

ORGANIC DERIVATIVES OF ATTAPULGITE—I. INFRARED SPECTROSCOPY AND X-RAY DIFFRACTION STUDIES

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(Received 8 March 1976)

Abstract—Highly significant differences are observed between the methyl derivatives of attapulgite, produced when this mineral is reacted with $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$, in the presence or in absence of HCl. In the first case, the corresponding infrared spectra show characteristic absorption bands due to the $\text{Si}(\text{CH}_3)_2$ radicals at 1260, 850 and 800 cm^{-1} as well as a shoulder at 960 cm^{-1} , the latter assigned to silanol groups. The 850 cm^{-1} frequency which is usually exhibited by trimethylsilicon compounds is also detected when $-\text{O}-\text{Si}(\text{CH}_3)_2$ radicals are grafted in the silicates, but only if HCl is present in the reaction. Neither this band nor the 960 cm^{-1} shoulder appear in the spectrum of the derivative synthesized in absence of HCl. A comparative study by both i.r. spectroscopy and X-ray diffraction does not reveal structural modifications in attapulgite after it has been methylated in absence of HCl. However, although the i.r. spectra of the HCl-methylated derivatives, prepared at different periods, do not indicate substantial structural perturbations, X-ray diffraction patterns show a gradual weakening of the peaks due to attapulgite, as reaction time increases; the intensity of the (110) order reflection is drastically reduced after a 165 hr attack. The most viable mechanism for the grafting of the dimethylsiloxy units in attapulgite is through the HCl induced silanol sites. When the reaction is taking place in anhydrous benzene medium (absence of HCl), dimethyldiethoxysilane may be hydrolyzed by a fraction of water contained in attapulgite; the hydrolysis products which do incorporate on the surface of the silicate are identified by i.r. spectroscopy.

INTRODUCTION

The synthesis of methyl derivatives of silicate minerals ranging from ortho to tectosilicates, by a procedure involving hexamethyldisiloxane and HCl as modifying agents, has been described (Lentz, 1964). Furthermore, organic derivatives of some phyllosilicates have been prepared following this procedure, as well as employing agents like organochlorosilanes and HCl; i.e. the production of organic derivatives of chrysotile and vermiculite has been reported by Mendelovici (1967) and Castelein (1968) respectively.

The present work describes the preparation of methyl and phenyl derivatives of attapulgite and their study by infrared absorption spectroscopy and X-ray powder diffraction.

Dimethyldiethoxysilane, a difunctional alkoxy silane, has been used as source of methylsiloxy radicals in order to synthesize the methyl derivatives of attapulgite, in presence or absence of HCl. The low volatility, lack of corrosivity and other properties, make organoalkoxy silanes more suitable than organohalosilanes for these kinds of reactions.

EXPERIMENTAL

Materials

Georgia API 43 attapulgite as supplied by Ward's Natural Science Establishment, ground to pass a 100 mesh sieve, was used in all the experiments. Quartz was detected in the material which was examined by X-ray powder diffraction.

The chemical reagents as well as solvents were of analytical or spectroscopic grade (Merck). The silanes, dimethyldiethoxysilane (b.p. 113°), diphenyldiethoxysilane (b.p. 303°), diphenylmethylchlorosilane (b.p. 295°), and hexamethyldisiloxane (b.p. 101°), supplied by K & K Laboratories or Fluka, were used as received.

Methylation in presence of HCl

One gram of attapulgite was refluxed at about 70° with 70 ml of HCl (37%), 70 ml of isopropanol and 7.00 ml of dimethyldiethoxysilane ($d^{20^\circ} 0.848$). The reaction was carried out in a three neck round bottomed flask for variable intervals (5–120 hr). After 5 hr treatment, the solid was removed from the flask, washed with methanol (spectroscopic grade) until free of Cl^- , then extracted with benzene in a Soxhlet apparatus for 24 hr and then dried in the oven over-

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night. For the other periods of reaction the methanol washing step was omitted; one treatment was carried out for 165 hr.

In another experiment attapulgite was treated with hexamethyldisiloxane for 8 hr, according to the preparation previously described for chrysotile, by Fripiat and Mendelovici (1968).

Methylation in absence of HCl

One gram of attapulgite was refluxed with 7.00 ml of dimethyldiethoxysilane (DMDES) dissolved in 100 ml of anhydrous benzene. (Benzene containing 0.0003% H_2O was dried through a 4 Å molecular sieve column). A tube containing $CaCl_2$ was adapted at the top of the vertical condenser in order to trap moisture. After 8 hr, the extracted solid was quickly removed and dried in an oven at 100°C.

Phenylation

The modification of attapulgite by diphenyldiethoxysilane and diphenylmethylchlorosilane was performed in similar experimental conditions as those described for the methylation in presence of DMDES and HCl, but the experiment lasted 20 hr for the phenyl derivatives.

Instrumentation

The i.r. spectra were recorded on 476 and 377 Perkin-Elmer double beam grating spectrophotometers, in the range of 4000–400 cm^{-1} . For the solids study, 1% discs were prepared using KBr (spectroscopic grade) as dispersant. An evacuable die was used for the preparation of these discs.

In order to record the spectra of liquids, a few drops of the hydrolyzed dimethyldiethoxysilane fraction, separated from the HCl or benzene media, were placed between two NaCl windows. The windows were adequately mounted into the corresponding cell and fitted in the i.r. spectrophotometer.

X-ray powder diffraction patterns of powdered and oriented samples were run in a Norelco diffractometer, using nickel filtered $Cu K_\alpha$ radiation. The X-ray unit was operated at 36kV and 20mA (4 sec. time constant). The scanning speed was 1° $2\theta/min$.

RESULTS

Methylation of attapulgite by DMDES in presence of HCl

The i.r. spectra shown in Fig. 1 reflect, first of all, the modifications carried out on attapulgite (starting material), (Fig. 1a) after a 5 hr treatment. These changes are evident by the appearance of absorption bands at 2960–65, 1382, 1260, 850 and 800 cm^{-1} due to the methyl groups attached to silicon (Wright and Hunter, 1947), on the spectra of the methanol washed product (Fig. 1b) and benzene extracted solid (Fig. 1c). The spectrum of the latter displays a decrease in the intensity of the above mentioned bands, whose assignments are listed in Table 1. In addition, it also reveals a weak shoulder at 955–960 cm^{-1} (Fig. 1c) not detected in the spectrum of the starting material (Fig. 1a). The frequency at 960 cm^{-1} has been assigned to a Si–O–H vibration in HCl-treated attapulgite (Mendelovici, 1973).

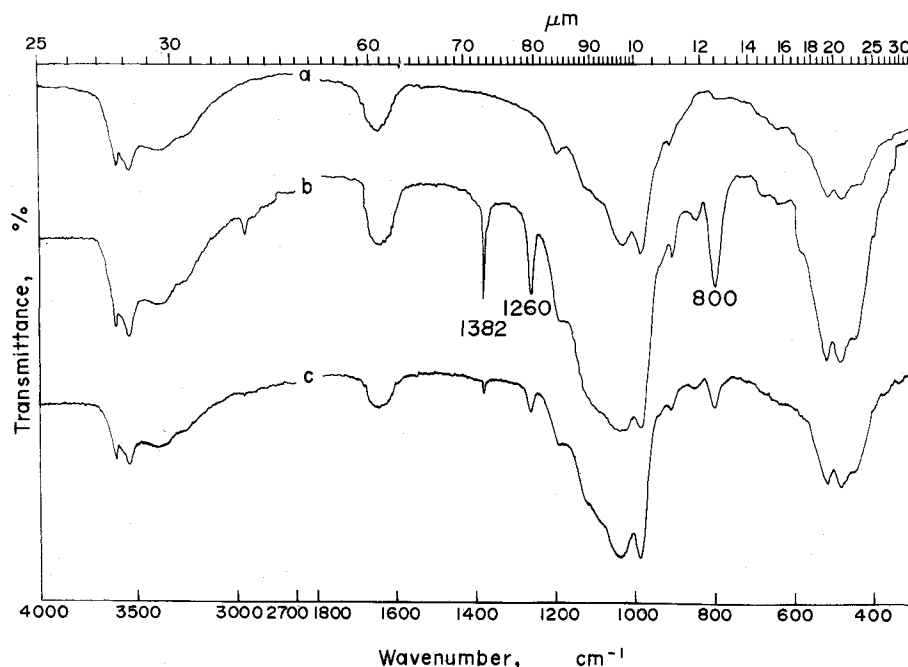


Fig. 1. I.R. spectra (1% KBr discs) of: (a) natural attapulgite (starting material); (b) methanol washed solid produced after 5 hr refluxing with DMDES and HCl; (c) the same as (b) but after (soxhlet) benzene extraction.

Table 1. Main i.r. bands of the derivatives of attapulgite prepared from DMEDES in presence of HCl

$\lambda(\mu\text{m})$	Absorptions (cm^{-1})	Assignments
2.76	*3620w	ν $M^{VI}\text{-OH}$
2.81	*3555m	ν as physisorbed H_2O
2.94	*3400m	ν s physisorbed H_2O
3.37	2965vw or w	ν CH
6.04	*1655st	δ physisorbed H_2O
7.23	1382w	δ as CH
7.93	1260st	δ s CH or ρ CH_3
8.34	*1198Sh	ν Si-O-Si
9.70	*1030v st	
10.15	*985v st	δ Si-O-H
10.41	960w Sh	
10.99	*910m	δ $M^{VI}\text{-O-H}$
11.76	850m	(see Discussion)
12.50	800st	Si-C and ring structure
19.60	*510m	Si-O and or Si-O- M^{VI}
21.05	*475m	
23.25	*430w	

* The same absorptions are also shown in the spectrum of natural attapulgite.

w—weak; m—medium; v—very; st—strong; Sh—shoulder; M^{VI} —hexacoordinated metallic cation; as— asymmetric; s—symmetric; ν —stretching; δ —deformation; ρ —rocking.

In Fig. 2 are reproduced the i.r. spectra of the benzene extracted products, corresponding to the reaction of attapulgite at different periods (a–e), as well as the spectrum of the oil separated from the acid hydrolysis of DMEDES (Fig. 2f), which is typical of a polydimethylsiloxane. Note an intensification of the bands attributed to the organic groups (Table 1), as

the reaction time increases from 5 to 120 hr (Fig. 2a–e). On the other hand, these spectra do not indicate any significant changes in the position or the intensity of the absorption bands arising from the vibrating species inherent to the octahedral or tetrahedral layers of the unmodified mineral. The assignment of the frequencies also are listed in Table 1.

Methylation of attapulgite in absence of HCl

Figure 3 shows the i.r. spectra of natural attapulgite (Fig. 3a) and of the solid resulting from reaction of the silicate with DMEDES in anhydrous benzene (Fig. 3b). The latter exhibits the frequencies at 1260 and 800 cm^{-1} , both registered when methylation is carried out in presence of HCl (Fig. 1b and c). However the absorptions at 960 and 850 cm^{-1} , also appearing in Fig. 1c are missing in the spectrum of Fig. 3b. The band at 850 cm^{-1} seems to be shifted to a weak shoulder about a maximum at 860 cm^{-1} , at the same position of hydrolyzed DMEDES (Fig. 2f). The 850 cm^{-1} absorption will be further discussed.

X-ray powder diffraction

The powder diffractograms in Fig. 4 show attapulgite before reaction and after methylation in the absence or presence of HCl, the latter at 20 and 165 hr.

When HCl is not included in the treatment the pattern of the methylated material does not differ substantially from that of the starting material (Fig. 4a). However, when the mineral is methylated by DMEDES in the presence of HCl, the peaks due to attapulgite are gradually weakened. After the 165 hr

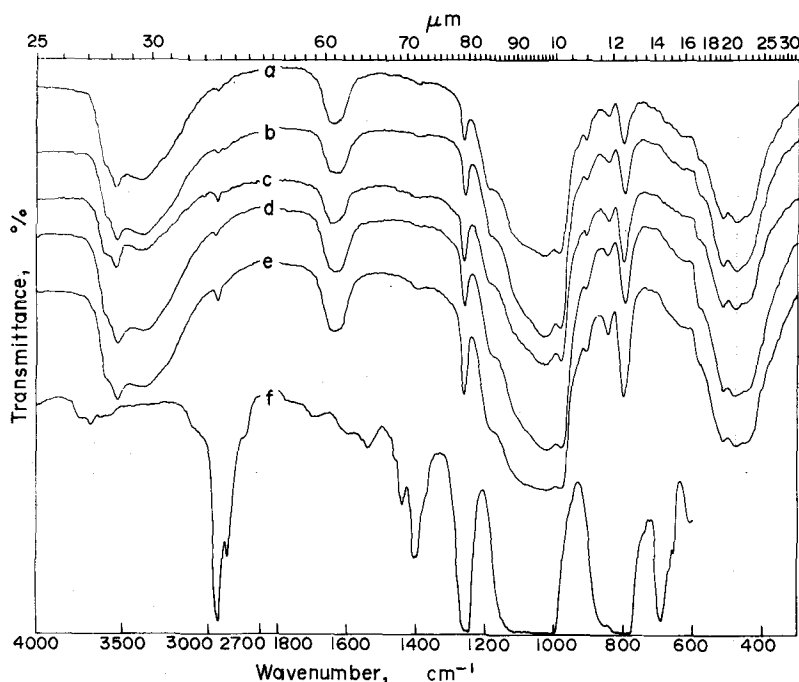


Fig. 2. I.R. spectra of: (a) soxhlet extracted attapulgite after 5 hr reaction with DMEDES (in HCl); (b) the same after 14 hr; (c) after 20 hr; (d) after 40 hr; (e) after 88 or 120 hr; (f) oil separated from the acid hydrolysis of DMEDES (NaCl windows).

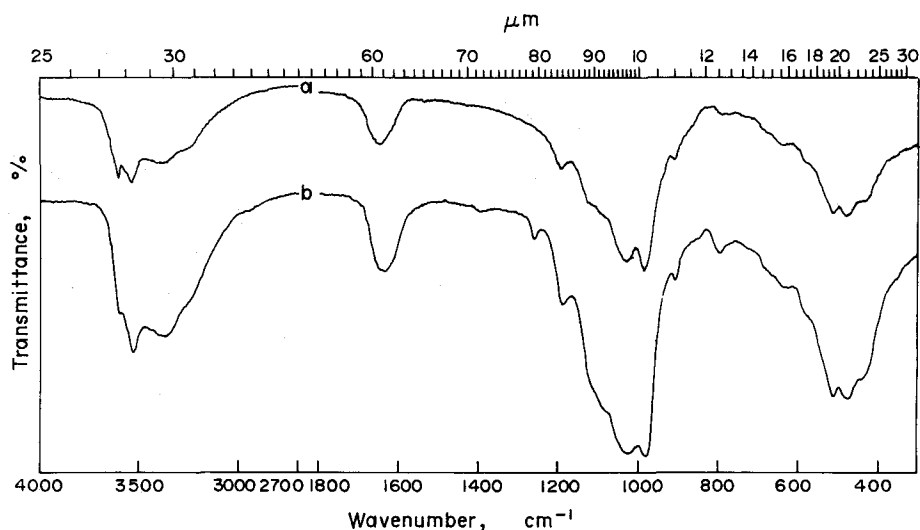


Fig. 3. Infrared spectra of KBr discs of: (a) natural attapulgite; (b) after 8 hr refluxing with DMDES in anhydrous benzene (absence of HCl).

attack all of the intensities of the reflections of attapulgite, especially the one corresponding to the (110) order, have been considerably reduced. The diffraction peaks due to quartz, detected in the natural mineral, are noticeable at all the stages of the treatment.

Modification of attapulgite by miscellaneous organic radicals

So far, we have studied the reaction of attapulgite with DMDES, grafting thereby dimethylsiloxy radicals $-\text{O}-\text{Si}(\text{CH}_3)_2$ in the mineral. The i.r. spectra in Fig. 5 reflect the results of grafting trimethyl (Fig. 5a), monomethyl (Fig. 5b) and no methylsiloxy groups (Fig. 5c) in the silicate in the presence of HCl. The source of these radicals were hexamethyldisiloxane, methylphenylchlorosilane and diphenyldiethoxysilane, respectively.

A careful examination of Fig. 5 reveals the appearance of the 850 cm^{-1} absorption only in the spectrum of the trimethylated derivative (Fig. 5a). As expected, the other two spectra show weak absorption bands due to the $\text{Si}-\phi$ groups, both at 1330 , 791 and 695 cm^{-1} (Fig. 5b and c). The $\text{Si}-\text{phenyl}$ bands which should appear between 9 and $10\text{ }\mu\text{m}$ (Young *et al.*, 1948) are overlapped by the strong absorptions arising in this region from the $\nu\text{Si}-\text{O}$ vibrations in the siloxane backbone of attapulgite.

DISCUSSION

Formation of the methyl derivatives in presence of HCl

Mendelovici (1967) and Zapata *et al.* (1971) described the mechanism prevailing in the modification of chrysotile by organochlorosilanes in acid medium. In the light of these studies and our actual results,

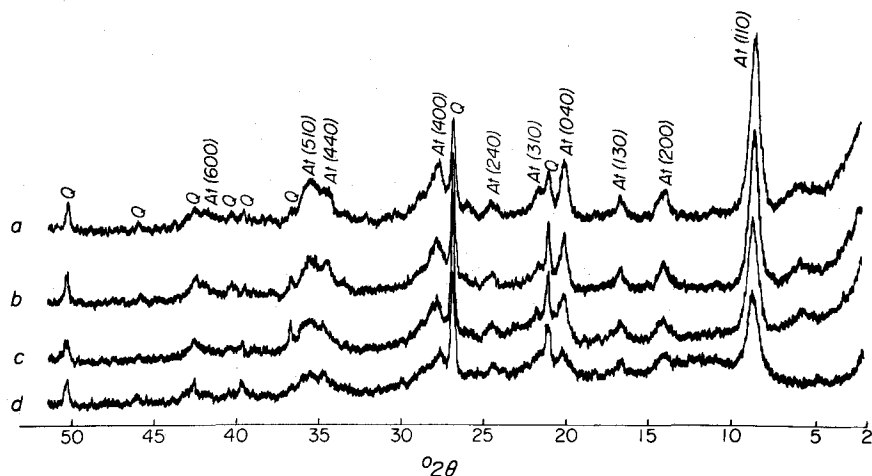


Fig. 4. X-ray diffractograms (powder specimens) of: (a) natural attapulgite; (b) after methylation in anhydrous benzene medium; (c) after 20 hr attack with DMDES and 6N HCl; (d) after 165 hr attack with DMDES and 6N HCl. At = Attapulgite; Q = Quartz.

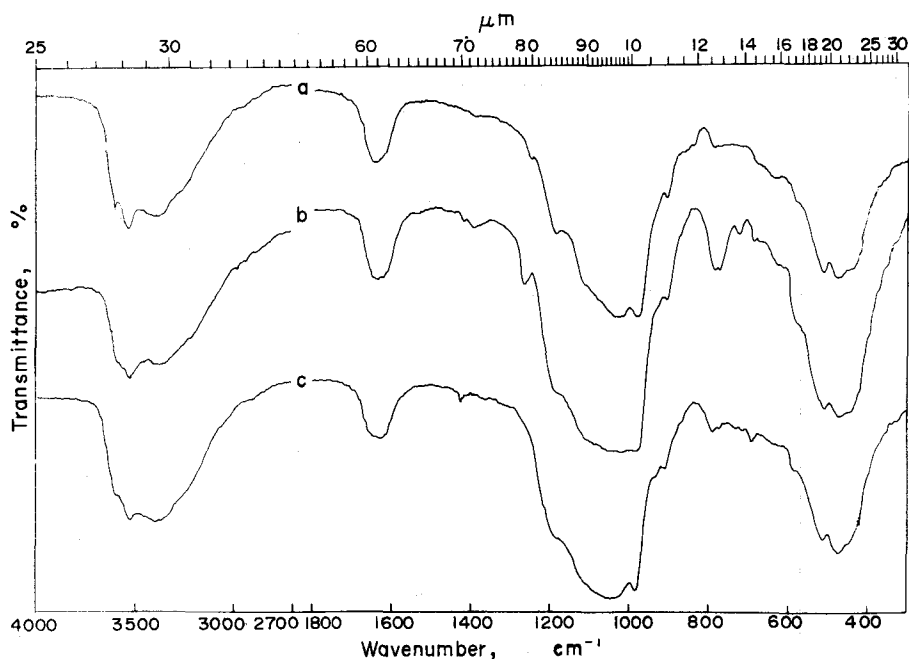
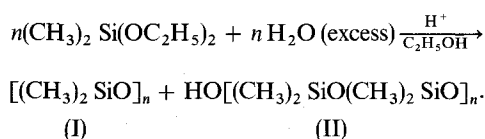


Fig. 5. Infrared spectra (KBr discs) of the derivatives of attapulgite prepared from: (a) hexamethyldisiloxane, (b) diphenylmethylchlorosilane, (c) diphenyldiethoxysilane.

an attempt is made to explain the modification of attapulgite by a difunctional alkoxy silane.

Hydrolysis of $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ in strongly acid media or in the presence of a water miscible solvent—both conditions prevailing in our experiments—favors the production of cyclic (I) or low molecular weight linear polymers (II) (Barry and Beck, 1962); accordingly the following reaction scheme is proposed:



When attapulgite is included in the reaction mixture, there is a competition among the hydrolysis products of fraction (II) for bonding to the mineral. After an exhaustive benzene extraction of the solid separated from the reaction mixture, only chemically bonded dimethylsiloxy radicals remain grafted in the mineral (via silanol sites); the non bonded fraction, presumably formed by the more volatile dimethylpolysiloxanes, being dissolved in benzene. This fact explains the decrease in intensity of the absorption bands due to the methyl groups at, 2960, 1382, 1260 and 800 cm^{-1} in the i.r. spectra of the extracted derivative (Fig. 1b and c). Another aspect of this hydrolysis is the competition between DMEDES and attapulgite for (excess) HCl, resulting from both processes radicals with SiOH terminal groups. Taking into account that the reaction occurs in a polar media, $(\text{H}_3\text{O})^+$ are available for the protonation of silanols, promoting thus the formation of siloxanes bridges (Si—O—Si) by a condensation mechanism between the

mineral's active sites (silanols) and the protonated organosilane. The kinetics governing this reaction will be presented in a further communication.

When attapulgite is refluxed only with conc. HCl (in the absence of an organosilane), the octahedral layer is dissolved after 5 hr treatment, as inferred from an i.r. spectroscopic study (Mendelovici, 1973). The acid attack causes the conversion of the multiple Si—O—Si absorptions from attapulgite to a characteristic band at 1090 cm^{-1} . However, the i.r. spectra of the methyl derivatives obtained after 5, 20, 40 hr, etc. show no changes in the frequencies arising from the Si—O—Si, Si—O—M, M—OH and H—O—H vibrations (where M is an octahedral cation), of attapulgite, except the appearance of the weak shoulder at 960 cm^{-1} (Figs. 1 and 2).

Nevertheless, structural perturbations in the mineral modified by DMEDES and HCl are interpreted from the X-ray powder diffraction results. Thus, even after a 20 hr reaction the diffraction peaks due to attapulgite are already weakened and, after 165 hr drastically reduced (Fig. 4), indicating mostly attack on the octahedral layer.

Formation of the methyl derivative of attapulgite in absence of HCl

On the basis of a comparative study from both i.r. spectroscopy and X-ray powder diffraction studies, it may be deduced that no structural perturbations are displayed by attapulgite after its reaction with DMEDES in a benzene medium. The i.r. spectrum of the resulting solid does not exhibit the frequencies at 960 and 850 cm^{-1} , both marked in the spectrum of the derivative synthesized in presence of HCl.

The above mentioned observations suggest, first of all, that in absence of HCl, the reaction is taking place on the surface of the mineral. On the other hand as induced silanol sites are not generated (the 960 cm^{-1} absorption not shown), an alternative mechanism should be proposed for the incorporation of the methylsiloxy groups.

Explaining the mechanism of hydrolysis of triethyl-ethoxysilane by hydrated silica, Bascom and Timmons (1972) assume an acid catalyzed process, in which a hydroxy-water network develops, H-bonded between silica silanols. For the hydrolysis to occur these authors invoke a proton transfer from the more acidic surface silanols of silica to Si-O bonds of the alkoxysilane, through the adsorbed water network.

The i.r. spectrum of the organosilicon liquid separated from the reaction of attapulgite with DMDES in benzene, shows characteristic absorptions due to Si-O-Si species at about 1020 and 1080 cm^{-1} , the same frequencies being marked in the spectrum of HCl hydrolyzed DMDES (Fig. 2f). On the other hand if attapulgite is replaced by kaolinite in this experiment, the incorporation of the organic groups does not occur. Kaolinite presents a quite different qualitative and quantitative water configuration from attapulgite.

The only conclusion we may deduce at this stage of our experiments is that the acid surface of attapulgite must have some catalytic effect in promoting the hydrolysis of DMDES and that water contained in this mineral plays a paramount role in this mechanism.

In this case the energy involved in the bonding of the organic groups to the silicate is different from that prevailing in the methylated derivative prepared in the presence of HCl. Experimental evidences which will be published elsewhere support this statement.

Origins of the 800 and 850 cm^{-1} absorptions

The principal i.r. bands attributed to the $\text{Si}(\text{CH}_3)_2$ groups, common to the spectra of both derivatives, obtained in the presence (A) or absence (B) of HCl, are detected at 1260 and 800 cm^{-1} . The latter has been assigned to the Si-C stretching mode, whereas the 1260 cm^{-1} frequency to the symmetrical deformation of CH in CH_3 or methyl rocking vibration (Wright and Hunter, 1947). However the 800 cm^{-1} band also appears in the spectrum of attapulgite attacked by HCl (in absence of silane) and could be related in this case to a ring structure vibration. Thus, we may conclude that for the (A) derivative of attapulgite, the 800 cm^{-1} frequency corresponds to a coupled band, arising from ν Si-C and ring vibrations (Fig. 1c).

The origin of the 850 cm^{-1} absorption is more complex. As it has been mentioned before it is only shown in the spectrum of the (A) derivative but not in the one of the (B) derivative (absence of HCl). In order to find out more information about this peculiar absorption, we boiled the (B) derivative of attapulgite

(the one prepared from DMDES in benzene) with 6N HCl for 24 hr, washed the solid until free of Cl^- and dried it in the oven. Its spectrum shows definitively the appearance of a band at exactly 850 cm^{-1} , not detected in the case of HCl-treated attapulgite (in absence of silane). This may be interpreted as some sort of rearrangement of the methylsiloxy groups when HCl intervenes, matched by alterations in the structure of the mineral. Acid catalyzed rearrangements of methylpolysiloxanes are not unfrequent in organosilicon chemistry (Patnode and Wilcock, 1945).

The presence of HCl being necessary for the appearance of the 850 cm^{-1} frequency when DMDES is used as source of $-\text{O}-\text{Si}(\text{CH}_3)_2$ radicals, we employed in some similar experiments silanes of heterogeneous functionality; the silanes involved in the modification of attapulgite, combine eventually phenyl with methylsiloxy groups. The corresponding i.r. spectra show the band at 850 cm^{-1} only for the products prepared in presence of reagents possessing trimethyl or dimethylsiloxy groups.

This leads us to conclude that the 850 cm^{-1} frequency only appears when $-\text{O}-\text{Si}(\text{CH}_3)_n$ ($n = 2$ or 3) are grafted on attapulgite and if HCl is present in the reaction medium.

Acknowledgements—The author wishes to express his gratitude to Dr. Ch. Garris from the Mechanical Engineering Department of I.V.I.C. for his assistance in the correction of the manuscript.

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