

Complexation of molecular oxygen with nitroxide radicals adsorbed on the surface of silica and MCM-41

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Low temperature nitroxide–dioxygen complexation is observed for nitroxide stable radicals adsorbed on a surface.

Nitroxide stable radicals are widely used as paramagnetic probe molecules for dynamic and structural investigations of liquids, polymers, biological samples, *etc.*^{1–3} Information on physical and chemical properties of nitroxides is useful. An unknown phenomenon of a considerable decrease or complete disappearance of ESR spectrum of nitroxide in porous Teflon AF-2400 and polyvinyltrimethylsilane (PVTMS) matrices at low temperatures in the presence of molecular oxygen has been experimentally found recently.⁴ A similar effect was found for a liquid solution saturated with oxygen.^{4,5} In all cases, the disappearance of ESR spectra is reversible, the ESR signal is completely restored when samples are heated or oxygen is moved off. These observations were explained as a consequence of complexation of nitroxide radicals with molecular oxygen. No data on stoichiometry, spin multiplicity and structure of nitroxide–dioxygen complexes have been reported.

To study the nitroxide–dioxygen complexation, a high concentration of oxygen in samples, as well as a high probability of molecular collisions of oxygen and nitroxide molecules at low temperature, is a necessary experimental condition. These conditions are satisfied when nitroxide molecules are adsorbed on an adsorbent with a high surface. The subject of this investigation is the oxygen-induced vanishing of ESR spectra of nitroxides adsorbed on silica and MCM-41.[†]

Influence of molecular oxygen on ESR spectra of TEMPO adsorbed on silica surface is shown in Figures 1 and 2. Similar results were obtained for the radical TEMPON. No significant difference was found between silica and MCM-41 adsorbents.

Figure 1 shows the broadening of ESR spectrum of adsorbed radical at room temperature. Strong broadening of spectral lines causes a decrease of component intensities. Continuous gradual broadening or narrowing was observed, when the amount of oxygen increased or decreased. In spite of apparent decrease of spin concentration, double integration of spectrum shows that the number of paramagnetic particles insignificantly changes in

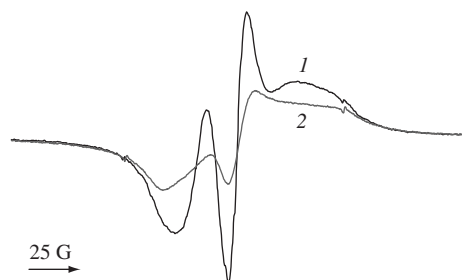


Figure 1 ESR spectra of TEMPO adsorbed on silica surface (1) under vacuum and (2) in the presence of 106 Torr O₂ at 293 K.

the presence of oxygen. The decrease is ~10–12% for TEMPO on silica or 8–10% for TEMPON on MCM-41. These values are close to experimental errors for integration of broadened spectra. Obviously, the broadening observed at 293 K is induced by exchange interaction of nitroxide and oxygen molecules. This effect is used for the determination of oxygen concentrations in liquid and biological objects.^{8–14} The observed strong broadening effect is caused by high oxygen concentration and accessibility of adsorbed radicals for oxygen molecules.

The change of ESR spectrum after oxygen inflow at 77 K is presented in Figure 2, which shows the spectra normalized to

[†] The stable radicals 2,2,6,6-tetramethylpiperidine oxyl (TEMPO) and 2,2,6,6-tetramethyl-4-oxopiperidine oxyl (TEMPON) were used without additional purification. Experiments were carried out in quartz ESR ampoules with an inner diameter of ~3 mm equipped with a vacuum valve. The weighed quantity of silica (specific surface of 290 m² g⁻¹) or MCM-41 (specific surface of 900 m² g⁻¹) was placed in an ampoule so that the layer height was 15–20 mm. The ampoule was evacuated to 10⁻³ Torr during 2 h at room temperature; then, it was maintained for 2.5 h at 350°. Heating was executed by steps of 50° and keeping during 30 min at each temperature.

Paramagnetic probe adsorbed on surface from gas phase, as equilibrium vapour pressure at 293 K is known to be 1.17×10⁻² Torr for TEMPON⁶ and 0.8 Torr for TEMPO.⁷ For that, evacuated ampoule had been connected for 3–5 min with volume filled by the saturated vapour of stable radical. Then, powder adsorbent was stirred. After the absorption procedure, the ESR spectra changed slowly. This process reflects diffusion of radicals on surface. Uniform distribution of radical particles on adsorption surface was achieved during three to seven days. The number of paramagnetic particles in a sample was about 6.15×10¹⁸ g⁻¹. It was chosen so that surface concentration was no more than one particle per 400 Å² to avoid the dipole–dipole broadening of ESR spectra.

The ESR spectra were recorded using a Varian E-3 spectrometer. Sufficient low modulation amplitude and power level were used to exclude any distortion of spectra. Temperature dependences were obtained using a flow nitrogen cryostat. The precision of temperature control was ±2 °C. The number of paramagnetic particles was determined by double integration of ESR spectrum and comparison of obtained area under the absorption curve with the similar area for the ESR spectrum of a single crystal of CuCl₂·2H₂O. The Curie law was used for calculation of true number of paramagnetic particles from spectra recorded at different temperatures.

Influence of oxygen on ESR spectra was recorded by the following way. An evacuated ampoule was placed in ESR spectrometer resonator and then connected with the volume with oxygen at chosen pressure. The pressure was recorded using a pressure sensor (Honeywell) connected to PC numerical recorder. The kinetics of changing ESR signal was recorded on one point (largest peak) of spectrum. After 10 min, the whole ESR spectrum was recorded.

Adsorption isotherm of oxygen was obtained by measurements of oxygen pressure before and after connecting a calibrated volume filled with oxygen with the ampoule containing a weighed amount of adsorbent.

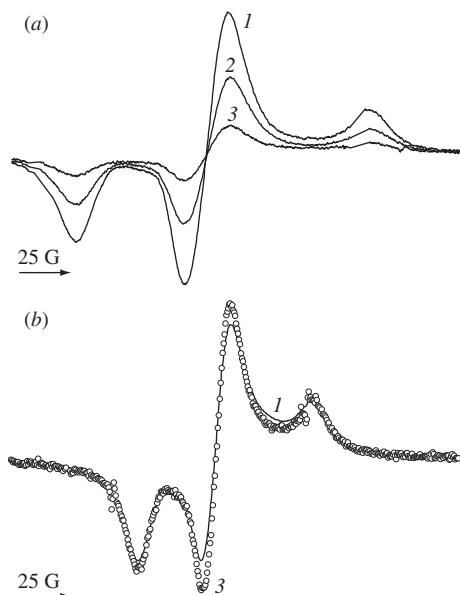


Figure 2 (a) ESR spectra of TEMPO adsorbed on silica surface, 77 K: (1) evacuated sample, (2) in the presence of 0.1 Torr O₂; (3) in the presence of 70 Torr O₂; (b) the spectra (1) and (3), normalized to spectrum areas.

the area under absorption curve in the presence and absence of oxygen. One can see that the residual spectrum has the same shape as the initial one. Positions and ratios of components, as well as line widths, in spectrum in the presence of oxygen coincide within experimental errors with the parameters of spectrum in a vacuum. Thus, an apparent decrease of number of paramagnetic particles is observed without sufficient broadening of spectrum. The residual number of paramagnetic particles is 8–10% from initial. This effect is reversible. Evacuation of oxygen at 77 K leads to recovery of spectrum amplitude without variation of spectrum shape, although full recovery at 77 K takes an extremely long time. The spectra are completely restored at heating to 293 K and evacuation.

The above effect of reversible disappearance of ESR signals is similar to phenomena observed earlier in polymer matrices⁴ and liquid solution.⁵ The difference consists in the different degrees of disappearance. In the case of adsorbed radicals, the effect is more observable than in liquid solutions. On the other hand, contrary to polymer matrices incomplete disappearance is observed in our experiments. Obviously, small fraction of adsorbed radical is incapable for interaction with dioxygen, possibly due to difference in strength or structure of adsorption site. The results show that complexation of nitroxide radicals with dioxygen is a general property independent of media.

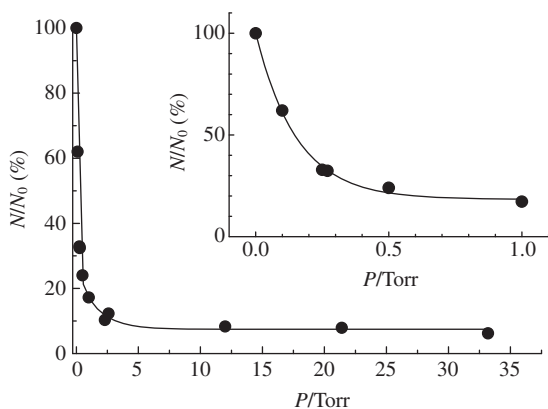


Figure 3 Portion of the particles observed by ESR vs. oxygen pressure; TEMPO on silica surface, 77 K; incut represents initial part of the dependence.

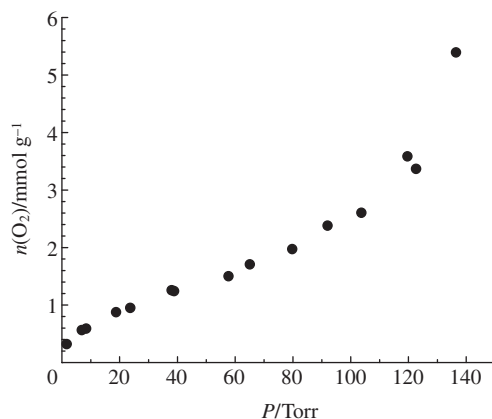


Figure 4 Adsorption isotherm for oxygen on silica surface with the nitroxide radical TEMPO, 77 K.

The dependence of the number of paramagnetic centres observed by ESR on oxygen pressure is presented in Figure 3.

The adsorption isotherm of oxygen on silica surface at 77 K is presented in Figure 4. The adsorption isotherm is independent of the presence of stable nitroxide radicals within experimental errors. It is expected result if we take into account that the number of nitroxide probe molecules in our experiments is 20–200 times less than the number of adsorbed oxygen molecules. Figure 4 shows that isotherm is a S-shape curve typical of polymolecular adsorption.

Comparison of Figures 3 and 4 makes clear that the decrease of ESR signal occurs when oxygen pressure is insufficient for formation of the dense adsorption layer. The temperature dependence of observed number of paramagnetic particles at constant oxygen pressure is presented in Figure 5. The amount of adsorbed oxygen is shown in Figure 5 for comparison. It is seen that interaction between nitroxide and dioxygen molecules is observed under small surface concentration of oxygen (small filling degree).

Under the assumption of simple equilibrium $R^{\text{ads}} + O_2^g \rightarrow RO_2^{\text{ads}}$ equilibrium constant of nitroxide-dioxygen bonding can be obtained from the curve in Figure 5. The temperature dependence of equilibrium constant is $\ln K = -\Delta H/RT + \Delta S/R$. Enthalpy of the interaction of gaseous oxygen with adsorbed nitroxide $\Delta H = -17.1 \pm 2.3 \text{ kJ mol}^{-1}$ was found from linear dependence of $\ln K$ on $1/T$. This value should be compared with evaporation heat of liquid oxygen that is 6.83 kJ mol^{-1} and with enthalpy of oxygen adsorption on silica gel that is $-9.53 \text{ kJ mol}^{-1}$.¹⁵ The comparison shows that interaction energy of dioxygen and nitroxide molecules corresponds to weak bonding.

The kinetic measurements showed that the specific time of ESR spectral change is significantly less than the specific time of equilibrium attainment. For example, when oxygen pressure

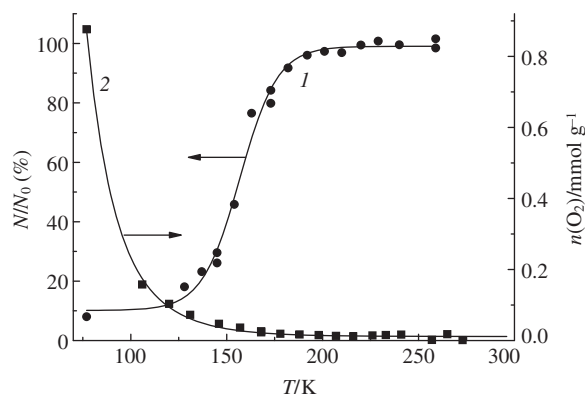


Figure 5 Temperature dependence of (1) the fraction of nitroxide radicals observed by ESR and (2) amount of adsorbed oxygen at 20 Torr.

is 25–30 Torr, half time of ESR signal decrease is ~1 s, but adsorption equilibrium is formed during ~7 s.

Thus, the ESR spectra of nitroxides at room temperature demonstrate broadening that depends on oxygen pressure. The low temperature behaviour of nitroxide in the presence of oxygen differs essentially from features observed at room temperature. The majority of nitroxide molecules in the presence of molecular oxygen exists in two distinct low temperature states: ESR silent state and native state that demonstrates ordinary ESR spectrum. The transformation of one state to another occurs when surface concentration of oxygen is ~10 times more than nitroxide surface concentration. The oxygen concentration required for this transformation is far insufficient to form a surface monolayer. The characteristic time of nitroxide–dioxygen interaction is less than the specific time of adsorption equilibrium. All presented results are arguments for low temperature specific complexation of nitroxide and oxygen molecules. In spite of small bond energy, complex obviously has a certain structure that defines ESR properties.

The composition of the nitroxide–dioxygen complex can be just a matter of speculations. The diamagnetic complex between two nitroxide radicals and one dioxygen molecule discussed earlier⁵ seems to be low probable as nitroxides are scarcely fixed on surface in the form of pairs with appropriate distance. Further investigations are necessary to clarify composition and structure of the complex.

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