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Evolution of Polycopperorganosiloxanes in the Course of a Catalytic Reaction of CCl_4 Addition to a Multiple Bond

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Abstract—The catalytic activity of linear and network oligomer copperorganosiloxanes immobilized on the surface of Silochrome in a reaction of CCl_4 addition to olefins was studied. It is likely that the reduction of Cu(II) ions to Cu(I) is a step in the catalytic radical reaction studied. This process also occurs in the absence of reagents at relatively low temperatures. The reaction occurs more readily in linear polycopperorganosiloxanes than in the network oligomers, which is consistent with the catalytic activity. The studied catalytic reaction is characterized by an unusual dependence of the activity of polycopperorganosiloxanes on metal concentration.

INTRODUCTION

Polycopperorganosiloxanes (PCOSs) immobilized on silica catalyze a number of organic reactions [1, 2]. It was found previously [2] that network and linear PCOSs (see the figure in [2]) catalyze the reactions of CCl_4 with alkanes (C–Cl bond metathesis). In this work, we examined the behavior of these compounds with the catalytic addition of CCl_4 to olefins of different structures.

It is well known that the formation of the $CCl_3^{\bullet}$ radical is the first step of the test reaction [3]. In the presence of copper compounds, the process primarily occurs in accordance with the following reaction scheme [4]:

$$\mathrm{Cu(I)} + \mathrm{CCl_4} \longrightarrow \mathrm{Cu(II)Cl} + \mathrm{CCl_3^{\bullet}},$$

$$\mathrm{CCl_3^{\bullet}} + \mathrm{RCH{=}CHR'} \longrightarrow \mathrm{RCH^{\bullet}CH(R')CCl_3},$$

$$\mathrm{RCH^{\bullet}CH(R')CCl_3} + \mathrm{Cu(II)Cl} \longrightarrow \mathrm{RCHClCH(R')CCl_3} + \mathrm{Cu(I)},$$

where Cu(I) and Cu(II)Cl are the reduced and oxidized forms of the catalyst, respectively.

The final step—the regeneration of Cu(I) ions—suggests a catalytic character of this process. It follows from the reaction scheme that the presence of Cu(I) ions in the system is necessary for initiating the reaction. Although PCOSs contain only Cu(II) ions [5], they also catalyze the process in the absence of reducing agents. In this work, to reveal the nature of this activity, we studied the transformations of structurally different PCOSs in the course of the CCl_4 reactions with 1-octene and allyl chloride

$$\mathrm{CCl_4} + \mathrm{C_6H_{13}CH{=}CH_2} \longrightarrow \mathrm{C_9H_{16}Cl_4},$$

$$\mathrm{CCl_4} + \mathrm{CH_2ClCH{=}CH_2} \longrightarrow \mathrm{C_4H_5Cl_5}.$$

Previously [6], in the reaction of CCl_4 with allyl chloride in the presence of copper compounds with donor ligands, we found unusual behavior (S-shaped kinetic curves, low rates of conversion as compared with other olefins, and unusual product composition) associated with the formation of a catalyst–substrate complex. A comparative study of these reactions for structurally different olefins may provide additional information on the mechanism of PCOSs transformations. It was also of interest to compare the catalytic activities of network PCOSs, in which the coordination number of copper is equal to 4, and linear oligomers, in which the coordination number can formally be equal to 2 in the absence of external donors.

EXPERIMENTAL

Oligomeric network and linear PCOSs were prepared according to published procedures [2, 5, 7, 8]. The table summarizes the composition of the test catalysts. The preparation of catalysts supported on a surface of Silochrome was described elsewhere [5].

The procedures of catalytic experiments, reaction conditions, and the analysis of products were analogous to those described in [6]. The reaction was performed in sealed glass ampules. The products were analyzed by GLC.

The EPR spectra were measured on a Varian E-3 radiospectrometer at 77 K using thin-walled tubes with i.d. 4 mm. To determine the numbers of paramagnetic centers in the samples, we used double integration of the spectra with respect to a side reference sample of

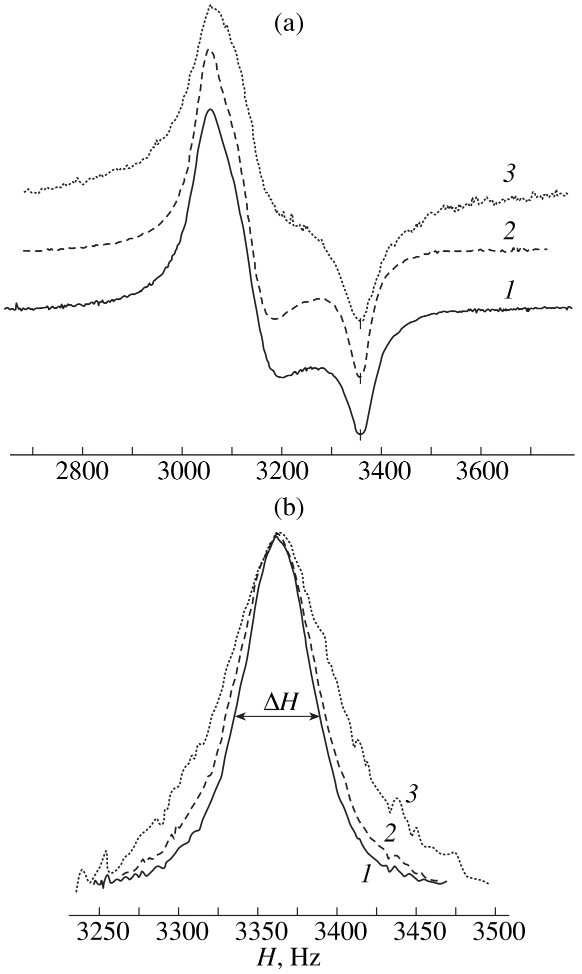

Fig. 1. EPR spectra of supported PCOS (sample 2) at 77 K: (a) (*1*) after long standing in air in the absence of reagents, (*2*) on the addition of allyl chloride and CCl_4, and (*3*) after thermostating at 130°C for 2 h; (b) line shapes of the high-field components of spectra *1–3* (line amplitudes are normalized).

ruby and a comparison with the signal from a $CuCl_2 \cdot 2H_2O$ single crystal with a known concentration of spins. The experimental spectra were treated with the use of an automated data acquisition system.

The diffuse reflectance spectra in the visible region were measured on an SF-17 instrument.

RESULTS AND DISCUSSION

Freshly prepared PCOSs immobilized on silica exhibited no signals in the EPR spectra. Although PCOSs contain only bivalent copper, it is likely that the majority of Cu(II) ions occur as Cu–O–Cu units, which are undetectable by EPR spectroscopy [5].

After being allowed o stay in air, the PCOS samples exhibited EPR signals from Cu(II) ions, whose amount was no higher than 5% of the total number of copper ions in the sample (Fig. 1, spectrum *1*). The evacuation of the catalyst at room temperature resulted in the disappearance of the EPR spectrum. The spectrum appeared again when the samples contacted with substances prone to coordination with Cu(II) ions, for example, DMF or H_2O. Thus, the appearance and disappearance of an EPR signal under these conditions is completely reversible. We believe that the coordination of an additional ligand molecule may affect the geometry of the environments of some (probably, terminal) copper ions, which are more weakly bound to oxygen in PCOSs.

The thermostatting of polyphenylorganosiloxanes (above 150 or 70°C for network or linear compounds, respectively) in a vacuum resulted in the following changes, which are indicative of the reduction of Cu(II) to Cu(I): (1) the bands due to *d–d* transitions at 750–800 nm, which were detected in an initial catalyst, disappeared from the electronic diffuse-reflectance spectra; and (2) with the addition of a water–alcohol solution of *ortho*-phenanthroline, which slowly decomposes PCOSs, in the absence of oxygen, an absorption band with a maximum at 450 nm, which is typical of Cu(I) complexes with nitrogen-containing ligands [9], appeared in the optical spectra. In the spectra of thermally untreated samples, only absorption at 600 nm, which is characteristic of Cu(II) complexes, was observed upon the addition of *ortho*-phenanthroline.

Generally, it is evident that the reduction of copper ions, which is required for the catalytic reaction under study, occurs in the thermal treatment of PCOSs even in

Composition and structure of test PCOS

Sample no.	Structure	Organic substituent	Cu content, wt %		Si/Cu,* atom/atom
			of initial PCOS	of supported catalyst	
1	Network	Ph	18.1	2.30	2.15
2	Linear	Ph	5.0	0.86	6.00
3	Linear	Me	11.2	0.60	6.50
4	Linear	Ph	5.0	0.47	6.00
5	Linear	Ph	5.0	0.27	6.00

* In the initial compound.

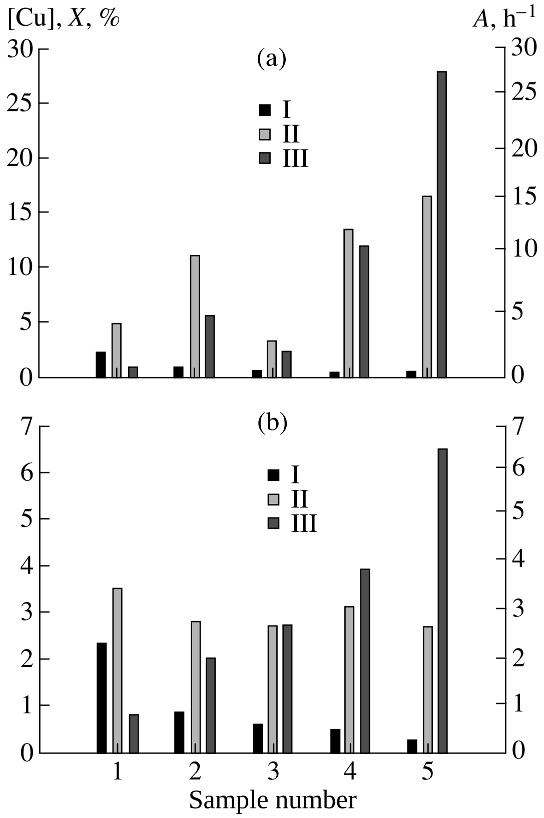

Fig. 2. Catalytic activity of supported PCOS in the reaction of CCl_4 addition to (a) 1-octene or (b) allyl chloride: (I) [Cu], %; (II) X, %; (III) A, h^{-1}. Reaction conditions: 0.05 g of PCOS; 0.05 g of an olefin; 0.45 ml of CCl_4; reaction temperature, 130 (with octene) or 140°C (with allyl chloride).

the absence of substrates. In this case, linear PCOSs are reduced much more easily than the network oligomers.

Figure 2 illustrates data on the catalytic activity of PCOSs in the reaction of CCl_4 with octene. For catalyst samples 1–5, we estimated the olefin conversion (X) in 1 h of reaction and the specific activity $A = ([Ol]_0 - [Ol])/([Cu]t)$, h^{-1}, where $[Ol]_0$ and [Ol] are the initial and final olefin concentrations, respectively; [Cu] is the catalyst concentration; and t is the reaction time. It can be seen in Fig. 2 that linear PCOSs are more active than network PCOSs, all other factors being the same; with linear PCOS, phenyl derivatives are more active than methyl derivatives (samples 2 and 3). Because the reaction also occurred with a low yield on the pure support at temperatures above 140°C, the conversion of allyl chloride on a PCOS was determined by subtracting the conversion on SiO_2 from the total conversion of the olefin.

The reaction of allyl chloride with CCl_4 was slow on all of the examined siloxanes (in 3 h, the conversion was no higher than 10%). The product composition was also significantly different from that in the rapid process with the participation of octene. Along with the addition of CCl_4, the additive and substitutive chlorination to form di- and trichloropropanes also took place. In contrast, 1,1,1,3-tetrachlorononane was the only reaction product in the case of octene. The product composition was almost independent of the structure of the siloxane.

In our opinion, the activity of network PCOSs is low because the Cu atom in network PCOSs is strongly coordinated to four oxygen atoms, whereas the reduction of the Cu(II) ion results in the formation of an anionic complex of Cu(I), for which a coordination number of 2, or more rarely 3, is typical [10]. Thus, the reduction of Cu(II) ions required for the catalytic process will be accompanied by the degradation of a PCOS network to hinder the reaction.

The reduction of Cu(II) can take place by the interaction with both organic groups of the siloxane and an olefin. The low activity of a PCOS in a reaction of CCl_4 with allyl chloride suggests that the olefin can hinder the formation and regeneration of active centers of the catalyst. Indeed, in the initiation of the reaction with benzoyl peroxide (i.e., with no catalyst), the rate of allyl chloride conversion was half as high as the rate of 1-octene conversion. The difference in the rates of these reactions was much greater in the case of PCOSs (Figs. 2a and 2b). Taking into account the considerable difference in product compositions, we can state that the above processes occurred via different mechanisms and the PCOSs underwent different transformations in these processes. This conclusion is consistent with the EPR data given below.

With the addition of CCl_4, 1-octene, or their mixtures to freshly prepared PCOS, the EPR spectrum can not be detected before or after reaction. At the same time, the addition of an allyl chloride–CCl_4 reaction mixture to, for example, linear polycopperphenylsiloxane (sample 2) resulted in the appearance of a spectrum (Fig. 2, spectrum *2*). The EPR spectrum of the catalyst was changed after 2 h of reaction (Fig. 2, spectrum *2*). This change manifests itself in a considerable broadening of the spectral line, probably, because of an increase in the dipole–dipole interaction. This fact is indicative of a decrease in the average distance between paramagnetic copper ions. After standing for 2 to 3 days in a reaction solution containing allyl chloride even at room temperature, the concentration of EPR-detectable copper ions in the catalyst further increased to reach 12% of the total metal content of the sample.

It is likely that copper ions are reduced by the interaction with organic groups of the siloxane. If olefins participated in the reaction at this step, we might expect the appearance of products of their oxidation in detectable amounts; however, this was not the case. Moreover, as demonstrated above, the reduction also readily takes place in the absence of reagents. The reaction mechanism remains unclear. However, it is evident that the nature of a substituent at the silicon atom will affect the reducibility and hence the catalytic activity of PCOS. Indeed, it can be seen in Fig. 2 that the replacement of phenyl groups with methyl groups decreases the catalytic activity of supported PCOSs in the reaction of CCl_4 with octene by a factor of more than two.

In addition to the catalyst structure and the nature of organic substituents, the metal content is a significant factor affecting the catalytic activity of siloxanes (Fig. 2). An opposite effect of copper concentration on the catalytic activity of PCOSs was also observed in other reactions with the participation of PCOSs [2]. It is our opinion that the dramatic decrease in the activity with increasing metal content of the catalyst can be explained by metal association to low-activity bridged structures. In this case, the coordination number of copper inevitably increases even in the case of initial linear PCOS. This is consistent with the fact that the formation of polynuclear copper complexes in the reaction of CCl_4 with allyl chloride inhibits the reaction via a free-radical mechanism [6]. Thus, substrates with low ability to coordinate metal ions and catalysts with low coordination numbers of the metal ion should be used to efficiently perform the reaction. These factors are primarily responsible for the activity of immobilized PCOSs in the synthesis and conversion of chlorinated hydrocarbons.

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