V. I. ZUBKOV, M. V. TIKHOMIROV, Academician K. A. ANDRIANOV,

S. A. GOLUBTSOV

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Abstract

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V. I. ZUBKOV, M. V. TIKHOMIROV, Academician K. A. ANDRIANOV,
S. A. GOLUBTSOV

MASS-SPECTROMETRIC STUDY OF INTERMEDIATE PRODUCTS OF THE INTERACTION OF SILICON WITH CUPROUS CHLORIDE

The existence of divalent silicon chloride—dichlorosilylene—has been experimentally demonstrated only for temperatures of 1000-1400° (^{1}). In a study of the mechanism of the reactions of direct synthesis of dialkyldichlorosilanes (^{2}), some of us suggested that cuprous chloride can react with silicon at relatively low temperatures (300-400°) with formation of an analogous compound of divalent silicon:

$$\mathrm{Si} + 2\mathrm{CuCl} \rightarrow 2\mathrm{Cu} + \mathrm{SiCl}_2. \tag{1}$$

The compound obtained either reacts with methyl chloride adsorbed on copper, with regeneration of cuprous chloride,

$$\mathrm{SiCl}_2 + 2\mathrm{CH}_3\mathrm{Cl}\cdot\mathrm{Cu} \rightarrow (\mathrm{CH}_3)_2\mathrm{SiCl}_2 + 2\mathrm{CuCl} \tag{2}$$

or, in the absence of methyl chloride, with an excess of cuprous chloride forms silicon tetrachloride:

$$\mathrm{SiCl}_2 + 2\mathrm{CuCl} \rightarrow \mathrm{SiCl}_4 + 2\mathrm{Cu}. \tag{3}$$

The possibility of formation of dichlorosilylene under the conditions of the synthesis of organochlorosilanes (at 300-400°) was confirmed by thermodynamic calculations and by a spectral study of the reaction of cuprous chloride with silicon at a temperature of 300°. Experiments involving transfer of the volatile product of the interaction of silicon with cuprous chloride through a porous wall (^{2}) showed that compounds of the dichlorosilylene type apparently exist in the gas phase at temperatures of 370-385°, but their composition remained unproved.

The mass-spectrometric study we carried out of the reaction mixture CuCl + Si showed that, even at low temperatures (180°), the ratios of peak intensities in the mass spectrum correspond to the presence in the reaction products of a

Fig. 1

Figure 1: Fig. 1

compound of formula $SiCl_2$. Thus, the course of the reaction of cuprous chloride with silicon according to schemes 1-3 is confirmed. We studied the mass spectra of the final reaction product—silicon tetrachloride—and of the gaseous products of the interaction of silicon with cuprous chloride.

Experimental Part

The work was carried out on an MI-1305 mass spectrometer with an ion source somewhat modified for studying gaseous products of the reaction of a solid reaction mixture during its heating (instead of a porcelain inlet tube, a heated glass ampoule with the reaction mixture was placed in the source). A mixture* of cuprous chloride (chemically pure grade, additionally purified by treatment with hydrochloric acid and washed with alcohol) and silicon (Kr-1 grade, with particles 75-250 μ in size) in a ratio of $3:8$ (by weight) was placed in ampoule 1 (Fig. 1), which was equipped with an external tungsten heater 5. The temperature of the ampoule was measured by thermocouple 4, located on its outer surface. The gaseous reaction products entered the ionization chamber of source 2 through an opening in platinum diaphragm 3. Through the same ampoule, silicon tetrachloride could also be introduced into the ion source. The ion currents were measured with an SI-01 ion counter.

Fig. 1

The mass spectrum of silicon tetrachloride is given in (^{5}); however, the need to work under entirely different conditions did not allow us to make use of the published data.* Therefore, first of all the mass spectrum of the final reaction product—silicon tetrachloride—was recorded. The part of the mass spectrum of silicon tetrachloride of interest to us, recorded at an ionizing-electron energy of 20 eV, is given in Table 1. The maximum intensity in the spectrum of silicon tetrachloride is exhibited by peaks with the ratio of ion mass m to its charge e equal to 133 and 135 ($^{28}Si^{35}Cl_3^+$ and $^{30}Si^{35}Cl_3^+ + {}^{28}Si^{35}Cl_2{}^{37}Cl^+$). The intensity of the peak with ratio $m/e = 98$ ($^{28}Si^{35}Cl_2^+$) in our case is only 2.4% of the intensity of peak 133. The intensity of the peak with ratio $m/e = 63$ ($^{28}Si^{35}Cl^+$) under our conditions is an order of magnitude smaller than the intensity of peak 98.

The intensity ratios of the isotopic varieties of molecular and fragment ions ($I/I_{\max}$), formed upon ionization by electron impact in the ion source, to the intensity of the maximum peak for the given fragment were calculated by the formulas given in works (^{3}-^{4}). The same ratios obtained experimentally agreed

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* Prepared by Z. V. Belikova.

with the calculated values within 0.001-0.02 (for $SiCl_2$ up to 0.005), which indicates that we were dealing precisely with $SiCl_2$ and fragments of the molecule of the final product $SiCl_4$. The reaction mixture was heated in high vacuum to a temperature of 180°. Mass spectra of the reaction products were recorded both with simultaneous admission of silicon tetrachloride vapor into the reaction zone and without its admission (Table 1).

Table 1

Relative intensity (I/I_{133}) of peaks in the mass spectrum

m/e	$SiCl_4,\ T = 20 \div 180^\circ$	$CuCl + Si,\ T = 180^\circ$
98	0.024	0.161
100	0.016	0.106
133	1.000	1.000
134	0.052	0.053
135	1.004	0.995
136	0.046	0.052
137	0.354	0.362
138	0.015	0.016
139	0.042	0.045
168	0.476	0.413
169	0.030	0.017
170	0.604	0.539
171	0.028	0.023
172	0.310	0.277
173	0.016	0.009
174	0.073	0.061

The relative intensity of the peak with the mass-to-charge ratio $m/e = 98$ (I_{98}/I_{133}), caused by the formation of $SiCl_2$ in the reaction zone, increased in our case by more than a factor of 6.** Control experiments with admission of silicon tetrachloride into the source ampoule, heated to the same temperature, in the absence of the reaction mixture showed that such a change in the intensity of the peak with $m/e = 98$ cannot be associated with thermal decomposition of $SiCl_4$. It follows from this that the relative increase of the peak with $m/e = 98$ may be regarded only as a consequence of the formation of dichlorosilylene in the reaction zone.

[*] The mass spectra of silicon tetrachloride and of the reaction products, from which Table 1 was compiled, were recorded in one experiment at an ionizing voltage of 20 V (in order to eliminate errors from doubly charged mercury and possible impurities).

[**] The magnitude of the indicated ratio apparently also depends on random changes in the geometry of the system.

The results presented, in our opinion, are direct experimental proof that the intermediate product of the interaction of silicon and cuprous chloride is gaseous dichlorosilylene, $SiCl_2$.

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