

SYNTHESIS OF THE TRIMETHYLSILYLATION DERIVATIVE OF HALLOYSITE

KAZUYUKI KURODA AND CHUZO KATO

Department of Applied Chemistry, School of Science and Engineering,
Waseda University, Shinjuku-ku, Tokyo, Japan 160

(Received 7 March 1978)

Abstract—The trimethylsilyl derivative from halloysite was prepared by the reaction of halloysite powder with a trimethylsilylating reagent. The product was organophilic and the results of its infrared spectrum, X-ray powder diffraction pattern, and elemental analysis indicated that the trimethylsilylation occurred on silanol groups in the tetrahedral layer of halloysite after the acid decomposition of the octahedral layer. The thermal stability of the product was evaluated by means of differential thermal analysis. It was not possible to obtain the organic derivative from kaolinite by the same procedure. It is suggested that the differences in the reactivity between halloysite and kaolinite is due to the difference in susceptibility of the clay minerals to acid attack.

Key Words—Halloysite, Kaolinite, Synthesis, Trimethylsilylation.

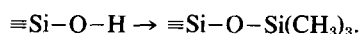
INTRODUCTION

Trimethylsilylation has been used for the synthesis of volatile derivatives from nonvolatile compounds (such as steroids and nucleosides) for the purpose of their gas-chromatographic analyses. However, trimethylsilylation is useful for the synthesis of organic derivatives from silicates, too. This reaction has been employed for studies of silicate structures and the analyses of their trimethylsilyl derivatives by gas chromatography have been reported (Lentz, 1964; Wu et al., 1970; Götz and Masson, 1970, 1971; Sharma et al., 1973; Currell et al., 1972).

The syntheses of inorganic polymers retaining a Si_2O_5 tetrahedral framework have been attempted by the reaction of phyllosilicate minerals with the trimethylsilylating reagent. Successful results in the preparation of sheetlike polymers from phyllosilicates have been reported by several workers (Frazier et al., 1967; Fripiat and Mendelovici, 1968; Linsky et al., 1971; Zapata et al., 1973), who investigated the trimethylsilylation of chrysotile.

It is well known that halloysite is easily attacked by acid, so it can be expected that silanol groups which are generated by the acid decomposition of the octahedral layer in halloysite are trimethylsilylated when the trimethylsilylating reagent is present.

Trimethylsilylation of silanol groups can be expressed by the following formula:



This paper describes the possibility of the synthesis of the trimethylsilyl derivative from halloysite.

Organic interlamellar complexes of halloysite have been studied by several investigators. Carr and Chih (1971) have reported the preparation of the various organic complexes of halloysite with polar organic compounds. The general review by Theng (1974) summa-

rizes most of the significant work on the preparation of organic complexes of halloysite. However, there have been no reports about the preparation of the trimethylsilyl derivative from halloysite.

EXPERIMENTAL

Materials

Halloysite from New Park, Utah (USA), was used in this work. This sample was fully hydrated and was checked by X-ray powder diffraction. The ground material was passed with a 325 mesh screen. Hexamethyldisiloxane, 2-propanol, and concentrated hydrochloric acid which were used as the trimethylsilylating reagent were reagent grade chemicals.

Trimethylsilylation procedure

The halloysite powder (2.25 g) was added to the mixture of hexamethyldisiloxane (30 ml), 2-propanol (22.5 ml) and hydrochloric acid (22.5 ml). The reaction mixture was refluxed (ca. 75°C) with stirring for 72 hr. The reaction mixture was cooled and the solid product was separated by filtration. The product was washed with 2-propanol and water once and followed by the further washing with acetone in a Soxhlet extractor for 3 hr.

Analyses

Infrared spectra were measured in KBr pellets with a Shimadzu IR-400 spectrometer. X-ray powder diffraction patterns were produced on a Shimadzu VD-11 diffractometer, using Ni filtered CuK_α radiation. Differential thermal analysis was carried out on a Shimadzu DT-20B. Sample weight was 5–10 mg, and $\alpha\text{-Al}_2\text{O}_3$ was used as a reference. The experiments were performed under a static air atmosphere at a heating rate of ca. 20°C/min.

RESULTS AND DISCUSSION

The resultant material (1.05 g) was a white solid having organophilic and hydrophobic properties. Figure 1

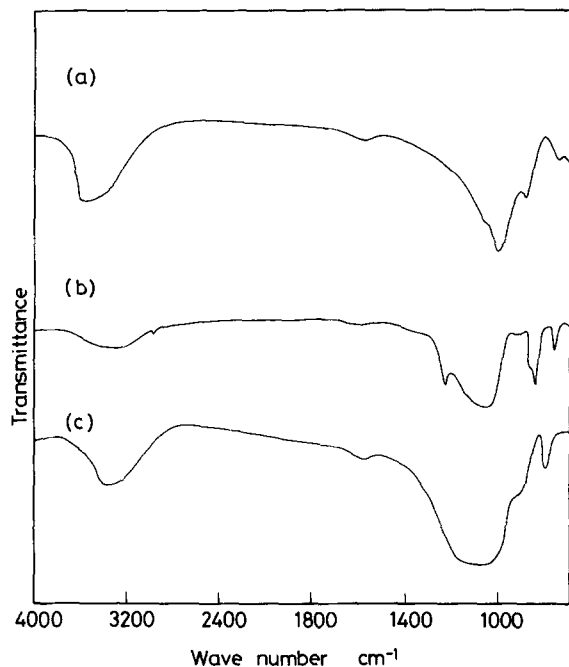


Fig. 1. Infrared spectra of (a) halloysite, (b) the trimethylsilylated product, and (c) the acid-treated product.

shows the infrared spectra of the starting material, the trimethylsilylated product and the product from halloysite treated with concentrated hydrochloric acid. The spectrum of the trimethylsilylated product showed the characteristic bands attributed to trimethylsilyl groups and silicate framework (2960 cm^{-1} ($\nu\text{-CH}_3$), 1260 cm^{-1} ($\delta\text{-CH}_3$), $1050\text{--}90\text{ cm}^{-1}$ ($\nu\text{-Si-O-Si}$), 840 cm^{-1} and 750 cm^{-1} ($\rho\text{-CH}_3$)).

X-ray powder diffraction patterns of (a) the original halloysite, (b) the trimethylsilylated product, and (c) the acid-treated halloysite are given in Figure 2. Figure 2(a) shows the typical pattern of hydrated halloysite. Figure 2(b) indicates the weak diffraction peak around $2\theta = 5.6^\circ$ ($d = 15.8\text{ \AA}$). Figure 2(c) shows that the product treated with acid is amorphous. It is suggested that the powder pattern (Figure 2b) indicates the formation of a new type organic derivative from halloysite and its structure seems to be lamellar. Because of the drastic experimental conditions, however, the original layer structure was wholly decomposed. The peak at $2\theta = 26.6^\circ$ (Figure 2b) seemed to be due to the presence of a small amount of quartz.

Table 1 gives the H and C analysis of the product and calculated values from the idealized trimethylsilyl derivatives from halloysite. H and C content in the product are in good agreement with the one calculated from the formula in which three hydrogens out of 10 in silanol groups were substituted by trimethylsilyl groups. Aluminon tests on the product indicate the presence of a trace amount of Al.

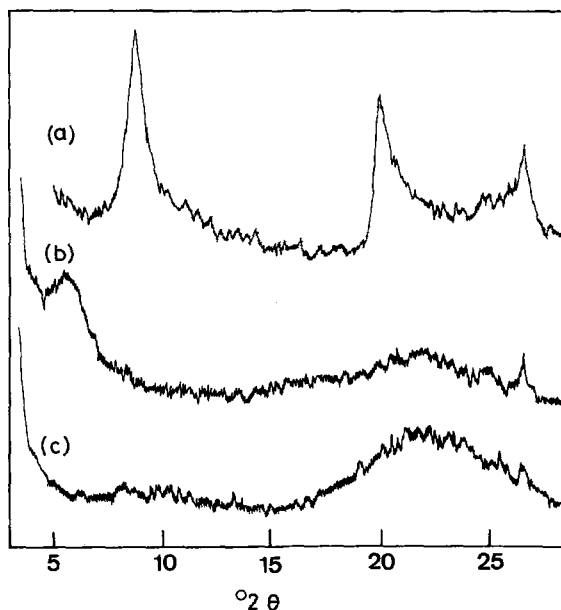


Fig. 2. X-ray powder diffraction patterns of (a) halloysite, (b) the trimethylsilylated product, and (c) the acid-treated product.

From the results described above, it is suggested that the trimethylsilylated product has a layer structure retaining a Si_2O_5 tetrahedral framework. The schematic representation is illustrated in Figure 3.

Figure 4 gives the micro-DTA curves of (a) halloysite and (b) the trimethylsilylated product. Figure 4(a) shows the typical pattern of the hydrated halloysite and the two endothermic peaks due to the dehydration of the interlayer water and hydroxyl groups, respectively.

Figure 4(b) shows the absence of endothermic peaks and the presence of one exothermic peak at 490°C attributed to the oxidative decomposition or combustion of the trimethylsilyl groups. The temperature at the initiation of the exothermic peak was higher than that for common organic compounds. The oxidation of the trimethylsilyl groups may be hindered due to the inhibition of diffusion by collapse of the layerlike organo-silicate structure. The infrared spectrum of the product heated up to 600°C by DTA showed no organic groups and it was found to be silica.

The same experimental procedure used for halloysite

Table 1. H and C data of the product and the calculated values from the idealized trimethylsilyl derivatives from halloysite.

Found		Calculated		
H (%)	C (%)	Idealized formula	H (%)	C (%)
4.1	11.5	$[(\text{CH}_3)_3\text{Si}]_4\text{Si}_4\text{O}_{10}$	6.4	25.5
		$[(\text{CH}_3)_3\text{Si}]_2\text{Si}_4\text{O}_8(\text{OH})_2$	4.8	17.1
		$[(\text{CH}_3)_3\text{Si}]_3\text{Si}_{10}\text{O}_{18}(\text{OH})_7$	3.8	11.9
		$[(\text{CH}_3)_3\text{Si}]_1\text{Si}_4\text{O}_7(\text{OH})_3$	3.4	10.3

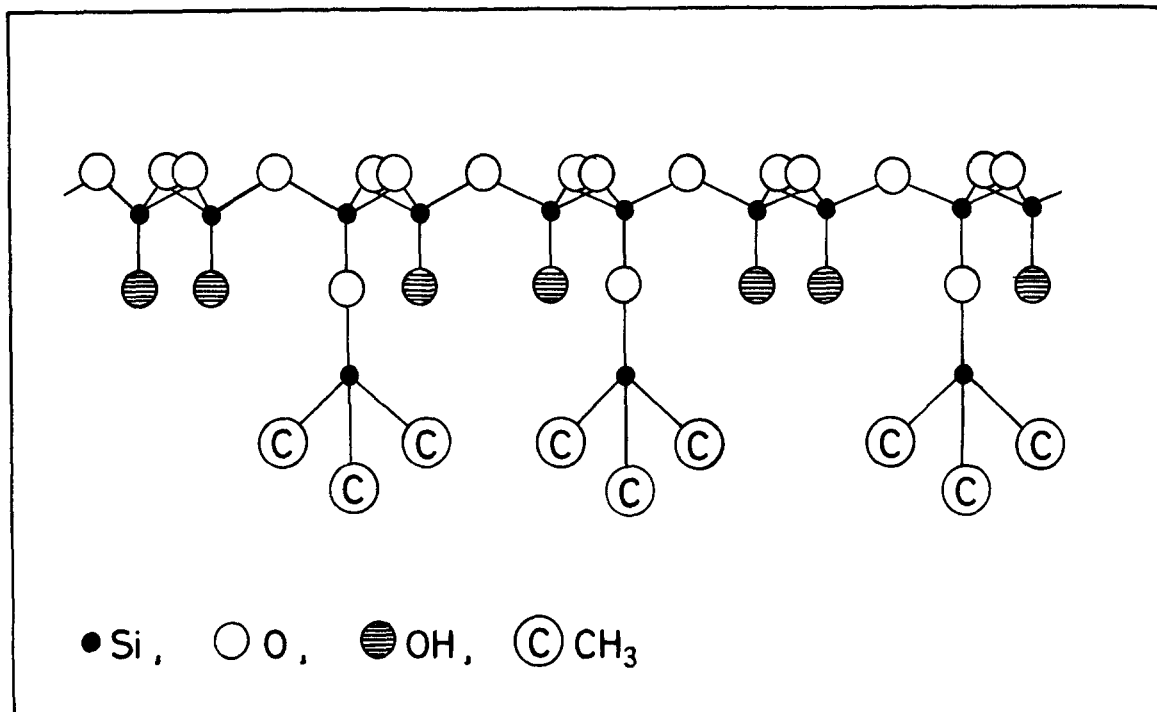


Fig. 3. Schematic representation of the trimethylsilylated product.

was applied to a standard sample of kaolinite (API No. 2). The product was analyzed by means of X-ray powder diffraction and infrared spectroscopy and the results indicated that no organic derivative was formed from kaolinite by this treatment. The difference between halloysite and kaolinite in reactivity for trimethylsilylation may be due to the fact that hydrochloric

acid can penetrate into the layer structure of halloysite and attack the octahedral layer. These results (the inertness of kaolinite) agree with the investigation by Currell et al. (1974), who surveyed the possibility of the trimethylsilylation of various types of silicate minerals.

Although the detailed reaction mechanism of the trimethylsilylation of halloysite has not been offered, the overall reaction may be postulated as follows:

- (1) The attack on halloysite by hydrochloric acid is initiated in the interlayer region.
- (2) The octahedral layers are decomposed and labile tetrahedral layers, having silanol groups on one side, are generated.
- (3) The silanol groups in the tetrahedral layers are partly trimethylsilylated by trimethylsilanol or trimethylchlorosilane formed by the reaction of hexamethyldisiloxane and hydrochloric acid.

ACKNOWLEDGMENTS

The authors wish to thank Mr. Masasumi Ishida for his experimental assistance.

REFERENCES

- Carr, R. M. and Chih, H. (1971) Complexes of halloysite with organic compounds: *Clay Miner.* **9**, 153-166.
 Currell, B. R., Midgley, H. G. and Seaborne, M. A. (1972) Trimethylsilylation of inorganic silicates: *J. Chem. Soc. Dalton Trans.*, 490-492.
 Currell, B. R., Midgley, H. G., Seaborne, M. A. and Thakur, C. P.

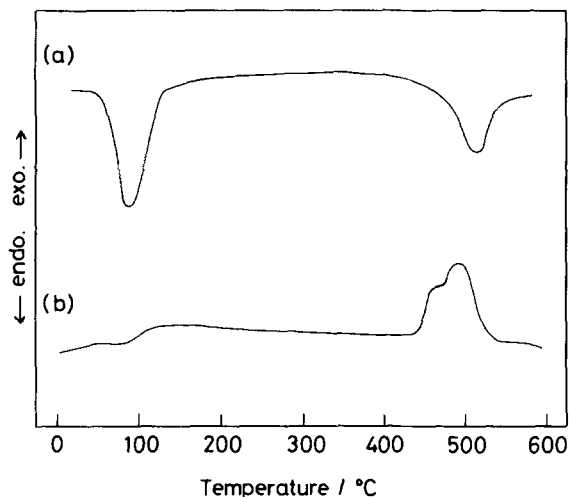


Fig. 4. Micro-DTA curves of (a) halloysite and (b) the trimethylsilylated product.

- (1974) Preparation of polyorganosiloxane from mineral silicates using the method of trimethylsilylation: *Br. Polym. J.* 6, 229–240.
- Frazier, S. E., Bedford, J. A., Hower, J. and Kenney, M. E. (1967) An inherently fibrous polymer: *Inorg. Chem.* 6, 1693–1696.
- Fripiat, J. J. and Mendelovici, E. (1968) Dérivés organiques des silicates. I. Le dérivé méthylé du chrysotile: *Bull. Soc. Chim. Fr.*, 483–492.
- Götz, J. and Masson, C. R. (1970) Trimethylsilyl derivatives for the study of silicate structures. Part 1. A direct method of trimethylsilylation: *J. Chem. Soc. A*, 2683–2686.
- Götz, J. and Masson, C. R. (1971) Trimethylsilyl derivatives for the study of silicate structures. Part 2. Orthosilicate, pyrosilicate and ring structures: *J. Chem. Soc. A*, 686–688.
- Lentz, C. W. (1964) Silicate minerals as sources of trimethylsilyl silicates and silicate structure analysis of sodium silicate solutions: *Inorg. Chem.* 3, 574–579.
- Linsky, J. P., Paul, T. R. and Kenney, M. E. (1971) Planar organosilicon polymers: *J. Polym. Sci. A2* 9, 143–160.
- Sharma, S. K., Dent Glasser, L. S. and Masson, C. R. (1973) Trimethylsilyl derivatives for the study of silicate structures. Part 3. Sodium silicate hydrates: *J. Chem. Soc. Dalton Trans.*, 1324–1328.
- Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions*, Chap. 6: Adam Hilger, London.
- Wu, F. F. H., Götz, J., Jamieson, W. D. and Masson, C. R. (1970) Determination of silicate anions by gas chromatographic separation and mass spectrometric identification of their trimethylsilyl derivatives: *J. Chromatogr.* 48, 515–520.
- Zapata, L., Meerbeek, A. V., Fripiat, J. J., Faille, M. D., Russelt, M. V. and Mercier, J. P. (1973) Synthesis and physical properties of graft copolymers derived from phyllosilicates. I. The chrysotile and vermiculite derivatives: *J. Polym. Sci. Polym. Symp.* 42, 257–272.

Резюме- Триметилсилил, дериват галлуазита, был получен реакцией порошка галлуазита с триметилсилиловым реагентом. Продукт реакции был органофильным и результаты исследований его инфракрасного спектра, диаграмм порошкового метода рентгеноструктурного анализа и элементный анализ указывают, что триметилсилилизация происходила в силаноловых группах в тетраэдрическом слое галлуазита после кислотного разложения октаэдрического слоя. Термальная стабильность продукта была оценена посредством дифференциального термального анализа. Органический дериват каолинита не мог быть получен с помощью аналогичной процедуры. Повидимому, различие в реактивности галлуазита и каолинита можно приписать различию в чувствительности глинистых минералов к воздействию кислоты.

Kurzreferat- Das Trimethylsilylderivat des Halloysit wurde durch Reaktion von Halloysitpulver mit einem Trimethylsilylierungsreagens präpariert. Das Produkt war organophil und die Resultate seines Infrarotspektrums, Röntgenpulverdiagrammes und elementare Analyse deuteten an, daß die Trimethylsilylierung an Silanolgruppen in der tetrahedratischen Schicht des Halloysit nach Säuredekomposition der oktahedratischen Schicht vorkommt. Die thermische Stabilität des Produkts wurde mit differentialer thermischer Analyse ermittelt. Das organische Derivat des Kaolinit, hergestellt in derselben Weise, konnte nicht erhalten werden. Es scheint, daß der Unterschied in der Reaktivität zwischen Halloysit und Kaolinit auf den Unterschied in der Anfälligkeit der Tonmineralien für den Säureangriff zurückzuführen ist.

Résumé- Le dérivatif triméthylsilyl de l'halloysite a été préparé par réaction de poudre d'halloysite avec un agent réactif triméthylsilylant. Le produit était organophyllique et les résultats obtenus de son spectre infrarouge, des diagrammes de diffraction aux rayons-X, et de l'analyse de l'élément ont indiqué que la triméthylsilylation s'est passée sur des groupes silanol dans les feuilletés tétraédriques de l'halloysite après la décomposition acide du feuillet octaédrique. La stabilité thermique du produit a été évaluée au moyen d'une analyse thermique différentielle. Le dérivatif organique de kaolinite par le même procédé n'a pas pu être obtenu. Il semble que la différence de réactivité entre l'halloysite et la kaolinite est attribuable à une différence de susceptibilité des minéraux argileux à l'attaque acide.