REACTIONS OF (CHLOROMETHYL)ETHOXY SILANES WITH AMINES

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It is known that the chlorine of a chloromethyl group attached to silicon can be replaced by other polar groups, namely by the alkoxy group under the action of sodium alkoxide [1, 2] and by the acetoxy group under the action of potassium acetate [2, 3]. Various amino derivatives are obtained when ammonia or amines are heated with trialkyl(chloromethyl)silanes, dialkoxy(chloromethyl)methylsilanes [8], (chloromethyl)pentamethyldisiloxane, and (chloromethyl)heptamethyldicyclosiloxane [7]. In the present investigation we studied the relative reactivities of chlorine in (chloromethyl)ethoxysilanes in reactions with various amines.

Unlike results reported in the literature, ours showed that the chlorine of (chloromethyl)ethoxysilanes is replaced by reaction with various aliphatic and aromatic amines at 20°. The identities of the compounds isolated indicated that the reaction of amines with alkoxy(chloromethyl)silanes proceeds by the equation:

$$2RNH_2 + ClCH_2(CH_3)_nSi(OH)_{3-n} \rightarrow RNHCH_2(CH_3)_nSi(OH)_{3-n} + RNH_2HCl$$

By the reactions of ethylamine with (chloromethyl)ethoxydimethylsilane and with (chloromethyl)diethoxydimethylsilane and of aniline with (chloromethyl)diethoxymethylsilane at 20° we obtained, respectively, N-[(ethoxydimethylsilyl)methyl]ethylamine in 65% yield, N-[(diethoxymethylsilyl)methyl]ethylamine in 56% yield, and N-[(diethoxymethylsilyl)methyl]aniline in 13.5% yield; these are accompanied by the hydrochloride of the base taken.

An investigation was made of the changes in the reactivity of chlorine in (chloromethyl)ethoxydimethyl-, (chloromethyl)diethoxymethyl-, and (chloromethyl)triethoxysilanes in their reactions with 2-aminoethanol, 2-(trimethylsiloxy)ethylamine, ethylamine, diethylamine, aniline, and N-ethylaniline. In the reaction of ethylamine with (chloromethyl)ethoxydimethylsilane for 560 hours at 20°, 75% replacement of chlorine by amino occurs; with (chloromethyl)diethoxymethylsilane there is 71% replacement, and with (chloromethyl)triethoxysilane there is 53% replacement. When the first two compounds are treated for the same time with diethylamine the replacement of chlorine is 72% and 64%, respectively.

An examination of the kinetic curves for the replacement of chlorine in all the (chloromethyl)ethoxysilanes in their reactions with ethylamine and diethylamine (Fig. 1) shows that at 20° replacement is rapid during the first 120 hours, but then slows down sharply. The reactions of the same three (chloromethyl)ethoxysilanes with aromatic amines (aniline and N-ethylaniline) at 20° are slower and result in a lower degree of replacement of chlorine than their reactions with ethylamine and diethylamine. Aniline reacts more readily than N-ethylaniline with (chloromethyl)ethoxysilanes (Fig. 2). Thus, in the reaction of aniline for 560 hours with (chloromethyl)ethoxydimethylsilane there is 49% replacement of chlorine, with (chloromethyl)diethoxymethylsilane there is 37%, and with (chloromethyl)triethoxysilane there is 26%. In the reactions of the (chloromethyl)ethoxysilanes with N-ethylaniline the replacement of chlorine is 35%, 22%, and 12.5% respectively. With the aromatic amines reaction is slow and there is no sharp difference in the rate of replacement between the start and end of the reaction (Fig. 2). A considerably faster reaction with a greater extent of replacement is found in the reactions of (chloromethyl)ethoxysilanes with 2-aminoethanol and 2-(trimethylsiloxy)ethylamine. Thus, in their reactions with 2-aminoethanol for 560 hours at 20°, (chloromethyl)ethoxydimethylsilane undergoes 90%
Fig. 1. Replacement of chlorine in (chloromethyl)ethoxysilanes in their reactions with ethylamine and diethylamine:
1) \( \text{ClCH}_2\text{Si(CH}_3\text{)}_2\text{OC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{NH}_2 \); 2) \( \text{ClCH}_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2 + + \text{C}_2\text{H}_5\text{NH}_2 \); 3) \( \text{ClCH}_2\text{Si(OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_5\text{NH}_2 \);
4) \( \text{ClCH}_2\text{Si(OC}_2\text{H}_5)_2 + (\text{C}_2\text{H}_5\text{)}_2\text{NH} \); 5) \( \text{ClCH}_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2 + (\text{C}_2\text{H}_5\text{)}_2\text{NH} \) .

Fig. 2. Replacement of chlorine in (chloromethyl)ethoxysilanes in their reactions with aniline and N-ethylaniline:
1) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{ClCH}_2\text{Si(CH}_3\text{)}_2\text{OC}_2\text{H}_5 \); 2) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{ClCH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 \);
3) \( \text{C}_6\text{H}_5\text{NH}_2 + \text{ClCH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 \); 4) \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH} + \text{ClCH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 \);
5) \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH} + \text{ClCH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 \);
6) \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5\text{NH} + \text{ClCH}_2\text{Si(OC}_2\text{H}_5\text{)}_2 \).

Conversion of (chloromethyl)diethoxymethylsilane 88% conversion, and (chloromethyl)triethoxysilane 69% conversion with replacement of chlorine. The corresponding figures for the reactions with 2-(trimethylsiloxy)ethylamine are 75%, 86.5%, and 68%. The reactions of (chloromethyl)ethoxysilanes with 2-aminoethanol and 2-(trimethylsiloxy)ethylamine are very rapid during the first 40 hours.

The greater extent of the replacement of the chlorine of (chloromethyl)ethoxysilanes when treated with aliphatic amines, rather than aromatic amines, must be attributed to the stronger basic character of the former. With respect to the readiness with which they react with (chloromethyl)ethoxysilanes at 20°, the amines can be placed in the following series:

\[ \text{HOC}_2\text{H}_4\text{NH}_2 \succ (\text{CH}_3)_3 \text{SiOC}_2\text{H}_4\text{NH}_2 \succ \text{C}_6\text{H}_5\text{NH}_2 \succ (\text{C}_2\text{H}_5)_2 \text{NH} \succ \text{C}_6\text{H}_5\text{NH}_2 \succ \text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH} \]