Silicate Minerals as Sources of Trimethylsilyl Silicates and Silicate Structure Analysis of Sodium Silicate Solutions

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Trimethylsilyl derivatives of silicate minerals—olivine, hemimorphite, sodalite, natrolite, and laumontite—have been prepared in which the silicate structure of the parent mineral is retained. The same technique was used to study the distribution of silicate structures in aqueous solutions of sodium silicates.

Introduction

The silicate minerals are now classified by mineralogists according to their crystal structure. The former classification based on a silicic acid theory was abandoned because it gave erroneous groupings, but if only the silicate portion of the structure is considered it can still be used to describe some of the minerals. By it the inorganic chemist then immediately recognizes these structures as orthosilicates, pyrosilicates, etc. The silicate structures within the silicate minerals are integral parts of complex, highly cross-linked, inorganic polymers, but some of the minerals react with acids, releasing their silicate portions as silicic acids. Although they are unstable, silicic acids will react with a monofunctional organosilicon compound to give a stable organosilyl silicate derivative of the acid.

The purpose of this paper is to describe work in which some silicate minerals have been simultaneously acid leached and trimethylsilyl end-blocked to yield specific trimethylsilyl silicates having the same silicate structure as the mineral from which they were derived and to show how this reaction scheme can be used to study the silicate structures present in sodium silicate solutions.

Part I. Silicate Minerals

Experimental

Olivine.—The source of olivine, $(Mg,Fe)_2SiO_4$, was Jackson County, North Carolina. The rock specimen was ground to pass a 100-mesh screen; 30 g. (19.13% Si) was slurried with water and added to the following mixture which had been stirring at room temperature for 1 hr.: 125 g. of ice, 150 ml. of concentrated HCl (36%), 300 ml. of isopropyl alcohol, and 200 ml. of hexamethyldisiloxane $\{[(CH_3)_3Si]_2O\}$. Stirring was continued for 48 hr. at room temperature. Then the mixture was filtered to separate 14.5 g. of solids which was found (by X-ray diffraction and Si analysis) to be identical with the olivine charged to the reaction. Therefore, only 15.5 g. of olivine was consumed in this experiment. The siloxane layer was separated, washed with water, refluxed under a Dean–Stark trap to remove any dissolved or suspended water, and stripped to a pot temperature of 135°. The contents of the flask, 51.6 g., were analyzed by gas chromatography. The product distribution was found to be 28.5 g. of $[(CH_3)_3Si]_4SiO_4$ and 3.56 g. of $[(CH_3)_3Si]_6Si_2O_7$.

Hemimorphite.—The source of hemimorphite, $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$, was Durango, Mexico. The specimen used in this experiment was composed of good crystals of hemimorphite on limonite. The crystals were separated from the limonite, ground in a mor-

tar and pestle to pass a 100-mesh screen, and 20 g. (10.5% Si) was slurried with water and added to the reaction mixture described for olivine. Stirring was continued for 2 hr. at room temperature. All of the mineral dissolved except for a trace of limonite. The mixture was filtered, and the siloxane layer was separated, washed with water, dried, and stripped to a pot temperature of 135°. The contents of the flask (36.8 g.) were analyzed by gas chromatography. The product distribution was 17.2% $[(CH_3)_3Si]_4SiO_4$, 20.2% $[(CH_3)_3SiO]_3SiOSi(OH)[OSi(CH_3)_3]_2$, 25.1% $[(CH_3)_3Si]_6Si_2O_7$, and 1.2% of a compound corresponding to a trisilicate derivative.

Sodalite.—The source of sodalite, $Na_8(Al,SiO_4)_6Cl_2$, was Bancroft, Ontario. The sodalite specimen was ground to pass a 100-mesh screen and analyzed by X-ray diffraction. Then 50 g. (17.05% Si) was added to the following mixture which had stirred 1 hr. 15 min. at 1–3°: 400 ml. of concentrated HCl, 300 g. of ice, 800 ml. of isopropyl alcohol, 75 ml. of $(CH_3)_3SiCl$, and 225 ml. of $[(CH_3)_3Si]_2O$. Addition time was 8 min., and stirring was continued for 50 min., during which the mixture was allowed to warm to room temperature. At this point some solids were suspended in the aqueous phase, but dissolved upon dilution with water, and thus they were shown to be salts formed by the reaction rather than unreacted sodalite. The siloxane phase was separated, washed with water, dried, and stripped to a pot temperature of 150°. The product (134.5 g.) was fractionally distilled through a spinning-band column to give 88 g. of a material boiling at 120–123° (41–43 mm.) identified as $[(CH_3)_3Si]_4SiO_4$ and 11.5 g. of residue. The residue was analyzed by gas chromatography and found to be composed of 7.9% $[(CH_3)_3Si]_4SiO_4$, 37.6% $[(CH_3)_3SiO]_3SiOSi(OH)[OSi(CH_3)_3]_2$, 27.6% $[(CH_3)_3Si]_6Si_2O_7$, 16.6% $(CH_3)_3SiO\{[(CH_3)_3SiO]_2SiO\}_3H$, and the remainder unidentified.

Natrolite.—The source of natrolite, $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$, was Lange Sundfiord, Norway. The mineral purchased as natrolite was a crystalline mass that did not appear to be contaminated with other mineral species. An X-ray diffraction pattern of the ground specimen confirmed that it was natrolite. Twenty grams (22.05% Si) of −100 mesh powder was slurried with water and added to a reaction mixture described under olivine. The mixture was stirred for 1 hr. and then filtered to separate the trace of unidentified solids. The siloxane phase was separated, washed, dried, and stripped to a pot temperature of 135°. The crude product in the flask weighed 52.5 g., and the results of gas chromatographic analyses are shown in Table I.

The conversion of g.l.c. data to a weight per cent basis was simplified by completing the trimethylsilyl substitution of those compounds containing hydroxyl groups without changing the nature of the silicate species. To effect complete trimethylsilyl substitution, 5.0 g. of the crude product was mixed with 7.56 g. of $[(CH_3)_3Si]_2O$ and 0.5 g. of Amberlyst 15 (a high surface area sulfonic acid functional ion-exchange resin) in a 1-oz. bottle. Adequate mixing of the system was ensured by attaching the bottle to a wheel and rotating the latter for 2 hr. at room temperature. The gas chromatograph and weight per cent data for this reaction mixture are given in Table II.

TABLE I

Compound	%
[(CH₃)₃Si]₂O	34.7
[(CH₃)₃Si]₄SiO₄	12.0
[(CH₃)₃SiO]₃SiOSi(OH)[OSi(CH₃)₃]₂	0.8
[(CH₃)₃Si]₆Si₂O₇	8.5
Unknown A	4.6
(CH₃)₃SiO{[(CH₃)₃SiO]₂SiO}₃H	30.1
Unknown B	1.6
(CH₃)₃SiO{[(CH₃)₃SiO]₂SiO}₃Si(CH₃)₃	7.5

TABLE II

Compound	G.l.c., %	Weight %
[(CH₃)₃Si]₂O	76.5	
[(CH₃)₃Si]₄SiO₄	4.0	6.1
[(CH₃)₃Si]₆Si₂O₇	3.2	6.25
Unknown A	1.6	
Unknown B	1.1	
(CH₃)₃SiO{[(CH₃)₃SiO]₂-SiO}₃Si(CH₃)₃	13.6	29.4

The unknowns A and B have not been isolated for identification. The linear trisilicates listed in Table I were isolated and identified in an earlier experiment with natrolite. The analytical data obtained are given.

Anal. Calcd. for $(CH_3)_3SiO\{[(CH_3)_3SiO]_2SiO\}_3H$: C, 33.3; H, 8.4; Si, 37.0; OH, 2.25; mol. wt., 756. Found: C, 33.55; H, 8.53; Si, 37.0; OH, 2.31; mol. wt., 692; b.p., 119–121° (0.1–0.2 mm.).

Anal. Calcd. for $(CH_3)_3SiO\{[(CH_3)_3SiO]_2SiO\}_3Si(CH_3)_3$: C, 34.8; H, 8.7; Si, 37.2; OH, 0.0; mol. wt., 828. Found: C, 34.57; H, 8.64; Si, 37.12; OH, 0.03; mol. wt., 748 (a crystalline solid).

Laumontite.—The source of laumontite, $CaAl_2Si_4O_{12}\cdot4H_2O$, was Cochise County, Arizona. The mineral specimen had laumontite crystals mixed with calcite crystals. The laumontite crystals were hand picked from the calcite, ground to pass a 100-mesh screen, and identified by X-ray diffraction. Ten grams (23.71% Si) was added to the reaction mixture described for olivine. Stirring was continued for 2 hr. at room temperature and then the mixture was filtered, yielding 0.1 g. of unidentified solids. The siloxane layer was separated, washed with water, dried, and stripped to a pot temperature of 130°. A g.l.c. analysis of the crude product (I) showed the following product distribution: 51% [(CH₃)₃Si]₂O, 1.0% [(CH₃)₃Si]₄-SiO₄, 30.3% II, and 17.7% III.

Then I was placed on the steam bath overnight to evaporate the [(CH₃)₃Si]₂O.

The remaining product was allowed to stand at room temperature for 9 days, during which time crystals formed. The mass was filtered to separate the crystalline phase from the oily liquid phase. The crystalline filter cake was washed with methanol, dried, and analyzed. The analysis of the material corresponds to the cyclic tetramer {[(CH₃)₃SiO]₂SiO}₄.

Anal. Calcd. for $\{[(CH_3)_3SiO]_2SiO\}_4$: C, 32.4; H, 8.11; mol. wt., 888. Found: C, 32.4; H, 8.43; mol. wt., 860.

The infrared spectrum confirms the cyclic structure (absorption band at 18.6 μ).

The analytical results for the oily filtrate correspond to those calculated for the cyclic tetramer derivative where one of the side groups is a hydroxyl.

Anal. Calcd. for $O[(CH_3)_3SiO]_2SiO[(CH_3)_3SiO]_2SiO[(CH_3)_3SiO]_2SiO[(CH_3)_3SiO]SiOH$: C, 30.9; H, 7.72; OH, 2.08. Found: C, 31.1; H, 8.09; OH, 2.21.

The infrared spectrum confirms the cyclic structure (absorption band at 18.6 μ).

It was determined that the liquid fraction above could be converted to {[(CH₃)₃SiO]₂SiO}₄ by allowing it to react with [(CH₃)₃Si]₂O in the presence of Amberlyst 15 catalyst.

Since it had been shown that the silicate structure derived from laumontite is a cyclic tetramer, a calibration curve for g.l.c. was prepared from the isolated derivative, and the laumontite experiment was repeated for the purpose of obtaining quantitative data. The crude product after the stripping operation weighed 22.3 g. It was then mixed with 34 g. of [(CH₃)₃-Si]₂O plus 2 g. of Amberlyst 15 and tumbled for 2 hr. at room temperature in order to complete the substitution with (CH₃)₃-Si– side groups. A g.l.c. analysis of this reaction product gave the following product distribution: 80.7% [(CH₃)₃Si]₂O, 0.3% [(CH₃)₃Si]₄SiO₄, 1.8% unknown, and 17.2% {[(CH₃)₃SiO]₂SiO}₄.

Using the calibration chart prepared with the {[(CH₃)₃SiO]₂-SiO₂}₄ obtained from the first laumontite experiment, the above reaction product (56.3 g.) was determined to contain 27.0% {[(CH₃)₃SiO]₂SiO}₄, or 15.2 g.

G.l.c. Analysis.—The gas chromatography analyses were run using a Model 720 F and M gas chromatograph programmed at 25°/min. to a maximum temperature of 350°. The peak areas were calculated and converted to weight per cent values using calibration curves that were prepared from known mixtures.

Results

The data are summarized in Table III as the percentage of the silicon originally present in the mineral which was recovered as a particular trimethylsilyl silicate. In the cases where two compounds are obtained representing the same silicate species, *i.e.*, [(CH₃)₃SiO]₃SiOSi(OH)[Si(CH₃)₃]₂ and [(CH₃)₃Si]₆-Si₂O₇, the data are totaled and summarized in the table as Si₂O₇. The silicates listed are SiO₄, Si₂O₇, Si₃O₁₀, and (SiO₃)₄, representing the monomer, dimer, trimer, and cyclic tetramer species, respectively.

Discussion

One of the universal characteristics of the silicon atom in the silicate minerals is that silicon is always in fourfold coordination with oxygen. The silicate minerals are divided into classes according to the manner in which these silicon–oxygen tetrahedra are related to one another. In turn, the silicate structures have a spatial relationship with metal atoms acting as bridges to separate the silicate skeletons while at the same time serving as cross links to give the mineral a rigid character. The molecular arrangement of the atoms has been determined by X-ray diffraction rather than by chemical methods. Before the development of X-ray technology one of the schemes used in an attempt to determine the structure of silicate minerals was to subject the mineral to the action of acids. It was found that some of the minerals were dissolved by acid, apparently yielding a soluble silica which later caused the solution to gel. Murata published a study in 1943 in which he related this property of the minerals to yield a soluble silica with the silicate structures as determined by X-ray diffraction.[1] He concluded that minerals producing a soluble silica when subjected to the action of acid were: (1) minerals containing silicate radicals of small molecular weight, namely orthosilicates, pyrosilicates, and possibly silicates containing ring structures of three silicon atoms and (2) those minerals with large continuous silicon–
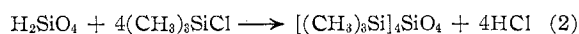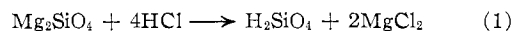
(1) K. J. Murata, *Am. Mineralogist*, **28**, 545 (1943).

Table III

Summary of Silicate Structures Derived from Minerals

Mineral	SiO₄	Si₂O₇	% of Si recovered as————————— Si₃O₁₀	(SiO₃)₄	Total
Olivine, $(Mg,Fe)_2SiO_4$	70.0	11.1			81.1
Hemimorphite, $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$	22.0	77.6	2.4		102.0
Sodalite, $Na_8(AlSiO_4)_6Cl_2$	76.0	8.7	2.5		87.2
Natrolite, $Na_2(Al_2Si_3O_{10}) \cdot 2H_2O$	10.0	13.1	67.5		90.6
Laumontite, $CaAl_2Si_4O_{12} \cdot 4H_2O$				80.9	80.9

oxygen networks that will disintegrate into units of low molecular weight such as the three-dimensional networks (tectosilicates) that contain aluminum in the ratio of at least 2 Al to 3 Si. Concerning point (2), Al can be substituted for Si in the silicate structure and the Al–O–Si linkage is cleaved by acid.

In this study the silicate species (or soluble silica) released from the mineral is allowed to react with a monofunctional organosilicon compound and the derivative identified and measured for quantitative data. The reaction sequence can be illustrated with the equations

$$Mg_2SiO_4 + 4HCl \longrightarrow H_2SiO_4 + 2MgCl_2 \quad (1)$$

$$H_2SiO_4 + 4(CH_3)_3SiCl \longrightarrow [(CH_3)_3Si]_4SiO_4 + 4HCl \quad (2)$$

The $(CH_3)_3SiCl$ for the trimethylsilylation reaction is derived from the interaction of HCl with $[(CH_3)_3Si]_2O$. The equation for this interaction shows that $(CH_3)_3SiOH$ is also a product.

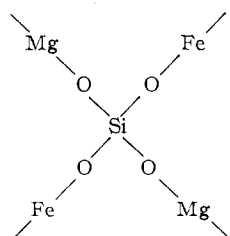$$[(CH_3)_3Si]_2O + HCl \rightleftharpoons (CH_3)_3SiCl + (CH_3)_3SiOH \quad (3)$$
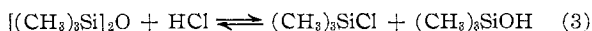
It is not known which species is the trimethylsilylating reagent. Either one is probably capable of reacting with a silicic acid.

The net result of the reaction is the replacement of the polyvalent metal atoms with the terminating trimethylsilyl group to yield a specific silicate species having the same silicate structure as the parent mineral.

It has been found that this reaction scheme does not give quantitative data because there are side reactions, but the major product of the reaction is the silicate species characteristic of the starting material. The side reactions will be described as they become evident.

The minerals examined in this study will be discussed individually because each one represents a different class or structure within a class.

Olivine is an orthosilicate mineral having Mg and Fe as the metaloxy groups separating the monomeric silicate skeletons. Although the following structural representation does not indicate the true spatial arrangement of the atoms in olivine, it serves the purpose of illustrating the orthosilicate character of the mineral. When olivine is subjected to a simultaneous acid

leaching–trimethylsilyl end-blocking reaction, the orthosilicate derivative $[(CH_3)_3Si]_4SiO_4$ is produced in 70.0% yield, and the pyrosilicate derivative $[(CH_3)_3Si]_6Si_2O_7$ produced accounts for 11.1% of the silicate mineral. The pyrosilicate derivative probably results from polymerization rather than from a similar silicate structure in the olivine mineral.

Hemimorphite is a zinc pyrosilicate, *i.e.*, two silicon atoms share one of the oxygen atoms, giving a disiloxane linkage. The pyrosilicate structures are isolated from the other silicate skeletons in the mineral by zinc atoms acting as metaloxy bridges between them.

When this mineral is simultaneously acid leached and trimethylsilyl end-blocked, the pyrosilicate derivatives $[(CH_3)_3SiO]_3SiOSi[OSi(CH_3)_3]_3$ and $[(CH_3)_3SiO]_3SiOSi(OH)[OSi(CH_3)_3]_2$ are produced. Together they account for 77.6% of the silicon analyzed in the mineral sample. In addition, the orthosilicate derivative $[(CH_3)_3Si]_4SiO_4$ is obtained representing 22.0% of the silicon.

The presence of such a large quantity of orthosilicate derivative was first assumed to have resulted from contamination of the hemimorphite by an orthosilicate mineral, but an examination of the X-ray diffraction pattern did not reveal a crystalline impurity. It is possible that a poorly crystallized orthosilicate impurity could be present as a contaminant in the mineral, and that it would not be revealed by X-ray analysis.

The experiment was repeated with the hemimorphite replaced by hexaethyl disilicate, $(C_2H_5O)_3SiOSi(OC_2H_5)_3$, whose purity could be established by gas chromatography. The appearance of a significant quantity of orthosilicate derivative indicated that here, and presumably also in the hemimorphite experiment, the orthosilicate derivative resulted from acid cleavage of the siloxane linkage. Additional studies using hexaethyl disilicate showed that the acid cleavage of the silicate siloxane linkage is temperature dependent, the higher the temperature the greater the extent of cleavage.

Cleavage of the siloxane bond upon hydrolysis of linear methyl silicates was observed by Schwarz and Knauff by determining that monosilicic acid was one of the products of the reaction.[2]

The experiment with hemimorphite demonstrates that depolymerization of the silicate structure can also be a side reaction.

The remaining three silicate minerals presented in this paper are from the class called tectosilicates. In

eral. When olivine is subjected to a simultaneous acid

(2) R. Schwarz and K. G. Knauff, *Z. anorg. allgem. Chem.*, **275**, 176 (1954).

this class every SiO_4 tetrahedra shares all its corners with other tetrahedra, giving a three-dimensional network.[3] Except for the silica minerals, all of the minerals in this class are aluminosilicates, *i.e.*, there are AlO_4 tetrahedra incorporated in the silicate network.

Sodalite is a sodium aluminosilicate having a three-dimensional structure with an Al:Si ratio of 1:1. The molecular arrangement is one of alternating AlO_4 and SiO_4 tetrahedra.[4] Since the SiO_4 tetrahedra are independent of each other (no siloxane linkages), the predicted product of a simultaneous acid leaching and trimethylsilyl end-blocking reaction would be the orthosilicate derivative. Formation of $[(CH_3)_3Si]_4$-SiO_4 in 76.0% yield shows that the chemistry is in agreement with the aluminosiloxane structure for sodalite established by X-ray diffraction.

Natrolite is a tectosilicate having an Al:Si ratio of 2:3. Their molecular arrangement is shown in the following sketch. Some of the oxygens associated with
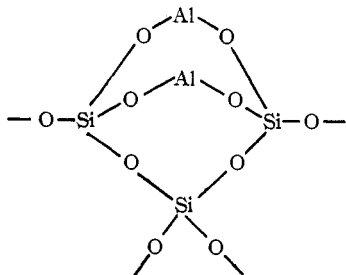
Al have been deleted in order to illustrate clearly the silicate structure. Examination of the sketch shows that in respect to the silicate network, natrolite can be described as containing linear trisiloxane chains. A trimethylsilyl-substituted linear trisilicate was produced from natrolite in an amount accounting for 67.5% of the silicon. In addition, orthosilicate and pyrosilicate derivatives accounting for 10.0 and 13.1%, respectively, of the silicon were also observed. Again it would seem that the latter products of the reaction probably result from acid cleavage of the trisilicate structure.

Laumontite is a tectosilicate having an Al:Si ratio of 1:2 and is an exception to the general rule that in order for an aluminosilicate to gelatinize it must have an Al:Si ratio of at least 2:3. A survey of the available literature did not disclose a structural picture or description of this mineral. Laumontite, when subjected to the acid leaching–trimethylsilyl end-blocking reaction, yielded a cyclic structure containing four silicon atoms, $\{[(CH_3)_3SiO]_2SiO\}_4$, in an amount accounting for 80.9% of the silicon.

Whereas the other polysilicate mineral structures gave significant quantities of lower silicate species because of acid cleavage of the siloxane bond, there were only trace quantities of a lower silicate produced with laumontite. Possibly the silicate ring structure is less vulnerable to acid attack than the linear silicate structures.

(3) L. Berry and B. Mason, "Mineralogy," W. H. Freeman and Co., San Francisco and London, 1959.

(4) W. L. Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, p. 267.

Part II. Sodium Silicates

Experimental

Preparation of Sodium Silicate Solutions.—Sodium orthosilicate and sodium metasilicate were purchased as solids from a laboratory supply house, and the others were commercial sodium silicate solutions ranging in SiO_2 concentration from 27 to 31.9%. The experimental solutions were prepared by dissolving enough sodium silicate in distilled water to give 1 M silicate concentrations. The solutions were stored in polyethylene bottles at room temperature for at least 8 days prior to the trimethylsilylation reaction in order to allow the mixture to equilibrate.

The sodium orthosilicate was assayed to determine its Na and Si content, but the other silicates were used according to the analyses supplied by the manufacturer.

Trimethylsilylation Reaction.—A mixture of 150 ml. of concentrated HCl (36%), 125 ml. of H_2O, 300 ml. of isopropyl alcohol, and 200 ml. of $[(CH_3)_3Si]_2O$ was stirred at room temperature for 1 hr. Then 100 ml. of the sodium silicate solution was added to it during a period of 3–6 min. while the temperature was maintained at 23–25°. The reaction mixture was stirred for 1 hr. at room temperature, and the siloxane phase was separated, washed twice with water, and then stirred for 2 hr. at room temperature with 2.5 g. of Amberlyst 15 in order to complete the substitution with $(CH_3)_3Si–$ groups. The latter reaction does not change the distribution of silicate structures in the presence of excess $[(CH_3)_3Si]_2O$; it merely reduces the number of chemical species present in the mixture and greatly simplifies the g.l.c. analysis. For example, both $[(CH_3)_3SiO]_3SiOSi(OH)$-$[OSi(CH_3)_3]_2$ and $[(CH_3)_3SiO]_3SiOSi[OSi(CH_3)_3]_3$ are produced in the trimethylsilylation reaction of sodium silicate. The Amberlyst 15 catalyzed reaction converts the first compound to the second compound so that the pyrosilicate derivative is represented by only one peak on the g.l.c. chromatogram. After the 2-hr. stir with Amberlyst 15 the mixture was filtered and the siloxane layer stripped to a pot temperature of 135°. The concentrated reaction product was weighed and analyzed by gas chromatography.

Analysis.—The volatile fraction of the reaction product was determined by measuring the weight loss after 3 hr. at 230°. Only the weight of the volatile fraction was used for calculating the yield of products detected by g.l.c. The nonvolatile portion of the reaction product was taken as the polysilicate fraction.

Results

The experimental results are summarized in Table IV. Only two sets of data are listed, the area % of the peaks on the g.l.c. chromatogram and the per cent of the sodium silicate accounted for as trimethylsilyl derivatives. The column headings are abbreviations of the silicate portion of the organosilyl derivatives. One of the column headings is $[(CH_3)_3Si]_2O$. This siloxane is solvent and excess reactant, not product.

The g.l.c. data are listed to indicate how much of the volatile crude product has been identified and, conversely, to show that some of the crude product is volatile but has not been identified. The silicate species that have been identified are monomer, dimer, linear trimer, and cyclic tetramer. The unidentified products of the reaction are probably higher homologs having either a linear or cyclic structure.

The quantity of silicate in the polysilicate derivative was calculated from the carbon analysis assuming that the only source of carbon is $(CH_3)_3SiO_{1/2}$ and the remaining weight is $SiO_{4/2}$.

Table IV

Summary of Silicate Structures Derived from Sodium Silicate Solutions

Na:Si ratio	SiO₂ concn., M	As per cent of chromatogram						As per cent yield					
		[(CH₃)₃Si]₂O	SiO₄	Si₂O₇	Si₃O₁₀	(SiO₃)₄	Total	SiO₄	Si₂O₇	Si₃O₁₀	(SiO₃)₄	(SiO₄/₂)x	Total
0.60:1	0	68.6	20.5	3.4	0.8	1.4	94.7	4.8	1.6	0.6	1.2	81.7	89.9
0.68:1	1	58.6	21.1	4.0	1.3	2.3	87.3	5.5	2.0	1.2	2.0	68.4	79.1
0.76:1	1	54.4	20.7	4.4	1.5	3.3	84.3	7.4	3.0	1.8	3.2	65.0	80.4
1.02:1	1	42.5	22.9	6.2	2.7	5.7	80.0	12.7	6.4	4.8	8.0	37.0	68.9
2:1	1	37.0	35.2	9.5	2.9	5.0	89.6	25.7	12.0	6.9	10.0	21.7	76.3
4:1	1	37.0	41.1	11.1	3.0	3.0	95.2	43.5	19.8	10.0	9.6	5.0	87.9
4:1	0.255	48.4	42.4	6.0	1.7	1.1	99.6	57.3	15.7	8.2	4.7	Trace	85.9
4:1	0.1	60.2	38.3	1.5	...	...	100.0	69.5	7.0	...	...	...	76.5
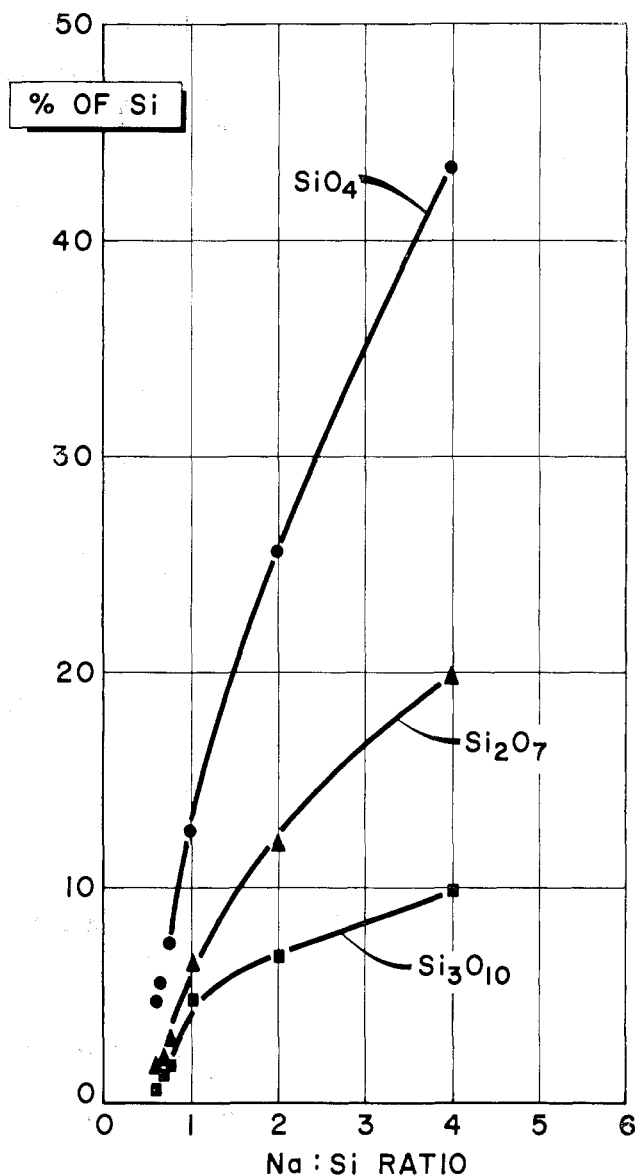
Fig. 1.—Distribution of monomer, dimer, and trimer silicates in 1 M sodium silicate solutions.

Fig. 2.—Cyclic tetramer silicate structure in aqueous solution *vs.* Na:Si ratio of the sodium silicate.

Total Si accounted for in this work ranges from 68.9 to 89.9%. Most of the unaccounted for Si probably could be traced to the unidentified products of the reaction. In fact, there is some correlation between the total of the g.l.c. data and the total material balance, the lower the g.l.c. total the lower the material balance.

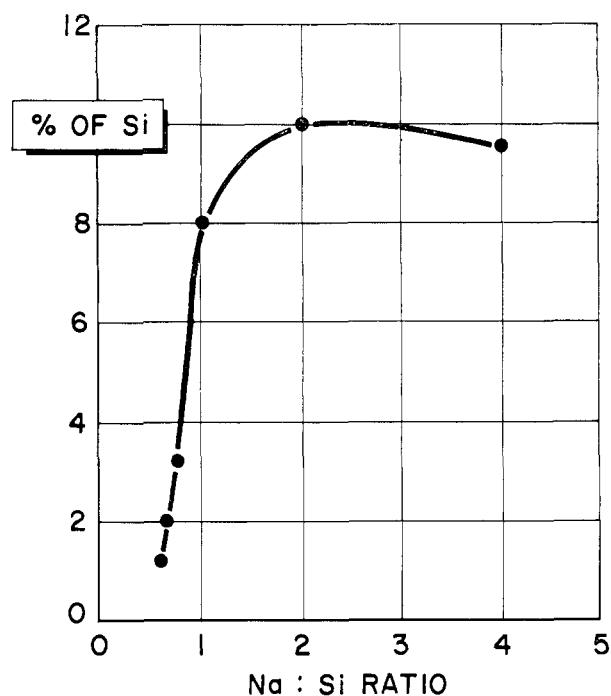The g.l.c. method of analysis is believed to have given better data in this study than a fractional distillation could yield because the only liquid product of the reaction is the orthosilicate derivative. All of the other identified products of the reaction are solids, which makes it most difficult to distil them quantitatively. A series was run in which the crude product was distilled to recover the orthosilicate derivative, and yields were obtained which are in excellent agreement with the g.l.c. data.

Discussion

Sodium silicate, one of the oldest commercial chemical products, still retains some secrets concerning its structures in aqueous solutions. If it is a crystalline member of the family, it has a specific silicate structure, but when it is dissolved in water there is no assurance that the structure remains unchanged because the alkaline medium is capable of reacting with the siloxane linkages.

Many experimental procedures have been used to study sodium silicates and their solutions in an attempt to define them, and undoubtedly many experimental approaches are needed to give the variety of informa-
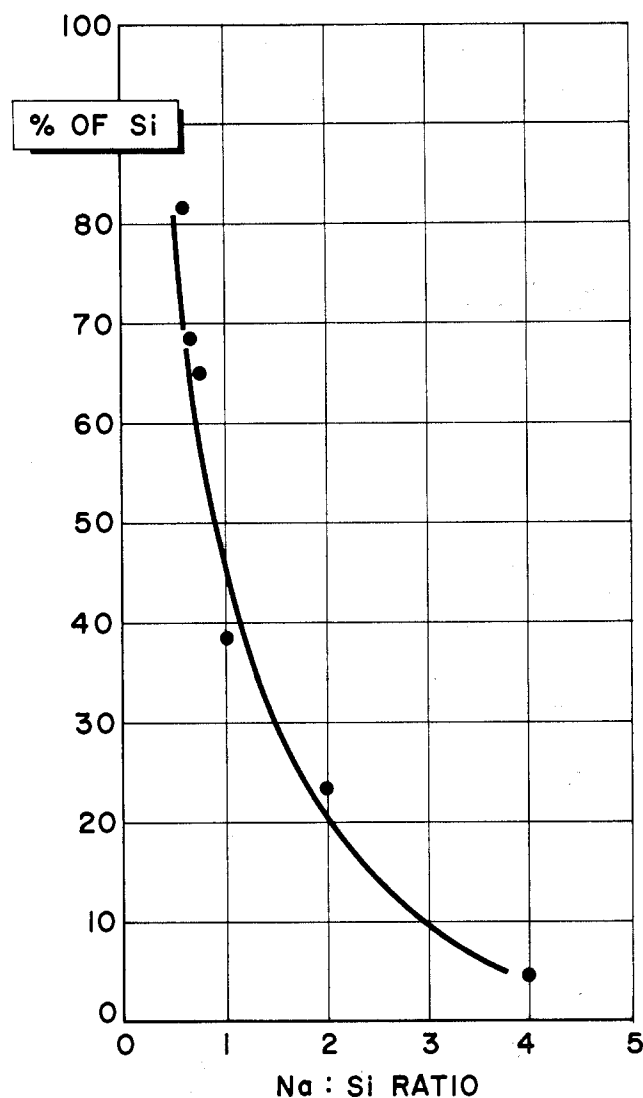
Fig. 3.—Polysilicate structure in aqueous solution *vs.* Na:Si ratio of the sodium silicate.

tion required. The data discussed in this paper have been obtained by a method which is new and contributes new information.

In part I of this paper it was shown that the acidification and trimethylsilylation of silicates does not give quantitative data because there are two side reactions involved, but valuable information can be obtained in spite of this limitation.

Only 43.5% of the silicate was recovered as the orthosilicate derivative in a 1 M sodium orthosilicate solution. There is a possibility that the solution contains only the orthosilicate species and the 43.5% yield is the maximum obtainable by this method of analysis, but three factors would tend to support the hypothesis that some of the silicate solution is polymeric: (1) such a low yield has never been experienced with an orthosilicate mineral, (2) a 9.6% yield of the cyclic tetramer species is an improbable product of a side reaction if the solution is entirely monomeric, and (3) higher yields of the orthosilicate derivative were found as the concentration of sodium orthosilicate decreased. This work shows that sodium orthosilicate solutions contain a variety of silicate structures. If this is a

valid observation, then there must be excess sodium ions which are not associated with the silicate anions.

A solution of sodium metasilicate was found to contain 25.7% monomer, 12.0% dimer, 6.9% trimer, 10.0% cyclic tetramer, and 23.3% of a polysilicate structure. Apparently a sodium metasilicate solution also contains a variety of silicate structures even though the sodium salt was a crystalline compound.

All of the sodium silicate solutions studied showed that an orthosilicate structure is present even when the silicate has a Na:Si ratio as low as 0.6:1. Figure 1 is a plot of the orthosilicate derivative obtained from the solutions having different Na:Si ratios. Included in this plot are the quantities of disilicate and trisilicate derivatives. The monomer is always found in greater quantity than the dimer, which is always found in greater quantity than the trimer, and all of these species generally decrease as the Na:Si ratio decreases. The yield of cyclic tetramer from the various sodium silicate solutions is plotted in Fig. 2. This species provides an exception to the trends observed in Fig. 1 in that the cyclic tetramer yield is nearly as great at a Na:Si ratio of 1:1 as it is at a Na:Si ratio of 4:1. The unidentified silicate species that were observed in the gas chromatograms appear to occur at a maximum quantity at a Na:Si ratio of 1:1.

In addition to the specific silicate species found, a polysilicate derivative of slightly varying composition has also been obtained in this study. A product of this type would be expected in the silicates generally referred to as the colloidal sodium silicates, but it was also found in a small quantity in the 1 M sodium orthosilicate solution and in significant quantity in the sodium metasilicate solution. The data are plotted in Fig. 3. The polysilicate derivative has not been identified, and, indeed, it probably is not a specific species. On the basis of its carbon assay, the $(CH_3)_3SiO_{1/2}:SiO_{4/2}$ ratio ranges from 1.32:1.0 to 1.05:1.0. Certainly the polysilicate derivative is not a linear material for, if it was, this ratio would be nearly 2:1. The polysilicate is probably an amorphous particle, and, if it is spherical, the particle diameter is in the range of 10–15 Å.

In summary, sodium silicate solutions having Na:Si ratios ranging from 4:1 to 0.6:1 have been found to contain SiO_4, Si_2O_7, Si_3O_{10}, $(SiO_3)_4$, and polysilicate structures. Other specific species are also present according to g.l.c. analysis, but they have not been isolated and identified. A sodium silicate solution appears to be an equilibrium solution because: (1) different concentrations produce a different distribution of products, and (2) the data show generally decreasing or increasing quantities of silicate structures over the spectrum of sodium silicate studies rather than predominant species at certain Na:Si ratios, except for the cyclic tetramer species.