Organometallic Chemistry

The photochemical interaction of polyphenylferrisiloxane with oligoorganosilanes

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The photochemical interaction of polyphenylferrisiloxane with some oligoorganosilanes in benzene solutions has been studied by UV, IR, ESR, and Mössbauer spectroscopy. Silylene species formed during photolysis of oligoorganosilanes react with the high-spin iron(III) to reduce the latter to low-spin iron(II). The formation of the low-spin state of iron(II) was supported by measurements of the magnetic moments. The insertion of the silylene species into the polymer chain to form the Fe—Si bond occurs due to the photoreaction.

Key words: polyphenylferrisiloxane, oligoorganosilanes, silylenes, magnetic moments, Mössbauer spectra.

Polyorganometallosiloxanes containing paramagnetic metal atoms are very promising from the viewpoint of preparation of artificial ferromagnetic materials.[1] One of these processes is the high-temperature pyrolysis of polyferri- and polycobaltoorganosiloxanes[2—4] resulting in the combination of paramagnetic atoms, which leads to the exchange interaction. Photochemical transformations of metallopolymers can also be a possible route for synthesis of magnetically ordered structures. However, data on photochemical reactions of polyorganometallosiloxanes are lacking. The photochemical reactions of transition metal compounds containing the disilanyl group resulting in the formation of stable silylene—transition metal complexes have been studied.[5] These processes have been studied in detail for iron derivatives, which are characterized by the stabilization of the metal atom by the cyclopentadienyl group and two carbonyl groups.[5] The photoreactions of high-spin iron(III) with oligoorganosiloxanes are not studied.

In this work, we studied for the first time the photochemical behavior of polyphenylferrisiloxanes (PPFS) in benzene solutions in the presence of several oligoorganosilanes. The latter, as known,[6] are sources of generated silylenes.

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Experimental

Samples of PPFS containing 9.56 and 15.76 wt.% iron prepared by the previously described procedure were studied.[1] The following oligoorganosiloxanes synthesized by known procedures were used: 2-phenylheptamethyltrisilane,[7] tris(trimethylsilyl)phenylsilane,[8] and dodecamethylcyclohexasilane.[9]

A PRK-4 medium-pressure mercury lamp (200 W) was used as the UV source.

Photolysis was carried out at a distance of 15 cm from the UV source in a sealed evacuated quartz ampule with continious cooling and stirring of the reaction mixture. The time of irradiation was 5—7 h.

The reaction product was precipitated *in vacuo* from an irradiated benzene solution of PPFS using thoroughly degassed hexane. It is a grayish powder, which slowly acquires an orange color during long exposure in air.

Mössbauer spectra were recorded on an MS-11013 spectrometer. Samples were prepared (in an argon atmosphere) in paraffin as pellets or in special cells as a powder. Sources of ^{57}Co in the Rh matrix with an activity of ~10 mCi were used. Mössbauer spectra were decoded by the SPECTR program (in the MSTools program complex[10]) developed in the Department of Physics, M. V. Lomonosov Moscow State University. The values of isomeric shifts are presented relative to α-Fe.

Magnetic moments were measured at 300 K by the Faraday method using a Setaram MTB-8 microbalance. Electronic absorption spectra were obtained on a Specord M-40 spectrophotometer. IR spectra were recorded on a Perkin—Elmer 577 instrument. ESR spectra were recorded on a Bruker ER200D spectrometer.

GLC analysis was carried out on a Tsvet-530 chromatograph (stainless steel column 0.3×200 cm, 5% SE-30 on solid Chromaton-N-AW-DMCS carrier, katharometer).

Results and Discussion

The capability of iron(III) to be reduced due to UV irradiation of its solutions has long been known.[11] Many organic substances, in particular, aromatic hydrocarbons, can serve as reducing agents.

We irradiated solutions of PPFS in benzene (5—10%) with UV light for a long time, but observed no properties of iron reduction. However, the addition of an equimolar (to the iron content) amount of 2-phenylheptamethylsilane to the system results rapidly in a change in the color of the irradiated solution from orange-brown to dirty-green (9.56 wt.% Fe) or greenish-black (15.76 wt.% Fe). A band at 670 nm, which was not observed in the spectrum of the starting PPFS, appears in the absorption spectrum of the solution. The chromatographic analysis of the irradiated solution showed that the reaction mixture contained no volatiles except hexamethyldisilane, whose amount corresponded to the complete photodecomposition of the initial trisilane according to the reaction

$$\mathrm{Me_3Si{-}SiMePh{-}SiMe_3} \xrightarrow{h\nu} \mathrm{:SiMePh + Me_3Si{-}SiMe_3}. \quad (1)$$

Similar phenomena were observed when other oligoorganosilanes were used, whose photodecomposition, as known,[6] is also accompanied by elimination of silylene:

$$\mathrm{(Me_3Si)_3SiPh} \xrightarrow{h\nu} \mathrm{:SiPhSiMe_3 + Me_3Si{-}SiMe_3}, \quad (2)$$

$$\mathrm{(Me_2Si)_6} \xrightarrow{h\nu} \mathrm{:SiMe_2 + (Me_2Si)_5}. \quad (3)$$

The product of the photochemical reaction is very sensitive to oxygen: the greenish color soon disappears in air, and the solution again becomes orange-brown. This suggests that the silylene species formed during the photolysis of oligoorganosilanes (reactions (1)—(3)) can reduce iron(III) contained in PPFS.

It was of interest to isolate the photoreaction product in the solid state and analyze it by Mössbauer spectroscopy in order to determine reduced forms of iron.

The Mössbauer spectrum of the PPFS sample isolated after the photochemical reaction with 2-phenylheptamethylsilane is presented in Fig. 1. The spectrum was recorded under conditions excluding oxidation, and its analysis showed the validity of the model (χ^2 = 0.99) providing for the presence of two main doublet forms (see Fig. 1, curves *2* and *3*), whose Mössbauer parameters are presented in Table 1.

It is noteworthy that the sample does not contain high-spin iron(II), whose region of isomeric shifts[12] does not include the values presented in Table 1. However, it is difficult to assign unambiguously the observed forms

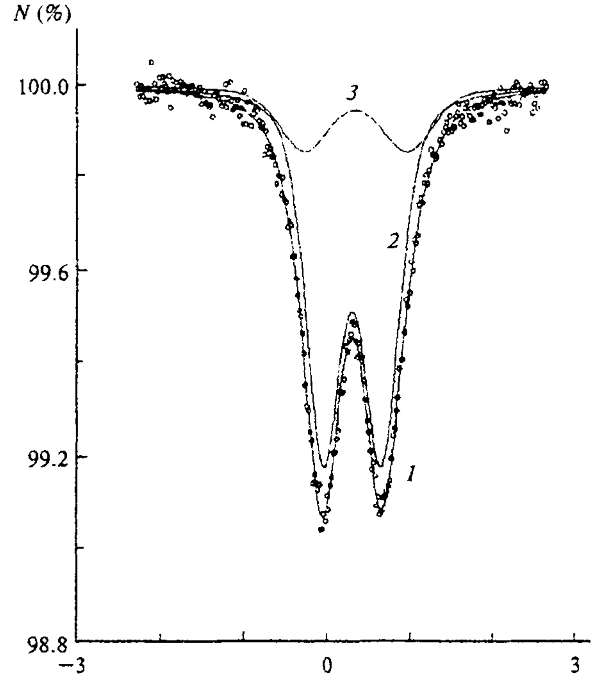


Fig. 1. Mössbauer spectrum of the product of the photoreaction of PPFS with 2-phenylheptamethyltrisilane (*1*) and partial spectra of suggested iron forms (χ^2 = 0.99) (*2* and *3*).

Table 1. Parameters of Mössbauer spectra and effective magnetic moments of iron (μ) in the initial PPFS (**1**) and product of the photoreaction (**2**)

Sample[a]	Partial doublet	IS[b]	QS[c]	S^d (%)	μ /μ_B
		mm s^{-1}			
1	*1*	0.33(2)	0.68(1)	84(1)	4.3(1)
	2	0.35(2)	1.3(2)	16(1)	
2	*1*	0.32(1)	0.70(1)	79(1)	1.9(1)
	2	0.36(1)	1.2(2)	21(2)	

[a] Iron content 9.56 wt.%. [b] Isomeric shift relative to α-iron. [c] Quadrupole splitting. [d] Fraction of partial doublet.

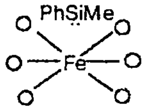
of iron on the basis of only Mössbauer spectroscopic data, because the Mössbauer parameters obtained can correspond to both low-spin iron(II) and high-spin(III) in the octahedral oxygen environment.

The ambiguity that appeared was eliminated by measuring the effective magnetic moments of iron in the samples of the initial and irradiated ferrisiloxane. Their values presented in Table 1 indicate that the low-spin form of iron is formed during the photochemical reaction. The starting ferrisiloxane and isolated product have similar Mössbauer spectra (see Table 1). Only some increase in the content of the doublet form with a higher quadrupole splitting is observed in the sample of irradiated PPFS. Thus, high-spin iron(III) in the starting ferrisiloxane is transformed into low-spin iron(II) due to the photochemical reaction.

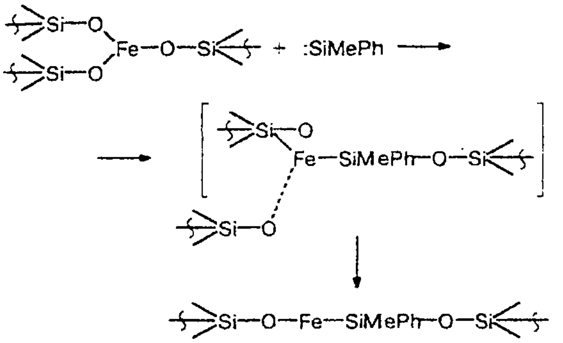
This conclusion agrees with the data of ESR spectroscopy. No ESR signals were observed in the starting PPFS at room temperature, which is typical of high-spin compounds of both tri- and bivalent iron. According to the available data,[1] the ESR spectra of the starting PPFS at low temperatures correspond to the spectra of the Fe^{3+} ions (high-spin d^5-configuration in weak crystalline field) and exhibit a signal with g = 2.003—2.006 close to the g-factor of free electron. At the same time, in the presence of 2-phenylheptamethyltrisilane, UV-irradiated benzene solutions of PPFS give at room temperature distinct ESR signals with the values of the g-factor different substantially from that presented above: for the sample containing 9.56 wt.% iron, g = 2.136; for the metal content of 15.76 wt.%, $g_\parallel$ = 2.48 and $g_\perp$ = 1.96. The anisotropy of magnetic properties observed for the sample with a higher content of iron should be mentioned. Perhaps, this is related to the formation of sufficiently large colloidal species containing paramagnetic atoms during the photolysis.

A noticeable deviation of the observed values of the g-factor from those typical of free electron confirms the formation of the covalent Si—Fe bond. It can be assumed that the reaction starts from the direct interaction of an electron pair of the silylene species with the d-orbitals of the iron atom in the octahedral oxygen environment.

The subsequent transformation of the intermediate



results in the formation of the σ-Fe—Si bond and rearrangement of siloxane units coordinated on the iron ion. The reduction of high-spin Fe^{III} in PPFS to low-spin Fe^{II} by the silylene species can be described by the following simplified scheme:



(4)

In fact, the band at 1250 cm^{-1} (Si—Me) appears in the spectrum of the photoreaction product precipitated with hexane. This band is absent in the starting PPFS and indicates that the silylene species is inserted into the polysiloxane chain.

The hydrolysis of the photoreaction product is chemical evidence for the formation of the Fe—Si bond. For example, the treatment of the reaction mixture *in vacuo* with acidified EtOH results in the appearance of a band at 2100 cm^{-1} (assigned to vibrations of the Si—H bond) in the IR spectrum of the product of reaction (5).

$$\geqslant\text{Si—Fe—} + \text{EtOH} \xrightarrow{H^+} \geqslant\text{Si—H} + \text{—FeOEt} \qquad (5)$$

It is noteworthy that the formation of the $\geqslant$Si—H groups cannot be explained by the insertion of silylene at the O—H bond of the hydroxyl groups of PPFS, since this band was not observed before hydrolysis in the spectrum of the photoreaction product.

Thus, we succeeded in preparing and isolating a stable compound containing the covalent Fe^{II}—Si bond stabilized in the polysiloxane matrix by the photochemical reactions of PPFS with oligoorganosiloxanes.

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