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Abstract

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Physicochemical Study of Complexes between Alkyl-(Aryl)-Chlorosilanes and Halides of Tetrasubstituted Ammonium

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A number of authors ([1–7]) have obtained interesting results concerning electrically conducting complexes of organoaluminum compounds with halides of alkali metals and tetrasubstituted ammonium, as well as with hydrides of alkali metals. An analysis of the literature data on the properties of halide compounds of Al and of the tetrahalides of elements of the fourth group shows that there is a certain similarity between them with respect to a number of properties. At the same time, the compounds of alkylaluminum display a similarity with respect to analogous properties with aluminum halides. On this basis we proposed that organoelement compounds of Si and Ge may form complexes analogous in their properties to the complexes of organoaluminum compounds.

The present work is devoted to the study of complex formation between CH_3SiCl_3, $(CH_3)_3SiCl$, $C_6H_5SiCl_3$, as well as $SiCl_4$ and NaCl, NaF, KF, CsCl, CsF, NH_4Cl, $(CH_3)_4NCl$, $(C_2H_5)_4NBr$, $(C_4H_9)_4NCl$, $(C_4H_9)_4NBr$, $(C_4H_9)_4NJ$, and ethylpyridinium bromide. The nature of the interaction of the organosilicon compound with the added salt was determined by chemical analysis and by measuring the electrical conductivity of the products obtained, and also visually, by observing dissolution of the salt.

The composition of the products obtained was determined by analysis for hydrolyzable chlorine ([9]), and in some cases for the total Cl content by argentometric titration ([10]).

The synthesis and measurements were carried out in an atmosphere of "pure" argon, dried by passage through P_2O_5. The synthesis was carried out in an apparatus with a reflux condenser and a magnetic stirrer. Heating was 35–40°, and the synthesis time was 3–12 hr, depending on the substance and the degree of dispersion of the salt. After synthesis the product was transferred into an apparatus for measuring electrical conductivity, which made it possible to separate the layers and to measure the electrical conductivity of each layer in the isolated state and in their joint presence. The reproducibility of the measurements of specific electrical conductivity in different experiments was

$\pm$10%, owing to the high viscosity of the substances obtained and the difficulty of complete separation.

The main results of the study are given in Table 1. For the remaining salts listed above, no interaction with the compounds was established. As a typical result for them, Table 1 gives the data for CsF.

The data on specific electrical conductivity and composition in the case of the interaction of $(CH_3)_3SiCl$ and CH_3SiCl_3 with tetrabutylammonium chloride and bromide refer to liquids supercooled to room temperature. In the case of CsF, the values of the specific electrical conductivity of the liquid phase after contact with the salt are given. The data obtained show that, in the case of halides of tetrasubstituted ammonium salts, interaction takes place provided that the alkyl radical is sufficiently long. In addition, the capacity for complex formation of tetrasubstituted ammonium halides increases as the radius of the anion decreases. CH_3SiCl_3 and $(CH_3)_3SiCl$ are similar in their behavior. In these compounds $(C_4H_9)_4NCl$

Table 1

No.	Organosilicon compound	Hydrolyzable Cl, %: theoretical	Hydrolyzable Cl, %: experimental	χ	CsF	$(C_2H_5)_4NBr$	$(C_4H_9)_4NBr$	$(C_4H_9)_4NCl$
1	$(CH_3)_3SiCl$	32.63	32.20	$3.4 \cdot 10^{-7}$	Does not dissolve	Does not dissolve; $\chi = 8.9 \cdot 10^{-7}$	$\chi = 1.1 \cdot 10^{-5}$	Complex forms; $\chi_k = 5\text{-}6 \cdot 10^{-4}$; $\chi_{bc} = 2.5 \cdot 10^{-5}$	Complex forms; $\chi_k = 6.0 \cdot 10^{-4}$; $\chi_{bc} = 3.4 \cdot 10^{-5}$
2	CH_3SiCl_3	71.15	70.30	$1.9 \cdot 10^{-7}$	Does not dissolve		$\chi = 1 \cdot 10^{-5}$	Complex forms; $\chi_k = 3 \cdot 10^{-4}$; $\chi_{bc} = 1.6 \cdot 10^{-5}$ (second layer)	Complex forms; $\chi_k = 4.2 \cdot 10^{-4}$; $\chi_{bc} = 4 \cdot 10^{-5}$

No.	Organosilicon compound	Hydrolyzable Cl, %: theoretical	Hydrolyzable Cl, %: experimental	χ	CsF	$(C_2H_5)_4NBr$	$(C_4H_9)_4NBr$	$(C_4H_9)_4NJ$	$(C_4H_9)_4NCl$
3	$SiCl_4$			$< 1 \cdot 10^{-7}$	Does not dissolve; $\chi < 1 \cdot 10^{-7}$		Salt decomposes	Complex forms; $\chi_k = 3.4 \cdot 10^{-4}$; $\chi_{bc} < 1 \cdot 10^{-7}$	Complex forms; $\chi_k = 1.15 \cdot 10^{-4}$; $\chi_{bc} < 1 \cdot 10^{-7}$
4	$C_6H_5SiCl_3$	50.28	50.45	$< 1 \cdot 10^{-7}$	Does not dissolve; $\chi < 1 \cdot 10^{-7}$	Does not dissolve; $\chi = 1 \cdot 10^{-7}$		Salt dissolves; $\chi = 7.4 \cdot 10^{-5}$	Salt dissolves; $\chi = 2.7 \cdot 10^{-4}$

Note. In all cases, the values of electrical conductivity χ, in $\Omega^{-1} \cdot cm^{-1}$, refer to room temperature, except for complexes with $SiCl_4$, for which χ was measured at 55°C.

dissolves with the formation of two layers. One of the layers approximately corresponds in its composition to a ratio of organosilicon compound to salt of $3 : 1$. At room temperature these complexes are viscous supercooled liquids, colorless or slightly yellowish. The second layer is a mobile colorless liquid consisting of the organosilicon compound with a small amount of dissolved salt. Its composition for $(CH_3)_3SiCl$ and CH_3SiCl_3 corresponds to a ratio of organosilicon compound to salt of $\sim 40 : 1$.

When $(C_4H_9)_4NBr$ is dissolved, analogous phenomena are observed. In the case of $(C_4H_9)_4NJ$, complexes could not be obtained. During the synthesis only a slight yellowing of the organosilicon compound is observed, with some increase in its electrical conductivity. $SiCl_4$ behaves analogously to CH_3SiCl_3 and $(CH_3)_3SiCl$, but the complexes formed are rather high-melting.

The properties of phenyltrichlorosilane (PhTCS) differ sharply from the properties of the organosilicon compounds described above. Tetrabutylammonium chloride and bromide dissolve in this compound without separation into layers, forming a yellow-colored solution, and have a considerable temperature coefficient of solubility; moreover, the solubility of the chloride is considerably higher than in methyl derivatives of silicon, while the electrical conductivities are lower. The electrical-conductivity values given in Table 1 refer to a PhTCS-to-salt ra-

tio equal to 5.4 : 1 in the case of the chloride (unsaturated solution) and 45 : 1 in the case of the bromide (saturated solution at room temperature).

Subsequently, the system $(CH_3)_3SiCl$–$(C_4H_9)_4NCl$ was chosen as the principal object of investigation. It was established that the composition of the layers practically does not depend on the holding time or on temperature. Table 2 gives data on the effect of temperature on the composition

Table 2

	25°	30°	35°	45°
Amount of hydrolyzable Cl in the complex, %	17.63	17.75	17.60	17.58
Amount of hydrolyzable Cl in the upper layer, %	30.76	30.59	30.79	30.67
χ, $ohm^{-1}\cdot cm^{-1}$ of the complex	$6.2 \cdot 10^{-4}$		$8.0 \cdot 10^{-4}$	$9.5 \cdot 10^{-4}$

of the substance formed and on the specific electrical conductivity of $(CH_3)_3SiCl$ –$(C_4H_9)_4NCl$. The independence of the composition of the complex from temperature is also indicated by the fact that the electrical conductivity of the complex at different temperatures in the presence of the second layer coincides with the electrical conductivity of the isolated complex.

Investigation of the behavior of the complexes $[(CH_3)_3SiCl]_3(C_4H_9)_4NCl$ with respect to various solvents (Table 3) showed that the strengths of the bonds of the three molecules of $(CH_3)_3SiCl$ in it are not identical: one molecule is bound more strongly than the other two.

Table 3

Solvent	$(C_4H_9)_4NCl$	$(CH_3)_3SiCl$	Complex $[(CH_3)_3SiCl]_3 \cdot (C_4H_9)_4NCl$
Heptane and cyclohexane	Does not dissolve	Mixes in all proportions with formation of a nonconducting solution	The solvent leaches out 2 molecules of $(CH_3)_3SiCl$; the remaining 1:1 complex is insoluble in heptane and cyclohexane
Benzene	At room temperature only traces dissolve; the solubility increases rapidly with increasing temperature	Analogous to heptane	The complex dissolves with formation of an electrically conducting solution. $\chi = 1.12 \cdot 10^{-5}$ $ohm^{-1} \cdot cm^{-1}$ (1 mole of complex per 100 moles of solvent) $\chi = 7.5 \cdot 10^{-4}$ $ohm^{-1} \cdot cm^{-1}$ (1 mole of complex per 10 moles of solvent)
Toluene	At room temperature only traces dissolve; upon heating the solubility increases	Analogous to heptane	The complex dissolves with formation of an electrically conducting solution $\chi = 0.71 \cdot 10^{-5}$ $ohm^{-1} \cdot cm^{-1}$ (1:100) $\chi = 5.25 \cdot 10^{-5}$ $ohm^{-1} \cdot cm^{-1}$ (1:10)

Next, electrolysis was carried out of the systems CH_3SiCl_3–$(C_4H_9)_4NCl$, $(CH_3)_3SiCl$–$(C_4H_9)_4NCl$, CH_3SiCl_3–$(C_4H_9)_4NBr$, and of solutions of $(C_4H_9)_4NCl$ and $(C_4H_9)_4NBr$ in $C_6H_5SiCl_3$. The electrolysis was carried

out with a Pt cathode and a Pt or Si anode, at room temperature without stirring. In all cases no deposition of silicon on the cathode could be observed (D_k = 0.25-10 A/dm^2).

Dissolution of low-resistance p-type Si was observed in the case of the systems CH_3SiCl_3–$(C_4H_9)_4NCl$, $(CH_3)_3SiCl$–$(C_4H_9)_4NCl$, and in solutions of $(C_4H_9)_4NCl$ in $C_6H_5SiCl_3$. For example, in the complex $[(CH_3)_3SiCl]_3(C_4H_9)_4NCl$ at D_a = 4 A/dm^2 silicon dissolves with a current efficiency close to 100% (calculated as Si^{+4}). The current density can be varied from 1 to 15 A/dm^2. The Si anode also dissolves in benzene solutions of the complex $[(CH_3)_3SiCl]_3(C_4H_9)_4NCl$ (1 mole of complex per 10 moles of benzene).

The results obtained, in addition to being of independent interest, indicate a certain similarity between the compounds studied and analogous Al compounds. These include, above all, the very fact of complex formation, which until now had been considered unlikely for alkyl derivatives of silicon. Further similarity is manifested in dissociation during complex formation, in the leaching of two molecules of $(CH_3)_3SiCl$ by aliphatic solvents, in the dependence of complex formation on the radius of the anion and the size of the cation, and in the anodic behavior during electrolysis. At the same time, substantial differences also occur, as, for example, in the cathodic behavior of the complexes during electrolysis.

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Note: Figure translations are in progress. See original paper for figures.