Brief Communications

Use of 1,4-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)butane as a probe for studying acid sites

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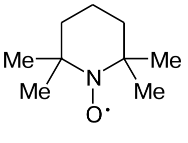
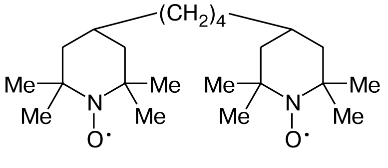
ESR spectroscopy was applied to study paramagnetic complexes of the nitroxyl biradical of 1,4-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)butane formed with $AlCl_3$ in a toluene solution and resulted from the interaction with the acid sites on the SiO_2 and γ-Al_2O_3 surface. This biradical in solution forms a complex with two $AlCl_3$ molecules, and a complex with two hydroxyl groups is formed on the SiO_2 surface. When the biradical is adsorbed on the γ-Al_2O_3 surface, complex formation is complicated because of steric hindrance preventing bidentate coordination.

Key words: 1,4-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)butane, paramagnetic complexes, aluminum chloride, silica, alumina, electron paramagnetic resonance.

Stable nitroxyl radicals, in particular, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), are widely used as spin probes for studying acid properties of the surface of heterogeneous catalysts and supports. Information on the structure of electron-acceptor sites and their strength and concentration can be obtained using nitroxyl radicals.[1] The nitroxyl radicals containing one >NO group are usually adsorbed *via* one-center mechanism. Two-center adsorption is often observed for the nitroxyl radicals containing another donor group in addition to >NO.[1,2] Therefore, it seemed of interest to study 1,4-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)butane (thereafter biradical **1**) containing two >NO groups as a probe. These groups are simultaneously radicals and electron-donors. A molecule of this biradical contains no other heteroatoms. Two NO-containing moieties, which structurally resemble TEMPO, are linked with each other through a mobile aliphatic hydrocarbon chain.



TEMPO



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Biradical **1** has previously been studied as an efficient inhibitor of radiation-chemical aging of *n*-octane[3] and

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a paramagnetic probe for studying conformational changes in Na,K-dependent ATPase.[4]

Experimental

The adsorbents used were γ-Al_2O_3 (trade mark A-1, Fe^{3+} content < 0.005 wt.%, S_{sp} = 185 $m^2 g^{-1}$) and SiO_2 (S_{sp} = 330 $m^2 g^{-1}$) prepared by hydrolysis of tetraethoxysilane (analytical purity grade) followed by drying and calcination at 773 K for 5 h.

Aluminum chloride was synthesized by the reaction of aluminum metal with gaseous chlorine and purified by sublimation.

The specific surface was measured on a GKh-1 gas meter by the chromatographic method using low-temperature adsorption (77 K) of nitrogen (using an N_2 (6 mol.%)—He mixture) followed by desorption at room temperature (from the desorption peak value).

The TEMPO radical was synthesized at our Laboratory using a known procedure.[5] TEMPO is represented by transparent dark red prisms with strong camphor odor (m.p. 311 K). Biradical **1** synthesized by an earlier published procedure[6] was kindly presented by A. I. Kokorin (N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences). Toluene (reagent grade) was purified by distillation and drying above sodium.

Samples of oxides were thermally treated (2 h in air and 2 h under 10^{-5} Torr at 743 K) in glass ampules equipped with a side branch with a sealed tube containing a glass ball. After the treatment was completed, the ampule was sealed from the vacuum setup, and the sample was transferred to the side branch, which was then sealed *in vacuo*. Glass balls with a toluene solution of biradical **1** (10^{-3} mol L^{-1}) were specially prepared. Then the balls with biradical **1** and adsorbent were transferred to an evacuated glass system with a branch, being simultaneously an ESR tube, where the balls were broken with magnetic bullets. The adsorbent and a solution of biradical **1** were mixed in the ESR tube, which was then sealed off.

ESR spectra were recorded on RE-1306 and Bruker EMX-6/1 radiospectrometers at a frequency of 9.5 GHz (in the X-range).

The ESR spectra were simulated using the SimFonia program.[7]

Results and Discussion

The spectra of the free biradical and complexes of TEMPO and biradical **1** with aluminum chloride in a toluene solution are shown in Fig. 1. The spectrum of biradical **1** in solution at 293 K (see Fig. 1, curve *1*) exhibits five components with a successive spacing of 7.9 G, which agrees with the literature data.[3] This spectrum pattern indicates spin exchange between the radical moieties upon their collision.[8,9] The $a_{iso}{}^{N}$ value (isotropic HFC constant with the ^{14}N nucleus) is 15.8 G. The interaction with $AlCl_3$ increased the $a_{iso}{}^{N}$ value to 20.7 G and resulted in the appearance of the HFS from the ^{27}Al nucleus ($a_{iso}{}^{Al}$ = 9.6 G). The ESR spectrum with similar magnetic resonance parameters is also observed for the complex of TEMPO with $AlCl_3$ (see Fig. 1). This suggests that the both nitroxyl groups of biradical **1** form complexes with $AlCl_3$ in solution. Spin exchange in the complex of biradical **1** with $AlCl_3$ is not manifested because, most likely, collisions of the radical moieties stop to occur. However, due to the dipole-dipole broadening, the ESR spectrum of the complex of biradical **1** has a broader linewidth (6.9 G) than that in the case of the TEMPO complex (3.4 G). For the TEMPO complex with $AlCl_3$ in a CCl_4 solution, the HFC constants are[10] $a_{iso}{}^{N}$ = 19.86 G and $a_{iso}{}^{Al}$ = 8.80 G, being somewhat lower than those measured in the present work. This is caused, most likely, by the solvation of the >NO groups by toluene molecules (dipole moment 0.37 D),[11] which is not manifested in a CCl_4 solution (dipole moment is zero). The spectra of the complexes of biradical **1** and TEMPO with $AlCl_3$ at low temperature are also similar, which agrees with the assumption on the formation of similar complexes by both >NO groups in biradical **1** (each group coordinates with one $AlCl_3$ molecule). Evidently, complex formation of biradical **1** and TEMPO in solution

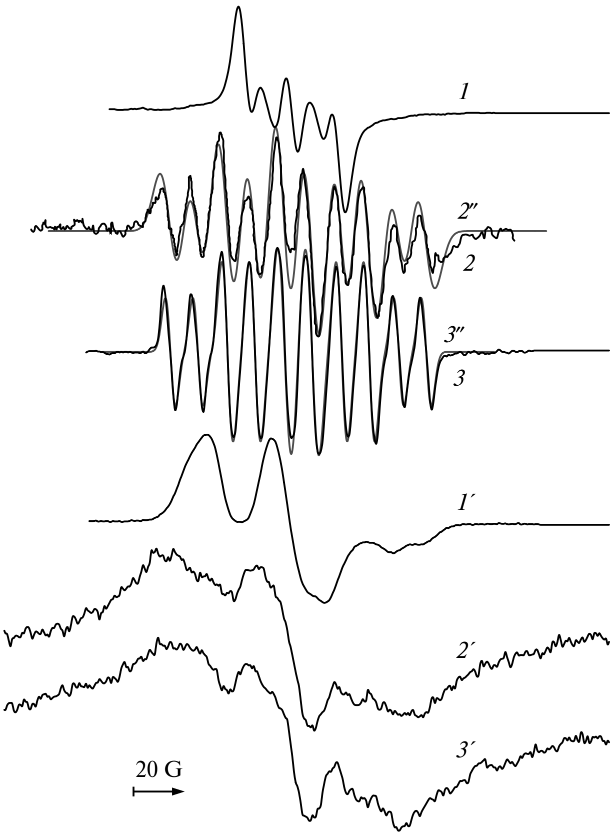

Fig. 1. ESR spectra of 10^{-3} *M* toluene solutions of biradical **1** (*1*, *1′*) and the complexes of biradical **1** (*2*, *2′*) and TEMPO (*3*, *3′*) with aluminum chloride at 293 (*1—3*) and 77 K (*1′—3′*). The model spectra are shown by dashed lines (*2″*, *3″*).

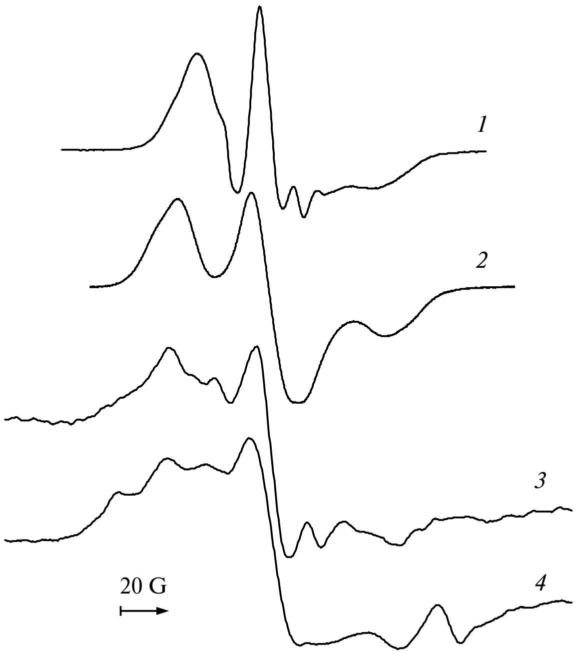

Fig. 2. ESR spectra of biradical **1** adsorbed on the SiO_2 (*1*, *2*) and Al_2O_3 (*3*, *4*) surface recorded at 293 (*1*, *3*) and 120 K (*2*, *4*).

occurs similarly, and both >NO groups can simultaneously form complexes.

The spectrum of biradical **1** adsorbed on the SiO_2 surface (Fig. 2) indicates restricted rotational mobility of the probe compared to the spectrum of free biradical **1** in solution. This is related, most likely, to the interaction of the >NO groups with the hydroxyl groups of the surface. It is known[1] that the interaction of TEMPO with the hydroxyl groups of the SiO_2 surface increases the HFC constant with the ^{14}N nucleus ($A_{\parallel}^{N}$) from 34.6 G (in a toluene solution) to 38 G. In the case of TEMPO, the $A_{\parallel}^{N}$ value can be determined by measuring a half of the distance between the ultimate extremes in the spectrum recorded at low temperature (usually 77 K). It could be expected that complex formation with the silanol groups would increase the $A_{\parallel}^{N}$ value in the case of biradical **1**. In fact, the distance between the ultimate components in the spectrum of the complex of biradical **1** on the SiO_2 surface (see Fig. 2, curve *2*) is longer than that for free biradical **1** in a toluene solution (see Fig. 1, curve *4*). Exact measurement of $A_{\parallel}^{N}$ is difficult because of dipole-dipole splitting D that bifurcates the ultimate components of the spectrum. Simulation of the spectra under assumption of $D = 3$ G and Lorentz lineshape suggested that the $A_{\parallel}^{N}$ value is 35 G for free biradical **1** and 38 G for the complex on the SiO_2 surface. This conclusion agrees with the data[9] according to which the bi- and monoradicals are solvated similarly.

It is most likely that the increased $A_{\parallel}^{N}$ value indicates the formation of both >NO groups in biradical **1** with the hydroxyl groups of the SiO_2 surface. Measurement of the dipole-dipole broadening in the ESR spectrum using a known procedure[9] gives the distance between the >NO groups equal to 1.32 nm, which is somewhat shorter than that for free biradical **1** (1.40 nm). This result is consistent with the assumption on the bidentate character of interaction of biradical **1** with the silica gel surface.

The spectrum of biradical **1** adsorbed on the Al_2O_3 surface is more complicated. A source of complexity can be a superposition of two spectra. One spectrum corresponds to the complex of biradical **1** with the surface coordinately unsaturated Al^{3+} cations and manifests the HFS from the ^{27}Al nucleus (nuclei). The second spectrum belongs to the complex of biradical **1** with the hydroxyl groups of the surface or with weaker Lewis acid sites (Al^{3+}). The difference between the spectrum of biradical **1** adsorbed on the Al_2O_3 surface and that of the complex with $AlCl_3$ in solution indicates steric hindrance preventing bidentate coordination.

The results obtained showed that biradical **1** can be used as a probe for studying the surface of solid oxide catalysts and adsorbents. Since the nitroxyl groups are linked through a flexible aliphatic bridge, the both groups can form a complex with the acid sites upon adsorption on the surface, which makes it possible to estimate the distance between these sites (in the case of SiO_2). However, for analysis of the magnetic resonance parameters of the surface complexes of probe molecules with the acid sites, the use of biradical **1** demonstrates no substantial advantages over the TEMPO monoradical, because the ESR spectrum of biradical **1** is broadened due to the dipole-dipole interaction.

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