Trimethylsilyl Derivatives for the Study of Silicate Structures. Part III.[1] Sodium Silicate Hydrates

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A study was made of the yield and distribution of the products formed when $Na_2H_2SiO_4,4H_2O$, $Na_2H_2SiO_4,5H_2O$, and $Na_2H_2SiO_4,8H_2O$ were treated by a direct method of trimethylsilylation reported previously. These soluble silicates are particularly prone to side reactions due to polymerisation of silicate ions in solution, yielding a distribution of products many of which are undetected chromatographically.

Quantitative yields of the expected orthosilicate derivatives were obtained only when vanishingly small concentrations of silicate were used. Further experiments with the mineral hemimorphite confirmed that, for a unified method of trimethylsilylation applicable to different structures, careful control of the water content in the reaction medium is essential. Improvements in the trimethylsilylation and chromatographic procedures are described.

THE structures of crystalline silicates have been studied mainly by *X*-ray diffraction. Recently chemical techniques have been developed [1-5] by which silicate ions may be extracted from crystalline and amorphous solids as their stable trimethylsilyl (TMS) derivatives and separated by gas–liquid chromatography (g.l.c.). The present paper describes the application of this technique to various sodium silicate hydrates whose crystal structures have already been determined by *X*-ray diffraction.[6-8] These were three of the so-called sodium metasilicate hydrates, whose formulae are commonly written Na_2SiO_3,xH_2O. The *X*-ray studies have shown that those used in this work all contain the anion $H_2SiO_4^{2-}$ [or $SiO_2(OH)_2^{2-}$]. They are thus more properly referred to as disodium dihydrogen orthosilicate hydrates, formulae $Na_2H_2SiO_4,(x\text{-}1)H_2O$.

Application of the technique to soluble silicates presents difficulties not encountered with the more sparingly soluble compounds studied previously. This is due mainly to the ease and rapidity with which discrete silicate ions undergo reorganisation reactions in solution. These reactions lower the yield of the main derivative and lead to the production of TMS derivatives of anions not present in the original material. It has been shown [1,2] that the labile nature of the orthosilicate ion in solution makes it difficult to trimethylsilylate quantitatively, even when extracted from sparingly soluble minerals such as the olivines. With the highly soluble hydrates employed in this work, the probability of side reactions due to a high concentration of orthosilicate ions in solution is increased. The study of these silicates is thus important for a more complete understanding of the method as a structural tool.

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[1] Part II, J. Götz and C. R. Masson, *J. Chem. Soc. (A)*, 1971, 686.

[2] Part I, J. Götz and C. R. Masson, *J. Chem. Soc. (A)*, 1970, 2683.

[3] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

[4] F. F. H. Wu, J. Götz, W. D. Jamieson, and C. R. Masson, *J. Chromatog.*, 1970, **48**, 515.

[5] B. R. Currell, H. G. Midgley, and M. A. Seaborne, *J.C.S. Dalton*, 1972, 490.

[6] K.-H. Jost and W. Hilmer, *Acta Cryst.*, 1966, **21**, 583.

[7] P. B. Jamieson and L. S. Dent Glasser, *Acta Cryst.*, 1966, **20**, 688.

[8] P. B. Jamieson and L. S. Dent Glasser, *Acta Cryst.*, 1967, **22**, 507.

EXPERIMENTAL

For most of the systematic work, B.D.H. technical grade 'sodium metasilicate pentahydrate' ($Na_2SiO_3,5H_2O$ or $Na_2H_2SiO_4,4H_2O$) was used. The other hydrates were prepared by recrystallisation at room temperature from aqueous solutions of the 'pentahydrate'. Hemimorphite, $Zn_4(OH)_2Si_2O_7,H_2O$, from Friedensville, Pa., U.S.A., used in some experiments, was the same as that employed in previous studies.[1,2] The purity of all solids was checked by *X*-ray powder diffraction. They were ground to pass 100 mesh for trimethylsilylation.

The method of direct trimethylsilylation,[1,2] in which the solid is allowed to react with trimethylchlorosilane in the presence of water, hexamethyldisiloxane, and isopropyl alcohol, was employed. A systematic study was made of the influence of all variables on the yield and chromatographic pattern of the products.

The g.l.c. analyses were performed with a Hewlett–Packard 5750 G chromatograph equipped with a flame ionization detector. As in previous work,[4] the column was of stainless steel, 12 ft. long and 1/8 inch i.d., packed with methyl silicone gum rubber SE-30, 3% on Chromosorb W, AWDMCS, 80—100 mesh. Nitrogen was used in place of helium as carrier gas. All gases were dried by passage through a molecular sieve.

The chromatographic conditions described previously [4] were modified as follows: nitrogen flow rate, 66 ml min^{-1}; air flow rate, 375 ml min^{-1}; hydrogen flow rate, 28 ml min^{-1}; injection port temperature, 330 °C; flame detector block temperature, 350 °C. The program used for the temperature of the column was: 110 °C, 3 min; 110—140 °C, 15 °C min^{-1}; 140—200 °C, 8 °C min^{-1}; 200—260 °C, 2 °C min^{-1}. These conditions yielded good linearity of response and the TMS derivatives of the silicate anions appeared in the chromatograms at lower temperatures than in the earlier work.

To determine yields, areas were converted to weight concentrations by calibration with standard solutions in hexamethyldisiloxane of the pure TMS derivatives of monomer (SiO_4^{4-}) and dimer ($Si_2O_7^{6-}$). These were prepared with the aid of a modified collection vent similar to that described elsewhere.[4]

RESULTS

Preliminary experiments using the unified trimethylsilylation procedure described previously [1] showed that the main product of trimethylsilylation of $Na_2H_2SiO_4,4H_2O$ was the TMS derivative of the orthosilicate ion, SiO_4^{4-}, in agreement with the known structure of this compound. A typical chromatogram is shown in Figure 1.

In quantitative studies with this procedure, however, the yield of the orthosilicate derivative was always lower than expected, and was generally of the order of 10—20% of theoretical. Attempts to improve the yield by varying the conditions of trimethylsilylation showed that an important parameter was the order of addition of the reagents. The following procedure was finally adopted for all quantitative studies:

A weighed amount of solid was added, with continuous stirring, to a mixture of hexamethyldisiloxane, isopropyl alcohol, and water in a 2 oz. glass jar equipped with a magnetic stirring bar. A measured volume of trimethylchlorosilane was added, the jar was capped, and stirring was continued for the 'reaction time' indicated. The upper (organic) layer was then transferred by means of a dropping tube to a vial and weighed. Amberlyst * 15 ion exchange resin (*ca.* 1 g) was added, a small stirring bar was introduced, and the system was stirred overnight, or longer if required, until all peaks in the chromatogram due to partially trimethylsilylated derivatives had merged and the trimethylsilylation was complete.

An important feature of the above technique is the addition of the trimethylchlorosilane as the final step in the reaction procedure. Addition of this reagent at an earlier stage invariably led to erratic results and low yields, particularly when small amounts of solid were employed. Moreover, the elimination of the distillation step used in previous techniques not only simplifies the procedure, but also avoids uncertainties due to losses on distillation and other effects to be discussed in a subsequent communication.

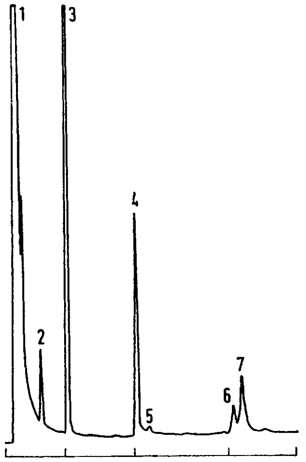

FIGURE 1 Typical chromatographic pattern for $Na_2H_2SiO_4$,-$4H_2O$. The peaks are due to: (1) solvent; (2) blank; and TMS derivatives of (3) SiO_4^{4-}; (4) $Si_2O_7^{6-}$; (5) $Si_3O_9^{6-}$; (6) $Si_4O_{12}^{8-}$; (7) $Si_3O_{10}^{8-}$

Using the above technique, the influence of various parameters on the yield of orthosilicate derivative from $Na_2H_2SiO_4,4H_2O$ was studied. All experiments were done at room temperature and the volume of hexamethyldisiloxane in the reaction mixture was kept constant at 5 ml.

Effect of Water.—Previous work [1] has shown that water is essential for the trimethylsilylation of anhydrous silicates, and that the yield and chromatographic pattern are markedly influenced by the amount used. Figure 2 shows the effect of water on the yield of orthosilicate derivate under the conditions given in the caption. Prolonged Amberlyst treatment was required for the experiments with the highest yields. A significant feature of the results is the low yield of monomer derivative (<0·1%) in the absence of added water, in spite of the presence of water of hydration in the original material. The marked increase in the yield with added water and the establishment of a plateau are similar to the effects observed with olivine.[2]

Effect of Isopropyl Alcohol.—The role of isopropyl alcohol in the trimethylsilylation of silicates has not been fully established, although its presence is known to be essential in the trimethylsilylation of olivine.[1] Figure 3 shows its effect on the trimethylsilylation of $Na_2H_2SiO_4,4H_2O$ under the conditions specified in the caption. The yield is a

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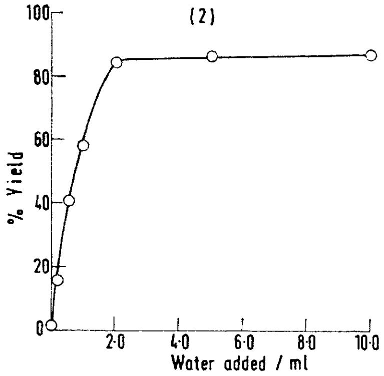
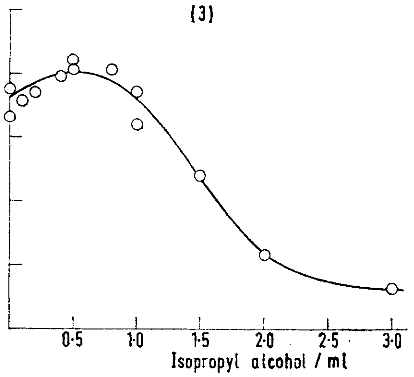
* Rohm and Haas, Philadelphia, U.S.A. *Not* Amberlite as incorrectly printed in Parts I and II.

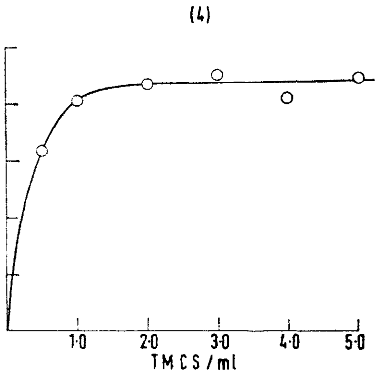
maximum at *ca.* 0·5 ml isopropyl alcohol, and decreases markedly as the volume is further increased. A similar decrease in the yield of the expected derivative with increasing isopropyl alcohol was observed with laumontite.[1]

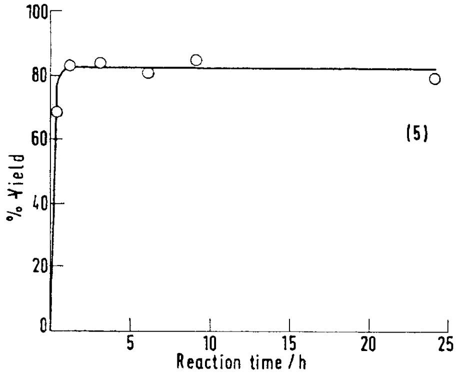
Effect of Trimethylchlorosilane.—Figure 4 shows the effect of varying the quantity of trimethylchlorosilane under the conditions specified in the caption. No reaction was observed in the absence of this reagent. The results are similar to those with olivine [1] and hemimorphite,[2] in that increase in the amount of reagent beyond a certain point has no effect on the yield; in the present case the critical amount is 2 ml.

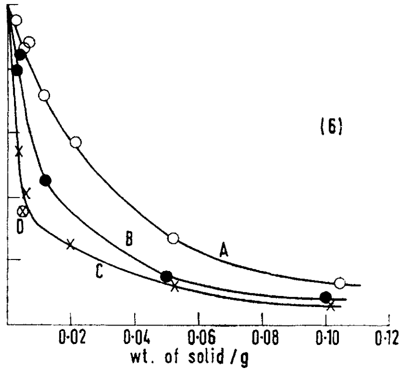
Effect of Time.—Figure 5 shows that the yield is independent of time after *ca.* 1 h, indicating that the material had all reacted within this period. Again, this result is similar to earlier ones using the method of direct trimethylsilylation.[1,2] Although the initial reaction is complete after 1 h, the trimethylsilylation was generally allowed to proceed overnight, as this decreased the time required for subsequent treatment with Amberlyst.











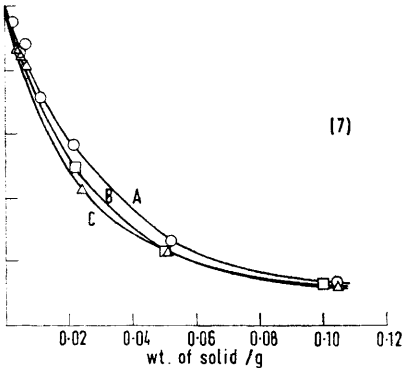


FIGURE 2 Percentage yield of orthosilicate TMS derivative plotted against the amount of water added. Other conditions: hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), $Na_2H_2SiO_4,4H_2O$ (4—5 mg) trimethylchlorosilane (4 ml), reaction time 12 h

FIGURE 3 Percentage yield of orthosilicate TMS derivative plotted against quantity of isopropyl alcohol used. Other conditions: hexamethyldisiloxane (5 ml), water (2 ml), $Na_2H_2SiO_4,4H_2O$ (3—4 mg), trimethylchlorosilane (4 ml), reaction time 12 h

FIGURE 4 Percentage yield of orthosilicate TMS derivative plotted against quantity of trimethylchlorosilane (TMCS) used. Other conditions: hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), water (2 ml), $Na_2H_2SiO_4,4H_2O$ (3·1—3·5 mg), reaction time 12 h

FIGURE 5 Percentage yield of orthosilicate TMS derivative plotted against reaction time. Other conditions: hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), water (2 ml), $Na_2H_2SiO_4,4H_2O$ (3·3—3·8 mg), trimethylchlorosilane (3 ml)

FIGURE 6 Percentage yield of orthosilicate TMS derivative plotted against the weight of $Na_2H_2SiO_4,4H_2O$ used. Other conditions: hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), trimethylchlorosilane (3—4 ml), with water A, 5 ml; B, 2 ml; and C, 0·4 ml. The single point D is not an experimental point, but was read from the curve in Figure 2 for 0·4 ml water. It can be seen that results from different series of runs agree well

FIGURE 7 Percentage yield of orthosilicate TMS derivative plotted against weight of solid used for the three different hydrates: A, $Na_2H_2SiO_4,4H_2O$; B, $Na_2H_2SiO_4,5H_2O$; C, $Na_2H_2SiO_4,8H_2O$

Effect of Solid.—Figure 6 shows the results obtained with various weights of solid, under the conditions specified in the caption. Curves are shown for experiments with 0·4, 2·0, and 5·0 ml water. In all the experiments, the yield of monomer derivative increased markedly with decreasing weight of solid and appeared to approach the theoretical value as the weight of solid became vanishingly small. A practical limit is reached at *ca.* 0·002 g, when errors in weighing and in measuring peak area become important. Figure 7 compares the results from each of the three different hydrates, using 5 ml of water in each case, other conditions being the same as for Figure 6. The slight differences observed are probably not significant.

DISCUSSION

It is evident that the highest yields of monomer TMS derivative from the hydrates employed in this work are obtained when the concentration of orthosilicate ions in solution is vanishingly small. Under these conditions, side reactions due to polymerisation of orthosilicate ions are minimised, and the yields approach the theoretical value as the solutions become infinitely dilute.

In line with this conclusion, it was observed that as the yield of orthosilicate derivative decreased, the proportion of TMS derivatives of higher anions in the products increased. Figure 8 shows this effect for the dimeric $Si_2O_7^{6-}$ ion; the ratio of the peak areas of the TMS derivatives of the monomeric and dimeric ions (SiO_4^{4-}/$Si_2O_7^{6-}$) is plotted against the volume of water employed (*cf.* Figure 2). As expected, the ratio increases continuously with increasing volume of water in the reaction medium. The effect is similar to that observed with olivine.[1]

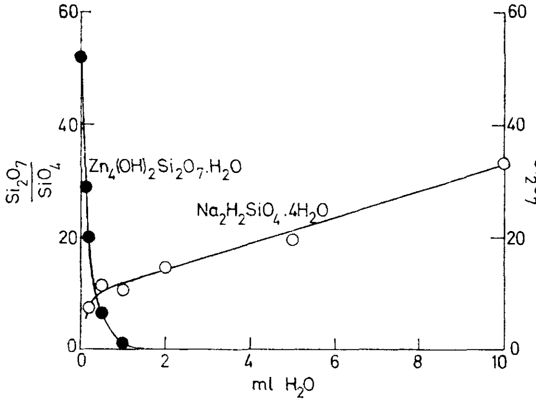


FIGURE 8 Ratio of peak areas of dimer to monomer derivatives from hemimorphite (Si_2O_7/SiO_4, left hand ordinate) and of monomer to dimer for $Na_2H_2SiO_4$,$4H_2O$ (SiO_4/Si_2O_7, right hand ordinate) plotted against volume of water employed

When large amounts of solid were used and the yields were low, as in some of the runs shown in Figures 6 and 7, a white solid was observed at the interface between the organic and aqueous layers. This was examined to see whether it might contain the missing material. *X*-Ray diffraction showed it to be amorphous. The i.r. spectrum showed strong bands characteristic of condensed silicate frameworks and weaker ones consistent with the presence of methyl groups attached to silicon. The solid charred on heating, and on ignition at 800 °C lost 20—30% of its weight. The white residue which remained was insoluble in common solvents but soluble in HF, and was therefore assumed to be amorphous silica. All these observations are consistent with the deduction that the white solid is mainly TMS derivatives of highly polymerised silicate anions, and its presence therefore accounts for the undetected silicate.

After trimethylsilylation, in some experiments the aqueous layer was evaporated to dryness. The white residue thus obtained was shown by *X*-ray powder diffraction to be sodium chloride. The weight of this residue always corresponded closely to that expected from the weight of sodium introduced, even when the yield of TMS derivatives was low. This confirms that the low yields were due to the formation of TMS derivatives of higher polymers, which cannot be detected by g.l.c., rather than to incomplete trimethylsilylation.

In all experiments the orthosilicate derivative was the main product detected, even though when yields were low it represented only a small fraction of the total silicate reacted. This agrees with the predictions of polymer theory[9] for the equilibrium distribution in a linear self-condensation; in theory, at equilibrium, the monomer is numerically the most abundant species for all extents of polycondensation. Extension of this theory to the silicates[10] has shown that a similar conclusion should apply.

The above establishes that for these sodium silicate hydrates undue losses of orthosilicate ions through polymerisation in solution, with consequent reduction in yields, can be avoided by using very small weights of solid or relatively large quantities of water or both. From the viewpoint of the method as an aid in structural studies it is desirable to examine the behaviour of other silicates under these conditions. For this purpose, the mineral hemimorphite was used, since its trimethylsilylation had already been studied in some detail.[1,2] (Ideally, one should have used a sodium pyrosilicate, but so far as is known, none exists).

Figure 8 shows the ratio of peak areas of the TMS derivatives of the dimer and monomer ($Si_2O_7^{6-}$/SiO_4^{4-}) plotted against volume of water employed in trimethylsilylation of hemimorphite under the same conditions as for $Na_2H_2SiO_4$,$4H_2O$. The ratio Si_2O_7/SiO_4 decreases markedly with increasing water content, so that conditions which favour high yields of the orthosilicate derivative from the sodium silicate hydrates are unsuitable for hemimorphite. Presumably, in dilute aqueous solution hydrolysis of the dimeric pyrosilicate ion produces substantial quantities of the monomer before trimethylsilylation is complete.

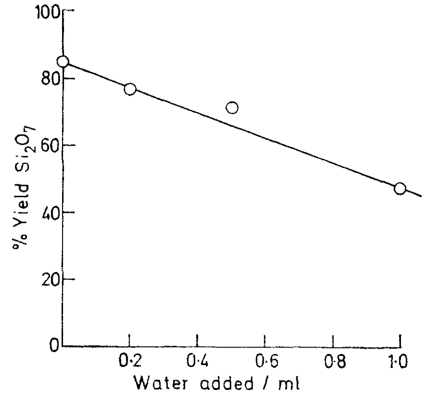


FIGURE 9 Effect of added water on the yield of dimer derivative from hemimorphite. Other conditions: hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), hemimorphite (3·8—4·5 mg), trimethylchlorosilane (3 ml)

The variation in the yield of dimeric derivative from hemimorphite with added water was studied; the results are plotted in Figure 9, which may be compared with

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[9] P. J. Flory, 'Principles of Polymer Chemistry,' Cornell University Press, Ithaca, New York, 1953.

[10] C. R. Masson, I. B. Smith, and S. G. Whiteway, *Canad. J. Chem.*, 1970, **48**, 1456.

Figure 2. A striking feature is that under the conditions indicated the yield of dimeric derivative from hemimorphite is 85% of theoretical in the absence of added water. This is in contrast to the behaviour of the sodium silicate hydrate (Figure 2) for which the addition of water is essential to obtain even a moderate amount of the product.

CONCLUSION

In Part II[1] of this work the difficulties in obtaining a unified method of trimethylsilylation applicable to silicates of different structures were discussed. It was concluded that it is essential to use controlled amounts of water to avoid undue polymerisation–depolymerisation of silicate ions in solution before trimethylsilylation is complete. The sodium silicates used in the present work present far greater difficulties than the other silicates studied previously. Because they are very soluble in water, high local concentrations of silicate ions can be produced which polymerise before trimethylsilylation has had a chance to occur. This is probably the explanation of the negligible amount of monomer derivative noted in the absence of water. Such high concentrations can be largely avoided by working with large amounts of water and/or very small quantities of solid, but the results with hemimorphite show that unacceptably low yields of the dimeric derivative are obtained under these conditions.

Figure 8 shows that, with 0·4 ml water, the ratio of peak areas Si_2O_7/SiO_4 from hemimorphite and SiO_4/Si_2O_7 from $Na_2H_2SiO_4,4H_2O$ are each approximately 10/1. The following procedure therefore summarises the conditions found to yield the orthosilicate derivative as the main product from the sodium silicate hydrates while retaining a high yield of dimeric derivative from hemimorphite. The solid (<100 mesh, 0·004 g) is added, with stirring, to a mixture of hexamethyldisiloxane (5 ml), isopropyl alcohol (0·5 ml), and water (0·4 ml). Trimethylchlorosilane (3 ml) is added and stirring is continued for at least 1 h at room temperature. The organic layer is separated and treated with Amberlyst 15 ion exchange resin until all multiple peaks have merged and the trimethylsilylation is complete.

The yield of monomer derivative from $Na_2H_2SiO_4,4H_2O$ under these conditions is *ca.* 40% of theoretical (Figure 2), the remainder appearing as TMS derivatives of higher anions, most of which are undetected chromatographically. Although the yield is low, the chromatographic pattern is acceptable for purposes of structural identification. Under the same conditions, the pattern from hemimorphite is also satisfactory and the yield of dimeric derivative (Figure 9) is 70% of theoretical.

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