(with respect to air oxygen rather than to a standard water) as an alternative to treatment with equilibrated carbon dioxide, sulfur dioxide, etc.[5]

We are indebted to the Research Committee of the University and to the Wisconsin Alumni Research Foundation for grants in aid of this work.

Summary

It has been found that the exchange equilibrium between water vapor and oxygen is rapidly established on a hot wire at 1800°A. and above, but much more slowly at lower temperatures. Water thus equilibrated with excess air increases in density by about 7 p. p. m., and the Dole effect is confirmed. Oxygen-abnormal water may be prepared conveniently by this method, and the oxygen isotope ratio of an unknown sample may be studied with its aid.

MADISON, WIS. RECEIVED DECEMBER 2, 1936

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[5] Dr. Charles H. Greene kindly writes as follows (December 22, 1936): "There is a small error in your result. The hot platinum in your apparatus brings the water vapor to the same isotopic composition as atmospheric oxygen. Water vapor, however, is slightly richer in O^{16} than the liquid water with which it is in equilibrium. Thus the liquid water in your apparatus, after equilibrium is attained, will be somewhat richer in O^{18} than atmospheric oxygen. From the results of Wahl and Urey, *J. Chem. Phys.* **3**, 411 (1935), I estimate the effect as 0.9 ± 0.3 p. p. m. This correction would bring your results into very good accord with our own."

If Dr. Greene's correction is accepted, our value of the Dole effect for liquid fresh water becomes 6.1 γ, assuming that complete equilibrium was reached.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 56]

The Oxybromides of Silicon

BY WALTER C. SCHUMB AND CAROLYN H. KLEIN

Although considerable information has been gathered concerning the oxychlorides of silicon,[1] little was known of the oxybromides of that element at the outset of this research. An investigation of the oxybromides of silicon was begun in 1934, with the object of isolating an homologous series of these compounds.

Of the various methods previously employed in the preparation of the oxychlorides, the ones which appeared most promising for adaptation to oxybromide preparation were the oxidation of the silicon tetrahalide, and the reaction of a mixture of oxygen and the halogen on silicon. In addition to these two successful methods, we have made studies of the oxidation of hexabromodisilane Si_2Br_6, silicobromoform $SiHBr_3$, and of Si_2OBr_6, as well as the effect of ozone and of silver oxide on silicon tetrabromide.

I. The Reaction of a Mixture of Oxygen and Bromine with Silicon and with Calcium Silicide.—The apparatus used in a study of the simultaneous effect of oxygen and bromine on silicon was similar to that used by Gattermann[2] for the preparation of silicon tetrabromide. A stream of oxygen, dried with calcium chloride, was bubbled through a trap of bromine (at 55°) at a rate of about 3 liters per hour (a velocity such that some oxygen bubbled through at the exit of the apparatus). The mixture of oxygen and bromine resulting was then passed over commercial silicon (averaging 97.5% Si) heated by a gas furnace to the desired temperature, about 700°. The product of the reaction was collected in a trap cooled in ice water.

The crude product was distilled fractionally, the excess bromine and silicon tetrabromide passing off first, followed by higher boiling material, which was collected up to 225° under a high vacuum. After repeated fractionation with an efficient column a separation of the compounds present in the mixture was effected. The combined results of two experiments, together with the formulas of the compounds isolated and identified by methods described below, are collected in Table I.

These substances all hydrolyze in the presence of moisture of the air, the speed being directly proportional to the volatility of the compound. They are miscible in all proportions with carbon tetrachloride, carbon disulfide, chloroform, and silicon tetrabromide. With the exception of the first and third, they have not been reported previously in the literature, and the two which were reported were prepared independently and by a different process.[3]

In order to determine the effect of a lower reaction temperature on the products formed, calcium silicide was used in another experiment in place of silicon, it being known that certain silicides react more readily with halogens at a lower temperature than does silicon itself. The reaction was carried out at a temperature of 180 to 200°, but in this case the product consisted almost wholly of hexabromodisilane, oxybromides being formed only in minute amounts. Evidently, in spite of an excess of oxygen, a Si–Si bond formed in preference to a Si–O–Si linkage.

Incidentally, the procedure just mentioned constitutes a far more satisfactory method of preparation of Si_2Br_6 than any hitherto described, as the yield is almost quantitative.

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[1] L. Troost and P. Hautefeuille, *Bull. soc. chim.*, [2] **16**, 243 (1891).

[2] L. Gattermann, *Ber.*, **22**, 186 (1889).

[3] H. Rheinboldt and W. Wisfeld, *Ann.*, **517**, 197 (1935).

TABLE I

Fraction	Appearance	Approx. no. g.	Approx. %	B. p., °C.	Mm.	F. p., °C.	Formula
I	Colorless liquid readily freezing to colorless tabular crystals	100	20.6	118	15	27.9 ± 0.1	Si_2OBr_6
II	Colorless liquid freezing in ice water to colorless solid	240	49.4	159	12	17.5 ± 0.2	$Si_3O_2Br_6$
III	Heavy white solid melting to colorless liquid	5	1.0	155	7	123–123.5	$Si_4O_4Br_8$
IV	Colorless liquid becoming very viscous on cooling and freezing to a glassy solid	60	12.4	122	<0.5	−91 ± 2°	$Si_4O_3Br_{10}$
V	Same	50	10.3	150	<0.5	−82 ± 2°	$Si_5O_4Br_{12}$
VI	Heavy colorless oil freezing in liquid air to glassy solid	30	6.2	160–180	<0.5	< −78°	Higher residue

II. The Reaction of Silicon Tetrabromide with Oxygen.—The silicon tetrabromide employed for the oxidation was prepared according to the method of Gattermann[2] by entraining bromine in a stream of carbon dioxide, and passing the resulting mixture over heated silicon. The oxidation of the tetrabromide was studied, early in the course of this research, between the temperatures 800 and 900°. It was found that, although the rate of oxidation was slow, the reaction proceeded all of the way to the formation of silica.

That further study of this reaction would be desirable was realized, but before this was accomplished a paper by Rheinboldt and Wisfeld[3] appeared, in which the results of their study of the same reaction are given. These workers found that the optimum temperature range for the formation of oxybromides is 670 to 695°; above this the reaction progresses to silica. Two oxybromides only were isolated by them, Si_2OBr_6 (m. p. began at 26.5°, but mostly at 28.5°, b. p. approx. 120° at 15 mm.) formed in small quantities, and $Si_4O_4Br_8$ (m. p. began at 121.5° but mostly at 123.5°, b. p. 170° at 15 mm.), formed in large quantities. The work of these authors was repeated and the results obtained are summarized in Table II.

TABLE II

Fraction	Product G.	Product %	Formula
I	18	14.4	Si_2OBr_6
II	37	29.6	$Si_3O_2Br_8$
III	38	30.4	$(SiOBr_2)_4$
IV	13	10.4	$Si_4O_3Br_{10}$
V	12	9.6	$Si_5O_4Br_{12}$
VI	7	5.6	Higher residue

From this table it can be seen that $(SiOBr_2)_4$, formed only as a trace by the simultaneous action of oxygen and bromine on silicon, is obtained in large amounts by the oxidation of silicon tetrabromide, a fact which is in agreement with the results reported by Rheinboldt and Wisfeld. It is apparent, however, that appreciable quantities of several other compounds, not reported by them, are also formed in the reaction. The purification and analysis of these compounds is described below.

III. Other Methods Studied

a. Oxidation of Hexabromodisilane, Si_2Br_6.—Since oxybromides may be prepared by the oxidation of silicon tetrabromide, it was thought that the oxidation of such substances as hexabromodisilane and silicobromoform might be of interest. The Si–Si bond present in Si_2Br_6 would be expected to break to admit oxygen more readily than the Si–Br linkage of the tetrabromide. When, however, oxygen was bubbled through the hexabromodisilane (prepared as described in Section I), which was heated to 230 to 250°, and the resulting mixture was passed back and forth through a tube heated electrically to the desired temperature, it was found that below 250° oxidation is negligible, and above this temperature silicon tetrabromide and silica are formed. In a typical experiment, with the Si_2Br_6 kept at 250°, the oxygen stream at a rate of 3 liters per hour, and the furnace temperature 300°, in the course of seven hours, 10 g. of Si_2Br_6 was decomposed to form silicon tetrabromide and silica. The reaction is evidently $2Si_2Br_6 + O_2 = 3SiBr_4 + SiO_2$.

b. Oxidation of Silicobromoform, $SiHBr_3$.—In 1868 A. J. Besson reported that in the preparation of silicobromoform from silicon and hydrogen bromide he noted the formation of a trace of material crystallizing in yellow platelets, and, since some air got into his apparatus during the reaction, he thought this substance probably was an oxybromide of silicon. Consequently it was decided to study the oxidation of silicobromoform in some detail in the hope of isolating this yellow material. The silicobromoform was prepared by passing a stream of hydrogen bromide over heated silicon.[4]

Dry air was bubbled at a rate of about two liters an hour through a solution containing 10 g. of silicobromoform, diluted with an equal volume of silicon tetrabromide to retard the reaction, and the exit tube for the gas was protected by a drying tube. The mixture in the trap was warmed gradually to 90°, at which temperature a deposit of the appearance of silica gradually precipitated, but no yellow color appeared. The reaction was accompanied by a slow evolution of hydrogen bromide, and distillation of the material in the trap showed the other products to be silicon tetrabromide, silicon dioxide, and a white solid (probably silicoformic anhydride), which exploded on impact. The formation of this could be explained as due to the hydrolysis of silicobromoform by the water formed as a product of the oxidation of silicobromoform.

c. The Reaction between Silver Oxide and Silicon Tetrabromide.—About 80 g. of silicon tetrabromide was refluxed slowly with 20 g. of silver oxide (dried for twenty-four hours at 75°, two hours at 120°, and one hour at 140°). The dark brown color of the silver oxide slowly disappeared, being replaced by the yellow color characteristic of silver bromide, and at the end of thirty hours the process was completed. Distillation of the product showed that the reaction had gone quantitatively according to the equation

$$2Ag_2O + SiBr_4 \longrightarrow 4AgBr + SiO_2$$

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[4] See W. C. Schumb and R. C. Young, THIS JOURNAL, **52**, 1464 (1930).

With the hope of stopping the action intermediately, the experiment was repeated with the tetrabromide diluted with an equal volume of carbon tetrachloride, and the temperature was kept at 80°. After forty hours of refluxing the reaction was completed, but in this case, too, the oxidation had progressed to silica.

d. The Ozonization of Silicon Tetrabromide.—The effect of ozone on silicon halides apparently has not been investigated previously. It was thought that such a reaction might prove interesting, since ozone forms an oxygen linkage between two carbons in certain organic compounds.

A stream of ozonized oxygen (8% ozone) was bubbled at a rate of about 3 liters an hour through a trap containing 30 g. of silicon tetrabromide. Since little or no effect was observed at room temperature, the trap was warmed gradually. After a period of two hours at 45°, the solution became pale orange in color, but, since the reaction was so slight, the temperature was gradually raised to 75°, whereupon the color deepened at a noticeable rate. Since this color is necessarily due to bromine set free, dilution with silicon tetrabromide must prevent the reaction of the bromine with the ozone from becoming violent at this temperature.

At the end of twenty hours a few cc. of bromine had collected, and a deposit of a gelatinous-looking solid appeared on the walls of the traps. Distillation showed the products of the reaction to be bromine, silica, and a trace of a high boiling oil. In the hope of increasing the amount of the latter, ozonization of silicon tetrabromide was repeated with the addition of a diluent. For this purpose carbon tetrachloride was chosen, since it is unreactive with ozone. After thirty hours, with a mixture of equal volumes of silicon tetrabromide and carbon tetrachloride kept at 40°, sufficient oxidation had occurred to warrant a distillation of the product. The results obtained, however, did not differ materially from those found in the first trial.

e. Thermal Decomposition of Si_2OBr_6.—Several articles relating to the formation of higher oxychlorides from Si_2OCl_6 appeared in 1876.[5] Since large quantities of Si_2OBr_6 were already available, the effect of oxygen on this compound was tried, the method employed being identical with that used for the oxidation of hexabromodisilane. It was found that there was no reaction below 200°, at which temperature an exceedingly slow action occurs, resulting in the formation of silicon tetrabromide and silica, together with a trace of a high boiling oil. The rate of decomposition gradually increases as the temperature is raised, but even at 260°, close to the boilingpoint of the oxybromide, the reaction is very slow.

Any reaction occurring obviously is not an oxidation process, since no bromine is set free; it evidently proceeds for the most part according to the equation $2Si_2OBr_6 = 3SiBr_4 + SiO_2$, and to a very small extent in this manner: $4Si_2OBr_6 = 3SiBr_4 + Si_5O_4Br_{12}$. In either case the oxygen used plays no part in the process and any inert gas should serve as well; as was shown experimentally to be the case.

Purification of Products and Freezing Point Determinations.—The purification of fractions II, IV and V (Table I) was effected entirely by repeated fractional distillations. The type of column which proved most satisfactory was a two-foot (60 cm.) vapor-jacketed column of the Podbielniak type, with a solid glass spiral fitted into a Pyrex tube (outside diameter 8 mm.). For the purification of fraction I partial crystallization from its own liquor was used, as well as distillation. In the case of number III, fractional distillation was followed by two crystallizations from carbon disulfide, the crystals being separated from the solution in the absence of moisture by means of a sintered glass plate, and washed with fresh solvent.

Of the physical constants of the compounds obtained tabulated in Table I, the freezing points were quite sharp with the first three compounds, but some difficulty was experienced in obtaining accurate values in the case of the last two compounds. These liquids became increasingly viscous on cooling to the temperature of solid carbon dioxide, and upon immersion in liquid air froze to a colorless solid with a glassy appearance. Whether this was due to polymerization of the molecules on cooling is not known, but seems probable. Approximate freezing point determinations of these two compounds were made by immersion in alcohol cooled with liquid air.

Methods of Analysis and Molecular Weight Determinations.—In the analytical work required to establish the composition of the oxybromides prepared in this work, both the bromine and the silicon content were determined, gravimetrically, the former as silver bromide and the latter as silica. The percentage of oxygen was calculated by difference.

Molecular weight values were determined by the Beck-

TABLE III

ANALYTICAL DATA AND MOLECULAR WEIGHTS

Fraction	Si, %	Br, %	Mean ratio Si:O:Br	Mol. wt. (by f. p. method)
I		87.21		
	10.20	86.85	2:0.99:5.98	597
	10.17	86.77		573
Si_2OBr_6	10.14	86.96	2:1:6	552
II	11.23	84.50		838
	11.06	84.62	3:2.03:7.90	836
	11.11	84.45		795
$Si_3O_2Br_8$	11.11	84.65	3:2:8	756
III	13.46			895
	13.53	79.50		790
	13.66	79.15	1:0.92:2.05	856
$Si_4O_4Br_8$	13.72	78.43	1:1:2	816
IV	11.91	83.43		
	11.64	81.43	4:2.95:9.97	989
	11.70	83.39		930
	11.54	83.31		
$Si_4O_3Br_{10}$	11.67	83.33	4:3:10	959
V	12.03	82.33	5:4.05:12.00	1299
	12.02	82.46		1232
				1223
$Si_5O_4Br_{12}$	12.03	82.47	5:4:12	1163
VI	12.14	82.15		
	12.18	82.10	6:5.0:14.4	[a]
$Si_6O_5Br_{14}$	12.28	81.85	6:5:14	1367

[a] The results on this fraction, while less complete and less accurate than the preceding five, strongly indicate the presence of the oxybromide $Si_6O_5Br_{14}$.

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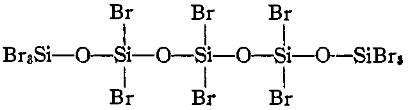
[5] L. Troost and P. Hautefeuille, *Ann. chim. phys.*, [5] **7**, 453 1876).

mann freezing point lowering method. Ethylene bromide (Eastman Reagent) which was used as the solvent in the molecular weight work, was dried by allowing it to stand over phosphorus pentoxide for twenty-four hours, after which it was fractionally distilled from fresh drying agent, giving a sample with a boiling point of 129.5 to 130°. The cryoscopic constant of ethylene bromide was taken as 12.50° per mole per 1000 g. of solvent.[6]

The fractions given in the following tabulation refer to those of Table I. The same weight of solvent, 54.73 g. (the contents delivered by a calibrated pipet), was used in each molecular weight determination.

The simplest conceivable oxybromide, $SiOBr_2$, like the corresponding chloride, is probably incapable of existence outside the vapor state, and in the liquid state polymerizes to $(SiOBr_2)_4$, or $Si_4O_4Br_8$. With the exception of $(SiOBr_2)_4$, the compounds are all members of the series of general formula $Si_nO_{n-1}Br_{2n+2}$, of which series $SiBr_4$ itself might be considered as the first member. Although there is evidence of a ring structure for $(SiOBr_2)_4$, the other substances are most probably straight-chain compounds, with an oxygen atom linked between each Si atom, such as



$$Br_3Si{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}\underset{Br}{\overset{Br}{Si}}{-}O{-}SiBr_3$$

Compounds containing the terminal linkage $-\underset{Br}{Si}{=}O$, although logically to be expected, apparently are not realized.

Summary

1. The following series of silicon oxybromides was prepared: $(SiOBr_2)_4$, Si_2OBr_6, $Si_3O_2Br_8$, $Si_4O_3Br_{10}$ and $Si_5O_4Br_{12}$, definite indication of the existence of $Si_6O_5Br_{14}$ (and perhaps of higher oxybromides) also being shown. All but the first compound belong to the homologous series $Si_nO_{n-1}Br_{2n+2}$. The compounds all hydrolyze readily in the presence of moisture, the rate of hydrolysis decreasing with a decrease in volatility. They are miscible in all proportions with CS_2, CCl_4, $CHCl_3$ and $SiBr_4$.

With the exception of the first two compounds (which were prepared independently in the present work, and by independent methods) these substances have not been reported previously, nor has as complete a series of any other silicon oxyhalides been prepared.

2. With the hope of obtaining oxybromides of silicon, the following reactions were studied: A, the simultaneous reaction of oxygen and bromine, both with silicon and with calcium silicide; B, the reaction of silicon tetrabromide with oxygen; C, the oxidation of hexabromodisilane; D, the oxidation and the thermal decomposition of Si_2OBr_6; E, the reaction of silicobromoform with oxygen; F, the effect of silver oxide on silicon tetrabromide; G, the ozonization of silicon tetrabromide. The first two methods resulted in the formation of large quantities of oxybromides. In no other case were appreciable quantities of oxybromides formed, the reaction progressing all of the way to silicon dioxide.

CAMBRIDGE, MASS. RECEIVED OCTOBER 30, 1936

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(6) "International Critical Tables," Vol. IV, p. 183.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

The Electrode Potential of the Iodine–Iodate Electrode at 25°[1]

BY WALTER O. LUNDBERG,[2] CARL S. VESTLING[3] AND J. ELSTON AHLBERG

The purpose of the present investigation has been to gather additional data necessary to determine more closely the standard potential at 25° for the electrode reaction

$$\tfrac{1}{2}I_2(s) + 3H_2O(l) = IO_3^- + 6H^+ + 5E^-$$

The value of the standard potential available until now is based upon the work of Sammet,[4] but several experimental factors contribute to considerable uncertainty in his results. The most important of these is that he measured the potential of the iodine–iodate electrode at 25° against a normal calomel potassium chloride electrode maintained at 18°. Furthermore, the liquid potentials with which he had to deal were relatively high, ranging up to 0.034 volt. The results of Sammet have been recalculated employing the activity coefficients of hydrogen ion as given by Lewis and Randall[5] and those of iodic

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(1) In part from a dissertation submitted by Walter O. Lundberg to The Johns Hopkins University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(2) Hormel Foundation Fellow in Chemistry, 1930–1934.

(3) Patrick Garvan Fellow in Chemistry, 1934–.

(4) Sammet, *Z. physik. Chem.*, **53**, 665 (1905).

(5) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York, 1923.