and polar bonds are present, the observed structure depends not only on the number of gauche interactions but also upon the distance between the interacting groups. With the long (2.219 Å) phosphorus–phosphorus bond we feel that the hydrogen atoms are too far apart to exert any influence on the molecular structure and it is the dominating effect of the lone electron pairs that determines the structure of biphosphine. In the solid phase, at least, these results are contrary to the structures found for other P_2Y_4 molecules but are, however, consistent with the X-ray crystal study performed by Nixon.[2]

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Registry No. P_2H_4, 13445-50-6; P_2D_4, 39863-38-2.

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Contribution of the Laboratoire des Hauts Polymeres,
Université de Louvain, 1348 Louvain-la-Neuve, Belgium

Esterification of Chrysotile–Asbestos by Allyl Alcohol

C. BLEIMAN and J. P. MERCIER*

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In this paper, a method is developed for grafting organic allylic ester groups onto the surface of hydrolyzed or chlorinated chrysotile. It is shown that the degree of esterification increases gradually in relation to the degree of hydrolysis. It is possible to obtain in this way a sheet-like organomineral polymer.

Introduction

Phyllosilicates like chrysotile, which possess a basic Mg(OH) surface, are known to be relatively inert. In particular, they do not respond to the action of silane coupling agents which are so effective with acidic silanols.[1] However, the octahedral layer of phyllosilicate can be eliminated by acid leaching. This treatment, which preserves the crystalline structure of the siloxanic planes, generates on the surface a very reactive acidic layer.

When this hydrolysis is carried out in the presence of halosilane or disiloxane, a condensation reaction takes place and a kind of sheetlike organomineral polymer is produced.[2] The basis for the approach was provided by Lentz,[3] who applied this type of synthesis to monomeric minerals like olivine, sodalite, or natrolite.

In this article a procedure to synthesize another polymeric organomineral material is described. This was obtained by allowing hydrolyzed or chlorinated chrysotile to react with allyl alcohol.

Experimental Section

General Information. The chrysotile–asbestos used in this work is grade 4 fibers from the western part of Canada. Their physical properties and their composition are reported in Table I.

Hydrolysis. The fibers were hydrolyzed in a 1:1 solution of concentrated hydrochloric acid (12 *N*) in 2-propanol, as described in a previous publication.[4] The hydrolyzed fibers were carefully washed with 2-propanol dispersed in benzene, and freeze-dried under vacuum. After elimination of the benzene, the widely open fibers were dried under vacuum at 60° for 24 hr. The degree of hydrolysis was expressed as the fraction (%) of the original magnesium which was eliminated.

Esterification. The reaction of esterification was carried out in a 500-ml vessel. Five grams of hydrolyzed chrysotile was refluxed for 4 hr under mild agitation with a mixture of 100 ml of pyridine and 100 ml of allyl alcohol (reagent grade). After cooling, the esterified fibers were separated from the solution by filtration. The esterified phyllosilicates were then extracted with ethyl ether in a Soxhlet apparatus for 4 hr to remove traces of unreacted reagents. The product was finally dried for 24 hr at room temperature under a pressure of 10^{-2} Torr and for 48 hr at 60° under 10^{-1} Torr.

Table I. Physicochemical Characteristics of the Fibers

A. Virgin chrysotile: Chemical analysis		A. Virgin chrysotile: Specific surface	B. Hydrolyzed chrysotile: Hydrolysis deg, %	B. Hydrolyzed chrysotile: Specific surface[5]
SiO_2	41.08%	BET, N_2[5] 14.38 m^2/g	20	65
Al_2O_3	1.01%		38	125
Fe_2O_3	2.63%		49	200
MgO + CaO	41.24%		62	285
Heat loss	14.53%		70	360
	100.49%		78	425

Table II. Esterification of Chrysotile–Asbestos

Degree of hydrolysis, %	Hydrolyzed fibers: % C	Hydrolyzed fibers: mequiv of OR/100 g[a]	Hydrolyzed fibers: No. of OR/100 nm^2 [b]	Chlorinated fibers: % C	Chlorinated fibers: mequiv of OR/100 g[a]	Chlorinated fibers: No. of OR/100 nm^2 [b]
20	1.3	37	335	1.9	54	515
38	2.6	75	362	2.9	85	402
49	3.1	91	276	4.9	148	443
62	4.9	148	312	6.9	216	458
70	5.4	164	274	7.4	233	390
78	7.6	241	342	9.2	300	425

[a] Milliequivalents of ester groups/100 g of inorganic substrate.
[b] Number of ester groups/100 nm^2.

Chlorination. In a second series of experiments, we submitted the hydrolyzed fiber to chlorination with thionyl chloride before carrying

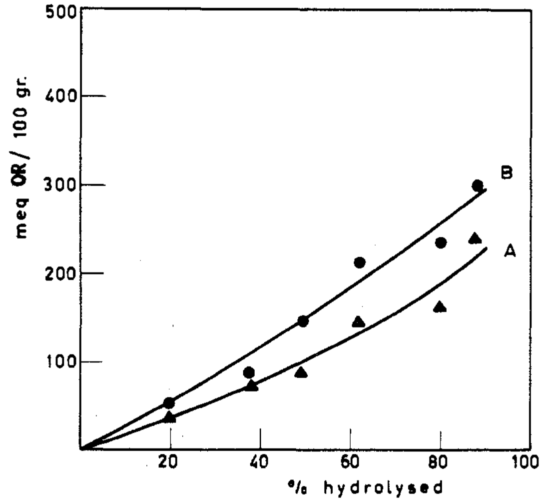

Figure 1. Esterification of chrysotile–asbestos by allyl alcohol: the units on the ordinate are expressed in milliequivalents of ester groups/100 g of inorganic substrate; degree of hydrolysis reported on the abscissa represents the fraction (%) of the original magnesium which was eliminated; curve A, hydrolyzed fiber; curve B, chlorinated fiber.

out the esterification. The procedure of chlorination is described in detail elsewhere.[4] This reaction substitutes Si–Cl groups for the silanol groups generated by hydrolysis.

Results and Discussion

The results obtained in this study are summarized in Table II and in Figure 1. One can see that the degree of esterification increases gradually with the degree of hydrolysis. This result clearly shows that esterification is only possible on the siloxanic surface. One also notices that the degree of coverage is relatively constant and does not depend on the degree of hydrolysis of the fiber. The mean degree of coverage is 316 OR groups/nm^2 for the hydrolyzed fibers and 400 OR groups/nm^2 for the chlorinated ones. This result represents a relative increase of about 26%. This increase in the degree of surface coverage could result from the higher reactivity of the Si–Cl groups as compared with that of the silanol groups.

If we compare our results with the figure obtained by Wartmann[6] for the esterification of silica gel chloride with short chain alcohols, we see that the degree of coverage obtained here is much higher. For example, for the esterification of 1-propanol, Wartmann grafted 168 OR/100 nm^2. It is our opinion that the higher degree of coverage obtained with chrysotile results from the very regular quasicrystalline structure of the surface produced by hydrolysis compared with the mainly amorphous surface of synthetic silica gel.

Iler[7] has calculated on a theoretical basis that there are between 800 and 900 OH groups/100 nm^2 of a silanolic surface. If we take into consideration the problem of steric hindrance introduced by the allylic ester groups, we may expect a maximum degree of substitution of 50%, i.e. between 400 and 500 OR groups/100 nm^2. The experimental values that we have obtained in this study are very close to this theoretical value, especially for the chlorinated fibers.

In conclusion, in this study, it has been shown that the reaction of esterification of hydrolyzed or chlorinated chrysotile is possible with an efficiency higher than that obtained for silica gel. This method is very convenient for grafting a continuous layer of organophilic groups onto the surface of phyllosilicates.

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Notes

Contribution from the Laboratoire de Chimie Minérale,
Equipe de Recherche Associée au CNRS,
Institut de Mathématiques et Sciences Physiques,
06034 Nice Cedex, France

Isolation of a Mixed Niobium Tantalum Alkoxide

Liliane G. Hubert-Pfalzgraf and Jean G. Riess*

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Dimeric niobium and tantalum alkoxides have been known for a long time[1] and have been the subject of many studies[2] and reviews.[3] Alkoxides containing both a transition metal and a group 1 or 2 metal are also well known, but there seems to be no report yet of a mixed alkoxide containing *two different transition metals.*[4] We now wish to report the preparation and isolation as a crystalline compound of a mixed-metal alkoxide of molecular formula NbTa(OCH$_3$)$_{10}$ (I), which appears to be the first mixed transition metal alkoxide isolated.

Results and Discussions

Compound I forms when niobium pentamethoxide and tantalum pentamethoxide are mixed in octane, toluene, or acetonitrile solutions, according to eq 1. In any of these

$$\mathrm{Nb_2(OMe)_{10} + Ta_2(OMe)_{10} \rightleftharpoons 2\,(MeO)_4Nb(\mu\text{-}OMe)_2Ta(OMe)_4} \qquad (1)$$

I

solvents the low-temperature proton NMR spectra (Figure 1), recorded immediately after mixing, show, in addition to the signals corresponding to the symmetric starting materials, the presence of four new signals in the region of the terminal methoxy groups and one additional signal in the region of the bridging methoxy group, as would be expected for the mixed-metal alkoxide of structure I. The relative areas of these new signals remain constant when the Nb(OCH$_3$)$_5$:Ta(OC-