

# THE HALIDES AND OXYHALIDES OF SILICON<sup>1, 2</sup>

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*Received January 11, 1942*

The preparation and some of the properties of the silicon halides, oxyhalides, and related compounds are briefly described, with special reference to the results of recent research in this field. A comparison is offered of the compounds of silicon with those of carbon and of the elements in Group IV a; similarities and differences are pointed out. The possible application of the oxyhalides of silicon to the synthesis of silicon resins is suggested.

Recent interest in the preparation of silicon resins, the commercial possibilities of which have attracted the attention of a number of industrial research laboratories, suggests a consideration of recent developments in the study of the silicon halides and oxyhalides, from which such products may be derived. The halides and related compounds, such as the oxyhalides, the halohydrides, and the alkyl and aryl silicon halides, present a number of points of theoretical as well as practical importance. Especially worthy of emphasis are the differences in properties exhibited by silicon in these compounds in comparison with those of its analog, carbon, in spite of the strong resemblances in formula shown by the corresponding compounds of the two elements.

Table 1, while not complete, is intended to summarize the relative power of carbon, silicon, titanium, zirconium (and hafnium), and thorium to combine with the halogens. The similarities in the formulas of the compounds of silicon and carbon are clearly to be seen, as well as the differences between these two elements and the other elements constituting Group IVa of the Periodic Table. Sharp contrasts are to be noted, as follows: (a) the absence of chain compounds of titanium, zirconium, or thorium; (b) instead, the existence in the case of titanium and zirconium of halides in the trivalent and bivalent states; (c) the absence of haloforms, MeHX<sub>3</sub>, and other halohydrides of all the elements other than carbon and silicon. For convenience recent work upon the silicon halides and related compounds will be discussed for the most part in the order of their arrangement in table 1.

## I. FLUORIDES

Aside from the well-known tetrafluoride, SiF<sub>4</sub>, discovered in 1771 by Scheele, the only other silicon fluoride that has been established definitely is the second member of the homologous series Si<sub>n</sub>F<sub>2n+2</sub>, that is, Si<sub>2</sub>F<sub>6</sub>, which was prepared by

<sup>1</sup> Presented December 31, 1941, before the Sixth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, which was held at Columbus, Ohio.

<sup>2</sup> Contribution No. 89 from the Research Laboratory of Inorganic Chemistry, Massachusetts Institute of Technology.

E. L. Gamble and the writer in 1932 by the fluorination of  $\text{Si}_2\text{Cl}_6$  with zinc fluoride (10). At low temperatures it is a colorless solid which sublimes at atmospheric pressure, its vapor pressure becoming 760 mm. at  $-19.1^\circ\text{C}$ ; its melting point is  $-18.5^\circ\text{C}$ . at 780 mm. It is very rapidly hydrolyzed to form "silicoöxalic acid" (or 1,2-bis(oxyoxo)disilane), silicic acid, and fluosilicic acid.

TABLE I  
*Halogen compounds of the elements of Group IVa*

HALIDES	ELEMENTS				
	Carbon	Silicon	Titanium	Zirconium (Hafnium)	Thorium
Fluorides.....	$\text{CF}_4$	$\text{SiF}_4$	$\text{TiF}_4$	$\text{ZrF}_4$	$\text{ThF}_4$
	$\text{C}_2\text{F}_6$	$\text{Si}_2\text{F}_6$	$\text{TiF}_3$	$\text{ZrF}_3$	
	$\text{C}_2\text{F}_4$				
	$\text{CHF}_3$	$\text{SiHF}_3$			
	$\text{CH}_2\text{F}_2$				
	$\text{CH}_3\text{F}$				
Chlorides.....	$\text{CCl}_4$	$\text{SiCl}_4$	$\text{TiCl}_4$	$\text{ZrCl}_4$	$\text{ThCl}_4$
	$\text{C}_2\text{Cl}_6$	$\text{Si}_2\text{Cl}_6$	$\text{TiCl}_3$	$\text{ZrCl}_3$	
	$\text{C}_2\text{Cl}_4$	$(\text{SiCl}_2)_x$	$\text{TiCl}_2$	$\text{ZrCl}_2$	
	$\text{C}_6\text{Cl}_6$	$(\text{SiCl})_x$			
	$\text{CHCl}_3$	$\text{SiHCl}_3$			
	$\text{CH}_2\text{Cl}_2$	$\text{SiH}_2\text{Cl}_2$			
	$\text{CH}_3\text{Cl}$	$\text{SiH}_3\text{Cl}$			
Bromides.....	$\text{CBr}_4$	$\text{SiBr}_4$	$\text{TiBr}_4$	$\text{ZrBr}_4$	$\text{ThBr}_4$
	$\text{C}_2\text{Br}_6$	$\text{Si}_2\text{Br}_6$	$\text{TiBr}_3$	$\text{ZrBr}_3$	
	$\text{C}_2\text{Br}_4$		$\text{TiBr}_2$	$\text{ZrBr}_2$	
	$\text{C}_6\text{Br}_6$				
	$\text{CHBr}_3$	$\text{SiHBr}_3$			
	$\text{CH}_2\text{Br}_2$	$\text{SiH}_2\text{Br}_2$			
	$\text{CH}_3\text{Br}$	$\text{SiH}_3\text{Br}$			
Iodides.....	$\text{CI}_4$	$\text{SiI}_4$	$\text{TiI}_4$	$\text{ZrI}_4$	$\text{ThI}_4$
		$\text{Si}_2\text{I}_6$	$\text{TiI}_3$	$\text{ZrI}_3$	
	$\text{C}_2\text{I}_4$	$\text{Si}_2\text{I}_4$			
	$\text{C}_6\text{I}_6$				
	$\bullet\text{CHI}_3$	$\text{SiHI}_3$			
	$\text{CH}_2\text{I}_2$	$\text{SiH}_2\text{I}_2$			
	$\text{CH}_3\text{I}$	$\text{SiH}_3\text{I}$			

The instability of the Si—Si bond is responsible for failure to prepare higher members of the series, such as  $\text{Si}_3\text{F}_8$ , from the corresponding chlorides.

The direct fluorination of silicon or of its alloys is a very vigorous reaction, the temperature at the zone of contact rising to incandescence; hence it is not surprising to find in this case that only the tetrafluoride can be obtained, the Si—Si linkages existing in the crystalline element being broken during the reaction.

So-called *subfluorides* of silicon, of unknown composition, have been reported by several investigators, including St. C. Deville (19) and Troost and Hautefeuille (20), who employed various methods intended to reduce the tetrafluoride. However, attempts by Ruff (7) to repeat this work were unsuccessful, nor could he obtain evidence of a subfluoride by means other than those previously tried. The evidence for the existence of such lower fluorides therefore must be considered as questionable. Similarly, up to the present the existence of silicon oxyfluorides has not been established.<sup>3</sup>

The absence of subfluorides of silicon is directly associated with the fact that silicon, like carbon and—somewhat unexpectedly—like thorium, but unlike the other elements in the fourth periodic group, is uniformly quadrivalent in its halogen compounds. Although lower halides, such as  $(\text{SiCl}_2)_x$  and even  $(\text{SiCl})_x$ , have been formed by reduction of silicon tetrachloride with hydrogen under proper conditions, these unsaturated polymerized substances are not to be regarded as lower valence compounds of silicon.

Mention of the ease of hydrolysis of hexafluorodisilane,  $\text{Si}_2\text{F}_6$ , leads to the observation that the fluorine compounds of silicon deviate in several particulars from the otherwise constant behavior of the halides toward water, i.e., a vigorous and usually complete replacement of halogen by hydroxyl with accompanying condensation to produce siloxane linkages,  $\text{Si—O—Si}$ . In the case of silicon tetrafluoride, however, owing to the comparatively small atomic radius of the fluorine atom, a coordination number of six for the silicon atom is assumed in the formation of soluble fluosilicic acid, in addition to insoluble hydrous silica. Various mechanisms for this reaction have been suggested, but a plausible interpretation appears to be that the complete replacement of the fluorine atoms by hydroxyl and the consequent formation of hydrous silica and hydrofluoric acid is at once followed by interaction of these products, with solution of the silica to a greater or less extent, forming fluosilicic acid. Toward the halogen atoms of larger atomic radius silicon does not show a coordination number greater than four.

Another instance of exceptional behavior on the part of the fluorides of silicon is found in the case of the triphenylhalosilanes,  $(\text{C}_6\text{H}_5)_3\text{SiX}$ . The ease of hydrolysis of these substances decreases from iodide to fluoride, as the strength of the  $\text{Si—X}$  bond increases, so that  $(\text{C}_6\text{H}_5)_3\text{SiF}$  is said to be unaffected by water (6), whereas the corresponding chloro and bromo compounds are rapidly hydrolyzed, forming silicols.

## II. CHLORIDES

The interaction of elementary silicon, or better, of a silicon alloy, with chlorine differs from the direct fluorination of silicon in that notable quantities of the higher chlorides of the series  $\text{Si}_n\text{Cl}_{2n+2}$  may be obtained, especially if the

<sup>3</sup> Since the presentation of this review, H. S. Booth and R. A. Osten at a meeting of the American Chemical Society held in Buffalo, New York, September 8, 1942, have reported the successful preparation of an oxyfluoride,  $\text{Si}_2\text{OF}_6$ , from  $\text{Si}_2\text{OCl}_6$  by means of antimony trifluoride, together with several intermediate fluorochloro derivatives of disiloxane.

temperature employed is held as low as practicable. At high temperatures the tetrachloride is almost exclusively formed, a fact which led Martin (5) to conclude that the initial compounds produced on chlorination of silicon are the most complex, with chains of Si—Si linkages, such as were present in the element itself; in the presence of excess chlorine, and aided by higher temperatures, these linkages are progressively broken down, yielding finally the tetrachloride.

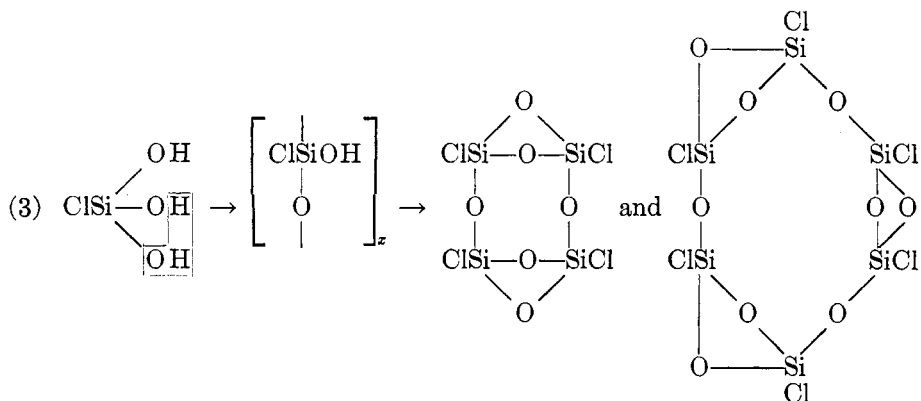
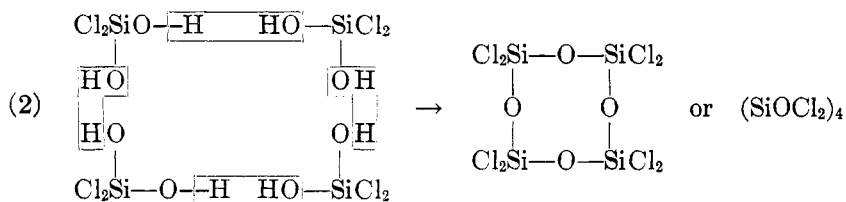
For the preparation of these higher chlorides we have found (12) that commercial "calcium silicon," containing 60–65 per cent silicon and 35–30 per cent calcium, gives the best results. From the crude reaction product yields of hexachlorodisilane,  $\text{Si}_2\text{Cl}_6$ , up to 25 per cent were obtainable, rapidly diminishing proportions of  $\text{Si}_3\text{Cl}_8$  and higher halides also being formed.

It is perhaps of interest to note that, instead of elementary chlorine, certain anhydrous metal chlorides, such as cuprous or cupric chlorides or lead chloride, may be used; in some instances the tetrachloride is obtained in a practically pure condition on heating the mixture of metal chloride and silicon. This displacement reaction is of rather general application; thus we have prepared samples of silicon tetraiodide from heated mixtures of cuprous iodide or of red mercuric iodide and silicon, some purification of the product here being found necessary. Likewise, the reaction between cuprous bromide and silicon yields silicon tetrabromide, and the tetrafluoride results from heating a mixture of silicon powder and lead fluoride.

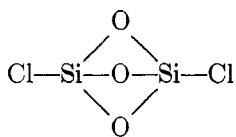
As to the unsaturated silicon chlorides, only the polymerized dichloride,  $(\text{SiCl}_2)_x$ , and the monochloride,  $(\text{SiCl})_x$ , are reported to have been prepared (15, 16), the former by reduction of the tetrachloride with hydrogen in a glow discharge from aluminum electrodes, the latter by the "cracking" of  $\text{Si}_{10}\text{Cl}_{22}$  (or of  $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$ ) in an inert atmosphere. The "dichloride" is described as a white stable solid, which is soluble in methyl alcohol and is decomposed violently by water with evolution of hydrogen. The "monochloride,"  $(\text{SiCl})_x$ , is said to be a yellow amorphous solid, changing reversibly to orange red between  $180^\circ$  and  $200^\circ\text{C}$ ., and to be inflammable in air at  $100^\circ\text{C}$ . No report has appeared as yet in confirmation of this work; however, from similar but unsuccessful attempts to prepare the corresponding bromides, we conclude that the yields of the unsaturated halides obtainable by this process must be very meagre.

In connection with Schwarz' work, it is interesting to observe that the remarkable compounds,  $\text{Si}_{10}\text{Cl}_{22}$  (17) and  $\text{Si}_{10}\text{Cl}_{20}\text{H}_2$  (18), obtained by him by the reaction of the tetrachloride and its decomposition products with hydrogen in a so-called "hot-cold" tube, represent the longest straight-chain compounds of silicon known, with a formula weight in the case of  $\text{Si}_{10}\text{Cl}_{22}$  of 1060. Oddly enough, intermediate chlorides which might have been expected to form, such as  $\text{Si}_6\text{Cl}_{14}$  to  $\text{Si}_9\text{Cl}_{20}$ , inclusive, were not observed in the reaction product.

From what we know of the hydrolysis of halides of other elements, it might be inferred that the interaction of water with the tetrahalides of silicon should proceed stepwise, with the formation of such intermediate compounds as  $\text{SiCl}_3\text{OH}$ ,  $\text{SiCl}_2(\text{OH})_2$ , and  $\text{SiCl}(\text{OH})_3$ , which on condensation would yield oxychlorides containing siloxane linkages. Thus:



The first two of these oxychlorides are well-established compounds; the third corresponds to a compound of unknown molecular weight,  $(\text{Si}_2\text{O}_3\text{Cl}_2)_x$ , reported by Troost and Hautefeuille (21), the existence of which, however, is not supported by adequate experimental data. In its simplest forms it would be represented by a dimeric structure containing three oxygen atoms bridged between two silicon atoms, as in



This substance, as well as the dimeric and trimeric forms of  $\text{SiOCl}_2$ , have not been isolated. Furthermore, none of the structures represented under (3) are probable, inasmuch as the bridging of two or three oxygen atoms between two silicon atoms violates the structural requirements known to hold among silicates.

Except under special conditions provided to retard the progress of hydrolysis, such intermediate compounds, if formed, are not isolated. In recent experiments, not yet completed, we have established the fact that, by diluting the silicon halide with anhydrous ether (or other organic solvents) and using a moist organic solvent, such as moist ether, as the hydrolytic medium, the hydrolysis of silicon tetrachloride may be controlled so as to form appreciable quantities of oxychlorides. The success of these experiments upon the partial hydrolysis of the tetrachloride suggests that even in the case of the tetrafluoride

the restraining influence of dilution of the reacting substances by inert solvents might conceivably lead to the isolation of the oxyfluorides of silicon.

### III. BROMIDES

As with the chlorides of silicon, an homologous series of bromides,  $\text{Si}_n\text{Br}_{2n+2}$ , is known, the first member of which, the tetrabromide, is a liquid. The succeeding members of the series,—known definitely only as far as  $\text{Si}_4\text{Br}_{10}$ ,—are white crystalline solids. Their reactions, notably hydrolysis and ammonolysis, follow closely those of the corresponding chlorides.

A satisfactory method of preparation of hexabromodisilane,  $\text{Si}_2\text{Br}_6$ , was found accidentally by us a few years ago in an experiment intended to yield the oxybromides of silicon. With the aim of simultaneously oxidizing and brominating silicon, and in order to operate at as low a reaction temperature as possible, a mixture of oxygen and bromine vapor was passed over calcium silicide at 180–200°C. The product obtained consisted almost entirely of hexabromodisilane with but minute amounts of oxybromides, whereas, when elementary crystalline silicon was subjected to similar treatment, the main product formed was a mixture of the oxybromides. Evidently the energetic combination of the calcium in the silicide with oxygen facilitates the union of the silicon atoms—probably covalently linked together in  $\text{CaSi}_2$ —with bromine at a sufficiently low temperature to avoid splitting the Si—Si linkages.

### IV. IODIDES

Less work has been done with the iodides of silicon than with the other halides of this element, in part, perhaps, because of the unstable character of these compounds on exposure to air and to light. Thus the tetraiodide, a white crystalline solid, which is obtainable, for example, when the vapors of iodine, entrained in a current of carbon dioxide, are passed over hot silicon, turns dark when left in a sealed glass tube in direct sunlight. Iodine also is liberated when the compound is left in contact with the air. Besides the tetraiodide, only the second member, hexaiododisilane,  $\text{Si}_2\text{I}_6$ , of the homologous series  $\text{Si}_n\text{I}_{2n+2}$  has been reported. It is a white crystalline solid, prepared by heating the tetraiodide with finely divided silver in a sealed tube at about 300°C.

The unsaturated compound  $\text{Si}_2\text{I}_4$ , tetraiododisilene, described as an orange-colored solid, is reported to result, together with the tetraiodide, from the thermal decomposition of hexaiododisilane. It represents the analog of the polymerized dichloride,  $(\text{SiCl}_2)_x$ .

### V. HALOSILANES

In recent work on the iodo compounds of silane by Emeléus and coworkers (2), most of the gaps left in the list of known halosilanes have been filled. All of the possible compounds of the general formula  $\text{SiH}_n\text{X}_{4-n}$  had been recorded previously except the mono- and di-iodosilanes,  $\text{SiH}_3\text{I}$  and  $\text{SiH}_2\text{I}_2$  (also styled "silyl" and "silylene" iodides), and the corresponding fluoro compounds. The iodo compounds have now been prepared by the reaction of silane with hydrogen

iodide at 80°C. under reduced pressure. Both substances are decomposed by light and have pungent odors. Monoiodosilane boils at 149.5°C. and melts at -1°C.; the diiodo compound boils at 45.4°C. and melts at -57°C.

In connection with the properties of these halosilanes it is perhaps worth recalling that some of them form explosive mixtures with ordinary air. We have experienced the explosion of a flask containing silicochloroform (trichlorosilane) while the apparatus was standing undisturbed at room temperature, the only explanation being the probable presence of air in the flask. Silicoiodoform similarly forms explosive mixtures with air. Silicobromoform when poured through the air burns brilliantly, liberating much smoke.

#### VI. MIXED HALIDES

In addition to the compounds listed in table 1 there may be mentioned the mixed halides formed by carbon and silicon (and to a less important degree by titanium), in which two or three different halogens are linked to carbon or silicon. Some of these compounds of silicon have long been known; others have been prepared only recently. Thus, while complete series of silicon chlorobromides, chloriodides, and bromiodides are recorded, the isolation of some of which dates back many decades, the fluorochlorides were first described in 1932 (1, 11), the fluorobromides in 1936 (8), and two fluorochlorobromides,  $\text{SiFClBr}_2$  and  $\text{SiFCl}_2\text{Br}$ , in 1937 (9). As would be expected, these compounds exhibit properties resembling those of the binary halides from which they are derived.

The preparation of a silicon mixed halide with four different atoms attached to the silicon, as in  $\text{SiFClBrI}$  or  $\text{SiHFClBr}$ , which would present the interesting possibility of optical isomerism, as yet has not been realized.

#### VII. OXYHALIDES

A few years ago a study of the various possible methods of preparation of the silicon oxybromides was carried out in our laboratory (14). In this study it was found that the reaction of a mixture of oxygen and the halogen with heated silicon, or the oxidation of the silicon tetrahalide, gave the most satisfactory results. By each of these methods a crude product was obtained which on careful fractionation proved to be a mixture of six or more oxybromides, all but one of which belonged to the homologous series  $\text{Si}_n\text{O}_{n-1}\text{Br}_{2n+2}$ . The exceptional case was the cyclic tetramer,  $(\text{SiOBr}_2)_4$ . Previous fragmentary work on the oxychlorides had not revealed the existence of such series, although they were to be expected. More recently we have established in another investigation (13) the fact that an entirely analogous series of oxychlorides exists, probably extending considerably beyond  $\text{Si}_7\text{O}_6\text{Cl}_{16}$ , which was the highest member isolated. All of these substances except the tetramer  $(\text{SiOCl}_2)_4$ —a colorless, crystalline solid—are colorless, oily liquids, which are hydrolyzed in the presence of moisture (the lower members most readily), and are miscible with carbon tetrachloride, chloroform, carbon disulfide, or silicon tetrachloride. They are converted by absolute ethyl alcohol into the corresponding ethyl esters, which are colorless, oily liquids with high boiling points and are hydrolyzed only very slowly,

even by water at 100°C. The ester produced from  $\text{Si}_2\text{OCl}_6$  and cyclohexanol was found to be a white crystalline solid, melting at 217.1–217.6°C. and soluble in the solvents previously mentioned and in ether and alcohol. Further investigation of these substances is in progress with a view toward their possible utilization in the production of silicon resins, which appear up to the present to have been derived exclusively from the tetrahalides, such as silicon tetrachloride. Thus in the recent work of Hyde and De Long (3), dihalosilanes containing phenyl groups, prepared from silicon tetrachloride by means of the Grignard reaction, were hydrolyzed with aqueous hydrochloric acid and resinous products were obtained which, if the treatment were not too prolonged, remained soluble in organic solvents. Hydrolysis products derived from alkyl-substituted dihalosilanes likewise gave resinous materials when air was passed through the heated liquids.

Interest in the production of such resinous substances containing silicon is naturally to be expected, since by the partial replacement of carbon atoms by silicon a product possessing superior properties in some respects may be anticipated, such as an increased stability at elevated temperatures.

The opening of this field of research, with its prospects of considerable industrial importance, illustrates once again the hazardous character of a prediction that any particular line of investigation has been exhausted of further possibilities of development. Thus in a lecture a few years ago, Kipping (4), who, more than any other single investigator, has contributed to our knowledge of organosilicon chemistry, concluded his remarks with the statement that in his opinion no likelihood of further notable developments existed in this branch of silicon chemistry. However, in the progress of science the certainties of today have a habit of becoming the uncertainties of tomorrow. So it is not at all surprising to find now that investigations are actively being pursued in various laboratories with the object of uncovering the possibilities which lie in the field of silicon plastics. It is perhaps a little premature to assert that great developments are at hand in this direction, since for large-scale industrial application the economics of the problem are as important as the basic chemical discoveries. Nevertheless, enough has been learned to prove the truth of the contention that in this, as in other instances, while the door to further opportunity in research sometimes may appear closed, it is never locked.

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