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Intermolecular rearrangement of cobalt phenylsiloxanes

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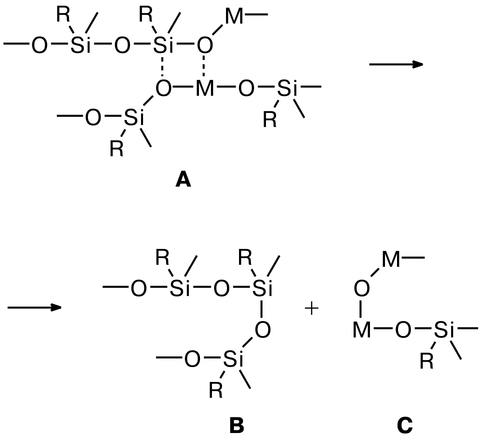
Intermolecular rearrangement of cobalt phenylsiloxanes was studied. The rearrangement leads to the formation of compounds with metal oxide moieties in the organosiloxane structure and is accompanied by a change in the spectral characteristics of cobalt(II), determined by the second coordination sphere of the metal. The rate-determining step is the decomposition of an intermediate complex formed upon the coordination of the metal siloxane moieties.

Key words: metal-containing organosiloxanes, cobalt(II), UV spectroscopy, IR spectroscopy, kinetics of rearrangement.

The intermolecular rearrangement of metal-containing organosiloxanes leading to the metal redistribution in the siloxane matrix proceeds through the formation of intermediate coordination complex **A** and its transformation into oligosiloxanes **B** and **C** *via* the scheme[1]



M = Fe, Co, Ni, Cu

The formation of the metal oxide moieties —M—O—M— due to the rearrangement was confirmed by magnetic measurements[2] and, in some cases, by X-ray diffraction studies.[3] To date, the rearrangement has been demonstrated mainly for examples comparing compositions of the starting and target products.[1]

In this work, the kinetics of this process and details of its mechanism were studied for the first time. The most appropriate compounds for the study are cobalt organosiloxanes, because they are characterized by the easiest deep rearrangement affording a compound with a high metal content and simultaneously polysiloxane containing no metal.[4] Changes accompanying this process can be detected by spectroscopy.

It has previously been found that the $\mathrm{Co^{II}}$ atom in the siloxane structure can be in the hexa-[5] and tetracoordinate[6] states, and the tetracoordinate state is formed in the presence of highly basic silanolate anions and does not tend to rearrangement. Therefore, cobalt phenylsiloxanes (CPS) containing no stabilizing silanolate anions were chosen for the study. The CPS were synthesized *via* metathesis of metal halide with the crystal solvate of sodium organosilanolate

$$2/3\,n\,[\mathrm{PhSi(ONa)O}]_3\cdot 6\mathrm{PrOH} + n\,\mathrm{CoCl_2} = \underset{\mathbf{1}}{[(\mathrm{PhSiO_{1.5}})_2(\mathrm{CoO})]_n} + 2n\,\mathrm{NaCl} + 6n\,\mathrm{PrOH}.$$

The resulting compound **1** is unstable on boiling in nonpolar solvents and rearranges to CPS with an increased metal content and polysiloxane containing no metal

$$\underset{\mathbf{1}}{[(\mathrm{PhSiO_{1.5}})_2(\mathrm{CoO})]_n} \longrightarrow n/m\,\underset{\mathbf{2}}{[(\mathrm{PhSiO_{1.5}})(\mathrm{CoO})]_m} + n/k\,(\mathrm{PhSiO_{1.5}})_k.$$

The UV spectra of compound **1** contains a band at 565 nm with the molar absorption coefficient ε = 20.3 L (mol cm)$^{-1}$. This band is characteristic of hexacoordinate $\mathrm{Co^{II}}$ complexes,[7] which is confirmed by the low ε value (for the tetracoordinate Co complexes, ε is 1—2 orders of magnitude higher[8]). The rearrangement of compound **1** to **2** is accompanied by a decrease in the intensity of this band, which was spectrally detected.

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Below we present a change in the absorbance of the band at 565 nm (*A*) for a solution of CPS **1**.

τ/min	0	840	1320	2190	2640
A	0.48	0.38	0.35	0.27	0.24

The decrease in the intensity of the band at 565 nm is accompanied by the appearance of a band at 370 nm, which is also attributed to hexacoordinate Co complexes.[8] However, measurements in this region are impeded due to a disguising influence of the intense absorption band of the solvent.

It can be assumed that differences between the Co^{II} ions in compounds **1** and **2**, being in both cases in hexacoordinate complexes $[CoO_6]$, are determined by the second coordination sphere. In other words, in compound **1** the O atoms of the coordination sphere are in metal siloxane moieties Si—O—Co, whereas in compound **2** the most part of coordinated O atoms compose metal oxide moieties Co—O—Co. A similar difference (without estimation of the process kinetics) has previously[9] been detected spectrally using γ-resonance spectroscopy for the Fe^{III} complexes in the organosiloxane structure.

A linear plot $\ln D_0/D_\tau$—τ was obtained from the UV measurements (Fig. 1).

This plot formally corresponds to the first order of a reaction with an average apparent constant of $4.5(\pm 0.5)\cdot 10^{-6}\cdot s^{-1}$. The first order of the reaction indicates that the rate-determining step of the rearrangement is the decomposition of an intermediate complex to form compounds with an increased (compared to the initial value) metal content.

Since the changes observed could be a consequence of a possible oxidation of cobalt(II), we measured effective magnetic moments μ_{eff} for compounds **1** and **2**. The μ_{eff} values were obtained at 296 K and amounted 3.92 μ_B for **1** and 4.12 μ_B for **2** (theoretical value μ = 3.87 μ_B). They indicate that high-spin paramagnetic Co^{II} ions with configuration d^7 are present in both cases, and in the second case, the content of the ferromagnetic component is somewhat higher, which is characteristic of CPS with metal oxide moieties.[2]

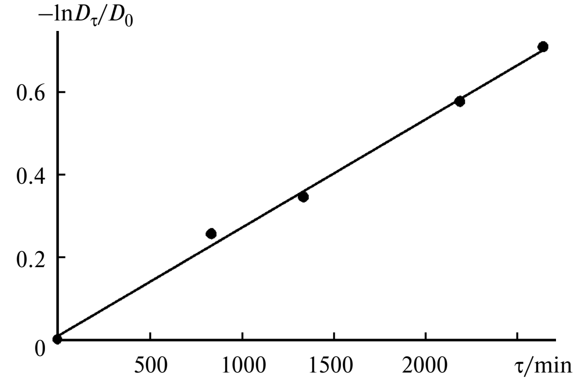

Fig. 1. Kinetic plot for the rearrangement of compound **1** to **2**.

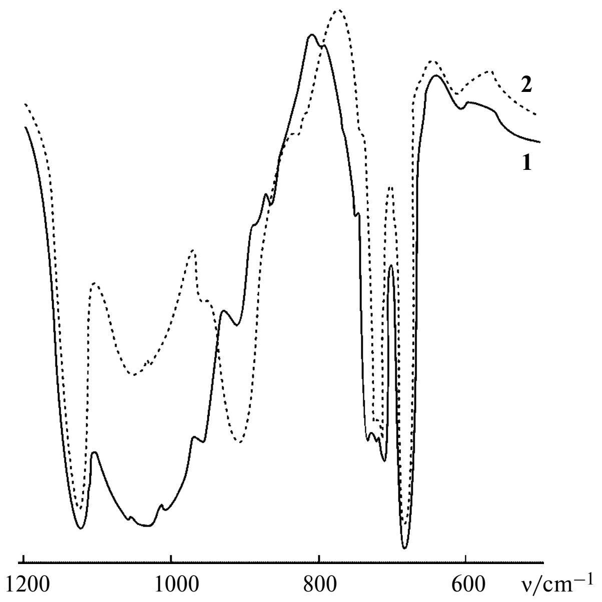

Fig. 2. IR spectra of compounds **1** and **2**.

The IR spectra of compounds **1** and **2** contain coinciding bands at 1120 cm^{-1} (Ph—Si group) and at 720 cm^{-1} and 680 cm^{-1} (monosubstituted Ph ring), and differences are observed in a region of 900—1000 cm^{-1} (Fig. 2.).

The IR spectrum of compound **1** exhibits a broad intense band at 940—1100 cm^{-1} (vibrations of the Si—O—Si groups), which partially disguises a band at 900 cm^{-1} (vibrations of the Si—O—Co group). The spectrum of compound **2** contains a band at 940—1100 cm^{-1} with a lowered intensity and an intense band at 900 cm^{-1}. These differences resulted from the rearrangement decreasing the silicon content and increasing the metal content. The spectral data indicate that compound **2** contains a noticeable number of Si—O—Si units, which, being compared with the composition of this compound (atomic ratio Si : Co ≈ 1), can confirm additionally that complex **2** contains the metal oxide moieties Co—O—Co.

Thus, the rearrangement found affords compounds containing highly basic O atoms of the metal oxide groups in the coordination sphere of the metal, which appears as a change in the spectral characteristics of the coordination entity $[CoO_6]$. The rate-determining step of the process is the decomposition of the intermediate complex formed upon the coordination of the metal siloxane moieties of CPS.

Experimental

IR spectra were recorded on a Specord M-82 spectrometer for samples as a suspension in Nujol between KBr plates. UV spectra were obtained on a Specord M-40 spectrophotometer in an interval of 300—700 nm for a solution of compound **1** in toluene with a concentration of 0.237 moles of Co^{II} L^{-1} using a quartz cell with an optical path length of 0.1 cm.

The magnetic susceptibility χ was measured on a VSM-155 vibromagnetometer. Effective magnetic moments were calculated by the Curie formula: $\mu_{eff} = \sqrt{(3KT_{\chi})/N}$, where χ is the specific magnetic susceptibility, K is the Boltzmann constant, T is temperature (K), and N is the number of metal atoms.

Cobalt phenylsiloxane 1 was obtained by the reaction of $[PhSi(ONa)O]_3 \cdot 6PrOH$ [2] (8.4 g, 10 mmol) dissolved in a mixture of toluene (20 mL) and propanol (15 mL) with $CoCl_2$ (1.95 g, 15 mmol) in propanol (15 mL). The reaction was carried out with a permanent pH control of the aqueous extract to achieve an equimolar Na^+ to Cl^- ratio in the reaction system. The addition of cobalt(II) halide was ceased after a neutral reaction medium was attained. After NaCl separation, the target product was precipitated from the reaction mixture with excess heptane. The light blue amorphous product was dried *in vacuo*. The yield was 4.55 g (91%). Found (%): Si, 17.05; Co, 17.20. $C_{12}H_{10}O_4Si_2Co$. Calculated (%): Si, 16.85; Co, 17.68.

Cobalt phenylsiloxane 2 was obtained by the dissolution of compound **1** (4.05 g) in toluene (50 mL). The resulting solution was used for UV spectral studies. Then it was concentrated to 15 mL and refluxed for 17 h until an insoluble precipitate formed. The precipitate was separated from the solution by centrifuging, washed with toluene, and dried *in vacuo*. The dark green amorphous product was obtained in 91% yield (2.25 g). Found (%): Si, 14.06; Co, 28.12. $C_6H_5O_{2.5}SiCo$. Calculated (%): Si, 13.76; Co, 28.87. The solution obtained after the separation of CPS **2** was concentrated and precipitated with heptane. The yield of a colorless resin-like product was 1.39 g (89%). Found (%): Si, 21.10; C, 56.21. $C_6H_5O_{1.5}Si$. Calculated (%): Si, 21.74; C, 55.78.

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