was deemed advisable to add a further 20 c.c. of alcohol and warm once more. Finally, the alcohol was distilled off. The distilled alcohol contained much hydrogen chloride and a small amount of some volatile silicon compound, since on diluting with water a slight milkiness occurred.

The liquid left in the flask was now subjected to fractional distillation under diminished pressure. The distillation began about $77^\circ/18$ mm., and the thermometer rose slowly but steadily up to 220° , at which point the distillation was stopped.

A small quantity of viscid oil remained in the flask. The distillates were colourless oils free from chlorine, and three fractions were collected: (1) b. p. $77-90^\circ/18$ mm.; (2) $90-145^\circ/18$ mm.; (3) $145-220^\circ/18$ mm. It was evident that the product was a complex mixture, and that the reaction:

had not taken place. The separate fractions were fractionally distilled, and the fraction of lowest boiling point was proved to consist almost entirely of tetraethoxysilicomethane, $\text{Si}(\text{OEt})_4$. It evolved no hydrogen with potassium hydroxide (proving the absence of directly linked silicon atoms; see *Ber.*, 1912, **45**, 2097; 1913, **46**, 3289), and was completely hydrolysed to silicic acid by water (0.2164 gave 0.0633 SiO_2 on decomposing with concentrated sulphuric acid. $\text{Si}=13.7$. $\text{Si}(\text{OEt})_4$ requires $\text{Si}=13.6$ per cent.). The fact that a considerable proportion of tetraethoxysilicomethane was thus obtained showed that there had occurred a very considerable disruption of the $\cdot\text{Si}\cdot\text{Si}\cdot\text{Si}\cdot$ chain present in the trisilicon octachloride when the latter was treated with alcohol.

The fractions of higher boiling point were also re-distilled, but it was impossible to isolate any fraction of constant boiling point, and with each successive distillation a large portion of the liquid to be distilled became converted into liquids of higher boiling points—evidently polymerised or complex decomposition products. This was made certain by analysing the products; for example, the fraction collected between 90° and $145^\circ/18$ mm. contained $\text{Si}=17.46$, and 1 gram, when treated with potassium hydroxide, evolved about 18 c.c. of hydrogen.

The fraction collected between 145° and $220^\circ/18$ mm. con-

tained $\text{Si}=20.2$, and 1 gram, when treated with potassium hydroxide, evolved 24.9 c.c. of dry hydrogen at N.T.P.

Since octaethoxysilicopropane, $\text{Si}_3(\text{OEt})_8$, requires $\text{Si}=19.1$ and 1 gram should evolve with potassium hydroxide 100.8 c.c. of hydrogen at N.T.P., the above analyses serve to show that an almost complete decomposition of the octaethoxysilicopropane had occurred, either before or during the process of distillation.

It was thought, therefore, that since octaethoxysilicopropane would certainly not bear distillation under diminished pressure, better results would be obtained by simply treating the trisilicon octachloride with alcohol, without attempting to isolate the product by distillation.

For this purpose 12.3 grams of pure silicon octachloride were placed in a distilling flask provided with a reflux condenser, and 23 grams of pure ethyl alcohol were gradually added.

After the vigorous action which had set in had subsided, the liquid was warmed on the water-bath to expel the excess of hydrochloric acid. Traces of a volatile silicon compound escaped with the hydrogen chloride, because an incrustation collected at the top of the reflux condenser. The excess of alcohol was removed by distilling on the water-bath, and twice there was added about 30 c.c. of alcohol, which was then distilled off in order to expel traces of dissolved hydrogen chloride. During the distillation of the alcohol a current of dry hydrogen was passed through the liquid in order to help the removal of the dissolved hydrogen chloride. The liquid so obtained was almost clear, and was rendered quite clear by filtering through a layer of recently dried asbestos. When thrown into water, it floated on the surface in oily drops, which were only slowly decomposed with the formation of a white solid. The liquid, when filtered from the solid and acidified with nitric acid, did not give a precipitate with silver nitrate. Since no trace of chlorine could be detected, and since the liquid evolved hydrogen with potassium hydroxide, it was thought that the action $\text{Si}_3\text{Cl}_8 + 8\text{EtOH} = \text{Si}_3(\text{OEt})_8 + 8\text{HCl}$ had proceeded to completion. Consequently an analysis was made.

The silica was determined in the usual way by decomposing with concentrated sulphuric acid:

0.2824 gave 0.1044 SiO_2 . $\text{Si}=17.4$.

1.0 " , with potassium hydroxide, only 42.3 c.c. H_2 (dry)
at N.T.P.

Since the formula $\text{Si}_3(\text{OEt})_8$ requires $\text{Si}=19.1$, and 1 gram should evolve with potassium hydroxide 100.8 c.c. of dry hydrogen, the above figures show that the rupture of the molecule of octaethoxysilicopropane had proceeded to nearly 60 per cent. Attempts

to isolate octaethoxysilicopropane were, therefore, abandoned, as, with the means at the author's disposal, there seemed no prospect of isolating it in a pure condition.

Action of Methyl Alcohol on Trisilicon Octachloride.—It was thought that possibly the methoxy-compound, $\text{Si}_3(\text{OMe})_8$, would prove more stable than the ethoxy-compound, and so attempts were made to prepare it. 18.42 Grams of trisilicon octachloride were treated with 44 grams of pure methyl alcohol (purified by metallic calcium and silver oxide). The action proceeded with development of heat and the evolution of hydrogen chloride, exactly as was the case with ethyl alcohol. The liquid was warmed on the water-bath in order to complete the action, and the excess of alcohol was distilled off on the water-bath in a current of dry hydrogen. There finally remained, after the complete removal of the alcohol, 12.2 grams of a colourless liquid. This was subjected to fractional distillation under 14 mm. pressure. The temperature rose slowly from 90° to $140^\circ/14$ mm., whilst the liquid slowly distilled uniformly in drops. At the last temperature about one-third of the liquid remained as a viscid oil. It was evident that no fraction of constant boiling point could be isolated, and that a complex mixture of decomposition products had resulted.

Thus the distillate, boiling between 90° and $170^\circ/13$ mm., was analysed in the usual way:

0.2681 gave 0.1381 SiO_2 . $\text{Si} = 24.2$.

1 gram gave with potassium hydroxide only 36.6 c.c. H_2 (dry) at N.T.P.

$\text{Si}_3(\text{OMe})_8$ requires $\text{Si} = 25.5$ per cent., and 1 gram should yield with potassium hydroxide 134.5 c.c. H_2 (dry) at N.T.P.

Hence the chains of directly united silicon atoms, as judged by the evolution of hydrogen with potassium hydroxide, were almost completely destroyed.

The decomposition had not proceeded so far in the oil which had not distilled. This was found to contain $\text{Si} = 27.6$, and 1 gram gave 68.2 c.c. H_2 (dry) with potassium hydroxide.

When treated with water the oils were decomposed with the formation of white solids, which evolved hydrogen with potassium hydroxide and ammonia, and were readily combustible. When the oils were treated with ammonia solution they were violently decomposed, with the evolution of hydrogen and formation of silicic acid.

The preceding experiments indicated that there seems little prospect, with the means at the author's disposal, of preparing a pure specimen of octamethoxysilicopropane, $\text{Si}_3(\text{OMe})_8$, as this substance, if formed at all, will not bear distillation.

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This great instability of derivatives containing a chain of three silicon atoms directly linked led the author to investigate the relative stability of mesosilicic acid, $\text{HO}_2\text{Si}\cdot\text{Si}(\text{OH})_2\cdot\text{SiO}_2\text{H}$, and silico-oxalic acid, $\text{HO}_2\text{Si}\cdot\text{SiO}_2\text{H}$. Thin layers of these acids were prepared by pouring a little of the chlorides Si_3Cl_8 and Si_2Cl_6 on to a smooth wooden surface and exposing to atmospheric moisture for some hours. On testing these layers by means of a hot wire or by friction, it was found that the mesosilico-oxalic acid exploded more readily than the silico-oxalic acid. The film of mesosilico-oxalic acid would, when rubbed, often blaze up like gunpowder, whereas the effect was much less pronounced with silico-oxalic acid.

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