Effect of Amberlyst 15 Cation-exchange Resin on the Products of
Trimethylsilylation of Hexameric Ring Silicates

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Chemical and structural transformations induced by proton-donor catalysts (Amberlyst 15 cation-exchange resin and trichloroacetic acid) have been studied using the silicate derivatives $\text{Si}_4\text{O}_{18}(\text{SiMe}_3)_6$ and $\text{Si}_2\text{O}_{18}(\text{SiMe}_3)_{12}$ as model compounds. The experiments were performed in hexamethyldisiloxane solutions using a standard quality Amberlyst 15. Gas chromatography with a glass capillary column was used for detection of the composition changes in the reaction mixtures. Present and former results have permitted a probable structural presentation of the reaction pathways to be made. The transformations tend to produce structures containing only tetrameric siloxane rings when starting from cyclic and polycyclic silicate derivatives containing trimeric, (pentameric), or hexameric siloxane rings. Three different reaction types are suggested for the interpretation of the transformations. Amberlyst 15 was found to contribute significantly to side reactions during the Amberlyst treatment following the trimethylsilylation of silicates under the usual conditions employed.

TRIMETHYLSILYLATION of low-molecular-weight silicate systems has been widely used since 1964 when Lentz reported that trimethylsilyl esters of silicates were relatively volatile and fairly stable compounds, soluble in organic solvents. The technique of trimethylsilylation usually precedes gas chromatographic (g.c.) and mass spectrometric (m.s.) investigations, in order to volatilize the silicate species while preserving its original structure. However, when silicates of known structure are examined using any of the recommended trimethylsilylation techniques, it appears that most of the silica is lost and/or recovered as derivatives of anions other than those originally present in the parent compound. This indicates the occurrence of undesirable side reactions, which are, in the opinion of Götz and Masson,2 polymerization and depolymerization processes taking place before trimethylsilylation has been completed, and hydrolysis of the trimethylsilyl derivatives themselves.

Recently Calhoun and Masson and ourselves have stressed the importance of controlling the pH during the silylation reaction to avoid these disturbing side reactions. Most investigators agree that trimethylsilylation cannot be completed without after-treatment of the organic phase (hexamethyldisiloxane solution) of the reaction mixture with Amberlyst 15 cation-exchange resin for several hours. This after-treatment is supposed to promote the proton–trimethylsilyl exchange in some residual shielded OH groups in the silicate skeleton.

Calhoun and Masson have also found that, besides completing the trimethylsilylation, Amberlyst 15 may interconvert certain trimethylsilyl–silicate isomers and contribute to the occurrence of other side reactions.

In an earlier paper we proposed a new trimethylsilylation method for aqueous silicic acid solutions, using bis(trimethylsilyl)acetamide as the silylating agent. In this method after-treatment with Amberlyst proved to be unnecessary. In another paper on tetraethylammonium silicates we reported that using the silylation method developed by Tamás et al. trimethylsilyl ester formation was again complete without Amberlyst treatment.

In this paper we demonstrate the contribution of strong acids (Amberlyst 15 and trichloroacetic acid) to the side reactions of the trimethylsilylation procedure. It is shown that these acids give rise to characteristic chemical transformations of the trimethylsilyl silicates themselves.

The chemical processes discussed here were examined in reaction mixtures containing hexamethyldisiloxane and Amberlyst or trichloroacetic acid. Crystalline tetraethylammonium silicate and dioptase were chosen as the model systems. The anionic component of crystalline tetraethylammonium silicate is a double trimeric ring silicate and that of dioptase is a hexameric ring silicate. The original structure of tetraethylammonium silicate is shown in Figure 1(a) and that of dioptase in Figure 1(b). The dioptase structure is pictured in the simplified form used for all silicates and their trimethylsilyl derivatives throughout this paper.

**Figure 1** Structures of the model compounds
Making use of the abbreviations, \( \text{Si}(O_{15})_4 = \text{SiO}_2 = Q \) and \( \text{Me}_5\text{SiO}_{15} = L \), the trimethylsilylated product from tetraethylammonium silicate can be designated as \( Q_8L_{12} \) and that from dioptase as \( Q_6L_{12} \).

**EXPERIMENTAL**

The preparation and trimethylsilylation of crystalline tetraethylammonium silicate have already been reported.\(^7\) The chromatogram of the silylation product showed one main peak with area 92%; the elemental composition of the corresponding structure being \( \text{SiO}_{15}(\text{SiMe})_4 \).

**Trimethylsilylation of Dioptase.** \( \text{Cu}_{15}\text{SiO}_{14} \cdot 6\text{H}_2\text{O} \).—A mixture of hexamethyldisiloxane (5 cm\(^3\)), dimethylformamide (10 cm\(^3\)), and \( \text{SiMe}_2\text{Cl} \) (5 cm\(^3\)) was stirred for 15 min at room temperature. Dioptase powder (39.7 mg) was then added and stirring was continued for a further 30 min. The addition of 100 \( \mu \text{l} \) of the internal standard solution (6 mg of \( n \)-tetradecane in 1.352 \( \mu \text{g} \) of \( n \)-heptane) followed, and the mixture was washed with water (9 \( \times \) 25 \( \mu \text{g} \)).

The yield of silylation measured by g.c. was 6\% (\( \text{SiO}_2 \)). The chromatogram had one main peak, the retention value of which was characteristic of 12 \( \text{SiMe}_2 \) groups; area: 70\%; mass number of the corresponding compound: 1332.\(^8\)

**Standardization of the Amberlyst Resin.**—Amberlyst 15 ion-exchange resin was supplied by Serva Feinbiochemica, Heidelberg. In order to standardize the ion exchanger, the contents of a freshly opened container were spread out on a plate in a thin layer and heated in an oven at 80 °C for 4 h. After cooling in a desiccator, the resin was stored in a dry place.

**Characterization of the Amberlyst Resin.**—Experience gained over the years has shown that different batches of Amberlyst 15 have different activities in the completion of silylation reactions. We have also learned that the contribution of Amberlyst 15 to proton–trimethylsilyl exchange is preceded by the cleavage of an \( \text{Si}-\text{O}-\text{Si} \) bond in hexamethyldisiloxane on addition of the protonated Amberlyst 15. It was therefore expected that \( \equiv \text{Si}-\text{O}-\equiv \text{Si} \) bonds in longer methylosiloxane chains would likewise be cleaved by Amberlyst 15.

For practical reasons, based on our experience, the rate of disappearance of the dodecamethylpentasiloxane peak in the chromatogram, in the presence of Amberlyst 15, was chosen as the characteristic feature of Amberlyst activity. For comparison, pure Amberlyst 15 from the same bottle without any pretreatment and after the standardization procedure was used to treat dodecamethylpentasiloxane (1 mg), \( n \)-heptane (500 \( \mu \text{g} \)), standard quality Amberlyst 15 (20 mg), and a stock solution of the internal standard (25 \( \mu \text{g} \)) were then added.

Comparison of the curves in Figure 2 shows the effect of the standardization procedure. At the same time, the upper curve characterizes the standard quality Amberlyst 15 used throughout this work. Both curves reflect dodecamethylpentasiloxane consumption in the absence of hexamethyldisiloxane.

The heat treatment of Amberlyst 15 at 80 °C represents a drying process, which does not alter the chemical composition or the structure of the resin.\(^9\) As a result of standardization the nature of the catalysed reaction remains unchanged, but the activity of the catalyst is increased.

**Amberlyst Treatment of \( \text{SiO}_{15}(\text{SiMe})_4 \) and \( \text{SiO}_{15}(\text{SiMe})_2 \).**

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A solution of \( \text{SiO}_{15}(\text{SiMe})_4 \) (ca. 1.5 cm\(^3\)) (0.2 mg of \( \text{SiO}_2 \) per 1 cm\(^3\) of hexamethyldisiloxane) was evaporated to dryness; hexamethyldisiloxane (200 \( \mu \text{l} \), \( n \)-heptane (200 \( \mu \text{l} \)), and Amberlyst 15 (40 mg) were then added.

A solution of \( \text{SiO}_{15}(\text{SiMe})_2 \) (4 cm\(^3\)) (0.09 mg of \( \text{SiO}_2 \) per 1 cm\(^3\) of hexamethyldisiloxane) was evaporated to dryness. Hexamethyldisiloxane (1 cm\(^3\)), standard quality Amberlyst 15 (500 mg), and a stock solution of the internal standard (50 \( \mu \text{l} \)) were then added.

Both samples were shaken at 20 °C for several days.

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**FIGURE 2 Characterization of Amberlyst.** Recovery of the original weight, \( w(0) \), of dodecamethylpentasiloxane according to the chromatograms after Amberlyst treatment for \( t \) h; dodecamethylpentasiloxane (1.3 \( \times \) 10\(^-4 \)) mmol per 1 mg of Amberlyst in \( n \)-heptane without any treatment of the original ion-exchanger (\( \circ \)); and after drying the original ion-exchanger according to the procedure given in the text (\( \times \)).

From time to time 0.5–4 \( \mu \text{l} \) aliquots were directed injected into the gas chromatograph.

**Treatment of \( \text{SiO}_{15}(\text{SiMe})_4 \) with Trichloroacetic Acid.—** To 1 cm\(^3\) of a \( \text{SiO}_{15}(\text{SiMe})_4 \) solution (0.9 mg \( \text{SiO}_2 \) per 1 cm\(^3\) of hexamethyldisiloxane) was added trichloroacetic acid (170 mg) to obtain a 1.0 mol dm\(^{-3}\) solution of trichloroacetic acid. The sample was shaken and injected into the gas chromatograph as before.

**Gas Chromatography.**—A Hewlett-Packard model 5830A device equipped with a flame-ionization detector and capillary inlet system model 18740A was used. The column (20 m \( \times \) 0.25 mm diameter) was of Pyrex glass. The stationary phase was OV-1 (phase ratio 3:1; 600) and the carrier gas was nitrogen. Operating conditions were: linear velocity, 30 cm s\(^{-1}\); injection-port temperature, 280 °C; detector block temperature, 300 °C. The temperature of the column was increased at 10° min\(^{-1}\) from an initial temperature of 115 °C to a final temperature of 300 °C. \( n \)-Tetradecane was used as internal standard. The percentage values in Figures 4–6 denote the area percentages, corrected by the following individual flame-ionization detector response factors (= amount/area): \( n \)-tetradecane, 1; \( Q_2L_{12} \), 2.5; \( Q_3L_{12} \), 2.0; \( Q_5L_{12} \), 1.7; \( Q_6L_{12} \), 3.3; \( Q_8L_{12} \), 1.3; \( Q_9L_{12} \), 1.5.
RESULTS

Chemical Transformations of QeL₆—The processes occurring during Amberlyst treatment are qualitatively demonstrated by the series of chromatograms in Figure 3. Peak assignments were performed partly with the help of reference materials [Q₂L₆, Q₄L₁₀ (1), Q₆L₁₆ (11), and Q₈L₁₆] and partly by g.c.-m.s. [Q₂L₆, Q₆L₁₂ (1), Q₆L₁₂ (1a), and Q₆L₁₂ (II)]. The composition of the silylation mixture remained unchanged over several months if Amberlyst was absent.

FIGURE 3 Chromatograms taken during Amberlyst treatment of QeL₆: dodecamethylpentasiloxane internal standard peak (S₁); n-tetradecane internal standard peak (S₂); Q₂L₆ (1); Q₄L₄ (2); Q₆L₆ (3); Q₆L₁₆ (11) (6); Q₆L₁₂ (1) (6); Q₆L₁₂ (1a) (7); Q₆L₁₆ (11) (8); Q₆L₁₀ (9) and (10). Designations of Q₆L₁₁ (I) and Q₆L₁₃ (II) correspond to those in ref. 3. For the g.c. conditions see the text.

FIGURE 4 Concentration changes during the Amberlyst treatment of QeL₆. Area percentages corrected by individual flame ionization detector response factors. For conditions used for the Amberlyst treatment, see the Table.
The plots in Figure 4 show the concentration changes against time for the main reaction participants. Besides the corrected area percentage values, percentages of SiO₂ were also calculated in several cases, by means of the internal standard added to the samples in known concentrations. No significant losses were found in the summarized SiO₂ values during Amberlyst treatment.

![Figure 4](image)

**Figure 4** Concentration changes during the treatment of Q₆L₄ and 1 mol dm⁻³ trichloroacetic acid. Area percentages corrected by individual flame-ionization detector response factors

The diagrams show clearly the sequence and the different rates of reactions (1)—(5). The formation, and subsequent conversion, of Q₆L₁₀ (I) seems to reach a steady state at a rather low concentration.

In the diagram of Figure 5 the effect of trichloroacetic acid on the hexamethyldisiloxane solution of Q₆L₄ is demonstrated. The curves verify reactions starting from isomer (III) found already by Calhoun and Masson³ in the Amberlyst treated silylation product of dioptase. Based on the diagrams, the consecutive reactions and the reaction rates are as given in equations (6)—(10). As a result of experiments carried out under more or less similar conditions, Calhoun and Masson³ reported similar, though faster, changes in composition for the 20—170 h period of Amberlyst treatment; however, in contrast to our results, they found

![Figure 5](image)

**Figure 5** Concentration changes during the treatment of Q₆L₄ and 1 mol dm⁻³ trichloroacetic acid. Area percentages corrected by individual flame-ionization detector response factors

**Chemical Transformations of Q₆L₄—**The results of the Amberlyst treatment of the dioptase silylation product are illustrated in Figure 6. The sample contained one Q₆L₁₂ isomer as the main component. This was identified as

![Figure 6](image)

**Figure 6** Concentration changes during the Amberlyst treatment of Q₆L₁₂ (III). For conditions used for the Amberlyst treatment, see the Table. Area percentages corrected by individual flame-ionization detector response factors
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Amberlyst-H + Me$_3$Si -O-SiMe$_3$ $\rightleftharpoons$ Amberlyst-SiMe$_3$ + HO-SiMe$_3$. (II)

Cl$_3$COOH + Me$_3$Si -O-SiMe$_3$ $\rightleftharpoons$ Cl$_3$COOSiMe$_3$ + HO-SiMe$_3$. (IIa)

Figure 7  Mechanism of the type (i) and type (ii) reactions using the trimethylsilylated double trimeric ring as an example

two systems. In both reaction pathways the concentration of Q$_{4}$I$_{12}$ (I) increases monotonously and finally it becomes the main component of both reaction mixtures.

DISCUSSION

The Role of Amberlyst 15 and Trichloroacetic Acid.---
Reactions (1) to (10), listed above, represent three types of reactions. (i) In reactions (1), (2), (3), (5), and (10) a decrease in the condensation degree of the molecular structure via cleavage of one skeletal $\equiv$Si-O-Si$\equiv$ bond followed by trimethylsilylation can be observed. (ii) In reaction (7) the condensation degree of the molecular structure increases, as the cleavage of two substituent $\equiv$Si-O-Si$\equiv$ bonds is followed by the formation of a new skeletal $\equiv$Si-O-Si$\equiv$ bond. (iii) In reactions (4), (6), (8), and (9) isomerization occurs via intramolecular rearrangement. Most probably the cleavage of one skeletal and one substituent $\equiv$Si-O-Si$\equiv$ bond is followed by siloxane bond rearrangement and OSiMe$_3$ group migration.

The role of Amberlyst 15 and trichloroacetic acid is obviously the participation in, or the catalysis of, these reactions. The mechanisms of type (i) and type (ii) reactions are similar to that of the well known equilibration processes of organosiloxanes, which can be catalyzed, among other agents, by proton-donor acids including the H$^+$-form of cation-exchange resins.$^{12}$ Type (i) reactions clearly postulate the presence of a trimethylsilylating agent, e.g. Amberlyst + hexamethyldisiloxane.

Obviously the $\equiv$Si-O-Si$\equiv$ bond is also split by trichloroacetic acid. Accordingly, Figure 5 demonstrates the occurrence of the same reactions in the same sequence. Owing to the low reaction rate, however, the type (iii) reaction could not be observed. This indicates that (i) in proper conditions, similar to equilibrium (11), (11a) takes place as well (cf. Figure 7); (ii) the transitional product Cl$_3$CCOOSiMe$_3$ may be regarded as a 'silylating

In conclusion, a rough approximation of the mechanism of type (i) and type (ii) reactions may be given. If X represents the Amberlyst matrix or the Cl$_3$CCOO$^-$ anion, then in addition to (11) and (11a), the reactions (12) and (13) (Figure 7) also occur. (The trimethylsilylated double trimeric ring serves only as an example in Figure 7.)

According to the mechanism of the type (i) reaction Amberlyst attacks concurrently hexamethyldisiloxane and a skeletal $\equiv$Si-O-Si$\equiv$ bond of the trimethylsilylsilicate. The H$^+$-form of the Amberlyst exerts a catalytic effect. However, regarding the huge excess of hexamethyldisiloxane compared to the silicates in our experiments, most of the catalyst is presumably consumed by means of reactions (11) and (11a). According to the mechanism of the opposite type (ii) reaction, Amberlyst attacks two substituent $\equiv$Si-O-Si$\equiv$ bonds [reaction (13)]. This attack is followed by reaction (12), then by reaction (11), each in reversed direction. This
opposite pathway is found, however, only in case of the \( Q_{6L10} \rightarrow Q_{6L12} \) transformation; hexamethyldisiloxane is produced instead of being consumed.

**Structures and Stabilities of the Reaction Products.**—

There have been ten components detected as the main initial, transitional, and end-products of the reactions starting from \( Q_{6L6} \) and \( Q_{6L12} \) (cf. Figure 3). The reaction pathway includes, however, only molecules with four different elementary compositions (\( Q_{6L6} \), \( Q_{6L8} \), \( Q_{6L10} \), \( Q_{6L12} \)). Considering only the type (i) reaction and the fact that \( Q_{6L6} \) with a definite structure is the common starting material of the reaction products, the numbers of the possible geometric isomers for the remaining three compounds are: two for \( Q_{6L8} \), six for \( Q_{6L10} \), and nine for \( Q_{6L12} \) (cf. ref. 13 and Figure 8).

![Figure 8](image-url)  
*Figure 8* Chemical and structural transformations of \( Q_{6L6} \) and \( Q_{6L12} \) (II) induced by proton-donor catalysts. See text for description of reaction types (i), (ii), and (iii).

On the other hand, it is seen from Figure 3 that regarding only the important reaction participants, both \( Q_{6L6} \) and \( Q_{6L8} \) are represented by one, \( Q_{6L10} \) by two, and \( Q_{6L12} \) by three peaks in the chromatograms. These facts are sufficient for presenting the reaction pathway in the form of a most probable structural representation.

The entire pathway starting from \( Q_{6L6} \) and resulting in \( Q_{6L12} \), which may be realised in principle by type (i) reactions, is shown in Figure 8. It is evident that when type (ii) reactions are considered, the same pathway will apply in the opposite direction. Encountering also type (iii) reactions, the number of the possible geometric isomers would increase further and the scheme of the reaction pathway becomes rather confusing. Therefore type (ii) and type (iii) reactions are shown only in those cases when their existence is experimentally proved.

The occurrence of all transformations given on the left-hand side of Figure 8 follows from the experimental results discussed; there is no evidence for the participation in the transformations of the structures shown on the right-hand side of Figure 8. The comparatively high difference between the number of the possible and realised transformations suggests certain preferences of definite reaction routes.

In order to follow the pathway of type (i) reactions in Figure 8, one can start from the fact that the structures of \( Q_{6L10} \), \( Q_{6L10} \) (I), and \( Q_{6L10} \) (II) are known from previous work.\(^{7,11}\) These structures predetermine the structure of the transitional \( Q_{6L6} \) species, provided that only one-step type (i) reactions are to be considered both in the production and consumption of \( Q_{6L4} \).

Curves in Figure 4 furnish evidence for the stability of \( Q_{6L10} \) (I) and for the intermediate character of \( Q_{6L10} \) (II). Therefore, in the third reaction sequence mainly \( Q_{6L10} \) (II) is transformed into \( Q_{6L12} \) by one-step type (i) reactions.

Of the three possible reaction routes starting from \( Q_{6L10} \) (II) in Figure 8, mainly one, leading to the isomer \( Q_{6L12} \) (II), is operative and this product is further converted into \( Q_{6L12} \) (I), as can be seen in Figures 4 and 6. In order to select the proper structure for the intermediate \( Q_{6L12} \) (II), one can rely on its analogous behaviour to the \( Q_{6L10} \) (II) structure. Hence it is assumed that the cyclopentasilicate structure is the most probable one for \( Q_{6L12} \) (II).

Disregarding the cyclohexasilicate structure, three cyclotetrasilicate structures remain for the most stable \( Q_{6L12} \) (I) isomer, i.e., for the product which seems to be the preferred one in the present reaction route (cf. Figures 4 and 6). It is evident from the chromatograms in Figure 3 that \( Q_{6L12} \) (I) is actually represented by two peaks (peak nos. 6 and 7). (Most probably all the three peaks would be observed on improving the separation conditions in the g.c. column.) The existence and importance of the type (ii) reaction in certain cases follows from Figure 6. This type of reaction is demonstrated therefore in Figure 8, starting from the silylation product of dioptase, \( Q_{6L12} \) (III).

Two arguments may be given for the cyclohexasilicate structure of this trimethylsilyl ester. (i) Several observations speak for the maintenance of the original silicate structure \(^8\) when trimethylsilylation is performed either by bis(trimethylsilyl)acetamide or by the Tamás method, but without Amberlyst treatment.\(^4,17\) (ii) Taking into account the usual elution behaviour of members of certain homologous series in g.c., the retention value of the \( Q_{6L12} \) (III) peak points also to the cyclohexasilicate structure.\(^{11,14}\) Additional information is offered by the curves in Figure 6: slow type (i) reactions starting from \( Q_{6L10} \) (I) have also been found (dotted-line...
These reactions also contribute to the formation of QsL12 (1) isomers. The structural scheme outlined above suggests the first conclusion: all reactions occurring in the course of Amberlyst treatment tend to transform cyclic and polycyclic trimethylsilyl silicate anion structures, containing cyclotrisiloxane, cyclopentasiloxane, and cyclotetrasiloxane units, into structures containing only cyclotetrasiloxane units.

The absence of the structures shown in the right-hand side of Figure 8 underlines the main tendency of the transformations, namely the preferred cleavage of \( \equiv \text{Si-O-Si} \equiv \) bonds in cyclotrisiloxane structural units. This preference follows from the strained bond system of the trimeric siloxane ring. The structures made up of cyclotetrasiloxane units or cyclotetrasiloxane chain combinations seem to be especially stable and represent therefore the end-products of the transformations discussed.

Further it can be concluded that chemical reactions of the trimethylsilyl silicates catalyzed by Amberlyst 15 play an important role in side reactions observed in the course of the trimethylsilylation procedures including after-treatment with Amberlyst.\(^1\)\(^-3\) Hexamethyldisiloxane, the usual solvent in trimethylsilylation reactions, always takes part in the side reactions when \( \equiv \text{Si-O-Si} \equiv \) bond cleavage may occur upon proton catalysis.

The Role of Different Reaction Conditions in the Transformations of Trimethyl Silicates induced by Proton-donor Catalysts.—The experiments and their interpretation outlined above suggest the decisive influence of several experimental factors on the nature and rate of the transformations discussed.

The data in the Table demonstrate that the experiments reported here were performed under reaction conditions similar to those used in previous investigations\(^4\)\(^-6\) in the course of Amberlyst-treatment following the trimethylsilylation of silicate species. Experimental details and a discussion on the particular effects of the silicate concentration, proton concentration, the nature of the proton source and that of the solvent will be published separately.

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**Comparison of conditions of Amberlyst treatments**

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<th>Compound</th>
<th>Skeletal SiO(_2)/mg</th>
<th>Hexamethyldisiloxane/μl</th>
<th>Dibenz/μl</th>
<th>Amberlyst/μg</th>
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* Based on recovery data of silylation measured by g.c. * Experiments repeated by ourselves.

**REFERENCES**