Structural features of catalytically active oligoorganometallosiloxanes

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Copper- and (copper, aluminum)-containing organosiloxanes were studied by spectroscopic methods. It was found that in organometallosiloxanes (OMS) with an increased content of copper (Si/Cu = 1 : 1), Cu atoms are rather uniformly distributed in the siloxane matrix. All compounds under study are complexes characterized by d-d-transitions in copper ions with a constant coordination number of the metal atom. The intensity of the d-d-transition band increases as the copper content increases. ESR studies demonstrated that in the compounds under consideration, a change from mononuclear paramagnetic centers to clusters, in which copper ions are linked by strong spin-exchange interactions, occurs as the copper content increases. The catalytic activity of the above-mentioned compounds in isomerization reactions of 3,4-dichlorobutene-1 was studied. It was found that copper atoms serve as catalytic centers.

Key words: organometallosiloxanes, polynuclear complexes, ESR spectroscopy, catalysis.

Organometallosiloxanes (OMS) containing alternating RSi-O-Si(R)O- and RSi-O-M-O groups (M is a transition metal) are characterized by a number of interesting properties. In particular, an efficient metalmetal interaction in OMS leads to the appearance of peculiar magnetic properties, for example, to ferromagnetic and antiferromagnetic interactions in σ -bonded clusters and ordinary clusters, respectively.¹ Recently, it was found that individual OMS and OMS supported on mineral carriers exhibit high catalytic activity.^{2,3} In this respect, oligomeric OMS are of considerable interest. Because of their chemical features, it is possible to introduce additional metal atoms into these compounds, which allows one to prepare heterometallic derivatives, whose compositions change almost continuously. Structural data on oligometric OMS are virtually unavailable although individual crystalline compounds have been studied in considerable detail. 4,5

In this work, complex spectral studies of amorphous oligomeric copper-containing OMS (both homometallic (only Cu) and heterometallic (Cu+Al)) were performed. Our results were compared with the catalytic activity of the above-mentioned oligomers. Syntheses of oligomeric OMS were carried out according to a known procedure.⁶ The molecular weights of the oligomers under study were 3500-6000 (ebullioscopy in benzene). Their compositions are given in Table 1.

Results and Discussion

The IR spectra of the dimers under study are shown in Fig. 1. All have a narrow intense band at 1130 cm^{-1} ,

Oligo- mer	Fragment of the oligomer unit	Composition (%)				
		Si	Cu	Al	Si : Al	Si : (
1	PhSi - O - Cu - O - Si(Ph) - O - Al - O - O - O - O - O - O - O - O - O -	15.8	1.8	3.4	3.8	20.0
2	PhSi-O-Cu-O-Si(Ph)-O-Al-O-	12.9	8.3	3.4	3.1	3.5
3	PhSi-O-Cu-O-	12.7	14.0		_	2.0
4	PhSi-O-Cu-O-	8.6	20.0	_		1.0

Table 1. Compositions of the studied compounds

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Fig. 1. IR spectra of oligomers 1-4 (the numbers of the spectra correspond to the numbers of the oligomers in Table 1).

which corresponds (see Ref. 7) to vibrations of the Ph-Si group. The IR spectra in the regions of vibrations of Si-O-Si groups (1100-1030 cm⁻¹) are different depending on the particular compound. Oligomers 1 and 2 are characterized by a broad intense band typical of amorphous OMS. The IR spectrum of oligomer 3 has two well-resolved bands at 1060 and 1040 cm⁻¹ instead of one band and a broad band at 980 cm⁻¹. The bands at 1060 and 1040 cm⁻¹ correspond to vibrations of Si-O-Si groups. The fact that these bands are well resolved indicates that the structure of 3 is more ordered than those of oligomers 1 and 2. The band at 980 cm^{-1} , which is absent in the case of derivatives with a low content of copper, is assigned to vibrations of the Si-O-Cu groups.⁸ Finally, in the spectrum of 4 only bands at 1130 and 980 cm⁻¹ are intense, which agrees well with the above-mentioned assignment. The disappearance of absorption bands of the Si-O-Si groups demonstrates that the metal atoms are rather uniformly distributed in the oligomer. Otherwise, fragments with a predominant concentration of Si-O-Si and Cu-O-Cu

Table 2. UV spectral data for oligomers 1-4

Oligomer	λ/nm	٤*
1	690	18.8
2	709	21.5
3	709	32.2
4	709	42.5

* Values of ε were calculated per 1 g-at. of copper.

groups would be observed, which would be reflected in the shape of the spectrum. The introduction of aluminum has virtually no effect on the spectrum: the bands of the Si-O-Al and Si-O-Si groups overlap because of the close values of the weights of the Al and Si atoms.

The electronic spectra of oligomers 1-4 have a single band in the low-frequency region of the spectrum. The position of this band depends only slightly on the composition of OMS (Table 2).

The charge transfer bands $O \rightarrow Cu$ in the spectra are masked by intense absorption of the phenyl groups. The obtained values of λ and ε are typical of d-d-transitions in the Cu^{II} ion⁹ and do not carry unambiguous information on the geometry of the environment about the Cu atom. The position of the band remains unchanged, which indicates that the coordination number of the metal atom is constant in the series of the oligomers under study.

The ESR spectra of the oligomers under study are shown in Fig. 2. The spectrum of oligomer 1 with a minimum content of copper is characterized by an



Fig. 2. ESR spectra of oligomers 1-3 (see Table 1). Ia, the spectrum was recorded at 77 K and all other spectra were recorded at 298 K; 1, 2, 2a, 3, the spectrum was obtained for a solution (the concentration in toluene was $5 \cdot 10^{-2}$ mol L⁻¹); in the other cases, the spectra were obtained for powders.

Levitsky et al.

axial symmetry. The parameters of the spectrum are as follows: $a_{\parallel} = 12.76$ mT, $g_{\parallel} = 2.348\pm0.005$, and $g_{\perp} = 2.086\pm0.005$. Analysis of the shapes of the spectra shown in Fig. 2 demonstrates that they correspond to several different structures. Therefore, the above-mentioned parameters are, overall, efficient. Based on the spectra obtained, it can be stated that the complex has the tetragonal geometry. Presumably, the Cu^{II} ion has a distorted octahedral configuration in the ground state b_{\lg} with localization of the unpaired electron at the $3d_{x^2-y^2}$ orbital $(g_{\parallel} > g_{\perp} > 2).^{10,11}$ The ESR spectral data are unambiguously indicative of the absence of substantial Cu—Al interactions in Al-containing OMS (no evidence of splitting at the Al atom).

The ESR spectrum of oligomer 2 has a singlet with $g = 2.19\pm0.01$ against a background of components (which belong to two paramagnetic centers) of the multiplet spectrum. In the spectrum of the oligomer in toluene, the lines of the paramagnetic centers are absent and only a singlet ($g = 2.20\pm0.01$; the line width is 13 ± 1 mT) is observed. This singlet is typical of systems characterized by strong spin-exchange interactions in Cu^{II} ions.¹²

The ESR spectrum of oligomer 3, in which the copper content is an order of magnitude higher compared to "magnetically dilute" oligomers 1 and 2, is a complex superposition of signals from several different structures. The large widths of the spectral lines are indicative of strong magnetic dipole-dipole and spinexchange interactions in the ions.

Therefore, in the series of the compounds under study, a transition from the paramagnetic centers to the coordination clusters in which the Cu ions are linked by strong spin-exchange interactions occurs as the copper content increases.¹ Taking into account the available data on the structures of crystalline OMS,^{4,5} it can be assumed that the environment about copper ions is formed by four oxygen atoms (an approximately square configuration). The other two oxygen atoms, which are located along the symmetry axis C_4 , belong to the remote Si-O-Al or Si-O-Cu groups. The ESR spectra are inconsistent with the trigonal configuration typical of five-coordinate copper. The complicated shapes of the spectra are apparently associated with irregular structures of amorphous oligomeric complexes in which different modes of alternation of Si, Cu, and Al atoms, which are separated by oxygen bridges, are possible. The Cu-Al interaction is virtually absent. The effect of Al on the arrangement of the electronic levels and on the magnetic properties of copper ions is insignificant.

It was of interest to study the catalytic properties of OMS as a function of the nature of the metal ion in a series of compounds of analogous compositions. To estimate the catalytic properties of OMS oligomers, we used the reaction of isomerization of 3,4-dichlorobutene-1 (3,4-DCB) to 1,4-dichlorobutene-2 (1,4-DCB)

Previously,² using this reaction as an example, it has been demonstrated that copper-containing phenylpolysiloxane supported on silica gel exhibits high catalytic activity. The typical kinetic curves, which were obtained with the use of oligomers 2 and 3, are shown in Fig. 3. It can be seen that, in all cases, autoacceleration is observed. This autoacceleration is most pronounced for samples with high copper contents (curves 3-5 in Fig. 3). The formation of a more active form of the catalyst in the course of the reaction is a possible cause of autoacceleration. Portions of the curves obtained under conditions of existence of macroscopically homogeneous solutions are shown in Fig. 3. When large reaction times were used, precipitates, whose compositions corresponded to the initial OMS, were formed, which is apparently indicative of cross-linking or additional polymerization of the initial oligomeric OMS. In this case, isomerization was not slowed down. A comparison of curves 3 and 6 (see Fig. 3) demonstrates that in the case of OMS with equal contents of copper, the extent of the reaction after 40-80 min depends only slightly on the presence of aluminum. Apparently, copper is the only active metal. This result is not obvious because isomerization of DCB proceeds at a high rate at Lewis acid centers of aluminum halides or even of aluminum oxide.¹³ The absence of a strong effect of aluminum on the activity of the catalyst is apparently attributable to the fact that virtually all aluminum atoms in OMS are coordinatively saturated and do not exhibit pronounced Lewis acidity. Another important result, which calls for more detailed



Fig. 3. Kinetic curves of accumulation of *trans*-1,4-dichlorobutene-2 upon isomerization of 3,4-dichlorobutene-1

Curve	1	2	3	4	5	6
Catalyst	3	3	3	3	3	2
Cu content						
in a solution,						
10 ⁻³ /mol L ⁻¹	2.17	3.62	7.24	1.08	1.45	6.10

investigation, is the decreased activity (estimated from the conversion at specific intervals), which we observed in homogeneous solutions of OMS, compared to that observed previously for OMS supported on the surface of silica gel.²

Experimental

The IR spectra were recorded on a Specord M-82 instrument as Nujol mulls between KBr plates. The UV spectra were obtained on a Specord M-40 instrument in the range of 500-900 nm using a 0.1-cm cell.

The ESR spectra were recorded on a Brucker ER-200D radiospectrometer (3-cm range) using 4.0 mm-diameter thinwalled quartz tubes at 77 and 298 K. The magnetic field was calibrated using diphenylpicrylhydrazyl (g = 2.0036) and Mn^{2+} ions in the MgO matrix as the standards. The values of the g factor, g_{\parallel} and g_{\perp} , and the hyperfine interaction constant A_{\parallel} were calculated from the ESR spectra according to recommendations.¹⁴

Aluminocopperphenyl- and copperphenyloligosiloxanes were prepared according to a procedure reported previously.⁶ The intermediate compound, the cyclic sodium phenylsiloxanolate of composition [PhSi(ONa)O]₃ · 8 H₂O (5), whose structure has been reported previously,15 was synthesized according to a known procedure.¹⁶ Water of crystallization was removed by azeotropic distillation with p-xylene. A 5% solution of anhydrous metal halide in n-butanol was added with stirring to a 10% solution of dehydrated compound 5 in n-butanol (20 °C). In all cases, the exchange reaction was carried out using an initial reagent ratio such that the sodium to chloride ions ratio was equimolar. The completion of the exchange reaction was determined from attainment of neutrality of the aqueous extract of the reaction medium. The reaction mixture was stirred at 50-60 °C for 1 h and filtered off. The resulting filtrate was concentrated on a rotary evaporator to one-half of the initial volume. The final product was reprecipitated with hexane, filtered off, and dried in vacuo (15-20 Torr) at 100 °C. Oligomer 1 was prepared by the reaction of compound 5 (4.8 g, 10 mmol) with AlCl₃ (1.17 g, 8.8 mmol) and CuCl₂ (0.24 g, 18 mmol) in a yield of 3.2 g. Analogously, oligomer 2 was prepared from compound 5 (4.8 g, 10 mmol), AJCl₃ (0.8 g, 6 mmol), and CuCl₂ (0.81 g, 6 mmol) in a yield of 3.4 g. Oligomers 3 and 4 were prepared by fractional reprecipitation with hexane from a single reaction system (compound 5 (4.8 g, 10 mmol) and CuCl₂ (2.02 g, 15 mmol)) in yields of 3.6 and 0.8 g, respectively.

The experiments on isomerization of 3,4-dichlorobutene-1 were carried out in toluene solutions in sealed glass tubes. A weighed sample was dissolved in a solution of 3,4-dichlorobutene-1 in toluene with an initial concentration of olefin of 1.94 mol L^{-1} . Then the sample was rapidly heated to 100 °C (at room temperature, the rate of isomerization was negligibly small), kept at this temperature with intense stirring for a certain time, and rapidly cooled to room temperature. The content of the tube was analyzed by GLC (3700 chromatograph, flame ionization detector, column with 10% Silicon 8E-30 on Chromaton). Because the detector was equally sensitive to both isomers of DCB, their concentrations were determined from the ratio of the areas of the chromatographic peaks. Analysis with the use of the standard compounds demonstrated that the major isomerization product was the *trans*isomer of 1,4-DCB. The yield of the *cis*-isomer was no more than 5% of the total amount of 1,4-DCB.

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