Trimethylsilyl Derivatives for the Study of Silicate Structures. Part 7.[1] Calcium Silicate Structures

By **Harry P. Calhoun** and **Charles R. Masson,*** Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada B3H 3Z1

A detailed study was made of the yield and products of trimethylsilylation of calcium orthosilicate ($Ca_2[SiO_4]$), rankinite ($Ca_3[Si_2O_7]$), and pseudowollastonite ($Ca_3[Si_3O_9]$) under various experimental conditions. With hexamethyldisiloxane, chlorotrimethylsilane, and isopropyl alcohol as reagents, in the absence of added water $Ca_2[SiO_4]$ yielded predominantly $SiO_4(SiMe_3)_x(Pr^i)_{4-x}$ (x = 1—4) and a lesser amount of $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ (x = 2—6), $Ca_3[Si_2O_7]$ gave predominantly $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ (x = 2—6), and $Ca_3[Si_3O_9]$ gave predominantly $Si_3O_9(SiMe_3)_x(Pr^i)_{6-x}$ (x = 2—6) and $Si_3O_{10}(SiMe_3)_x(Pr^i)_{8-x}$ (x = 3—8). Mixed trimethylsilyl–isopropyl derivatives were converted to the fully trimethylsilylated derivatives $SiO_4(SiMe_3)_4$, $Si_2O_7(SiMe_3)_6$, and $Si_3O_{10}(SiMe_3)_8$ on treatment with Amberlyst 15 ion-exchange resin in the presence of hexamethyldisiloxane. In the trimethylsilylation of $Ca_2[SiO_4]$ reaction of the mineral itself is complete within *ca.* 6 min at room temperature, under the conditions employed, and the majority of unwanted side reactions which yield Si_2O_7 and Si_3O_{10} derivatives occur during the first 3—4 min. Side reactions may be suppressed by increasing the proportion of isopropyl alcohol and decreasing that of $Ca_2[SiO_4]$ in the reagents. The presence of both isopropyl alcohol and chlorotrimethylsilane is necessary for reaction to occur. Isopropyl alcohol may be replaced by either ethyl alcohol or water, although the yield is reduced. When isopropyl alcohol is replaced by water, only the fully trimethylsilylated derivatives are formed. The mechanism of the reaction is discussed and experimental conditions are described which give highest yields of the desired products.

SINCE introduced by Lentz,[2] the method of trimethylsilylation has been studied extensively as a means of identifying silicate structures with discrete anions. The method is particularly useful for amorphous silicates such as glasses and metallurgical slags,[1,3-7] the constitution of which cannot be determined readily by other means. It has also been used to study the change in constitution of a glass on devitrification,[4,7] the conversion of hemimorphite into willemite,[8] aluminium–silicon ordering in melilites,[9] anionic distributions in sodium silicate solutions,[2,10,11] and portland cement pastes.[12-16]

In spite of its attractive features, the method suffers from some inherent limitations. (a) It is confined mainly to structures which can be solubilized by leaching with acids. In acidic media, trimethylsilylation is believed to proceed initially by stepwise replacement of cations in the structure by protons to yield the corresponding silicic acid groups which then react with the trimethylsilylating agent, usually chlorotrimethylsilane, to yield the stable trimethylsilyl derivatives. Yields from minerals (*e.g.* beryl) which are resistant to acid leaching are usually low, even when such minerals contain discrete orthosilicate groups (*e.g.* zircon, garnet). Some minerals (*e.g.* thorite, uranothorite), although they gelatinize with acid according to Murata,[17] are also resistant to trimethylsilylation.

(b) Side reactions, leading to formation of silicate structures not present in the original material, often occur. These are generally considered to be of two types: (i) condensation of silicic acid groupings released by acid leaching, before trimethylsilylation is complete and (ii) hydrolytic cleavage of siloxane linkages in the original structure. The nature and extent of these unwanted reactions vary with the conditions of trimethylsilylation, the most important variable in this respect being the proportion of water in the reagent mixture.[18] For this reason, care is necessary in interpreting the results for materials of unknown structure, particularly with respect to the minor products of trimethylsilylation.

(c) A number of incompletely trimethylsilylated derivatives are usually formed along with the desired product. When the Lentz method [2] is employed these have been characterized as mono-hydroxyl compounds [2] [$Si_2O_7(SiMe_3)_5(H)$, $Si_3O_{10}(SiMe_3)_7(H)$, $Si_4O_{12}(SiMe_3)_7(H)$] or as mono-isopropyl derivatives [19] [$SiO_4(SiMe_3)_3(Pr^i)$, $Si_2O_7(SiMe_3)_5(Pr^i)$, $Si_3O_9(SiMe_3)_5(Pr^i)$, $Si_4O_{12}(SiMe_3)_7(Pr^i)$, $Si_3O_{10}(SiMe_3)_7(Pr^i)$]. Kuroda and Kato [20] found that the incompletely trimethylsilylated derivatives formed in the trimethylsilylation of hemimorphite by the direct method [18] were the mixed trimethylsilyl–isopropyl derivatives $Si_2O_7(SiMe_3)_5(Pr^i)$, $Si_2O_7(SiMe_3)_4(Pr^i)_2$, and $Si_2O_7(SiMe_3)_3(Pr^i)_3$. To complete the trimethylsilylation it is usually necessary to resort to final treatment with Amberlyst 15 ion-exchange resin in the presence of an excess of hexamethyldisiloxane. Occasionally, treatment with Amberlyst 15 catalyses other side reactions.[21]

It is clear that the yield and chromatographic pattern depend on the nature of the cations as well as the anions in the original structure and that optimum conditions for trimethylsilylation may vary from one cation to another. It was the purpose in the present work to confine attention to a series of silicates with a common cation. The calcium silicates were chosen for this purpose. Three calcium silicates are known which possess well defined anionic structures suitable for study by this method. These are calcium orthosilicate, $Ca_2[SiO_4]$, in which the silicate ions are present exclusively as orthosilicate groups SiO_4^{4-}, rankinite, $Ca_3[Si_2O_7]$, which has the pyrosilicate structure $Si_2O_7^{6-}$, and pseudowollastonite, $Ca_3[Si_3O_9]$, whose structure is that of a cyclosilicate with $Si_3O_9^{6-}$ groupings. An attractive feature in the choice of calcium as cation is that calcium silicates can be trimethylsilylated directly, without the aid of water, thus minimizing the possibility of reactions (i) and (ii) above. It was the aim also in the present work to make a detailed study of the incompletely trimethylsilylated derivatives found in the products before and during treatment with Amberlyst 15. Other approaches to the trimethylsilylation of calcium silicates include studies by Currell *et al.*[22] on akermanite and β-$Ca_2[SiO_4]$ and Lachowski[23] on mixtures of $Ca_3[SiO_5]$ and rankinite.

EXPERIMENTAL

Materials.—Calcium orthosilicate and rankinite were prepared from $Ca[CO_3]$ (B.D.H., AR grade) and SiO_2 (Mallinckrodt, reagent grade, prefired at 1 000 °C for 12 h) by repeated sintering of the mixed powders in stoicheiometric proportions in a platinum container at 1 400—1 450 °C and grinding. *X*-Ray diffraction of powdered specimens showed that the orthosilicate was γ-$Ca_2[SiO_4]$ and the pyrosilicate was rankinite. No unreacted CaO or SiO_2 was detected in either product. Pseudowollastonite was obtained by firing natural wollastonite (Sonora, Mexico; ground to pass 100 mesh) in a platinum crucible at 1 300 °C for 48 h. *X*-Ray diffraction showed the material to be pseudowollastonite with only a small impurity of unreacted wollastonite.

Trimethylsilylation.—The method of direct trimethylsilylation,[18] in which the solid is allowed to react with chlorotrimethylsilane in the presence of isopropyl alcohol and hexamethyldisiloxane, was employed. The proportions of the reagents were varied. In a typical experiment the solid mineral (50 mg), hexamethyldisiloxane (9 cm^3), and isopropyl alcohol (1 cm^3) were placed in a tightly capped glass jar and stirred vigorously at room temperature by means of a Teflon coated magnetic stirring bar. Chlorotrimethylsilane (2 cm^3) was added and stirring was continued for 4 h. The hexamethyldisiloxane (upper) layer was removed and concentrated by distillation to remove unchanged chlorotrimethylsilane. The residue was examined by gas–liquid partition chromatography as described previously.[24] Amberlyst 15 ion-exchange resin (2 g) was added to the residue (*ca.* 8 g) and the resulting mixture was stirred at room temperature in a capped glass vial. Samples (*ca.* 3 μl) for gas chromatographic analysis were removed at various times. After all mixed derivatives had been converted to fully trimethylsilylated derivatives, absolute yields were measured. These are expressed as weight % Si in the mineral extracted as $SiO_4(SiMe_3)_4$, $Si_2O_7(SiMe_3)_6$, and $Si_3O_{10}(SiMe_3)_8$ and were determined by calibration against standard solutions of the pure trimethylsilyl derivatives in hexamethyldisiloxane. Combined errors in this procedure are estimated to be of the order of 5%. It was possible to express the results in terms of absolute yields only for solutions which contained fully trimethylsilylated derivatives. Standard solutions of the mixed derivatives were not prepared. For the latter the results are expressed in terms of peak areas or percentages of total peak area.

Mass Spectrometry.—All spectra were of the electron-impact type. For SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_3O_9^{6-}$ derivatives 70 eV spectra were obtained on a Finnigan 4000 gas chromatograph–mass spectrometer (g.c.–m.s.) employing a stainless steel column (3.6 m long × 3.2 mm diameter) packed with 3% SE-30 Ultraphase on Chromosorb W, 80—100 mesh. For these compounds the *m/e* values of the molecular ions do not exceed 666 and adequate mass spectra could be obtained with the g.c.–m.s. unit. For derivatives of the $Si_3O_{10}^{8-}$ ion, molecular ions with *m/e* values up to 828 were present and for these derivatives it was necessary to collect the compounds in glass capillary tubes and determine the mass spectra on a separate instrument.

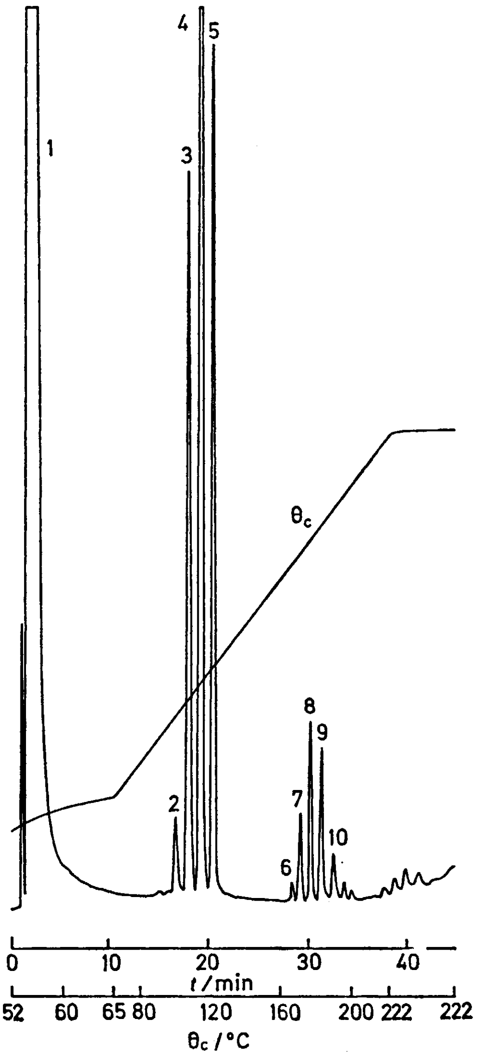

FIGURE 1 Chromatogram of product of trimethylsilylation of $Ca_2[SiO_4]$ before treatment with Amberlyst 15. Peaks correspond to $O(SiMe_3)_2$ (1), $SiO_4(SiMe_3)(Pr^i)_3$ (2), $SiO_4(SiMe_3)_2(Pr^i)_2$ (3), $SiO_4(SiMe_3)_3(Pr^i)$ (4), $SiO_4(SiMe_3)_4$ (5), $Si_2O_7(SiMe_3)_2(Pr^i)_4$ (6), $Si_2O_7(SiMe_3)_3(Pr^i)_3$ (7), $Si_2O_7(SiMe_3)_4(Pr^i)_2$ (8), $Si_2O_7(SiMe_3)_5(Pr^i)$ (9), and $Si_2O_7(SiMe_3)_6$ (10). Reagents for trimethylsilylation: 50 mg mineral, 9 cm^3 $O(SiMe_3)_2$, 1 cm^3 i-C_3H_7OH, 2 cm^3 $SiMe_3Cl$

These compounds were analysed by means of a Dupont/CEC model 21-110B mass spectrometer as described in a previous communication.[24]

RESULTS

Mass Spectra of Mixed Trimethylsilyl–Isopropyl Derivatives.—Typical chromatograms of the products of trimethylsilylation of $Ca_2[SiO_4]$, $Ca_3[Si_2O_7]$, and $Ca_3[Si_3O_9]$ before treatment with Amberlyst 15 ion-exchange resin are shown in Figures 1, 2, and 3 respectively. The identities of the peaks, as established by mass spectrometry, are given in the captions.

All derivatives gave a peak at $M - 15$, corresponding to loss of $CH_3\cdot$ from the molecular ion. This peak was generally the most useful for identification purposes.

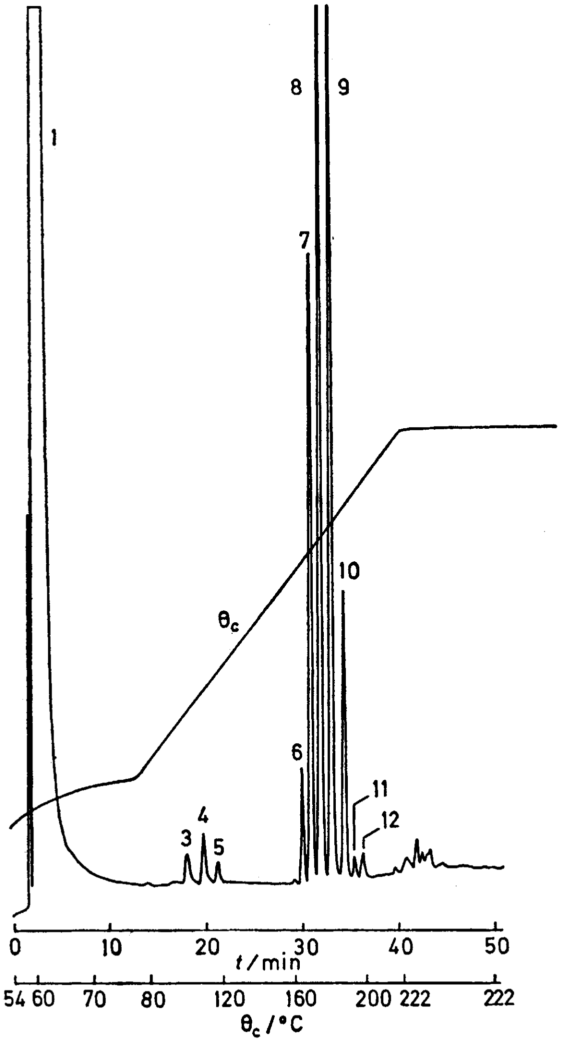

FIGURE 2 Chromatogram of product of trimethylsilylation of $Ca_3[Si_2O_7]$ before treatment with Amberlyst 15. Peaks 1 and 3—10 as in Figure 1; 11, not identified; 12, $Si_3O_9(SiMe_3)_6$. Reagents for trimethylsilylation: same as for Figure 1

In most cases, the molecular ion was too weak to be of importance for identification of the compound. For the Si_3O_{10} derivatives, however, the intensity of the molecular ion peak increased and that of the $M - 15$ peak decreased as the number of isopropyl groups on the molecule increased. Hence the molecular ion peaks were useful for identifying $Si_3O_{10}(SiMe_3)_4(Pr^i)_4$ and $Si_3O_{10}(SiMe_3)_3(Pr^i)_5$.

The fully trimethylsilylated derivatives all gave a peak at $M - 103$, as reported previously [5,24] and ascribed to loss of $CH_2Si(CH_3)_2O\cdot$ and/or $Si(CH_3)_4$ from the $(M - 15)^+$ ion.

The monoisopropyl derivatives all exhibited a peak at $M - 73$, possibly due to loss of $C_3H_7\cdot + CH_3\cdot$ from the $(M - 15)^+$ ion.

Ion currents of varying intensities were observed at $M - 57$ and $M - 59$ for the mixed isopropyl–trimethylsilyl derivatives. The most significant of these were as shown below. These are tentatively ascribed to loss of C_3H_6 and C_3H_8 respectively from the $(M - 15)^+$ ions.

	$(M - 57)$	$(M - 59)$
$SiO_4(SiMe_3)_x(Pr^i)_{4-x}$	$x = 1$—2	
$Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$	$x = 2$—5	$x = 2$—5
$Si_3O_9(SiMe_3)_x(Pr^i)_{6-x}$	$x = 2$—5	
$Si_3O_{10}(SiMe_3)_x(Pr^i)_{8-x}$	$x = 3$—7	$x = 3$—7

The following derivatives could not be separated on the packed column employed: $Si_2O_7(SiMe_3)_6$ ($M = 606$) and $Si_3O_9(SiMe_3)_4(Pr^i)_2$ ($M = 606$) (peak 10); $Si_2O_7(SiMe_3)_5(Pr^i)$ ($M = 576$) and $Si_3O_9(SiMe_3)_3(Pr^i)_3$ ($M = 576$) (peak 9); $Si_2O_7(SiMe_3)_4(Pr^i)_2$ ($M = 546$) and $Si_3O_9(SiMe_3)_2(Pr^i)_4$ ($M = 546$) (peak 8); $Si_2O_7(SiMe_3)_3(Pr^i)_3$ ($M = 516$) and $Si_3O_9(SiMe_3)(Pr^i)_5$ ($M = 516$) (peak 7); $Si_2O_7(SiMe_3)_2(Pr^i)_4$ ($M = 486$) and $Si_3O_9(Pr^i)_6$ ($M = 486$) (peak 6). In

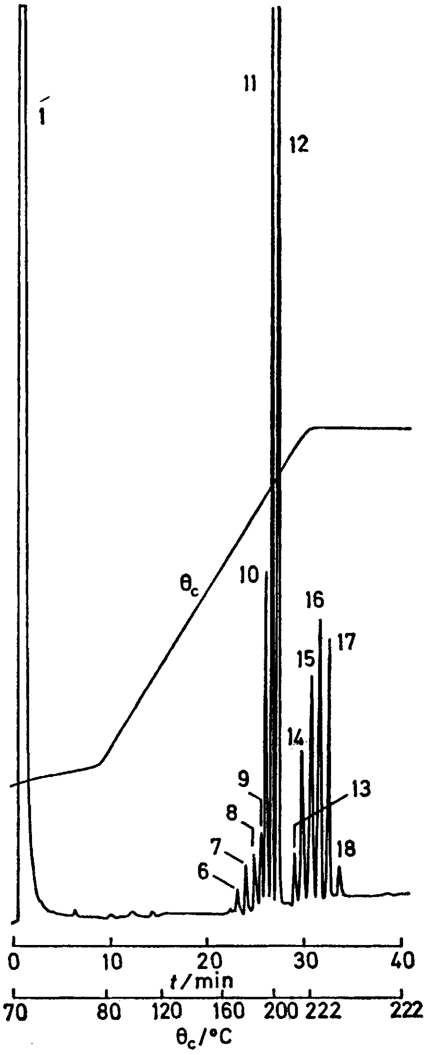

FIGURE 3 Chromatogram of product of trimethylsilylation of $Ca_3[Si_3O_9]$ before treatment with Amberlyst 15. Peaks correspond to $O(SiMe_3)_2$ (1), $Si_2O_7(SiMe_3)_2(Pr^i)_4 + Si_3O_9(Pr^i)_6$ (6), $Si_2O_7(SiMe_3)_3(Pr^i)_3 + Si_3O_9(SiMe_3)(Pr^i)_5$ (7), $Si_2O_7(SiMe_3)_4(Pr^i)_2 + Si_3O_9(SiMe_3)_2(Pr^i)_4$ (8), $Si_2O_7(SiMe_3)_5(Pr^i) + Si_3O_9(SiMe_3)_3(Pr^i)_3$ (9), $Si_2O_7(SiMe_3)_6 + Si_3O_9(SiMe_3)_4(Pr^i)_2$ (10), $Si_3O_9(SiMe_3)_5(Pr^i)$ (11), $Si_3O_9(SiMe_3)_6$ (12), $Si_3O_{10}(SiMe_3)_3(Pr^i)_5$ (13), $Si_3O_{10}(SiMe_3)_4(Pr^i)_4$ (14), $Si_3O_{10}(SiMe_3)_5(Pr^i)_3$ (15), $Si_3O_{10}(SiMe_3)_6(Pr^i)_2$ (16), $Si_3O_{10}(SiMe_3)_7(Pr^i)$ (17), and $Si_3O_{10}(SiMe_3)_8$ (18). Reagents for trimethylsilylation: same as for Figure 1

Figure 2, Si_3O_9 derivatives are present only in small amount, since peaks 11 and 12 together account for less than 1% of the total peak area (Figure 7). In Figure 3, Si_2O_7 derivatives account for *ca.* 4% of the total peak area (see below).

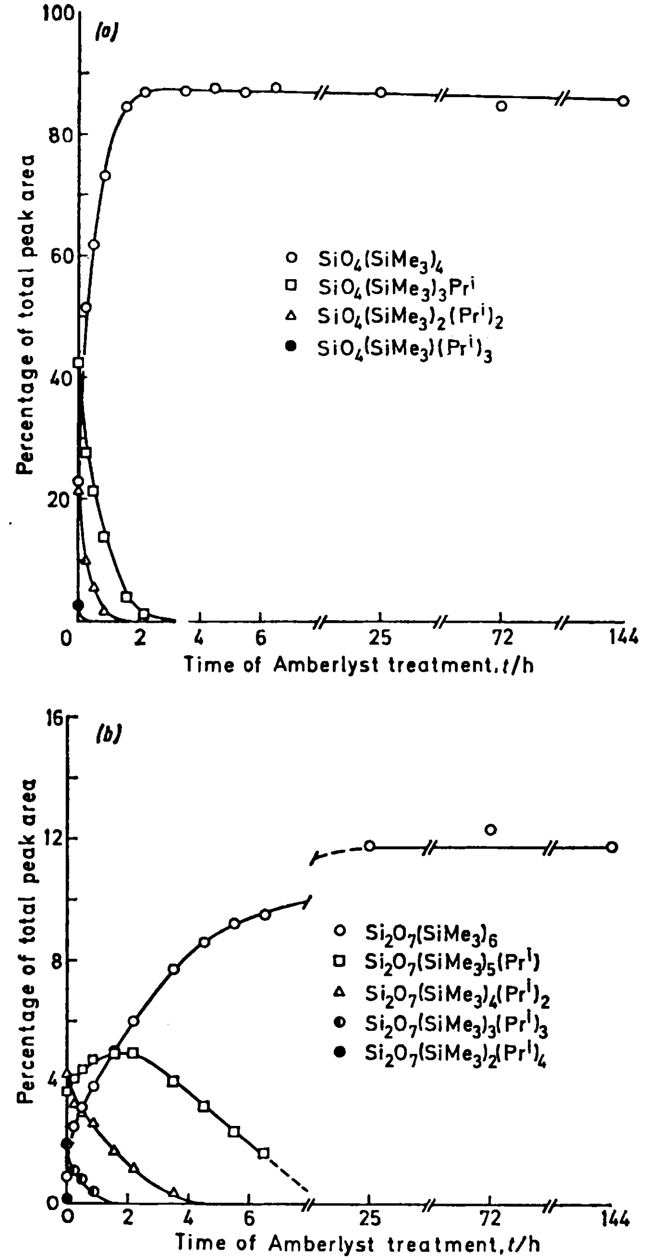

FIGURE 4 Effect of Amberlyst treatment on the products of trimethylsilylation of $Ca_2[SiO_4]$, (*a*) SiO_4^{4-} derivatives, (*b*) $Si_2O_7^{6-}$ derivatives. Reagents for trimethylsilylation: same as for Figure 1

Effect of Amberlyst 15 *Ion-exchange Resin.*—The effect of stirring the product of trimethylsilylation with Amberlyst 15 ion-exchange resin in the presence of an excess of hexamethyldisiloxane is shown in Figures 4—8. This resin catalyses the completion of the trimethylsilylation, causing a decrease in the peak area percentages due to mixed trimethylsilyl–isopropyl derivatives and a corresponding increase in the percentages due to fully trimethylsilylated derivatives. Trimethylsilylation of the SiO_4^{4-} ion was complete after 3 h treatment with Amberlyst 15 (Figure 4a). For the $Si_2O_7^{6-}$ ion, stirring times in excess of 25 h were required before all traces of mixed derivatives were removed [Figures 4(*b*) and 6]. This time could be reduced by increasing the amount of Amberlyst 15 added for a given weight of solution.

In the products of trimethylsilylation of $Ca_2[SiO_4]$ 89% of the total peak area can be attributed initially to SiO_4^{4-} and 11% to $Si_2O_7^{6-}$ derivatives. Stirring with Amberlyst 15 slowly decreases the total peak area percentage attributed to SiO_4^{4-} derivatives as shown in Figure 5. This is accompanied by a steady increase in the sum of the peak area percentages due to derivatives of the $Si_3O_{10}^{8-}$ ion. In the case of $Ca_3[Si_2O_7]$, 97.5% of the total peak area can be attributed to $Si_2O_7^{6-}$ derivatives before treatment with Amberlyst 15. Stirring with Amberlyst 15 slowly decreases this total as shown in Figure 7. This is accompanied by an increase in the peak area percentages due to derivatives of the SiO_4^{4-} and $Si_3O_{10}^{8-}$ ions as shown also in Figure 7. These trends indicate that the unavoidable final treatment with Amberlyst 15 to complete the trimethylsilylation contributes slightly to the extent of side reactions.

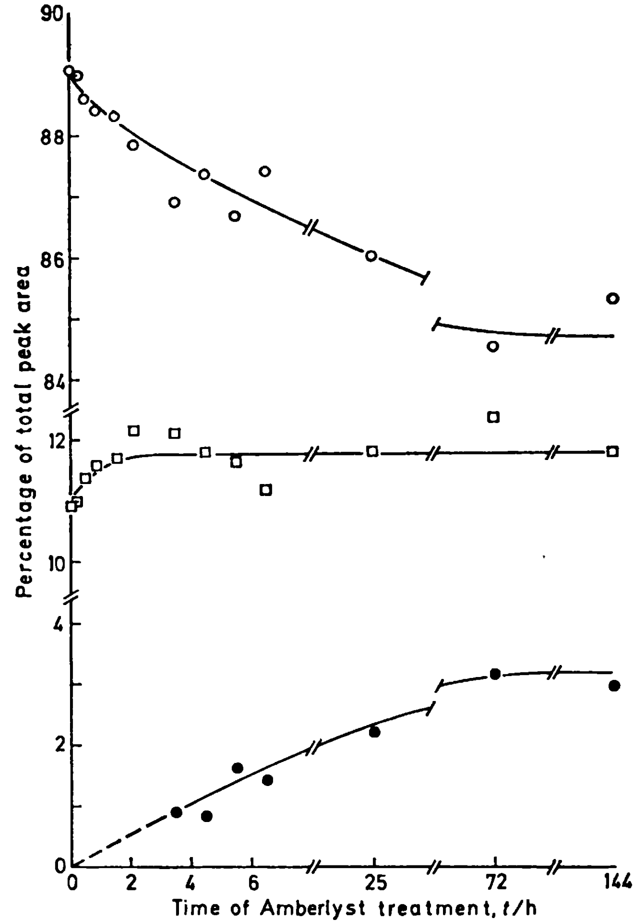

FIGURE 5 Effect of Amberlyst treatment on the total peak area percentages of $SiO_4(SiMe_3)_x(Pr^i)_{4-x}$ (○) $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ (□), and $Si_3O_{10}(SiMe_3)_x(Pr^i)_{8-x}$ (●) in the products of trimethylsilylation of $Ca_2[SiO_4]$. Reagents for trimethylsilylation: same as for Figure 1

The products of trimethylsilylation of $Ca_3[Si_3O_9]$ included mixed derivatives of Si$_2$O$_7^{6-}$, Si$_3$O$_9^{6-}$, and Si$_3$O$_{10}^{8-}$ ions (Figure 3). The effect of Amberlyst 15 was two-fold: (i) to convert mixed derivatives into fully trimethylsilylated derivatives in a complex manner and (ii) to break the Si$_3$O$_9$ ring and form derivatives of the Si$_3$O$_{10}^{8-}$ ion (Figure 8). When Amberlyst 15 treatment was complete (>168 h) the main product was Si$_3$O$_{10}$(SiMe$_3$)$_8$ (94% of total peak area). Small quantities of Si$_2$O$_7$(SiMe$_3$)$_6$ (4% of total peak area) and SiO$_4$(SiMe$_3$)$_4$ (2% of total peak area) were also present. [Although Si$_2$O$_7$(SiMe$_3$)$_6$ and Si$_3$O$_9$(SiMe$_3$)$_4$(Pr^i)$_2$ could not be distinguished, Si$_2$O$_7$(SiMe$_3$)$_6$ is less affected by Amberlyst 15 and is more likely to be present after Amberlyst 15 treatment is finished.]

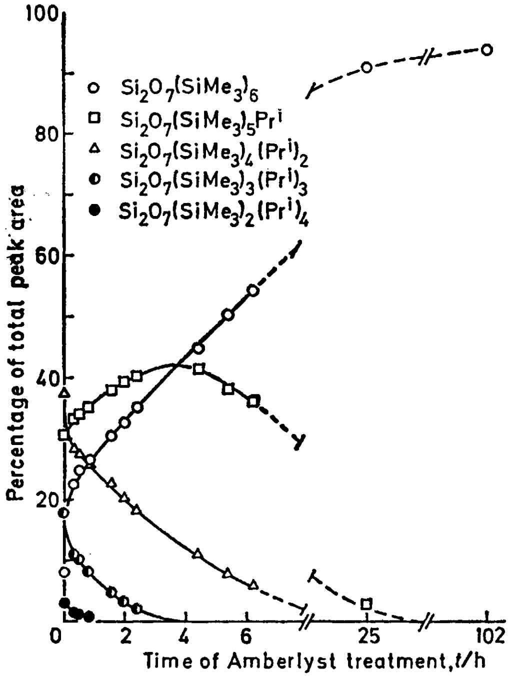

FIGURE 6 Effect of Amberlyst treatment on the products of trimethylsilylation of Ca$_3$[Si$_2$O$_7$]. Reagents for trimethylsilylation: same as for Figure 1

Effect of Reaction Time.—To investigate the mechanism, a detailed study was made of the change in chromatographic pattern for Ca$_2$[SiO$_4$] as a function of time For this purpose it was necessary to eliminate the distillation step. The reaction was allowed to proceed as described above for various times and was arrested by neutralizing the reaction medium with Na[HCO$_3$]. The Amberlyst treatment was omitted. The results are shown in Figures 9—13, where the relative proportions of the various products, expressed as percentages of the total peak area, are plotted against reaction time. As shown in Figures 9 and 10 the chromatographic pattern remained virtually constant during the first 25 min, except for slight changes during the earliest stage of reaction (up to 3 or 4 min). The initial products are, in order of decreasing abundance, the SiO$_4^{4-}$ derivatives with 1,2,0, and 3 and the Si$_2$O$_7^{6-}$ derivatives with 2,1,3,0, and 4 isopropyl groups.

With increase in time up to 336 h the proportions of these derivatives varied in the manner shown in Figures 11 and 12. The fully trimethylsilylated SiO$_4^{4-}$ derivative eventually became the major product, although a significant amount of the monoisopropyl derivative of this ion remained after 300 h (Figure 11) as well as significant amounts of the mono- and di-isopropyl derivatives of the ion Si$_2$O$_7^{6-}$ (Figure 12).

Figure 13 shows a plot of the sum of the peak area percentages of the Si$_2$O$_7$(SiMe$_3$)$_x$(Pr^i)$_{6-x}$ derivatives as a function of reaction time, taken from the data in Figures 10 and 12. It is clear that side reactions which lead to the formation of these derivatives are complete within the first 30 min and that the majority of these unwanted products are formed during the first 3—4 min of reaction.

The relative yield as a function of time is illustrated in Figure 14, in which the sum of the peak areas of the four SiO$_4^{4-}$ derivatives per microlitre of product is plotted against time. The yield is constant after *ca.* 6 min, showing that reaction of the mineral itself is complete in this period and is rapid compared with the final rearrangement of the products.

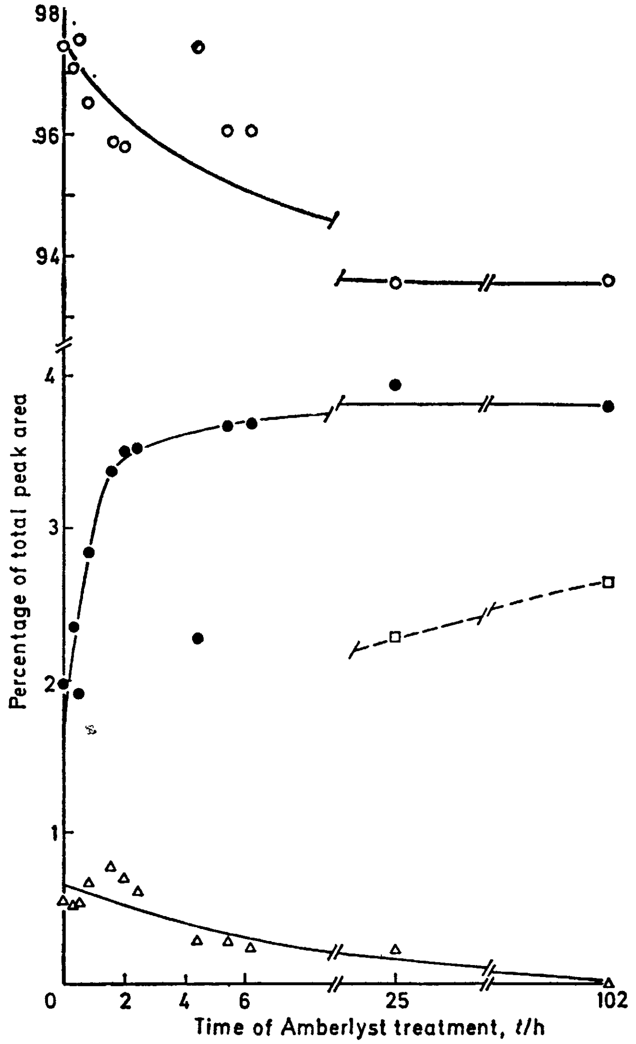

FIGURE 7 Effect of Amberlyst treatment on the total peak area percentages of Si$_2$O$_7$(SiMe$_3$)$_x$(Pr^i)$_{6-x}$ (○), SiO$_4$(SiMe$_3$)$_x$(Pr^i)$_{4-x}$ (●), Si$_3$O$_9$(SiMe$_3$)$_x$(Pr^i)$_{6-x}$ (△), and Si$_3$O$_{10}$(SiMe$_3$)$_x$(Pr^i)$_{8-x}$ (□) in the products of trimethylsilylation of Ca$_3$[Si$_2$O$_7$]. Reagents for trimethylsilylation: same as for Figure 1

Effect of Isopropyl Alcohol.—Absolute yields, expressed as weight % Si extracted from Ca$_2$[SiO$_4$] as SiO$_4^{4-}$, Si$_2$O$_7^{6-}$, and Si$_3$O$_{10}^{8-}$ derivatives are plotted in Figure 15 against the volume of isopropyl alcohol employed. Included is a plot of the total % Si recovered as these derivatives. No reaction was observed when the volume of isopropyl alcohol was 0.1 cm^3 or less, establishing that the presence of this reagent is essential for trimethylsilylation to occur. The total yield increased rapidly between 0.1 and 1 cm^3 then levelled off at *ca.* 90%. Above 0.5 cm^3 the % Si recovered as $Si_2O_7^{6-}$ and $Si_3O_{10}^{8-}$ derivatives decreased significantly, demonstrating that side reactions which lead to formation of these products can be partially suppressed by increasing the proportion of this reagent.

Effect of H_2O *and* C_2H_5OH.—It was shown that trimethylsilylation of $Ca_2[SiO_4]$ occurs when isopropyl alcohol is replaced by either water or ethyl alcohol in the reaction medium, although the yield is reduced.

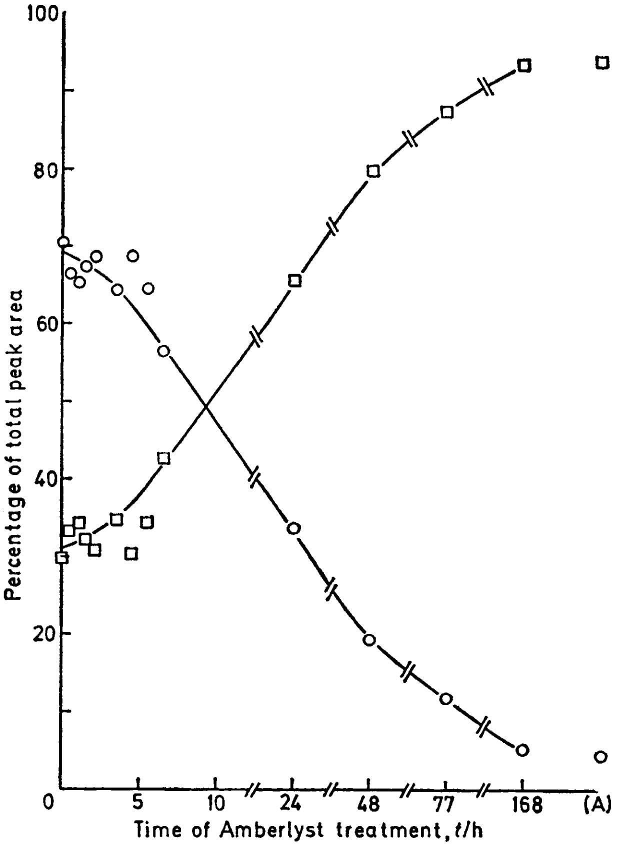

FIGURE 8 Effect of Amberlyst treatment on the total peak area percentages of $Si_3O_9(SiMe_3)_x(Pr^i)_{6-x}$ (○) and $Si_3O_{10}(SiMe_3)_x(Pr^i)_{8-x}$ (□) in the products of trimethylsilylation of $Ca_3[Si_3O_9]$. Reagents for trimethylsilylation: same as for Figure 1. (A) denotes additional 2 g Amberlyst 15 added and stirring continued for additional 24 h

The compound $Ca_2[SiO_4]$ (50 mg), hexamethyldisiloxane (10 cm^3), and water (4 cm^3) were stirred together, chlorotrimethylsilane (8 cm^3) was added, and reaction was allowed to proceed for 18 h. No multiple peaks were observed. The chromatographic pattern showed (area %): $SiO_4(SiMe_3)_4$ (79.8), $Si_2O_7(SiMe_3)_6$ (15.0), $Si_4O_{12}(SiMe_3)_8$ (3.3), and $Si_3O_{10}(SiMe_3)_8$ (1.9). The yield of $SiO_4(SiMe_3)_4$ accounted for only 20% by weight of the silicon in the $Ca_2[SiO_4]$.

Similarly, $Ca_2[SiO_4]$ (50 mg), hexamethyldisiloxane (9 cm^3), and ethyl alcohol (1 cm^3) were stirred together, chlorotrimethylsilane (2 cm^3) was added, and reaction

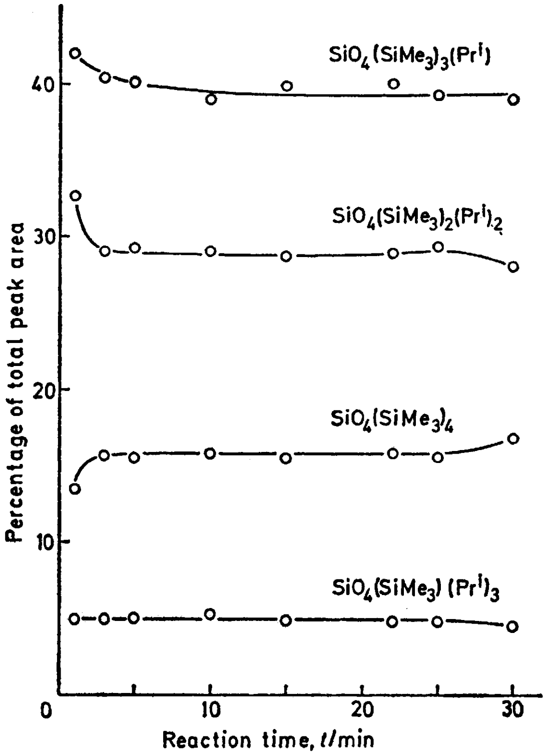

FIGURE 9 Effect of reaction time (0—30 min) on the distribution of SiO_4^{4-} derivatives in the products of trimethylsilylation of $Ca_2[SiO_4]$

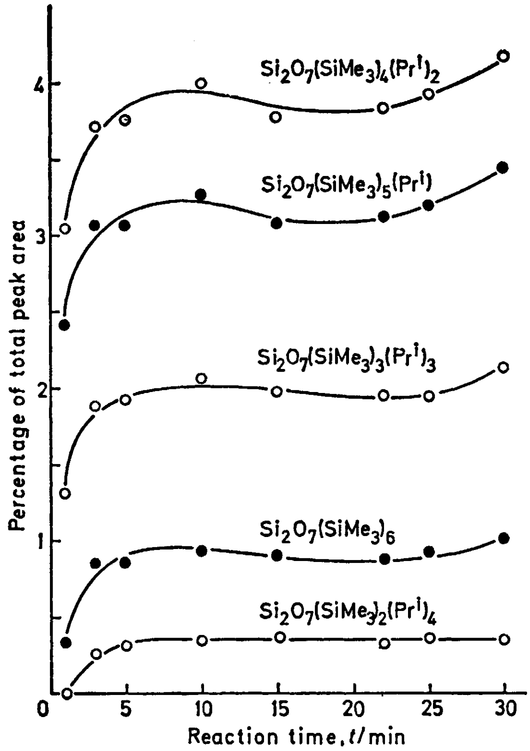

FIGURE 10 Effect of reaction time (0—30 min) on the distribution of $Si_2O_7^{6-}$ derivatives in the products of trimethylsilylation of $Ca_2[SiO_4]$

allowed to proceed for 4 h. Distillation of the product and treatment with Amberlyst 15 yielded (area %): $SiO_4(SiMe_3)_4$ (84.3), $Si_2O_7(SiMe_3)_6$ (12.5), and $Si_3O_{10}(SiMe_3)_8$ (3.2). The yield of $SiO_4(SiMe_3)_4$ was 63% and of $Si_2O_7(SiMe_3)_6$ 15%, for a combined yield of 78% of the silicon present in the mineral.

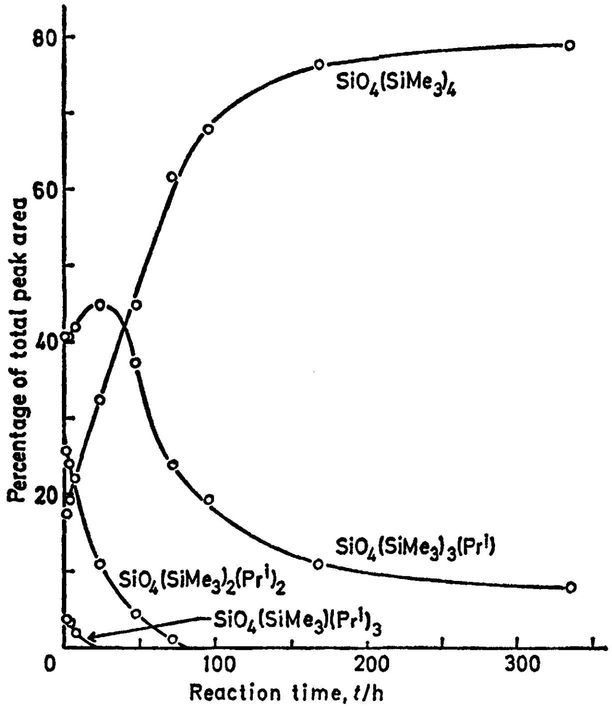

FIGURE 11 Effect of reaction time (0—336 h) on the distribution of SiO_4^{4-} derivatives in the products of trimethylsilylation of $Ca_2[SiO_4]$

Effect of $SiMe_3Cl$.—Experiments were performed in which chlorotrimethylsilane was omitted from the reaction medium, in attempts to prepare the pure isopropyl derivatives. No reaction was observed in the absence of this reagent. The yield of the SiO_4 derivative from $Ca_2[SiO_4]$ did not change significantly when the volume of this reagent was increased from 2 to 5 cm³.

Solid Products.—The solid products of the reaction with $Ca_2[SiO_4]$, $O(SiMe_3)_2$, $SiMe_3Cl$, and $i\text{-}C_3H_7OH$ were collected, dried overnight at 130 °C, and examined by *X*-ray diffraction. The product was hygroscopic and was identified as a mixture of $CaCl_2{\cdot}H_2O$ and $CaCl_2{\cdot}2H_2O$.

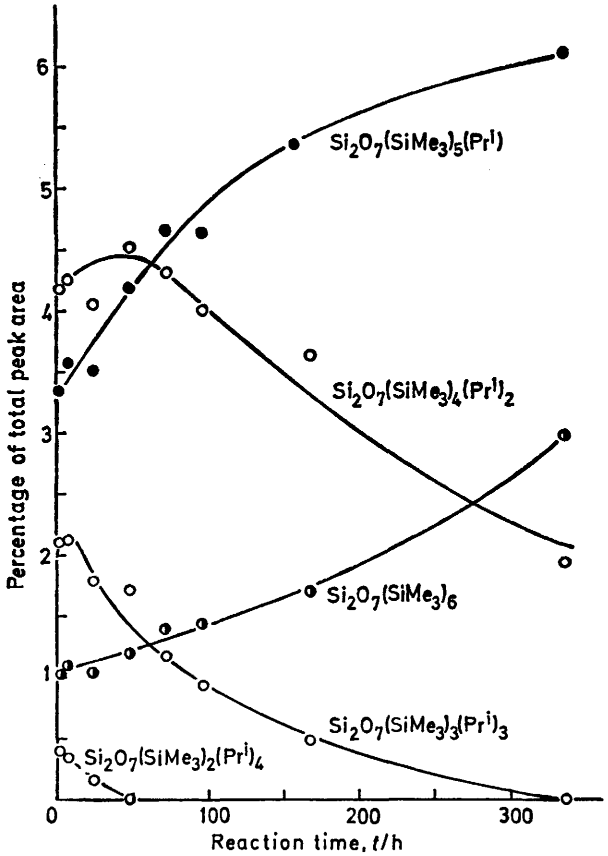

FIGURE 12 Effect of reaction time (0—336 h) on the distribution of $Si_2O_7^{6-}$ derivatives in the products of trimethylsilylation of $Ca_2[SiO_4]$

Absolute Yields.—Yields of $SiMe_3$ derivatives expressed as weight % Si in the mineral extracted as SiO_4^{4-}, $Si_2O_7^{6-}$,

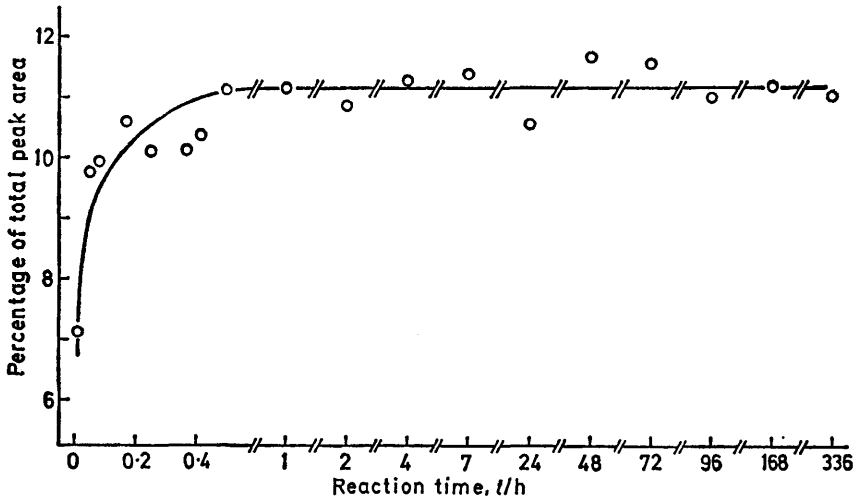

FIGURE 13 Effect of reaction time on the sum of the peak area percentages of $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ in the products of trimethylsilylation of $Ca_2[SiO_4]$

and $Si_3O_{10}^{8-}$ derivatives are presented in the Table for various experimental conditions. For $Ca_2[SiO_4]$ a combined yield of 83% was obtained for the conditions described in the Experimental section. This was increased to 96% by decreasing the weight of solid and increasing the volume of reagents. Best results were obtained with a larger proportion of isopropyl alcohol in the reaction medium. This reduces the extent of the major side reaction, resulting in a yield of 86% for SiO_4^{4-} and a combined yield of 94%. Further dilution with this proportion of reagents did not significantly improve the yield.

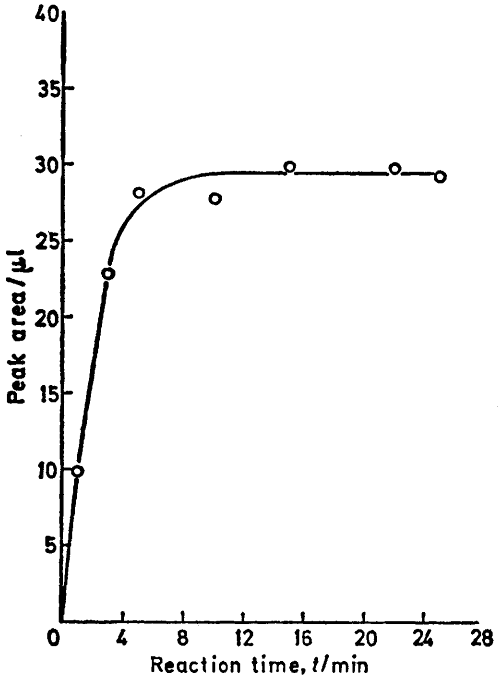

FIGURE 14 Sum of the peak areas of $SiO_4(SiMe_3)_x(Pr^i)_{4-x}$ per microlitre of solution as a function of reaction time in the trimethylsilylation of $Ca_2[SiO_4]$

For $Ca_3[Si_2O_7]$ side reactions which yield SiO_4^{4-} and $Si_3O_{10}^{8-}$ derivatives are minimal. The yield of $Si_2O_7(SiMe_3)_6$ was 96% for the most dilute solution. The yield dropped slightly for the more concentrated solutions. The conditions which gave the best overall results for $Ca_2[SiO_4]$ were applied to $Ca_3[Si_2O_7]$ for comparison. This lowered the yield of $Si_2O_7(SiMe_3)_6$ slightly. For $Ca_3[Si_3O_9]$ the $Si_3O_9^{6-}$ derivatives initially formed were slowly converted to $Si_3O_{10}^{8-}$ derivatives when the solution of products was stirred with Amberlyst 15. After treatment with Amberlyst 15 for 168 h (Figure 8) only traces of $Si_3O_9^{6-}$ derivatives remained and $Si_3O_{10}(SiMe_3)_8$ accounted for 93% of the total peak area. However, the yield of this derivative was only 15% of the theoretical value. This was increased to 24%

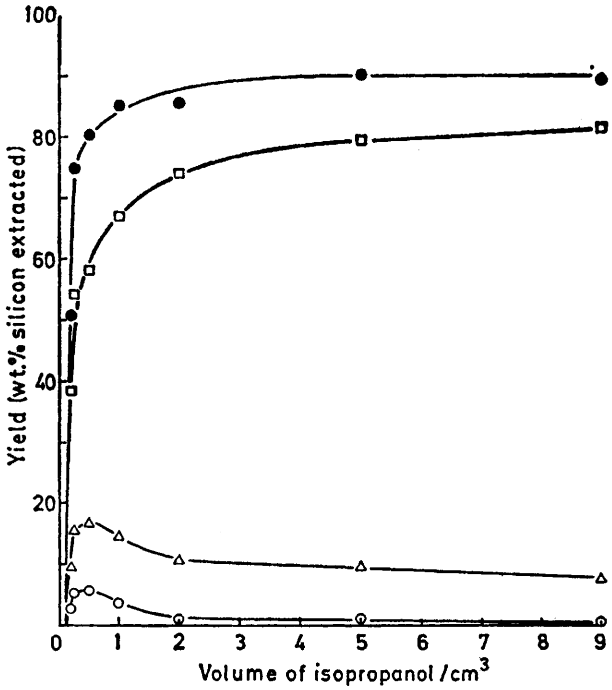

FIGURE 15 Effect of isopropyl alcohol on the percentage silicon in $Ca_2[SiO_4]$ extracted as SiO_4^{4-} (□), $Si_2O_7^{6-}$ (△), and $Si_3O_{10}^{8-}$ (○) derivatives. The upper curve (●) shows the total percentage silicon extracted as these derivatives. Other reagents for trimethylsilylation: 50 mg $Ca_2[SiO_4]$, 9 cm³ $O(SiMe_3)_2$, 2 cm³ $SiMe_3Cl$. Trimethylsilylation was completed by stirring the solution of the products in $O(SiMe_3)_2$ with Amberlyst 15

Yields of $SiMe_3$ derivatives from calcium silicates *

Mineral	Weight (mg)	Hexamethyldisiloxane (cm³)	Isopropyl alcohol (cm³)	Chlorotrimethylsilane (cm³)	$SiMe_3$ Derivative	Yield (wt. % Si)
$Ca_2[SiO_4]$	50.9	9	1	2	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	68 15
	10.3	27	3	6	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	83 13
	49.1	9	9	2	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	81 7
	47.8	9	9	5	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	80 9
	9.9	9	9	2	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	86 8
	3.5	14	14	2.8	$SiO_4(SiMe_3)_4$ $Si_2O_7(SiMe_3)_6$	86 9
$Ca_3[Si_2O_7]$	49.8	9	1	2	$Si_2O_7(SiMe_3)_6$	84
	10.4	27	3	6	$Si_2O_7(SiMe_3)_6$	96
	9.8	9	9	2	$Si_2O_7(SiMe_3)_6$	88
$Ca_3[Si_3O_9]$	52.5	9	1	2	$Si_3O_{10}(SiMe_3)_8$	15
	11.0	9	9	2	$Si_3O_{10}(SiMe_3)_8$	24

* Time of reaction 4 h; Amberlyst treatment 24 h.

by adding a larger quantity of isopropyl alcohol to the reaction medium.

DISCUSSION

The following sequence of reactions is tentatively proposed to account for the main observations. It is well known [25] that $SiMe_3Cl$ reacts with $i\text{-}C_3H_7OH$ according to equation (1). If base is not present to

$$SiMe_3Cl + i\text{-}C_3H_7OH \rightleftharpoons SiMe_3(OC_3H_7\text{-}i) + HCl \quad (1)$$

neutralise the HCl a complex equilibrium is set up. Hydrogen chloride can react with $i\text{-}C_3H_7OH$ according to equation (2) and the H_2O formed in this reaction can

$$HCl + i\text{-}C_3H_7OH \rightleftharpoons i\text{-}C_3H_7Cl + H_2O \quad (2)$$

hydrolyse $SiMe_3Cl$ to yield $O(SiMe_3)_2$ [equation (3)]. When $Ca_2[SiO_4]$ is present, O^- groups in the mineral are

$$H_2O + 2SiMe_3Cl \longrightarrow O(SiMe_3)_2 + 2HCl \quad (3)$$

protonated by HCl in the presence of H_2O to yield silicic acid groups [equation (4)] which then react with $SiMe_3Cl$

$$-\overset{|}{\underset{|}{Si}}-O^- + HCl \xrightarrow{H_2O} -\overset{|}{\underset{|}{Si}}-OH + Cl^- \quad (4)$$

and $SiMe_3(OC_3H_7\text{-}i)$ to yield various derivatives, *e.g.* equations (5)—(7). This sequence continues until an

$$-\overset{|}{\underset{|}{Si}}-OH + SiMe_3Cl \longrightarrow -\overset{|}{\underset{|}{Si}}-OSiMe_3 + HCl \quad (5)$$

$$-\overset{|}{\underset{|}{Si}}-OH + SiMe_3(OC_3H_7\text{-}i) \longrightarrow -\overset{|}{\underset{|}{Si}}-OSiMe_3 + i\text{-}C_3H_7OH \quad (6)$$

$$-\overset{|}{\underset{|}{Si}}-OH + SiMe_3(OC_3H_7\text{-}i) \longrightarrow -\overset{|}{\underset{|}{Si}}-OPr^i + SiMe_3OH \quad (7)$$

array of mixed trimethylsilyl–isopropyl derivatives of general formula $SiO_4(SiMe_3)_x(Pr^i)_{4-x}$ ($x = 1 - 4$) is formed. Subsequent replacement of isopropyl by trimethylsilyl groups proceeds slowly or is catalysed by Amberlyst 15 ion-exchange resin [equation (8)].

$$SiO_4(SiMe_3)_3(Pr^i) + Me_3SiOSiMe_3 \xrightarrow{\text{Amberlyst}} SiO_4(SiMe_3)_4 + SiMe_3(OPr^i) \quad (8)$$

Side reactions which yield derivatives of higher anions may be ascribed to the mutual interaction of silicic acid groups [equation (9)] in competition with reactions (5)—(7). Side reactions are minimized by decreasing the

$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O \quad (9)$$

quantity of mineral in reaction (9) or by adding excess of isopropyl alcohol, which increases the rates of reactions (6) and (7). Increasing the concentration of $SiMe_3Cl$ beyond a certain threshold value does not suppress the occurrence of side reactions as HCl, which is a product of both reactions (3) and (5), causes further protonation of O^- groups by reaction (4).

The main side reaction in the case of $Ca_3[Si_3O_9]$ is cleavage of the $Si_3O_9{}^{6-}$ ring during the reaction to form derivatives of the linear-chain ion $Si_3O_{10}{}^{8-}$. This process is continued during conversion of the mixed trimethylsilyl–isopropyl derivatives to fully trimethylsilylated derivatives, so that the end product is almost exclusively $Si_3O_{10}(SiMe_3)_8$. The lower yield for $Ca_3[Si_3O_9]$ is not fully understood. No significant amounts of higher derivatives were found under gas chromatographic conditions capable of detecting derivatives with up to 12 $SiMe_3$ groups per molecule.

While this paper was being prepared for publication the authors became aware of a recent study of Tamas *et al.*[14] in which the orthosilicates $\beta\text{-}Ca_2[SiO_4]$ and $Ca_3[SiO_5]$ were trimethylsilylated by a modified anhydrous technique, with dimethylformamide as solvent. The ratio of $SiO_4{}^{4-}$ to $Si_2O_7{}^{6-}$ derivatives reported by these authors for $\beta\text{-}Ca_2[SiO_4]$ (6.34) is somewhat lower than the best value (10.75) found in the present work for $\gamma\text{-}Ca_2[SiO_4]$. For $Ca_3[SiO_5]$, not examined in the present study, the ratio (11.6) is comparable. It has been reported [23] that the method of Tamas *et al.* also gives high absolute yields of the appropriate anion for mono- and di-silicates.

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