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Abstract

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CHLORINE DERIVATIVES OF KAOLIN AND CHRYSOTILE-ASBESTOS

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The creation in layered silicates of a reactive Si—Cl bond opens up broad possibilities for the synthesis of organic derivatives of such silicates (^{1}). A method is known for obtaining chlorine derivatives of silicagel ($^{2-5}$) and of one of the aluminosilicates—montmorillonite ($^{6-9}$)—which consists in replacing acidic hydroxyl groups by chlorine under the action of thionyl chloride:

$$\equiv \mathrm{Si{-}OH} + \mathrm{SOCl_2} \rightarrow \equiv \mathrm{Si{-}Cl} + \mathrm{SO_2} + \mathrm{HCl}. \qquad (1)$$

We investigated the action of thionyl chloride on kaolin and chrysotile-asbestos. Chinese kaolin from Suzhou (^{10}) and high-grade chrysotile-asbestos (crocidolite) from the Bazhenovsk deposit in the Urals were used as the initial silicates. Some of the samples, before being introduced into the reaction, were subjected to ultrasonic treatment in order to increase the number of surface groups $\equiv$ Si—OH (^{11}). Under the action of thionyl chloride on kaolin under the conditions recommended for obtaining montmorillonite chloride (^{7,8}), we were able to replace by chlorine only 8-11% of the initial content of hydroxyl groups, whereas in the case of montmorillonite the substitution reached 83-86%, and the substitution of hydroxyls in silicagel by reaction (1) was used for their quantitative determination (^{4}).

Such a substantial difference may be explained by the different arrangement of acidic hydroxyl groups on the surface of montmorillonite and kaolinite. The bulk of the structural hydroxyls of montmorillonite is uniformly distributed over the basal surface of its particles (^{12}). In this mineral the distance between neighboring hydroxyls located at the vertices of two silica-oxygen tetrahedra is 5.2 Å (^{13}). Mutual influence of OH groups at such a distance is not manifested (^{14}), and electrophilic attack of the oxygen atom of this group by a thionyl chloride molecule proceeds successfully (^{7}).

In contrast, the induced acidic hydroxyls of kaolin can be located only in regions with a disturbed structure (along particle boundaries, at defective sites on the surface), i.e., where the vertices of silica-oxygen tetrahedra appear at the surface. The smallest distance between such vertices is 2.6-2.7 Å, and thus a hydroxyl situated at one of the vertices may experience the influence of a hydroxyl group

Fig. 1

Figure 1: Fig. 1

(or oxygen atom) occupying the vertex of a neighboring tetrahedron. The hydrogen bond that arises between the oxygen atom and the hydroxyl group at distances smaller than 3.2 Å (14) increases the strength of the Si–O bond in the group ≡ Si–OH (15), which hinders its cleavage:

$$\mathrm{O} \ldots \mathrm{H{-}O{-}Si} \equiv .$$

In addition, one cannot fail to take into account the magnitude of the atomic radius of chlorine (1.035 Å), which increases in connection with the partially ionic character of the Si–Cl bond (30%) (16), which should also hinder the exchange of OH groups for chlorine.

The same hydroxyl groups, which are farther removed from the vertices of the nearest silico-oxygen tetrahedra, react with thionyl chloride as readily as the hydroxyls of montmorillonite (see Fig. 1). There is a certain similarity between the structural layers of serpentines (17) and kaolinite, manifested in the mutual arrangement of the octahedral and silico-oxygen layers, with the latter, by the vertices of the tetrahedra, facing one side–into the structural layer. In connection with this, the factors that determine the difficulties we observed in replacing the acidic hydroxyls of kaolin with chlorine also affect the interaction of thionyl chloride with chrysotile asbestos, whose acidic hydroxyls can be located only in places where the structure is disturbed (induced hydroxyls).

Fig. 1. **A**–Schematic representation of the network of silico-oxygen tetrahedra of montmorillonite with structural hydroxyls. **B**–The same for kaolinite, with several possible variants of the arrangement of induced hydroxyls.
1–silicon atom, **2**–oxygen atom, **3**–OH group.

It might have been expected that catalytic additions of chlorides of certain metals would lead to an increase in the chlorine content in kaolin chloride through heterolytic cleavage of the basic bonds of the aluminosilicate according to the scheme

$$\equiv \mathrm{Si} - \mathrm{O} - \mathrm{E} + \mathrm{SOCl_2} \xrightarrow{\mathrm{MCl}_n}$$

$$\rightarrow \equiv \mathrm{Si} - \mathrm{Cl} + \mathrm{E} - \mathrm{Cl} + \mathrm{SO_2},$$

where E is ≡ Si or = Al, and M is Al, Fe, Sn, etc., as occurs in the case of organosiloxanes. However, the presence of stannic chloride* did not lead to noticeable cleavage of the Si – O – E bonds, and the resulting chloro derivative contained practically the same amount of chlorine as the product obtained in the absence of a catalyst (see Table 1).

Table 1

Chloro derivatives of kaolin and chrysotile asbestos

Silicate	Chlorination method*	Cl content in the chloro derivative, %	Hydrolyzable Cl, %: boiling with water (4 h)	Hydrolyzable Cl, %: boiling with 25% ammonia (4 h)
Kaolin	7% solution of $SOCl_2$ in chloroform, 6 h (62°)	0.11	~0.05	–
Kaolin	$SOCl_2$, 16 h	0.16	0.12**	
Kaolin	$SOCl_2, SnCl_4$***, 16 h	0.14	0.07	0.18
Kaolin	$SOCl_2$, u.-v.****, 16 h	0.33	0.22	0.31
Chrysotile asbestos	$SOCl_2$, u.-v., 16 h	0.34	–	0.37
Chrysotile asbestos	$SOCl_2$, u.-v., 48 h	1.22	–	–

* All experiments, except the first, were carried out at the boiling temperature of thionyl chloride.
** After heating to the boiling temperature with a 2% solution of soda (4 h), 0.11% Cl was determined.
*** $SnCl_4$ was taken in amounts reaching up to 1% of the initial kaolin.
**** u.-v. = ultraviolet irradiation.

We were able to increase substantially the chlorine content in the chloro derivatives of silicates only with the aid of u.-v. irradiation of a mixture of the silicate and $SOCl_2$ at the boiling temperature of the latter. In u.-v. light thionyl chloride can

* In a preliminary experiment we established that, when thionyl chloride acts on hexamethyldisiloxane in the presence of $SnCl_4$, trimethylchlorosilane is formed in quantitative yield.

cleave the Si—O—Si bond in organosiloxanes with the formation of organochlorosilanes ([18]). This process, evidently, also takes place in the case of kaolin and chrysotile asbestos, and, along with the reaction of substitution of hydroxyls according to scheme (I), a reaction of homolytic cleavage of the bonds $\equiv$ Si—O—$\mathcal{E}$ occurs:

$$\equiv \mathrm{Si—O—}\mathcal{E} + \mathrm{SOCl_2} \xrightarrow{h\nu} \equiv \mathrm{Si—Cl} + \mathcal{E}\mathrm{—Cl} + \mathrm{SO_2},$$

where $\mathcal{E}$ is $\equiv$ Si, $=$ Al, or —Mg.

Kaolin chloride obtained in carrying out the photochemical reaction of kaolin with thionyl chloride contained twice as much chlorine as kaolin chloride obtained under the same conditions but without the use of ultraviolet light. By the action of thionyl chloride on chrysotile asbestos under ultraviolet irradiation, we obtained its chloro derivative with a content of more than 1% Cl.

The chloro derivatives of kaolin and chrysotile asbestos obtained contained, along with chlorine, unsubstituted acidic hydroxyl groups and, in contrast to montmorillonite chloride ([9]), in these derivatives the Si–Cl bond proved to be very resistant to hydrolysis. Thus, treatment of them with water at room temperature for 24 hours did not lead to cleavage of chlorine, while boiling with water for 4 hours hydrolyzed only two thirds of the total amount of chlorine in kaolin chloride.

Thionyl chloride does not destroy chrysotile asbestos either at room temperature or on heating, and the fibers of its chloro derivative retain the elasticity of the original asbestos.

Experimental Part

Preparation of samples. Before being introduced into the reaction, chrysotile asbestos was cut with scissors, and kaolin was subjected to elutriation (the fraction 0.1–3.0 μ was used). Both silicates were thoroughly dried ([11]). The chlorine content in the initial chrysotile asbestos was 0.17%; the initial kaolin contained no chlorine.

Procedure of the investigation. The experiments were carried out in a 100-ml quartz flask equipped with a reflux condenser connected to a Tishchenko bottle (conc. H_2SO_4). In experiments on photochemical chlorination, the flask was illuminated and heated with a PRK-4 mercury-quartz lamp placed at a distance of 15 cm from the bottom of the flask. After the experiment was completed, the reaction products were transferred into a dry box, where the silicate was separated from $SOCl_2$ and washed with absolute benzene until the absence of chlorine in the wash solvent (20 times), after which it was dried in a vacuum pistol (4 mm Hg) for 20 h at 135°.

Analysis. Chlorine was determined nephelometrically in the filtrate of an aqueous extract after fusion of the weighed sample with a tenfold amount of soda. An FEK-N-57 photocolorimeter with a green light filter was used. The analysis was based on the method for determining chlorine in minerals ([19]). A 0.02%

gelatin solution (0.2 ml each) was used as a protective colloid. The use of a more concentrated gelatin solution or larger amounts of it at low chlorine content retards the formation of the AgCl suspension. Its content was determined from a calibration curve constructed from a series of standard NaCl solutions. For a chlorine content from 0.01 to 0.10 mg, the most optimal portion of the curve proved to be from 0.02 to 0.07 mg. The size of the weighed samples was 5-20 mg. The samples were weighed in weighing tubes on an M-VM-20 balance. All operations for taking samples were carried out in a dry box. The accuracy of the analysis was ±5% relative. The reproducibility of the results obtained was ±10% relative. Acidic hydroxyl groups were determined by the method described earlier ([11]).

Hydrolytic stability of chloro derivatives of silicates was determined from the content of Cl^- ions in solutions after boiling the samples in water, in 2% Na_2CO_3 solution, and in 25% ammonia solution (see Table 1). After treatment of kaolin chloride, containing 0.13% Cl, with water—

for 24 hours at room temperature, the filtrate contained no chlorine.

Solubility of chrysotile asbestos in thionyl chloride was checked by a special experiment. Weighed portions of asbestos were kept for 80 hours in thionyl chloride at 25°. The average loss in weight of the samples after their separation from $SOCl_2$, washing with dry benzene, and drying at 130° was 0.5%, which did not exceed the possible error of this experiment.

Reaction of $SOCl_2$ with silicates. A. Without ultraviolet irradiation. A mixture of 3.0 g of kaolin containing 0.92% OH and 33.0 g of $SOCl_2$ was heated to boiling for 16 hours. The isolated derivative contained 0.13% Cl.

B. With ultraviolet irradiation. 1. A mixture of 2.5 g of kaolin (0.92% OH) and 40 g of $SOCl_2$ was irradiated and heated to boiling with a PRK-4 lamp for 14 hours. The chlorine content was 0.33%.

2. 1 g of chrysotile asbestos containing 1.37% OH and 40 g of $SOCl_2$. Irradiation time: 16 hours. Cl content: 0.34%.
3. The same experiment, lasting 48 hours, gave a chlorine derivative of chrysotile asbestos containing 1.22% Cl.

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