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TRIMETHYLSILYLATION OF BIOTITE

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Abstract—Organic solvent soluble organosilicate compounds retaining silicate backbone were obtained by the reaction between biotite and trimethylsilylating reagent. The soluble product which was formed at room temperature or at reflux temperature was a viscous liquid and was soluble in a wide range of organic solvents, but insoluble in water. Molecular weights of the soluble products and their thin-layer chromatograms made it clear that the soluble products consisted of several trimethylsilylated derivatives of silicic acids which were mainly the derivatives of mono- and disilicic acid. The influence of reaction temperature for the trimethylsilylation reaction also was discussed.

INTRODUCTION

Trimethylsilylation of silicates has been studied since Lentz (1964) reported the trimethylsilylation reaction of olivine, hemimorphite, natrolite and sodium silicate. The organic solvent soluble products prepared by the reaction were analyzed by gas–liquid partition chromatography and the distribution of silicate anions was discussed there. Götz and Masson (1970) and Sharma *et al.* (1973) applied this technique to the study of silicate structures, especially hemimorphite and sodium silicate hydrates. The preparation of organic derivatives of phyllosilicates by trimethylsilylation also has been studied by several workers (Frazier *et al.*, 1967; Fripiat and Mendelovici, 1968; Ruiz-Hitzky and Fripiat, 1976). Currell *et al.* (1974) reported the synthesis of trimethylsilylated products of a number of silicates, including biotite. However, except for the research by Currell *et al.*, no work has been known concerning the synthesis of organic derivatives of silicic acids which occur in the process of the acid decomposition of biotite.

Trimethylsilylation of silicates can be expressed as follows:

$$\equiv Si{-}O{-}M \xrightarrow{HCl/H_2O} \equiv Si{-}O{-}H$$

(M: metallic cation)

$$\equiv Si{-}O{-}H \xrightarrow{(CH_3)_3SiOH} \equiv Si{-}O{-}Si(CH_3)_3.$$

When biotite $\{K\}(Mg,Fe)_3[Si_3Al]O_{10}(OH)_2$ is leached with acid, fresh silicic acid occurs and it is trimethylsilylated in the presence of trimethylsilanol.

Trimethylsilylation reaction also gives novel information on the synthesis of inorganic polymers. In this paper, trimethylsilylation of biotite was studied for the purpose of the synthesis of inorganic oligomers retaining a silicate backbone.

EXPERIMENTAL

Material

The biotite used in this work was from Giridih, Bihar, India. Clean biotite crystals were ground to pass 100 mesh. The purity of the ground material was checked by the method of X-ray powder diffraction. Hexamethyldisiloxane, isopropyl alcohol and concentrated hydrochloric acid were obtained commercially.

Trimethylsilylation

Trimethylsilylation of biotite was carried out using the technique of Currell *et al.* (1974). Isopropyl alcohol (50 ml), concentrated hydrochloric acid (50 ml) and hexamethyldisiloxane (66.6 ml) were added to biotite powder (10 g). In this work, the reaction temperature was (A) room temperature or (B) reflux temperature (75°C). The reaction mixture was stirred for 72 hr and separated into an organic siloxane layer, an aqueous layer and a solid residue by centrifugation. Hexamethyldisiloxane in the organic layer was removed by evaporation under reduced pressure. The soluble product obtained from the organic layer was analyzed by infrared spectroscopy, molecular weight determination, TLC and thermal analysis. The solid residue (insoluble product) after washing with water, isopropyl alcohol and ether was analyzed by X-ray powder diffraction and infrared spectroscopy.

Analyses

Infrared spectra were measured in a KBr disk or a CCl_4 solution with a Shimadzu IR-400 spectrometer. X-ray powder diffraction patterns were produced on a Shimadzu VD-11 diffractometer, using Ni filtered Cu K_α radiation. Molecular weights were determined by the cryoscopic method in cyclohexane. Thin-layer chromatographic procedure followed that of Hoebbel and Wieker (1974). Semi-quantitative data of thin-layer chromatographic patterns were obtained by means of thin-layer stick chromatography on silica gel sintered sticks with a flame ionization detector (Okumura *et al.*, 1975). Differential thermal analysis was carried out on a Shimadzu DT-20B. Sample weight was about 5 mg and alumina was used as reference. The sample and the reference material were

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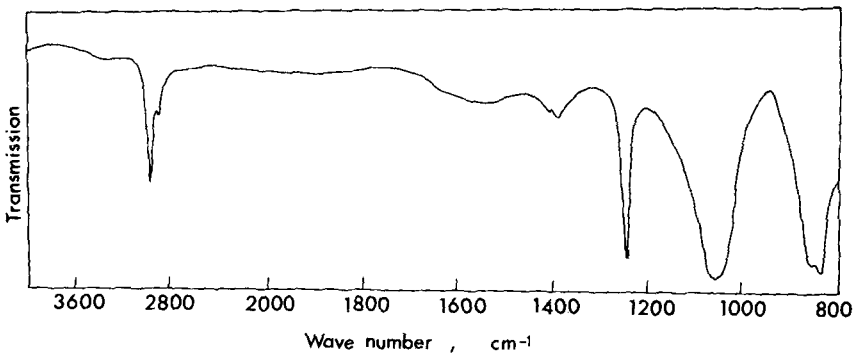


Figure 1. Infrared spectrum of the soluble trimethylsilylated product (A).

contained in aluminum sealed pans. The experiments were performed under a static air atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Organic solvent soluble products were transparent and viscous liquid, coloured yellow slightly. The yields of the soluble product formed by the reaction at room temperature, designated as the soluble product (A) hereafter, and the soluble product by the reaction at reflux temperature (the soluble product (B)) were 7.1 g and 9.5 g, respectively. The number-average molecular weight of the soluble product (A) was 780, while the molecular weight of the soluble product (B) was 565. The soluble product (A) was more viscous than the soluble product (B) and both of them did not dissolve in water.

Infrared spectrum of the soluble product (A) is given in Figure 1. The spectrum resembled that of hexamethyldisiloxane and showed no hydroxyl absorption. Major bands were assigned to CH (2960, 2895 cm^{-1}), $Si(CH_3)_3$ (1410, 1260 cm^{-1}), and SiOC and SiOSi (1060–70 cm^{-1} strong), indicating the trimethylsilylation of silanol groups in silicic acids which appeared in the decomposition of biotite. The spectrum of the soluble product (B) was identical with that of the soluble product (A).

The separation and identification of the trimethylsilylated products (A,B) was carried out by TLC. Figure 2(a) shows the thin-layer chromatogram of trimethylsilylated (mono-, di-, tri-, tetra-, cyclotri-, cyclotetra-, tricycloheptа-, pentacycloocta-) silicic acid, which has been reported by Hoebbel and Wieker (1974).

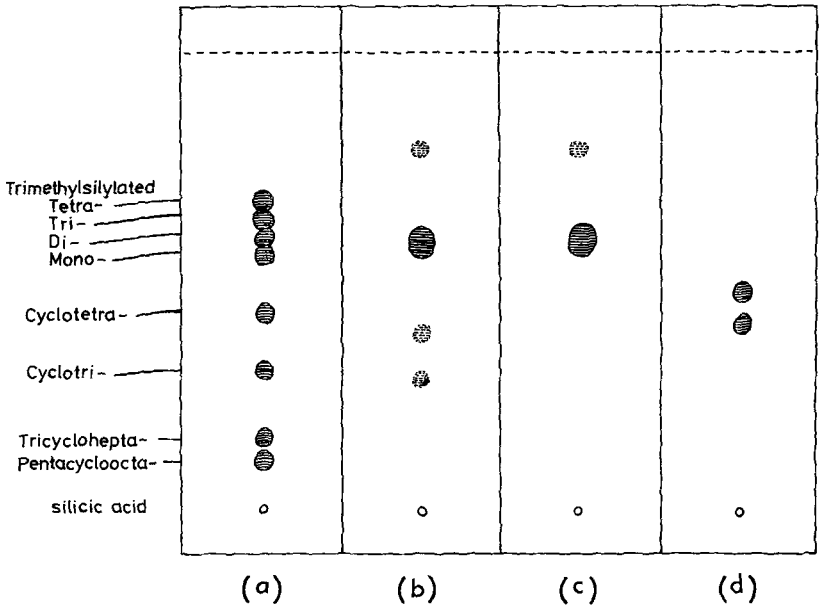


Figure 2. Thin-layer chromatograms of the trimethylsilylated products: (a) data from Hoebbel and Wieker (1974) on Al_2O_3–SiO_2 plate; (b) soluble product (A) on Al_2O_3–SiO_2 plate; (c) soluble product (B) on Al_2O_3–SiO_2 plate; (d) soluble product (A) on SiO_2 plate.

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Table 1. Theoretical molecular weights and R_f values of trimethylsilylated silicic acids

Trimethylsilylated silicic acid	Formula	Theoretical molecular weight	R_f*
Mono-	$[(CH_3)_3Si]_4[SiO_4]$	384	0.56
Di-	$[(CH_3)_3Si]_6[Si_2O_7]$	606	0.60
Tri-	$[(CH_3)_3Si]_8[Si_3O_{10}]$	828	0.65
Tetra-	$[(CH_3)_3Si]_{10}[Si_4O_{13}]$	1050	0.68
Cyclotri-	$[(CH_3)_3Si]_6[Si_3O_9]$	666	0.31
Cyclotetra-	$[(CH_3)_3Si]_8[Si_4O_{12}]$	888	0.44
Tricyclohepta-	$[(CH_3)_3Si]_{10}[Si_7O_{19}]$	1230	0.16
Pentacycloocta (Double four-ring-)	$[(CH_3)_3Si]_8[Si_8O_{20}]$	1129	0.11

* Data from Hoebbel and Wieker (1974).

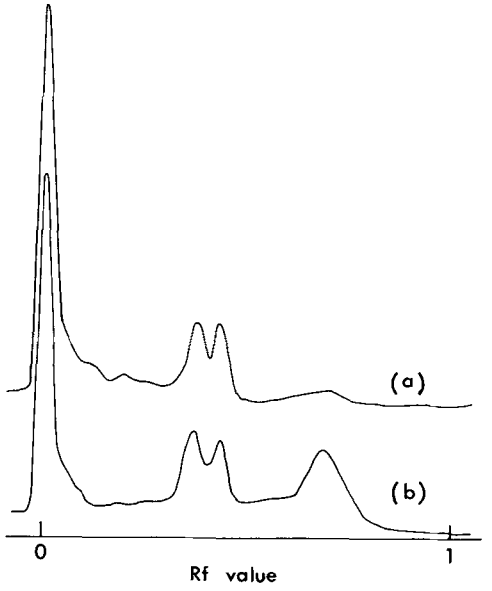


Figure 3. Thin-layer stick chromatograms on silica gel sintered stick with an FID scanner: (a) soluble product (A); (b) soluble product (B).

Theoretical molecular weights and R_f values* of the trimethylsilylated silicic acids are listed in Table 1. The chromatograms of the soluble products (A,B), which is given in Figure 2(b,c), revealed that the main products were the trimethylsilylated derivatives of low molecular silicic acids (mono- and disilicic acid). The spot at a high R_f value in Figure 2(b) or (c) could not be identified. Small amounts of cyclotri- and cyclotetra-silicic acid derivatives could be detected in Figure 2(b). Better separation was successful by use of the silica plate as shown in Figure 2(d). The derivatives which were developed to $R_f = 0.6$ on silica–alumina plate were separated into two components and their R_f values were 0.49 and 0.42 on silica plate.

Quantitative data were produced by means of thin-layer stick chromatography on silica gel sintered sticks with an FID scanner. The chromatograms of the soluble products (A,B) are shown in Figure 3. Central two peaks ($R_f \doteqdot 0.5$) corresponded to the two spots in Figure 2(d). The large peak at the starting point might be attributed to higher molecular weight silicic acid derivatives.

The quantity of higher molecular weight compounds, however, was small because a recorder response was almost proportional to the carbon content of each component. The small peak at a high R_f value corresponded to the unidentified spot in Figure 2(b) or (c). Number-average molecular weights of the soluble products and chromatograms in Figure 3 lead to the conclusion that the soluble products consist of trimethylsilylated silicic acids (mono-, di-, and polymeric silicic acid) and that the main products are the trimethylsilylated derivatives of mono- and disilicic acid. The molecular weight of the soluble product (B) was lower than that of the soluble product (A), which might be due mainly to the depolymerization of silicic acids under the drastic condition and partly due to the moderate existence of the unidentified compound.

Figure 4 shows DTA curve of the soluble product (A) formed by the reaction at room temperature. Thermal change was not observed up to 350°C. A large broad exothermic peak (360–500°C) indicated the combustion of trimethylsilyl groups. Similar thermal behavior was observed for the soluble product (B).

X-ray powder diffraction patterns of residues (insoluble products) are given in Figure 5.

The intensity of diffraction of the residue separated from the reaction mixture at room temperature was slightly diminished, while X-ray patterns of the residue at reflux temperature showed appreciable decomposition of the starting material, which agreed with the difference of the yields of the soluble products. The infrared spectra of the insoluble products showed no absorption bands due to the trimethylsilyl groups, indicating that trimethylsilylation did not occur on the solid residues. These results suggest that the trimethylsilylation reaction at reflux temperature proceeded faster than at room temperature.

* In chromatography, substances may be described by their migration relative to that of the developer. This ratio has been called the R_f value for linear flow in paper or TLC.

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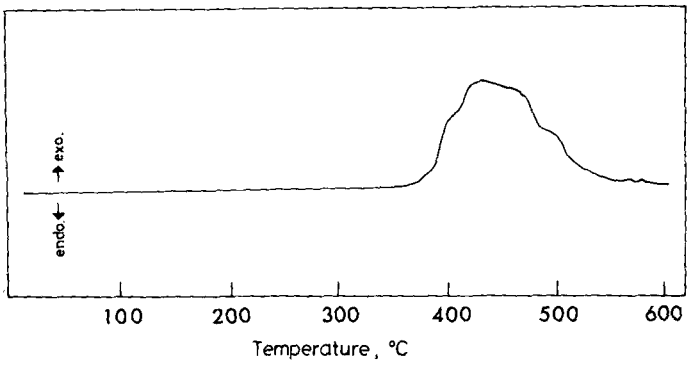


Figure 4. DTA curve of the soluble trimethylsilylated product (A).

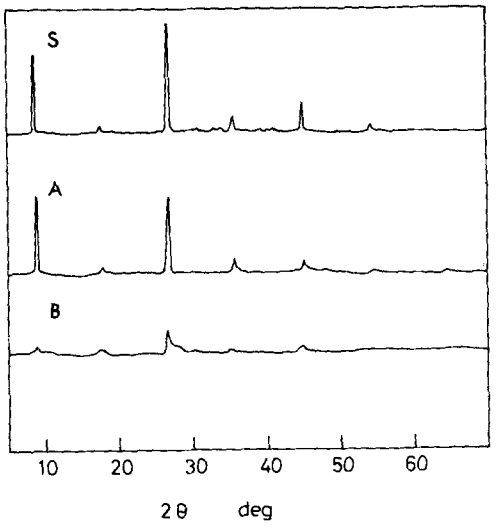


Figure 5. X-ray powder diffraction patterns of the insoluble products: (S) biotite; (A) solid residue at room temperature; (B) solid residue at reflux temperature.

The reaction process of the trimethylsilylation of biotite may be as follows:

(1) Hexamethyldisiloxane reacts with hydrochloric acid to give trimethylchlorosilane and (or) trimethylsilanol.

(2) Interlayer cation is removed by hydrochloric acid.

(3) Acid attack occurs (a) at Mg and Fe in octahedral layer and (b) at Al in tetrahedral layer.

(4) Low molecular silicic acids appear.

(5) Low molecular silicic acids are trimethylsilylated by the reaction with trimethylchlorosilane or trimethylsilanol.

According to Currell *et al.* (1974), the molecular weight distribution of soluble trimethylsilylated products may be influenced by (a) Al distribution in the tetrahedral layer and (b) polymerization–depolymerization equilibrium of low molecular silicic acids. Number-average molecular weights of the soluble products suggest that depolymerization of silicic acids is predominant under the refluxing conditions, which will be presented in a subsequent paper.

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