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Abstract

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The Action of Thionyl Chloride on the Siloxane Bond in an Ultrasonic Field

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Ultrasonic vibrations, owing to cavitation, are capable of inducing a variety of chemical processes (^{1}). We investigated the action of thionyl chloride on hexaalkyldisiloxanes and chrysotile asbestos in an acoustic field with a frequency of about 20 kHz and found that, upon sonication of a mixture of hexamethyldisiloxane with thionyl chloride in a molar ratio of 2:7, after 2 hours 27.5% trimethylchlorosilane is formed:

$$\mathrm{R_3SiOSiR_3 + SOCl_2 \xrightarrow{\text{ultrasound}} 2R_3SiCl + SO_2\uparrow}.$$

Hexaethyldisiloxane is cleaved by thionyl chloride under the same conditions by only 2%, and the increase in chlorine content in chrysotile asbestos after ultrasonic treatment in an $SOCl_2$ medium for 1 hour amounted to 0.4% of the weight of the asbestos. Comparison of these results with the cleavage of the siloxane bond in organosiloxanes (^{2}) and in certain silicates (^{3}) under the action of thionyl chloride in ultraviolet light, observed by us earlier, reveals a definite analogy between the influence of ultraviolet irradiation and acoustic vibrations on the course of these reactions.

In our opinion, the phenomenon of photochemical rupture of the $\equiv$ Si—O—Si $\equiv$ bond by thionyl chloride should be ascribed to a free-radical mechanism. Indeed, it is known that the S—Cl bond, under the action of light, is capable of decomposing with the formation of free chlorine radicals (^{4}). On the other hand, anhydrous thionyl chloride contains chlorine ions as a result of self-dissociation (^{5}) according to the scheme:

$$\mathrm{SOCl_2 \rightleftarrows SOCl^+ + Cl^- \rightleftarrows SO^{++} + 2Cl^-}.$$

Nevertheless, in the absence of a catalyst thionyl chloride does not act on silicates and organosiloxanes, although it readily converts the latter into the corresponding organochlorosilanes upon addition of HCl (^{6}) or $FeCl_3$ (^{3}). The use of ultraviolet light or ultrasound makes it possible to effect cleavage of the

$\equiv$ Si—O—Si $\equiv$ bond both in organosiloxanes and in silicates without resorting to a catalyst.

The similarity between the action of high-energy radiation and ultrasonic waves has already been noted (^{1}). It is logical to assume that the ultrasound-induced cleavage of the siloxane bond in the action of thionyl chloride on hexamethyldisiloxane and chrysotile asbestos proceeds by the same mechanism as the analogous photochemical process. An approximate calculation of the energies required for homolytic and heterolytic rupture of the Si—O and S—Cl bonds in the reactions under consideration also supports the assumption of the homolytic character of the cleavage. Thus, in the homolytic process, 169 kcal/mol is expended (104 kcal/mol for rupture of the Si—O bond and 65 kcal/mol for rupture of the S—Cl bond; the values are taken from Cottrell' s book (^{7})), whereas heterolytic decomposition requires 453.2 kcal/mol, i.e., 2.7 times more (to 169 kcal/mol one must add the ionization potentials of silicon and sulfur, i.e., respectively

187.9 kcal/mol and 238.8 kcal/mol (^{8}), and subtract from the sum the electron affinity energy for oxygen and chlorine, 56 kcal/mol and 86.5 kcal/mol, respectively (^{9}). This calculation does not take into account such factors as the influence of substituents on the remaining valences of silicon and the additional energy expenditures connected with the fact that the particles formed upon homolytic dissociation of molecules may be in an excited state. However, the former circumstance cannot substantially alter the calculations, while the latter is to some extent compensated by the possibility that the ions absorb additional energy, as occurs under the action of light rays (^{10}).

The participation in the cleavage reaction of the bond $\equiv$ Si—O—Si $\equiv$ of a catalyst capable of forming an active complex with a siloxane molecule (^{11}) and thereby lowering the high activation barrier of the reaction facilitates the heterolysis of the siloxane bond*. In the case of cleavage caused by photochemical or acoustic action on the reaction medium, homolysis appears to be more preferable.

The action of thionyl chloride in an acoustic field on organosiloxanes, in our opinion, differs somewhat from its action on chrysotile asbestos. In the first case, each of the reagents is capable of passing into the gaseous phase in the cavity of a cavitation bubble, where their molecules undergo activation processes. At the same time, chlorine radicals may be formed, which rupture the siloxane bond in the molecule $R_3SiOSiR_3$. This molecule may itself be in an excited state or even first decompose into radicals. What has been said does not exclude the possibility of parallel ion formation; however, as noted above, the homolytic mechanism is energetically more favorable and therefore should predominate. The course of this reaction in the gaseous phase is confirmed by the extremely low yield of triethylchlorosilane in the interaction of $SOCl_2$ with hexaethyldisiloxane. The latter has a high boiling point (231°) and evaporates incomparably less readily than hexamethyldisiloxane, which boils at 100°.

The reaction of thionyl chloride with chrysotile asbestos is a topochemical process. It is known that ultrasonic cavitation arises more readily at the interface between phases having different acoustic resistances ([12]). Therefore, cavitation bubbles appear in large numbers at the surface of the silicate crystal. When they collapse, a shock wave arises which can cause point destruction of the surface of chrysotile asbestos, accompanied by rupture of chemical bonds, including the bonds $\equiv$ Si—O—Si $\equiv$ or $\equiv$ Si—O—Mg—. The Si—O bond has an ionic character of 35 to 50% ([13]) and, upon mechanical destruction, can give both ions and radicals, both of which will be part of the crystal. These valence-unsaturated sites on its surface will be compensated by the active particles arising in the cavitation bubble, i.e., mainly by Cl· radicals. Taking into account that the reaction is accompanied by the evolution of sulfur dioxide, the process may be represented by the following scheme:

$$\mathrm{SOCl_2} \rightarrow \mathrm{SOCl} \cdot + \mathrm{Cl}\cdot$$

$$\equiv \mathrm{Si—O—Si} \equiv \rightarrow \equiv \mathrm{Si} \cdot + \cdot \mathrm{O—Si} \equiv$$

$$\equiv \mathrm{Si—O}^{\mathrm{Cl}\cdot} \rightarrow \equiv \mathrm{SiCl} + \cdot\mathrm{O}$$

$$\mathrm{SOCl}\cdot \xrightarrow{\mathrm{O}\cdot} \mathrm{SO_2} + \mathrm{Cl}\cdot$$

$$\equiv \mathrm{Si}\cdot \xrightarrow{\mathrm{Cl}\cdot} \equiv \mathrm{SiCl}$$

* The fact that the siloxane bond in kaolin proved resistant to the action of thionyl chloride even in the presence of a catalyst ($\mathrm{SnCl_4}$) ([3]) should be explained by the impossibility, for steric reasons, of forming an active complex on the kaolin surface.

As a result, chlorine atoms become chemically bound to the asbestos surface, i.e., a chlorinated silicate derivative is formed. This process is sometimes called chemisorption.

At the same time, chlorine radicals can attack, on the surface of the silicate crystal, the unbroken bonds $\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv$ or $\equiv \mathrm{Si} - \mathrm{O} - \mathrm{Mg}^{-}$, as occurs in photochemical chlorination, in which mechanical action on the surface is excluded. The chlorine content in asbestos after treatment with thionyl chloride in ultraviolet light for 16 h is lower than after acoustic chlorination for only 1 h. This fact indicates that, under acoustic action, mechanical disturbances of the surface play the decisive role.

The more highly developed the silicate surface, the greater the number of cavitation bubbles that occur for one and the same weight of it per unit time.

Therefore it was to be expected that unfluffed asbestos fibers would be chlorinated less readily than those previously comminuted. This view is confirmed by experimental data: the Cl content in samples of unfluffed asbestos after chlorination did not exceed 0.30%.

Experimental Part

Starting materials. Hexaalkyldisiloxanes were prepared by hydrolysis of the corresponding trialkylchlorosilanes, dried over P_2O_5, and distilled before introduction into the reaction. They had constants corresponding to the literature data. Thionyl chloride was redistilled twice immediately before use and had b.p. 75.9°, n_D^{20} 1.511 (lit.: b.p. 78.8°, n_D^{10} 1.527 (14); b.p. 76° (9)). Chrysotile asbestos (kryolite) was ground and dried before chlorination. The chlorine content in the initial chrysotile asbestos was 0.17%.

Experimental procedure. Sonication was carried out in a 150-ml beaker made of fluoroplastic-4, fitted with a tightly fitting lid of the same material. The lid had two openings; a thermometer was placed in one, and a reflux condenser connected to a Tishchenko bottle (conc. H_2SO_4) in the other. The beaker was placed on a magnetostrictive vibrator operating at a frequency of 19–21 kHz. The intensity was about 7 W/cm^2. The vibrator and the beaker were cooled with running water. The temperature of the reaction mixture did not exceed 50°.

Action of $SOCl_2$ **on hexamethyldisiloxane.** A mixture of 32.4 g (0.2 mole) of $(CH_3)_6Si_2O$ and 80 g (0.67 mole) of thionyl chloride was sonicated in 4 portions of 30 min each, with 15-min intervals for cooling the beaker. After sonication, 12 g (0.11 mole) of trimethylchlorosilane was isolated from the mixture by fractional distillation; its constants corresponded to the literature data (see (2)). Degree of conversion: 27.5%.

Action of $SOCl_2$ **on hexaethyldisiloxane.** A mixture of 24.6 g (0.1 mole) of $(C_2H_5)_6Si_2O$ and 40 g (0.34 mole) of thionyl chloride was sonicated in 8 portions of 15 min each, with 12-min intervals for cooling the beaker. Fractional distillation of the mixture after sonication gave 5.8 g of a product whose constants corresponded to the literature data for triethylchlorosilane (15). Degree of conversion: 2%.

Action of $SOCl_2$ **on chrysotile asbestos.** One gram of chrysotile asbestos was mixed with 130 g of thionyl chloride and sonicated in 3 portions of 20 min each, with 15-min intervals. It had previously been established that, without the action of ultrasound and light radiation, $SOCl_2$ does not act on this silicate (3). After sonication was completed, the asbestos was separated from $SOCl_2$ in a dry box and washed with absolute benzene until chlorine was absent from the wash solvent, after which it was dried for 15 h in a vacuum pistol (4 mm Hg, 135°). Chlorine determination was carried out by the method described—

···in the work (3). The Cl content in chrysotile asbestos after sonication was

0.58%. The hydrolytic stability of the chlorine in the sample was as high as in the samples obtained by the photochemical method.

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