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Dimethylvinylsilylation of $Si_8O_{20}{}^{8-}$ silicate anion in methanol solutions of tetramethylammonium silicate

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Abstract

1,3,5,7,9,11,13,15-octakis(dimethylvinylsiloxy)pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane $\{Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8\}$ has been synthesized by the reaction of dimethylvinylchlorosilane with the $Si_8O_{20}{}^{8-}$ silicate anion with the double eight-membered (Si_4O_4) ring in a tetramethylammonium silicate methanolic solution. Incompletely dimethylvinylsilylated derivatives of $Si_8O_{20}{}^{8-}$ with 1 and 2 silanol groups, $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_{8-n}(H)_n$ ($n = 1, 2$), have also been formed as intermediates in the course of formation of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$.

Introduction

A silicate species with the double eight-membered (Si_4O_4) ring ($Si_8O_{20}{}^{8-}$, the cubic octamer) is formed selectively by adding tetramethylammonium ions or other organic quaternary ammonium ions with three methyl groups to silicate solutions [1]. The structure of the cubic octamer corresponds to one of secondary building units in zeolite frameworks [2]. Therefore, it is expected that the species can be a starting material for synthesizing silica-based inorganic or inorganic-organic hybrid materials with controlled siloxane backbones.

For producing the latter materials from the cubic octamer, it would be necessary to synthesize its organic derivatives. Trimethylsilylation is one of the reaction methods to synthesize organic derivatives of silicates. Trimethylsilylation of silicates has been performed to elucidate silicate structures in silicate minerals and solutions [3]. Three basic methods have been reported for obtaining the trimethylsilyl derivatives [4–6]. In the method of Lentz [4], a mixture of concentrated hydrochloric acid, water, 2-propanol, and hexamethyldisiloxane [$(CH_3)_3Si$–O–$Si(CH_3)_3$, HMDS] is used as a trimethylsilylating reagent. A mixture of HMDS, trimethylchlorosilane [$(CH_3)_3SiCl$, TMCS], and 2-propanol and one of HMDS, TMCS, and dimethylformamide are the silylating reagents in the methods of Götz

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and Masson [5] and of Tamás [6], respectively. In the development of trimethylsilylation as a method for the study of silicate structures, much attention has been paid to avoiding breakdown of the original structures of silicate anions in minerals and solutions during derivatization. This is because under acidic conditions silicate anions are liable to polymerization and depolymerization.

Other organic derivatives of silicates have been synthesized on the basis of trimethylsilylation techniques. Hoebbel *et al.* [7,8] and Agaskar [9] reported the preparations of dimethylvinylsilyl, allyldimethylsilyl, chloromethyldimethylsilyl, and dimethylsilyl derivatives of the cubic octamer. The dimethylvinylsilyl derivative $\{Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8\}$ was synthesized by employing 1,3-divinyltetramethyldisiloxane $[(CH_2{=}CH)(CH_3)_2Si{-}O{-}Si(CH_3)_2(CH{=}CH_2)$, TMDVDS] and dimethylvinylchlorosilane $[(CH_2{=}CH)(CH_3)_2SiCl$, DMVCS] instead of respectively HMDS and TMCS, used in trimethylsilylation.

This study aimed to synthesize dimethylvinylsilylated derivatives of the cubic octamer by a single use of DMVCS. One reason for using DMVCS was to investigate whether introduction of dimethylvinylsilyl groups to $\equiv SiO^-$ sites in $Si_8O_{20}{}^{8-}$ would take place stoichiometrically and whether incompletely silylated derivatives would be formed. Although Hoebbel *et al.* [7] studied the reaction of DMVCS with the cubic octamer, the relationship between the amount of DMVCS used and the yield of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$, and the formation of by-products in the reaction have not been described. This paper reports the effect of amount of DMVCS and a reaction time on the formation of dimethylvinylsilylated derivatives of the cubic octamer.

Experimental

Preparation of a tetramethylammonium silicate methanolic solution in which $Si_8O_{20}{}^{8-}$ is the dominant component

The cubic octamer is dominant in a methanol solution of tetramethylammonium silicate when the SiO_2 concentration is 1.0 mol l^{-1}, the molar ratio of tetramethylammonium ions to SiO_2 is 1.0, and the molar ratio of water to SiO_2 is 10.0 [10,11]. The solution (20 ml) was prepared as follows. 4.48 ml of tetraethoxysilane was added to a mixture of 10 ml of 2.0 mol l^{-1} tetramethylammonium hydroxide pentahydrate methanol solution and 1.8 ml of water under stirring. Methanol was added to bring the total volume to 20 ml. Vigorous stirring at room temperature for one day resulted in the selective formation of the cubic octamer in solution.

Dimethylvinylsilylation of the cubic octamer

A 1 ml portion of the methanol solution of tetramethylammonium silicate was added dropwise to 5 ml of a solution of DMVCS in tetrahydrofuran (THF), which had been stirred for 5 min before the addition. THF is known to be effective for solvent extraction of silicate acids [12]. The reaction mixture was stirred for a given time at room temperature. Since the boundary of the organic and aqueous phases of the mixture was unclear after the reaction, water and hexane were added to separate the mixture clearly into two phases. The organic phase was removed for analysis. The amount of DMVCS and the reaction time were varied in order to investigate conditions for the formation of dimethylvinylsilyl derivatives of the cubic octamer. The amount of DMVCS used is represented as the DMVCS/SiO_2 ratio, *i.e.* the molar ratio of DMVCS to a SiO_2 component in a 1 ml portion of the methanol solution of tetramethylammonium silicate.

Analytical procedure

Products obtained by the dimethylvinylsilylation described above were analyzed by gas chromatography, gas chromatograph-mass spectrometry, and ^{29}Si NMR spectroscopy. Quantitative analysis with respect to $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ was performed with gas chromatography using tetradecane as an internal standard. ^{29}Si NMR spectra were obtained using hexamethylcyclotrisiloxane $\{[(CH_3)_2SiO]_3\}$ as an internal standard. A ^{29}Si NMR peak due to $[(CH_3)_2SiO]_3$ appeared at -8.342 ppm (reference: $Si(CH_3)_4$ at 0 ppm). For further details see ref. 13.

Results and discussion

Figure 1 shows portions of gas chromatograms of products in hexane solutions obtained by dimethylvinylsilylation with a reaction time of 1 h and DMVCS/SiO_2 ratios of (a) 4.0 and (b) 12.0, respectively.

A compound corresponding to a major peak, labelled A, on the gas chromatogram shown in Fig. 1 (b) is insoluble in methanol, so that the compound can easily be isolated and purified. In its mass spectrum, the $[M]^+$ ion occurs at m/z 1224, the $[M-15(CH_3\cdot)]^+$ ion at m/z 1209, the $[M-27(CH_2{=}CH\cdot)]^+$ ion at m/z 1197, and the $[Si(CH_3)_2(CH{=}CH_2)]^+$ ion at m/z 85. In the ^{29}Si NMR spectrum of the compound, only two peaks appear, at -109.118 and 0.531 ppm, assigned to $\mathit{Si}(OSi)_3[OSi(CH_3)_2(CH{=}CH_2)]$ and $\mathit{Si}(OSi)(CH_3)_2(CH{=}CH_2)$, respectively. These values are identical with those reported for $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ by Hoebbel *et al.* [7]. The compound is identified as the completely dimethylvinylsilylated derivative of the cubic octamer, $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$.

SiO_2 recovery is defined as the percentage of the SiO_2 component recovered as $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ against that in a 1 ml portion of the methanol solution of tetramethylammonium silicate. This varies with the DMVCS/SiO_2

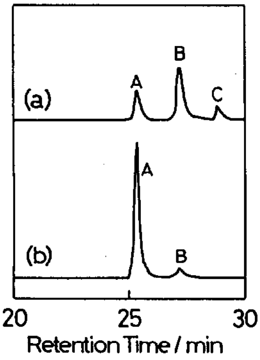

Fig. 1. Portions of gas chromatograms of products obtained by dimethylvinylsilylation at a reaction time of 1 h and DMVCS/SiO_2 ratios of (a) 4.0 and (b) 12.0. Peaks as follows: (A): $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$; (B): $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_7(H)$; (C): $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_6(H)_2$.

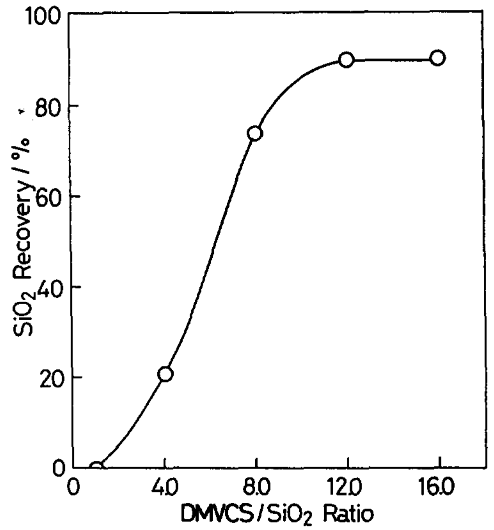

Fig. 2. Dependence of SiO_2 recovery of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ on the DMVCS/SiO_2 ratio in dimethylvinylsilylation (reaction time: 1 h)

ratio as shown in Fig. 2. Reaction time was constant (1 h), and the recovery increased with increasing DMVCS/SiO_2 ratio, becoming constant at 90% at DMVCS/SiO_2 ratios over 12.0.

Figure 3 shows the dependence of SiO_2 recovery on reaction time at a DMVCS/SiO_2 ratio of 12.0. The recovery of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ becomes constant at 90% for all reaction times above 30 min, indicating completion of dimethylvinylsilylation of $Si_8O_{20}{}^{8-}$ at this DMVCS/SiO_2 ratio.

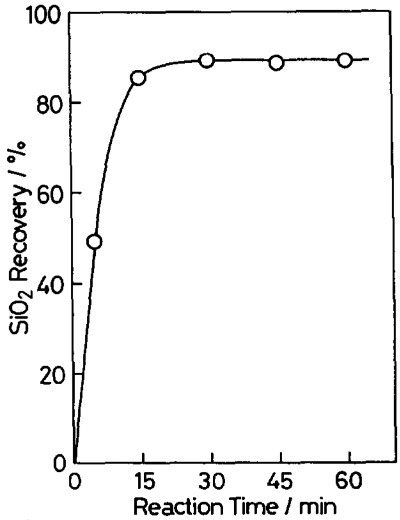

Fig. 3. Dependence of SiO_2 recovery of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ on the reaction time in dimethylvinylsilylation (DMVCS/SiO_2 ratio: 12.0)

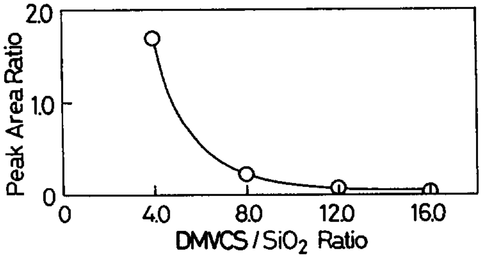

Fig. 4. Dependence of ratio of area of peak B to peak A on the DMVCS/SiO_2 ratio in dimethylvinylsilylation (reaction time: 1 h).

Compounds indicated by peaks B and C, as seen in Fig. 1(a), are also found after 5 min of a reaction at a DMVCS/SiO_2 ratio of 12.0 when $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ is formed with a SiO_2 recovery of 50%. However, they are just found as a trace after 30 min of reaction. This would indicate that these compounds are intermediates in the formation of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$.

The area ratio of peak B to peak A at a reaction time of 1 h increases with decreasing DMVCS/SiO_2 ratio (Fig. 4). This implies that the amount of the compound corresponding to peak B increases with decreasing ratio. Peak C is revealed only in a gas chromatogram of products obtained at a DMVCS/SiO_2 ratio of 4.0, indicating that these compounds are obtained when the amount of DMVCS is insufficient for the formation of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ at a 90% yield.

Unfortunately, all attempts to isolate the products corresponding to peaks B and C have so far been unsuccessful. However, a mixture of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ (peak A) and a compound corresponding to peak B is obtained. The ^{29}Si NMR spectrum of the mixture is shown in Fig. 5. Peaks a and b in Fig. 5 are due to $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$, as described above. Peaks c, d, and e are in the chemical shift range between -0.139 and $+0.184$ p.p.m. in relation to the peak assigned to the $\mathit{Si}(OSi)_4$ unit in $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$, suggesting that three non-equivalent $\mathit{Si}(OSi)_4$ units in the double eight-membered ring siloxane structure are involved in a compound indicated by peak B. Peak f appears in the chemical shift range due to peaks from the $\mathit{Si}(OSi)_3(O^-)$ unit. Actually, the chemical shift value of a peak due to the $\mathit{Si}(OSi)_3(O^-)$ unit in $Si_8O_{20}{}^{8-}$ is -99.2 ppm [11]. Since the intensity ratio of peaks c, d, e, and f is approximately 1 : 3 : 3 : 1, a compound corresponding to peak B has the double eight-membered ring siloxane backbone consisting of seven $\mathit{Si}(OSi)_4$ units and one $\mathit{Si}(OSi)_3(O^-)$ unit. A few peaks around peak b are due to the $\mathit{Si}(OSi)(CH_3)_2(CH{=}CH_2)$ site in $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$, indicating that the compound indicated by peak B also has this site. In addition, m/z for the $[M^+]$ ion of the compound is found by mass spectrometry to be 1140. From these facts, peak B would be assigned to $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_7(H)$, the incompletely dimethylvinylsilylated derivative of $Si_8O_{20}{}^{8-}$ with an unreacted silanol group.

The difference in retention times of peaks A and B in the gas chromatogram would be caused by replacement of a dimethylvinylsiloxyl group in $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ by a hydroxyl group. The difference is almost the

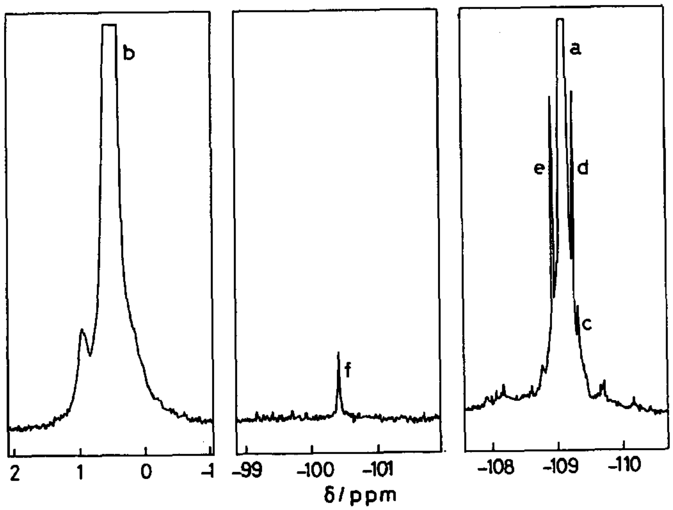

Fig. 5. Portions of the ^{29}Si NMR spectrum of a mixture of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ and $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_7(H)$. Chemical shifts of labelled peaks (ppm) are as follows: a, −109.118; b, 0.531; c, −109.326; d, −109.257; e, −108.934; f, −100.407.

same as that between peaks B and C. ^{29}Si NMR peaks of a mixture of compounds corresponding to peaks A, B, and C in Fig. 1(a) also appear only in three regions; −109.3 to −109.9 ppm from the *Si*(OSi)$_4$ unit, −100.8 to −101.2 ppm from the *Si*(OSi)$_3$(O$^-$) unit, and 0.9 to 0.0 ppm from the *Si*(OSi)(CH$_3$)$_2$(CH=CH$_2$) unit. In addition, an m/z for the $[M^+]$ ion from a compound corresponding to peak C is found to be 1056. From these facts, it is considered that peak C may be due to $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_6(H)_2$, a partially dimethylvinylsilylated product with the double eight-membered ring siloxane framework having two silanol groups. Formation of these compounds with unreacted silanol groups is consistent with the fact that these compounds are formed in the reaction at lower DMVCS/SiO$_2$ ratios and shorter reaction times.

Formation of $SiO_4[Si(CH_3)_2(CH{=}CH_2)]_4$ is also observed under all the reaction conditions investigated. This means that the $Si_8O_{20}{}^{8-}$ silicate anion is broken down to $SiO_4{}^{4-}$ during the reaction, although there are no other peaks that could be due to compounds with siloxane structures formed by cleavage of the $Si_8O_{20}{}^{8-}$ framework. On the other hand, recovery of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ is 90% even in a system with a DMVCS/SiO$_2$ ratio of 16.0, where a large amount of HCl would be formed. This suggests that cleavage of siloxane bonds in $Si_8O_{20}{}^{8-}$ barely takes place during the reaction.

At the early stage of the reaction, a white solid identified as tetramethylammonium chloride is precipitated. It is considered that the chloride ion from DMVCS reacts with tetramethylammonium ions as follows:

$$Si_8O_{20}[N(CH_3)_4]_8 + 8(CH_2{=}CH)(CH_3)_2SiCl \longrightarrow$$

$$Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8 + 8N(CH_3)_4 \cdot Cl$$

Thus formation of HCl, which causes the breakdown of siloxane bonds, would be depressed, resulting in the retention of siloxane bonds in the $Si_8O_{20}{}^{8-}$ backbone and a high yield of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ at even a high DMVCS/SiO_2 ratio.

This would also explain why $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ is not obtained at all in a system with a DMVCS/SiO_2 ratio of 1.0. If the reaction of DMVCS with $Si_8O_{20}{}^{8-}$ is stoichiometric, a reasonable yield of $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ should be obtained even with this DMVCS/SiO_2 ratio. This would be attributed to a side reaction of DMVCS, that is, the hydrolysis of DMVCS in the methanol solution of tetramethylammonium silicate to form TMDVDS.

$$2(CH_2{=}CH)(CH_3)_2SiCl + H_2O \longrightarrow (CH_2{=}CH)(CH_3)_2Si{-}O{-}Si(CH_3)_2(CH{=}CH_2) + 2HCl$$

Since this is reversible, the dimethylvinylsilylation reaction takes place if HCl is present with TMDVDS. In the present systems, however, chloride ions from DMVCS react with tetramethylammonium ions, making the reverse reaction from TMDVDS to DMVCS or dimethylvinylsilanol $[(CH_2{=}CH)(CH_3)_2SiOH]$ impossible, and so dimethylvinyl-silylation of $Si_8O_{20}^{8-}$ would not occur at ratio of 1.0. The presence of TMDVDS is confirmed as a product in all the systems before adding water and hexane.

$Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ is obtained in 60% yield after washing the crude product (obtained at a DMVCS/SiO_2 ratio of 12.0 and a reaction time of 1 h) twice with methanol. This low yield is due to the difficulty of removing $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_7(H)$ from the crude product. By adding DMVCS to a hexane solution of the crude product and stirring, however, $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_7(H)$ can be converted to $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$.

In conclusion, $Si_8O_{20}[Si(CH_3)_2(CH{=}CH_2)]_8$ was obtained at a SiO_2 recovery of 90% (60% after isolation by washing twice with methanol) by the reaction of DMVCS with $Si_8O_{20}{}^{8-}$ in the methanol solution of tetramethylammonium silicate at DMVCS/SiO_2 ratios above 12.0 and reaction times over 30 min. The cleavage of $Si_8O_{20}{}^{8-}$ caused by chloride ions from DMVCS was depressed because of the formation of tetramethylammonium chloride. Although the reaction was not stoichiometric, incompletely dimethylvinylsilylated products with silanol groups could be formed by controlling the DMVCS/SiO_2 ratio or the reaction time.

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