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The Oxychlorides of Silicon and the Corresponding Ethyl Esters

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The literature concerning the identity of the oxychlorides of silicon has been in a somewhat confused state since the original work of Friedel and Ladenburg[1] and of Troost and Hautefeuille.[2] The former investigators first prepared hexachlorodisiloxane, Si_2OCl_6, by passing the vapors of silicon tetrachloride through a porcelain tube packed with fragments of white-hot feldspar. The latter experimenters claimed to have prepared a series of oxychlorides by passing a mixture of chlorine and oxygen over heated crystalline silicon. However, as no analytical data were offered in support of the formulas of the oxychlorides reported, the results of their experiments are for the most part questionable, with the exception of the compounds Si_2OCl_6 and $Si_4O_4Cl_8$, which have been corroborated by the more recent work of Rheinboldt and Wisfeld.[3]

In a study of the oxybromides of silicon made in this Laboratory a few years ago,[4] it was learned that these compounds, with the exception of the tetramer, $(SiOBr_2)_4$, fall in an homologous series, $Si_nO_{n-1}Br_{2n+2}$, of which $SiBr_4$ may be considered the first member. The series extends definitely as far as $Si_6O_5Br_{12}$, and probably farther. Consequently it was felt that the oxychlorides of silicon likewise should be represented by such a series as $Si_nO_{n-1}Cl_{2n+2}$, together with the cyclical $(SiOCl_2)_4$. The monomeric form of the last compound, $SiOCl_2$, does not appear to exist, as it is well known that substances containing the Si=O linkage invariably undergo polymerization spontaneously with formation of Si—O—Si bonds.

Preliminary experiments in this Laboratory[5] employing a mixture of oxygen and chlorine, passed over heated silicon, had established the fact that this method of preparing a mixture of the oxychlorides is to be preferred to other possible methods, such as the interaction of silicon tetrachloride with oxygen at high temperatures.

The apparatus used in the present work consisted of a Pyrex tube containing 500 g. of commercial silicon (averaging 98% Si), which ranged in particle size from a fine powder to lumps about 1/4 inch in diameter. The tube was filled not much more than half full in order to allow a channel for the free passage of the gases even after the large increase in volume of the contents accompanying the reaction had occurred. The tube and contents were held in a hinged-type furnace (or an electric heating sleeve), which rested on an inclined plane, so that as each portion of the silicon became exhausted the heater could be moved down to a new position. Little additional heat needed to be supplied, since the heat of the reaction, once started, was sufficiently great to sustain the reaction. The attempt was made to regulate the heating and the rate of flow of the gases, in order to maintain a dull red glow in the tube and to avoid causing either a swelling or collapse of the walls of the glass tube.

Cylinder chlorine (2 vols.) and oxygen (1 vol.) were separately conducted through concentrated sulfuric acid drying tubes (preceded by traps to retain any of the acid sucked back) and mixed at a Y-joint just prior to entering the reaction tube. The products of the reaction were passed first into a receiver immersed in a hot-water-bath (80°) in order that the condensate might consist mainly of the oxychlorides, the lower boiling silicon tetrachloride largely passing on to a second receiver cooled with ice. The residual gases were vented through a calcium chloride tube and over the surface of concentrated sodium hydroxide solution into the hood. After thirty-six hours the first receiver contained about 300 cc. of liquid, colored yellow by the presence of some ferric chloride as well as by dissolved chlorine.

The reaction product from the first receiver was fractionally distilled, in part, at atmospheric pressure, to remove $SiCl_4$ and Si_2OCl_6, of each of which about 50 cc. was obtained, b. p. 57 and 137°, respectively; the rest was roughly separated into four fractions at 15 mm. pressure. The lowest boiling material was collected at 58°, the highest at 145° at this pressure. These four samples were subjected to a series of fractionations, recombination and refractionations, until one solid and five liquid products were obtained of sufficiently constant boiling points to warrant analysis and identification as compounds.

The fractionating column used was of the Podbielniak type, 4 feet long, electrically heated, containing a solid glass spiral fitted into an 8-mm. Pyrex tube.

The results of two such sets of experiments, including the formulas of the compounds isolated and identified by the methods described below, are summarized in Table I.

The melting point of the purest sample of Si_2OCl_6, as determined by the method employed in previous work on the oxybromides of silicon,[4] was found to be $-28.1 \pm 0.2°$, differing appreciably from −33°, the value first reported by Stock and co-workers.[6] With the exception of $Si_3O_2Cl_8$, the melting point of which was determined only approximately as −70°, and $Si_4O_4Cl_8$, m. p. 77°, as reported by

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(1) Friedel and Ladenburg, *Compt. rend.*, **66**, 539 (1868); *Ann.*, **147**, 355 (1868).

(2) Troost and Hautefeuille, *Bull. soc. chim.*, [2] **13**, 213 (1870); **16**, 243 (1871); **19**, 255 (1873); **35**, 360 (1881); *Ann. chim. phys.*, [5] **7**, 452 (1876).

(3) Rheinboldt and Wisfeld, *Ann.*, **517**, 197 (1935).

(4) Schumb and Klein, THIS JOURNAL, **59**, 261 (1937).

(5) Conducted by A. B. Levine, 1938.

(6) Stock, Somiesky and Wintgen, *Ber.*, **50**, 754 (1917).

TABLE I

EXPERIMENTAL RESULTS ON THE SILICON OXYCHLORIDES

Formula	B. p., °C. (15 mm.)	Mol. wt.			Analyses, % Silicon			Chlorine		
		Calcd.	Found		Calcd.	Found		Calcd.	Found	
Si_2OCl_6	137[a]	285			19.7	19.6		74.7	74.7	74.8
$Si_3O_2Cl_8$	76	400	397	412	21.1	21.2	21.2	70.9	70.8	70.8
$Si_4O_4Cl_8$	91	460			24.4	24.2	24.0	61.7	61.9	62.0
$Si_4O_3Cl_{10}$	109–110	515	485	480	21.8	21.9	21.7	68.9	68.8	69.0
$Si_5O_4Cl_{12}$	130–131	630	602	590	22.3	22.5	22.6	67.6	67.4	67.3
$Si_6O_5Cl_{14}$	139–141	745	704	681	22.6	22.6	22.7	66.7	66.8	66.8
$Si_7O_6Cl_{16}$	145–147	860	....		22.8	22.9	22.8	66.0	66.0	66.1

[a] 760 mm. pressure.

Rheinboldt and Wisfeld,[3] the other oxychlorides from $Si_4O_3Cl_{10}$ to $Si_7O_6Cl_{16}$, inclusive, were found to grow increasingly viscous on strong cooling, being converted to transparent, glassy solids when brought to liquid air temperature.

The analysis of the oxychlorides consisted of the gravimetric determination of chlorine and of silicon. The method employed for chlorine was based on that described by Baxter, Weatherill and Holmes[7] in the determination of the atomic weight of silicon. In this process weighed samples of the oxychloride contained in small, thin-walled, sealed glass bulbs, were hydrolyzed by breaking under water in a glass-stoppered Erlenmeyer flask, containing a slight excess of sodium hydroxide to react with the hydrochloric acid formed. The flask was shaken to ensure absorption of all the hydrogen chloride, the solution filtered, the filtrate acidified with nitric acid, silver nitrate added to precipitate the chloride, and the silver chloride weighed in the usual manner.

In the case of the analysis for silicon, the samples were likewise contained in sealed bulblets. The weight of the empty glass bulblet and the short piece of glass tubing connecting it (prior to sealing off) to the distillation apparatus in this case was determined as well as the weight of the sealed bulblet and sample. When the sample bulb had been broken under distilled water in a glass-stoppered Erlenmeyer flask and the flask well shaken, the contents of the flask, silica and glass, were transferred to a weighed platinum crucible, evaporated on a steam-bath, and ignited. From the weight of the glass *plus* silica the weight of the glass alone was subtracted, giving the weight of silica, from which the percentage of silicon in the sample could be calculated.

The molecular weights were determined by the Beckmann freezing point method, using ethylene dibromide (Eastman Kodak Co. reagent quality, dried over phosphorus pentoxide and fractionally distilled from fresh desiccant; b. p. 129.5–130.0°) as the cryoscopic solvent (k_F = 12.50). To prevent access of atmospheric moisture during measurements, the stirrer passed through a tube with a side-arm, through which a stream of well-dried nitrogen passed continuously. The sample was taken in a manner similar to that used in the analytical work, the sample bulb being placed in the solvent and broken just prior to observing the freezing point depression.

From the results in Table I it is evident that the oxychlorides of silicon, like the oxybromides, form an homologous series of straight-chain compounds, $Si_nO_{n-1}Cl_{2n+2}$, extending above $Si_7O_6Cl_{16}$, together with at least one compound of cyclical character, $Si_4O_4Cl_8$. With the exception of the last compound, which readily forms large, colorless, highly refracting crystals of prismatic habit, all of the compounds are colorless, oily liquids. They are all miscible with carbon tetrachloride, chloroform, carbon disulfide or silicon tetrachloride. They are incombustible, and hydrolyze more or less readily, the ease of hydrolysis decreasing with increasing molecular weight. Isolation of still higher members of the homologous series is attended with difficulty, as not only do the available quantities of these substances of higher molecular weight become small, but the increment in boiling point becomes progressively smaller as the chain lengthens, while the percentage differences in composition become so small as to make positive identification of the higher members questionable. The viscosity of the liquids increases with the higher members and when the attempt is made to distill them, the viscous oils begin to decompose with separation of silicon, even under pressures as low as 3–4 mm.

The Ethyl Esters

Although various esters derived from silicon tetrachloride have long been known and interest in the industrial applications of certain of these substances has increased in recent times, the esters derived from the silicon oxyhalides have attracted but little attention up to the present.

Only a few of these esters have been reported, including hexaethoxydisiloxane, $Si_2O(OC_2H_5)_6$,[8] the corresponding propyl compound, $Si_2O(OC_3H_7)_6$,[9] and the compound, $Si_4O_4(OC_2H_5)_8$, prepared by Troost and Hautefeuille[10] from absolute ethyl alcohol and $Si_4O_4Cl_8$.

In the present work the ethyl esters derived from Si_2OCl_6, $Si_3O_2Cl_8$, $Si_4O_3Cl_{10}$, and $Si_6O_5Cl_{14}$ were prepared from absolute ethyl alcohol and the separate oxychlorides. The alcohol was admitted dropwise into a receiver containing the oxychloride sample, which was heated in an oil-bath and a stream of thoroughly dried nitrogen or carbon dioxide was passed over the mixture to sweep out the hydrogen chloride formed. If this precaution was not taken,

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[7] Baxter, Weatherill and Holmes, THIS JOURNAL, **42**, 1194 (1920).

[8] Friedel and Crafts, *Ann. chim. phys.*, (4) **9**, 24 (1866); *Compt. rend.*, **61**, 794 (1865); Friedel and Ladenburg, *Ann.*, **147**, 362 (1868).

[9] Abati, *Gazz. chim. ital.*, **27**, II, 437 (1897).

[10] Troost and Hautefeuille, *Ann. chim. phys.*, (5) **7**, 472 (1876).

TABLE II

ESTERS PREPARED FROM SILICON OXYCHLORIDES

Oxychloride employed	Temp. of oil-bath, °C.	Resulting ester	B. p. range, °C.	Analyses, % Silicon Calcd.	Silicon Found		Carbon Calcd.	Carbon Found		Hydrogen Calcd.	Hydrogen Found	
Si_2OCl_6	105	$Si_2O(OC_2H_5)_6$	235	16.4	16.5	16.6	42.1			8.84		
$Si_3O_2Cl_8$	125	$Si_3O_2(OC_2H_5)_8$	268–273	17.6	17.8	17.8	40.3	40.8	40.8	8.46	8.61	8.42
$Si_4O_3Cl_{10}$	150	$Si_4O_3(OC_2H_5)_{10}$	290–5	18.4	18.2	18.3	39.3	39.5	39.2	8.25	8.12	8.05
$Si_6O_5Cl_{14}$	160	$Si_6O_5(OC_2H_5)_{14}$	300–10	19.2	19.5		38.3	38.0	38.2	8.03	7.94	8.02

the interaction of the hydrogen chloride formed with the alcohol produced sufficient water to hydrolyze the oxychloride and materially reduced the yield of the desired product. After the evolution of hydrogen chloride had ceased, the product was distilled at atmospheric pressure. The results of these experiments, including analytical data, are summarized in Table II.

All of these compounds were colorless, oily liquids, practically incombustible in air, miscible with carbon tetrachloride, carbon disulfide, and ethyl alcohol, and were little, if any, hydrolyzed in the presence of water, even after prolonged contact at 100°.

In the analysis of these compounds for silicon content, the weighed sample bulbs, prepared as previously described, were broken in a beaker under concentrated sulfuric acid. The organic matter was destroyed by fuming with a sulfuric–nitric acid mixture, and the resulting silica (and glass) was transferred to a platinum dish, ignited and weighed.

Attempts to prepare the ethyl esters by the interaction of ethyl alcohol with the appropriate silicon oxybromides were invariably unsuccessful, due to the fact that the hydrogen bromide formed reacts more readily with ethyl alcohol than is the case with hydrogen chloride, and the water resulting from this interaction hydrolyzes the oxybromide with the production of a silicic acid gel.

It was found possible, however, to prepare the ethyl esters from the silicon oxybromides by reaction with dry sodium ethylate. Solid sodium ethylate, prepared from absolute alcohol and clean sodium, was dissolved in hot alcohol, precipitated by cooling, filtered, washed with absolute alcohol and dried at reduced pressure by heating to 80° in an oil-bath. When the silicon oxybromide was added slowly, dropwise, to the sodium ethylate contained in a flask, a vigorous reaction took place and after the required quantity of oxybromide had been added, the flask was heated to 150°. On cooling, the reaction product was extracted with anhydrous ether, the ether was evaporated and the product distilled.

Summary

1. By the action of a mixture of chlorine (2 vol.) and oxygen (1 vol.) upon crystalline silicon at dull red heat, the following group of silicon oxychlorides was prepared, all of which, except the first, belong to the homologous series, $Si_nO_{n-1}Cl_{2n+2}$: $(SiOCl_2)_4$, Si_2OCl_6, $Si_3O_2Cl_8$, $Si_4O_3Cl_{10}$, $Si_5O_4Cl_{12}$, $Si_6O_5Cl_{14}$, $Si_7O_6Cl_{16}$. The series is believed to extend considerably beyond this. Only the first two of the compounds listed were previously known. The results cast some doubt upon the validity of the formulas of various other oxychlorides previously reported.

2. All of these substances except the tetramer, $(SiOCl_2)_4$—a colorless, crystalline solid—are colorless, oily liquids, increasing in viscosity with increasing complexity, miscible with carbon tetrachloride, chloroform, carbon disulfide or silicon tetrachloride. They all hydrolyze in the presence of moisture, the lower members being most speedily attacked.

3. By reaction with absolute alcohol the following ethyl esters were prepared: $Si_2O(OC_2H_5)_6$, $Si_3O_2(OC_2H_5)_8$, $Si_4O_3(OC_2H_5)_{10}$ and $Si_6O_5(OC_2H_5)_{14}$, of which only the first compound was previously known. These compounds are colorless, oily liquids with high boiling points and are practically incombustible in air. They are miscible with carbon tetrachloride, carbon disulfide and ethyl alcohol. They are little if any hydrolyzed by water, even after prolonged contact at 100°.

4. The esters were found not to be obtainable by the reaction of absolute alcohol with silicon oxybromides, but could be prepared from the oxybromides by means of sodium ethylate.

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