Preparation of Alkyl-substituted Partial Trimethylsilyl Silicates from Olivine

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The direct trimethylsilylation reaction of olivine has yielded partial trimethylsilyl derivatives of ortho- and di-silicates whose unsilylated silanol groups have been esterified with the alcohol used as the organic solvent in the trimethylsilylating reagent. Gas chromatographic–mass spectroscopic measurements indicate the presence of the tri-, di-, and mono-alkyl-substituted trimethylsilyl derivatives of monosilicic acid [$SiO_4(SiMe_3)_{4-n}R_n$; n = 1—3] in addition to the fully silylated monomeric derivative [$SiO_4(SiMe_3)_4$]. Dimeric derivatives have also been detected which contain both the completely trimethylsilylated derivative [$Si_2O_7(SiMe_3)_6$] and alcohol-esterified derivatives [$Si_2O_7(SiMe_3)_{6-n}R_n$; n = 1—4]. The ratio of the esterified products varies with the volume of alcohol or water in the silylating reagent as well as with the reaction time.

RECENTLY, trimethylsilylation has been applied to a number of silicates including amorphous materials in order to elucidate their structures.[1-21] The reaction may be expressed by equations (1) and (2), where M is a

$$\text{Si–O–M} \longrightarrow \text{Si–O–H} \qquad (1)$$

$$\text{Si–O–H} \xrightarrow[\text{reagent}]{\text{Trimethylsilylating}} \text{Si–O–SiMe}_3 \qquad (2)$$

metallic cation. The usual trimethylsilylation methods (Lentz method [1] and Götz and Masson method [2]) yield only crude products containing partial or incomplete trimethylsilyl derivatives, and the reactions are, therefore, normally completed by treatment with Amberlyst 15 cation exchanger.

The crude product from natrolite ($Na_2O{\cdot}Al_2O_3{\cdot}3SiO_2{\cdot}2H_2O$), trimethylsilylated by the Lentz method, was analyzed by Eglinton *et al.*,[22] who detected various trimethylsilyl mono-isopropoxy-derivatives of monosilicic acid and oligosilicic acids by means of gas chromatography–mass spectroscopy (g.c.–m.s.). On the other hand, when using the Götz and Masson method to study hemimorphite [$Zn_4(OH)_2Si_2O_7{\cdot}H_2O$], we found not only the trimethylsilyl mono-alkoxy-derivative but also the di- and tri-alkoxy-derivatives.[23] Hemimorphite has water of crystallization in its structure and the reaction of chlorotrimethylsilane with this water yields hydrochloric acid which gradually decomposes the silicate mineral.[2] Based on this esterification reaction, a ' silicate–organic copolymer ' was synthesized from hemimorphite and ethylene glycol in the presence of the trimethylsilylating reagent.[24]

The purpose of this study was to prepare and identify the alcohol-esterified partial trimethylsilyl derivatives obtained from olivine using the Götz and Masson method modified by the addition of various organic solvents. Although the recovery of silicate derivatives from olivine is low, this mineral is, nevertheless, useful as a source of orthosilicate.[3] Although Calhoun and Masson [25] have recently reported the preparation of mixed trimethylsilyl–isopropyl derivatives from calcium silicates, there have been no studies on the effect of different organic solvents on the products of the derivatization of olivine.

EXPERIMENTAL

Materials.—Olivine [approximate formula $(Mg_{0.8}Fe_{0.2})_2SiO_4$] from Miyakejima, Tokyo, was used, and ground to pass through a 100-mesh sieve. The purity of the ground material was checked by *X*-ray powder diffraction. Hexamethyldisiloxane, $Me_3SiOSiMe_3$, was obtained by the hydrolysis of chlorotrimethylsilane followed by a single distillation (100 °C). All the organic solvents (methanol, ethanol, isopropyl alcohol, n-butanol, and butan-2-one) were reagent grade chemicals.

Trimethylsilylation.—Trimethylsilylation of olivine was carried out by the method reported by Götz and Masson,[3] although the amount of organic solvent in the reaction mixture was larger than used previously. In a typical reaction, hexamethyldisiloxane (hmd) (9 cm^3), $SiMe_3Cl$ (3 cm^3), water (0.3 cm^3), and an organic solvent (10 cm^3) were mixed with stirring for 5 min. This was followed by the addition of olivine powder (0.5 g). The resulting mixture was stirred for 1 h, washed with water, and then filtered. The upper organic layer was separated and concentrated by removing the hmd under reduced pressure (*ca.* 20 mmHg †) for 2—3 h at room temperature. The products in the organic layer were analyzed by gas–liquid partition chromatography. The yield of the fully trimethylsilylated monomer [$SiO_4(SiMe_3)_4$] was 6 mg (*ca.* 0.5% of the total silica in the starting material) in the case of Pr^iOH and 14 mg (*ca.* 1.1%) in the case of n-butanol. These yields were determined by internal standardization using n-hexadecane. Yields of partial derivatives and dimer derivatives could not be calculated due to the difficulty in obtaining pure samples and their low yields.

Analyses.—Gas chromatographic analyses were performed on a Shimadzu GC-7A gas chromatograph with a stainless-steel column (length 2 m, internal diameter 3 mm) packed with 5% SE-30 on Shimalite W (60—80 mesh). The thermal conductivity detector temperature was 300 °C; injection temperature, 300 °C; programmed column temperature, 90 °C for 2 min, 90—270 °C at 8 °C min^{-1}, then 270 °C for 8 min; the carrier gas was H_2 (50 cm^3 min^{-1}).

Combined g.c.–m.s. studies were conducted using a Hewlett-Packard 5992A (quadrupole technique) with an ionizing energy of 70 eV. The g.c. column was of stainless steel (length 1.2 m and inside diameter 2 mm) packed with 2% OV-101. The column was operated at 16 °C min^{-1} in

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 eV ≈ 1.60 × 10^{-19} J.

the range 90—270 °C, using helium as a carrier gas at a flow rate of 30 cm^3 min^{-1}.

The 100-MHz ^1H n.m.r. spectra were recorded with a JEOL JNM PS-100 spectrometer using CCl_4 as solvent and $SiMe_4$ as standard.

RESULTS AND DISCUSSION

The gas chromatogram of the trimethylsilylated derivatives from olivine in the case of Pr^iOH is shown in Figure 1. The components designated as S1 and S2 have already been identified by mass spectrometry to be the fully trimethylsilylated derivatives of mono- and di-silicic acid respectively [S1, $SiO_4(SiMe_3)_4$; S2, $Si_2O_7(SiMe_3)_6$]. In addition to these fully silylated derivatives, the multiple peaks on the gas chromatogram indicated the presence of partially silylated derivatives.

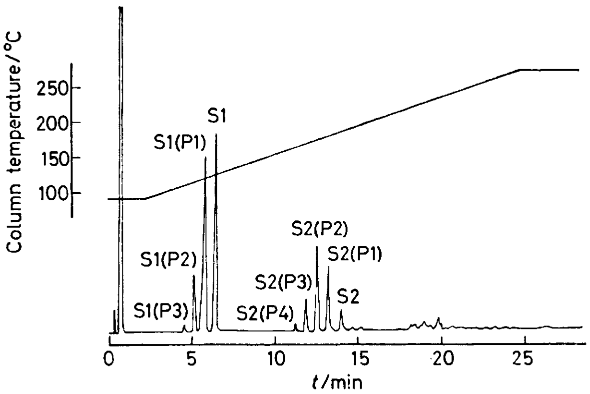

FIGURE 1 Gas chromatogram of the trimethylsilylated derivatives of olivine (organic solvent, Pr^iOH)

The multiple peaks from S2(P1) to S2(P4) are in the same pattern as the ones previously reported on the trimethylsilylation of hemimorphite, in which these peaks were identified to be the alkyl-substituted trimethylsilyl derivatives of disilicic acid $[Si_2O_7(SiMe_3)_{6-n}R_n]$.[23] Therefore, the peaks from S1(P1) to S1(P3) were assumed to be the alcohol-esterified trimethylsilyl derivatives of monosilicic acid. Although higher oligomeric derivatives could be detected at longer retention times than S2, these peaks were not investigated in this work because of their low yields and complicated mixtures.

The use of methyl, ethyl, or n-butyl alcohol in place of isopropyl alcohol brought about the variation of the chromatograms shown in Figure 2[(*a*)—(*c*)]. The retention times of the derivatives varied with the alcohol used in the trimethylsilylating reagent, although those of S1 and S2 were constant regardless of the organic solvent. On the other hand, the reaction products of olivine with a trimethylsilylating reagent containing butan-2-one gave a simple gas chromatogram showing only the presence of fully trimethylsilylated derivatives with a very small amount of an incomplete derivative (S1′) which was thought to be $SiO_3(OH)(SiMe_3)_3$, as shown in Figure 2(*d*).

Each g.c. peak was identified by g.c.–m.s. In the present work, no molecular-ion (*M*) peaks were detected. However, the $M - 15$ peaks which are characteristic of the trimethylsilyl derivatives of silicates were apparent, and these proved useful for the structure determination.[4,26] The spectrum of S1 had an $M - 15$ peak at 369, corresponding to the formula $SiO_4(SiMe_3)_4$ (molecular weight = 384). From S1 to S1(P3), the $M - 15$ peak decreased by 30 mass numbers which corresponds to the difference between $SiMe_3$ (73) and $CHMe_2$ (43), indicating substitution by isopropyl groups. A similar trend was observed in the series S1 to S1(B3) * with a separation of 16, indicating butyl substitution

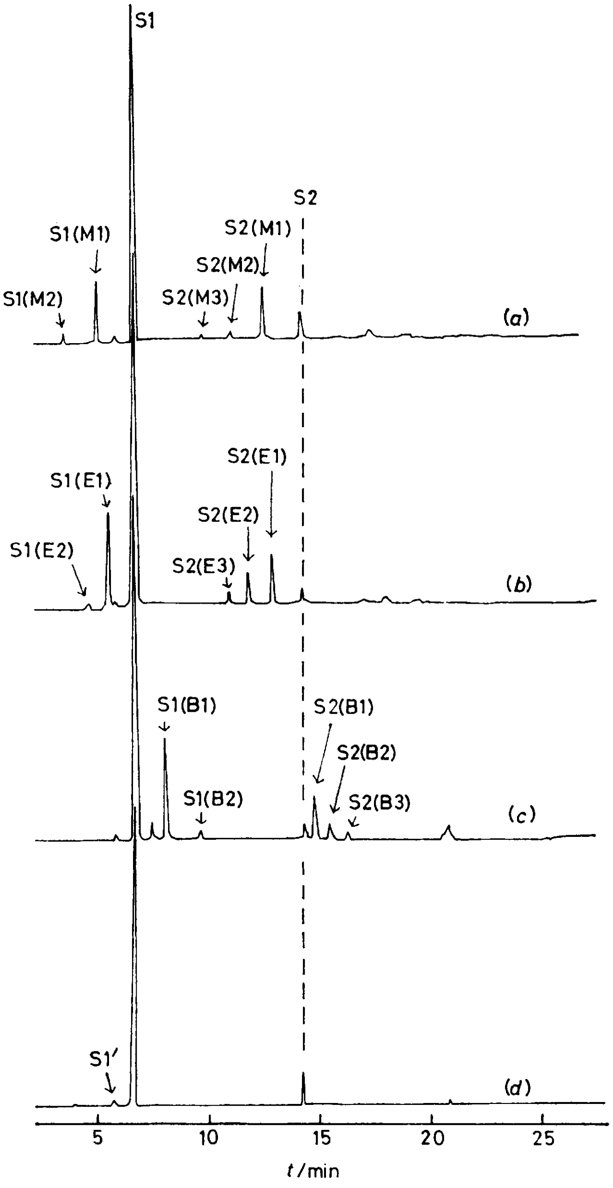

FIGURE 2 Gas chromatograms of the trimethylsilylated derivatives of olivine. Organic solvent: (*a*) methanol; (*b*) ethanol; (*c*) n-butanol; and (*d*) butan-2-one

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* The component S1(B3) could be detected by g.c.–m.s., although it does not appear on Figure 2(*c*).

[$SiMe_3$ (73) — C_4H_9 (57) = 16]. These results suggest that the components of S1(P1), S1(P2), and S1(P3) are mono-, di-, and tri-isopropyl-substituted trimethylsilyl derivatives [$SiO_4(SiMe_3)_{4-n}Pr^i_n$; $n = 1$—3] respectively, and that similar n-butyl-substituted trimethylsilyl derivatives [$SiO_4(SiMe_3)_{4-n}Bu^n_n$; $n = 1$—3] correspond to the components from S1(B1) to S1(B3). All the alcohol-esterified monomeric derivatives which appeared in the gas chromatograms are summarized in the Table. Dimeric derivatives from S2 to S2(P4) or S2(B3) were also analyzed by g.c.–m.s. and it was found that these multiple peaks, except for S2, were due to alkyl-substituted trimethylsilyl derivatives of disilicic acid [$Si_2O_7(SiMe_3)_{6-n}R_n$; $n = 1$—4], which were identical with our previous results on the trimethylsilylation of hemimorphite.[23] The ^{1}H n.m.r. spectrum of the component of S1(B1), which was obtained by preparative g.c., is given in Figure 3. The signals attributed to butyl groups could be detected and the proton ratio from the integral curve indicated the ratio of $SiMe_3$ to Bu^n to be 3 : 1. This finding strongly supported the formation of the mono-n-butyl-substituted trimethylsilyl derivative of monosilicic acid mentioned above.

Alcohol-esterified partial trimethylsilyl derivatives of monosilicic acid corresponding to g.c. peaks

Alcohol	G.c. peak	Formula
MeOH	S1(M1)	$SiO_4(SiMe_3)_3Me$
	S1(M2)	$SiO_4(SiMe_3)_2Me_2$
EtOH	S1(E1)	$SiO_4(SiMe_3)_3Et$
	S1(E2)	$SiO_4(SiMe_3)_2Et_2$
Pr^iOH	S1(P1)	$SiO_4(SiMe_3)_3Pr^i$
	S1(P2)	$SiO_4(SiMe_3)_2Pr^i_2$
	S1(P3)	$SiO_4(SiMe_3)Pr^i_3$
Bu^nOH	S1(B1)	$SiO_4(SiMe_3)_3Bu^n$
	S1(B2)	$SiO_4(SiMe_3)_2Bu^n_2$
	S1(B3)	$SiO_4(SiMe_3)Bu^n_3$

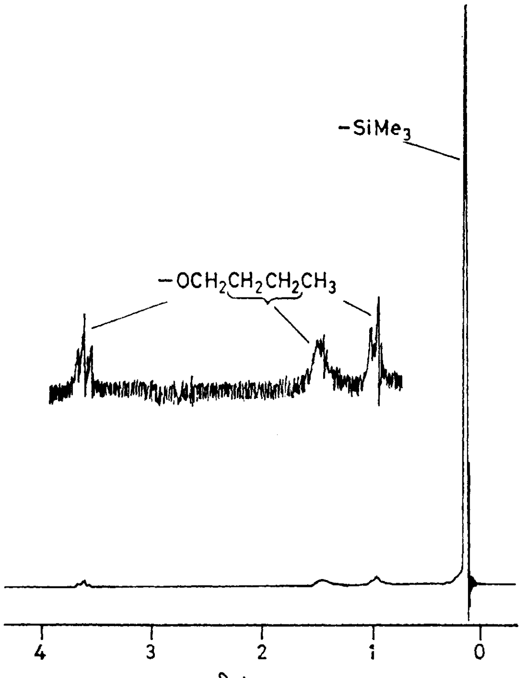

FIGURE 3 Proton n.m.r. spectrum of the component S1(B1)

From these results, it can be concluded that the reaction of olivine with the trimethylsilylating reagent containing an alcohol proceeds according to equation (3).

$$(Mg,Fe)_2SiO_4 \xrightarrow[\text{ROH}]{\text{Trimethylsilylating reagent}} SiO_4(SiMe_3)_{4-n}R_n\ (n = 0\text{—}3) + Si_2O_7(SiMe_3)_{6-n}R_n\ (n = 0\text{—}4) + \text{other polymeric species} \quad (3)$$

The simplification of the gas chromatogram in the case of butan-2-one is obviously due to the inability of butan-2-one to form an ester with the silanol group.

Figure 4 shows the effect of varying the volume of n-butanol on the ratio of peak areas of S1(B1) to S1. The proportion of the esterified product increases with an increase in the volume of n-butanol in the range 2—15 cm^3. The ratios of other (di- or tri-) esterified derivatives to fully silylated mono- or di-silicic acids also increase, at a different rate in each case.

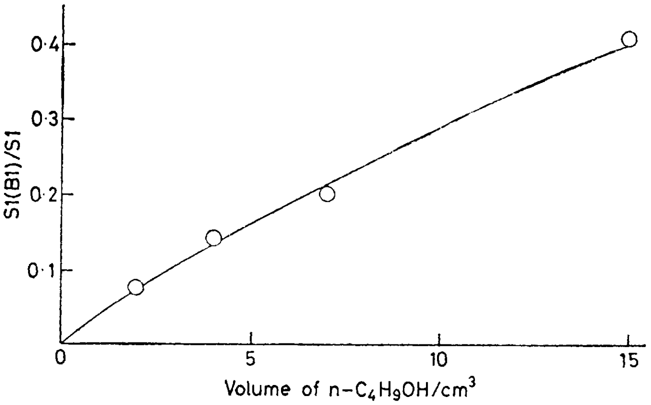

FIGURE 4 Effect of the volume of n-butanol on the ratio of peak areas of S1(B1) to S1. Reaction conditions: olivine (0.5 g); hmd (9 cm^3); $SiMe_3Cl$ (3 cm^3); water (0.3 cm^3); reaction time 1 h

The effect of the volume of water on the ratio of S1(B1) to S1 is shown in Figure 5. The proportion of the esterified derivatives decreases with an increase in the volume of water. Small amounts of water in the trimethylsilylating reagent react to completion with $SiMe_3Cl$ to produce HCl. The HCl decomposes the silicate structure, producing silanol groups, some of which react with the reagent and others which condense with alcohol. According to Calhoun and Masson's proposal [25] for the reaction mechanism, silanol groups may react with $SiMe_3(OR)$, formed by reaction between $SiMe_3Cl$ and alcohol, to produce ≡Si–O–R. Therefore, the effect of an excess of water is probably to prevent the esterification of silanol groups by the alcohol and the reaction of ≡Si–OH with $SiMe_3(OR)$, or to hydrolyse existing ester bonds.

The effect of reaction time on the ratio of S1(B1) to S1 is shown in Figure 6. On increasing the reaction

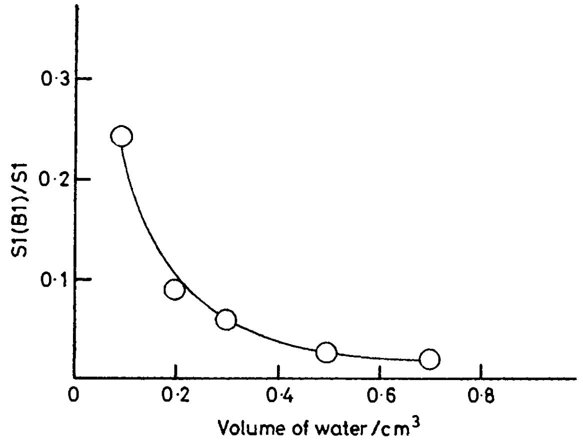

FIGURE 5 Effect of the volume of water on the ratio of peak areas of S1(B1) to S1. Reaction conditions: olivine (0.25 g); hmd (4.5 cm^3); $SiMe_3Cl$ (2.5 cm^3); n-butanol (5 cm^3); reaction time 1 h

time, the ratio dropped rapidly and eventually reached a constant level. This observation can be explained in terms of the hydrolysis of the resultant derivatives by the excess of water or HCl which was not used in the decomposition of the silicate mineral.

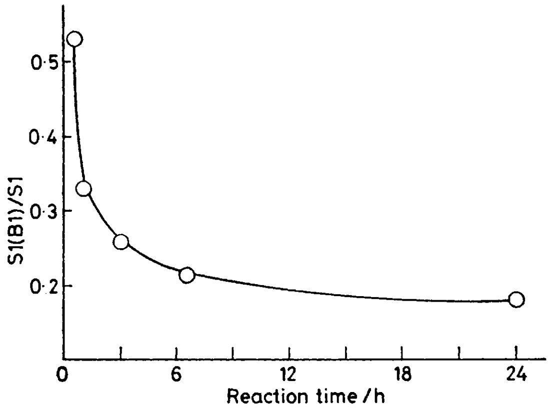

FIGURE 6 Effect of the reaction time on the ratio of peak areas of S1(B1) to S1. Reaction conditions: olivine (0.5 g); hmd (9 cm^3); $SiMe_3Cl$ (3 cm^3); water (0.3 cm^3); n-butanol (10 cm^3)

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