Mendeleev Commun., 1997, 7(6), 221–223

Interaction between singlet dioxygen and superoxide anion radical coordinated with vanadium(V) ion

Alexander E. Gekhman,[a] Natalia I. Moiseeva,[b] Vadim V. Minin,[a] Gennadii M. Larin[a] and Ilya I. Moiseev*[a]

[a] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 117907 Moscow, Russian Federation. Fax: +7 095 954 1279*

[b] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation*

Abnormal broadening of the $V^V(O_2^{\cdot-})$ EPR signal in the $V^V/H_2O_2/AcOH$ system known to generate singlet dioxygen has been observed; this effect suggests that $^1O_2$ serves as an effective relaxing agent, broadening the $V^V(O_2^{\cdot-})$ EPR signal.

Singlet dioxygen is known to oxidize free superoxide anion in solution according to reaction (1).[1,2]

$$^1O_2 + O_2^{\cdot-} \longrightarrow O_2^{\cdot-} + {}^3O_2 + 22\ \text{kcal mol}^{-1} \qquad (1)$$

In this paper we describe the first observations concerned with the influence of $^1O_2$ on vanadium(V) coordinated superoxide anion EPR spectra.

The coordinated superoxide radical anion $V^V(O_2^{\cdot-})$ was detected in the $V^V/H_2O_2/AcOH$ system in the course of catalytic decomposition of H_2O_2.[3,4] An octet with parameters $g = 2.01125\pm0.00005$ and $a_V = 0.00044\ \text{cm}^{-1}$ coinciding with those for the known vanadium complex with coordinated superoxide anion[5–7] was observed[†] (Figure 1, Table 1). The integral intensity of the observed signal grows smaller as H_2O_2 decomposes (Figure 2). To the best of our knowledge, this is the first time rather high (10^{-3}–10^{-4} M) steady-state concentrations of a complex with coordinated superoxide ion $V^V(O_2^{\cdot-})$ have been observed.

The shape of the spectra was found to change drastically depending on the gas atmosphere under which H_2O_2 was decomposed and the spectra were recorded.

Thus, a strong and well resolved octet was observed only when the EPR cell was purged with Ar or CO_2 [see Figure 1(*a*) and Table 1].

Under triplet dioxygen flow, the spectral parameters (*g* value and HFS constant, *a*) did not change but the lines of the octet were broadened by *ca.* 1.5 G [see Figure 1(*b*) and Table 1]. The observed broadening can be attributed to the dipole–dipole interaction involving $V^V(O_2^{\cdot-})$ and $^3O_2$.

A dramatic change in the spectrum shape was observed in experiments without any gas purging. In this case, the lines of the spectrum were broadened so much that the hyperfine structure of the spectrum became practically unresolved [see Figure 1(*c*) and Table 1].

The spectral lines become broadened in *ca.* 1 min after the Ar flow ceases. This suggests the presence of a volatile, very effective relaxing agent accumulating rapidly during H_2O_2 decomposition. Minor side products of the $H_2O_2/AcOH$ decomposition, such as CO_2, MeOH or MeOOAc, cannot serve as relaxing agents since the addition of these compounds was proved to have no effect on the shape of the spectra.

Table 1 EPR spectral parameters for the $V^V(O_2^{\cdot-})$ complex in $H_2O_2/V^V/AcOH$. $[V^V] = 10^{-2}$ M, $[H_2O_2]_0 = 1$ M, $[H_2O]_0 = 2.3$ M, 20 °C.

Purging gas	Time/min[a]	$g\pm0.0003$	$(a_V\pm0.2)/10^{-4}\ \text{cm}^{-1}$	$\alpha_V\pm0.2/\text{G}$[b]	Error[c]
Ar	12.0	2.0013	4.4	2.6	0.016
	18.8	2.0013	4.4	2.5	0.021
	40.0	2.0012	4.4	2.4	0.029
	72.0	2.0012	4.4	2.7	0.024
O_2	16.5	2.0012	4.5	4.0	0.018
	22.0	2.0013	4.5	4.0	0.016
	33.0	2.0013	4.5	3.8	0.016
	46.5	2.0013	4.5	3.8	0.020
	54.8	2.0012	4.5	3.8	0.017
no gas purging	3.5	2.0111	4.7	6.0	0.014
	8.5	2.0111	4.7	6.3	0.014
	35.0	2.0110	4.7	6.2	0.014
	48.0	2.0109	4.6	7.2	0.012
	67.0	2.0108	4.6	8.1	0.012

[a]The start of the run is the time of H_2O_2 addition to the catalyst solution. [b]The spectra obtained were processed according to ref. 8. Within the framework of the model used, broadening parameters were approximated by $\Delta H = \alpha + \beta m_I + \gamma m_I^2$, where m_I is the projection of the nuclear spin on the direction of the external magnetic field and α is a parameter accounting for all broadening effects; this parameter is the same for all HFS lines. The terms βm_I and γm_I^2 have been found to be *ca.* two orders of magnitude smaller than α and are not given in the table. [c]Root-mean square deviation.

The observed broadening (*ca.* 3.5–5.5 G, see Table 1) is much more pronounced than that normally observed for $^3O_2$ dipole–dipole interaction, which is usually *ca.* 1.5 G. For instance, we found that the spectrum of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl broadens by *ca.* 1 G under $^3O_2$ purging.

From other studies the $V^V/H_2O_2/AcOH$ system is known to generate complexes containing $^1O_2$ as a ligand, $V^V(^1O_2)$.[3,9] The complexes were found to transfer $^1O_2$ to an appropriate substrate like anthracene, alkenes, *et al.* in an oxidation reaction.[3,9] In the absence of the $^1O_2$ trapping agent, the complex is decomposed, evolving $^1O_2$ which is quenched *via* $^1O_2$/solvent interaction. Therefore, singlet dioxygen can be expected to occur in the $V^V/H_2O_2/AcOH$ system under steady-state concentrations. Under a constant gas flow, the concentration of dissolved $^1O_2$ should be lower than that in the absence of purging. So, the observed changes in the shape of the $V^V(O_2^{\cdot-})$ spectra can be rationalised from the point of view of an $^1O_2/V^V(O_2^{\cdot-})$ interaction.

An analogous unusual broadening of the EPR signal of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl has been observed during sensitised oxidation of the corresponding amine by singlet dioxygen.[10] The observed effect was not discussed in ref. 10, however.

In general, both free $^1O_2$ and its complex with vanadium(V) should be taken into consideration as possible relaxing agents. Fast equilibrium between these species could be expected, reaction (2).

$$(^1O_2)V^V \rightleftharpoons {}^1O_2 + V^V \qquad (2)$$

[†] EPR spectra were recorded using a Radiopan SE/X-2542 radiospectrometer (9450 MHz, 0.5 G modulation amplitude) at 255–293 K. 1,1-Diphenyl-2-picrylhydrazyl (DPPH), $g = 2.0036$, was used as the internal field marker. Methods of treatment and simulation of EPR data were described elsewhere.[8] The intensity of the $V^V(O_2^{\cdot-})$ signal was determined by using the 3rd and 4th components of the Mn/MgO EPR signal as a standard. $VO(acac)_2$, which is soluble in AcOH, was used as the starting compound for catalytic H_2O_2 decomposition. EPR experiments showed the V^{IV} signal of $VO(acac)_2$ to disappear after H_2O_2 portions were added to the V^V compound solution. In a typical experiment, 1 ml (9.7 mmol) of aqueous (9.67 M) H_2O_2 was added to 9 ml of glacial AcOH containing 10^{-2} M of $VO(acac)_2$. The solution obtained was placed into an EPR cell (i.d. 5 mm) equipped with two glass capillaries (i.d. 0.2–0.3 mm) which were connected to two vessels filled with O_2, Ar or CO_2, respectively. Gas was bubbled through the EPR cell during spectrum recording in the experiments with gas purging.

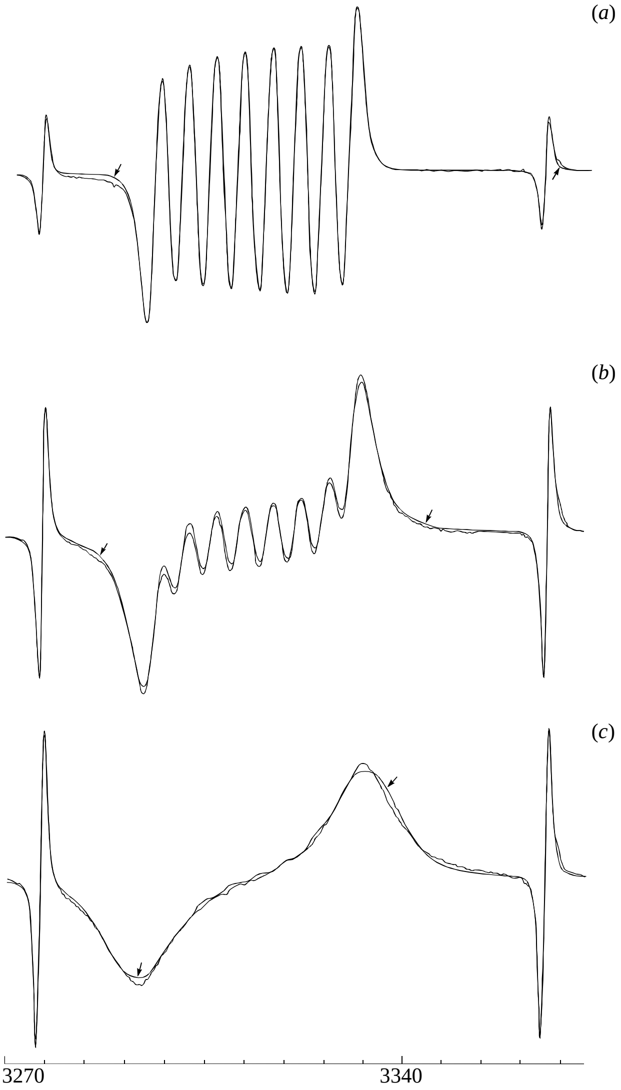

Figure 1 EPR spectra of $\mathrm{V^V(O_2^{\bullet-})}$ in the $\mathrm{H_2O_2/V^V/AcOH}$ system. $[\mathrm{V^V}] = 10^{-2}$ M, $[\mathrm{H_2O_2}]_0 = 1$ M, 20 °C; (*a*) with Ar purging; (*b*) with $\mathrm{O_2}$ purging; (*c*) without any gas purging. The arrows indicate approximate curves calculated according to ref. 8. The two lines edging the spectra at the high- and low-frequency fields are the 3rd and 4th components of the Mn/MgO EPR signal, respectively.

An inert gas flow can affect the steady-state concentration of $\mathrm{^1O_2}$ and, as a consequence, the concentration of the $\mathrm{V^V(^1O_2)}$ complex.

If both $\mathrm{^1O_2}$ molecule and superoxide radical anion were bound to the same vanadium atom, spin or electron exchange between the ligands could be expected, as has been observed[11] [*e.g.*, according to reaction (3)]:

$$\mathrm{(^1O_2)V^V(O_2^{\bullet-})} \rightleftharpoons \mathrm{(O_2^{\bullet-})V^V(^1O_2)} \qquad (3)$$

The observed change in the shape of the EPR spectra could be attributed to such an exchange. However, the oxidation of free $\mathrm{O_2^{\bullet-}}$ by free $\mathrm{^1O_2}$ is a diffusion-controlled reaction in $\mathrm{Me_2SO}$ [$(7\pm6)\times10^9$ $\mathrm{M^{-1}\,s^{-1}}$] and MeCN (1.6×10^9 $\mathrm{M^{-1}\,s^{-1}}$) solutions.[1] The reaction between the coordinated ligands, $\mathrm{O_2^{\bullet-}}$ and $\mathrm{^1O_2}$, resulting in a complex containing $\mathrm{^3O_2}$ molecule and superoxide anion radical, reaction (4), should be an even faster reaction.

$$\mathrm{(^1O_2)V^V(O_2^{\bullet-})} \rightleftharpoons \mathrm{(O_2^{\bullet-})V^V(^3O_2)} \qquad (4)$$

An enormously high broadening of the $\mathrm{O_2^{\bullet-}}$ EPR signal in a complex containing both $\mathrm{O_2^{\bullet-}}$ and $\mathrm{^3O_2}$ should be expected. The triplet dioxygen molecule, $\mathrm{^3O_2}$, should be a very poor ligand for $\mathrm{V^V}$ ion being expelled from the complex, reaction (5).

$$\mathrm{(O_2^{\bullet-})V^V(^3O_2)} \rightleftharpoons \mathrm{(O_2^{\bullet-})V^V} + \mathrm{^3O_2} \qquad (5)$$

However, the coincidence of the experimental EPR spectrum and a curve simulating the EPR spectrum under an approximation of homogeneous broadening suggests the occurrence of only one type of paramagnetic vanadium(V) complex (Figure 1). All attempts to record the signals of $\mathrm{V^{IV}}$ complexes in the $\mathrm{V^V/H_2O_2/AcOH}$ system failed. The assumption of the co-existence of a complex with well-resolved EPR signal, $\mathrm{V^V(O_2^{\bullet-})}$, and that with a broadened spectrum, $\mathrm{(O_2^{\bullet-})V^V(^3O_2)}$, is in disagreement with the experimental data. Thus, superposition of a well-resolved EPR signal and a broadened signal in a 1:1 ratio cannot be described by the model of homogeneous broadening of the spectrum of a single species (the deviations exceed 4%).

The interaction between $\mathrm{V^V(O_2^{\bullet-})}$ and free singlet dioxygen cannot be ruled out. Quenching of $\mathrm{^1O_2}$ with $\mathrm{V^V(O_2^{\bullet-})}$ according to reaction (6) could be an effective method of electron spin exchange and spin relaxation because of the gain in free energy during the $\mathrm{^1O_2(^1\Delta)}$ into $\mathrm{^3O_2(^3\Sigma)}$ transition (*ca.* 23 kcal $\mathrm{mol^{-1}}$).

$$\overset{\uparrow}{\mathrm{V^V(O_2^{\bullet-})}} + \overset{\uparrow\downarrow}{\mathrm{^1O_2}} \rightleftharpoons \overset{\downarrow}{\mathrm{V^V(O_2^{\bullet-})}} + \overset{\uparrow\uparrow}{\mathrm{^3O_2}} \qquad (6)$$

As a result, the EPR lines are broadened. The same mechanism can be operative in the 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl/$\mathrm{^1O_2}$ system.[10] Note that complex formation between the components of the latter system is impossible. So, reaction (6) seems to be a general pathway for the interaction between singlet dioxygen and free oxyl radical. However, in the case of $\mathrm{V^V(O_2^{\bullet-})/{}^1O_2}$, an additional avenue for $\mathrm{V^V(O_2^{\bullet-})/{}^1O_2}$ interaction seems to be possible.

It is an easy matter to see that the presence of dissolved $\mathrm{^1O_2}$ affects not only the shape of the EPR signal but also the kinetics of $\mathrm{V^V(O_2^{\bullet-})}$ disappearance (Figure 2). Under Ar flow, the decrease in the integral EPR intensity is described by first-order kinetics (Figure 2, curve *2*), while in the absence of Ar flow the reaction obeys zero-order kinetics (Figure 2, curve *3*). Thus, singlet dioxygen can be involved with $\mathrm{V^V(O_2^{\bullet-})}$ disappearance as well.

A redox reaction between $\mathrm{V^V(O_2^{\bullet-})}$ and $\mathrm{^1O_2}$ can be expected. Electron transfer from the $\mathrm{V^V(O_2^{\bullet-})}$ complex to $\mathrm{^1O_2}$ in AcOH solution should result in the formation of $\mathrm{HO_2^{\bullet}}$, reaction (7).

$$\mathrm{V(O_2^{\bullet-})} + \mathrm{^1O_2} \xrightarrow[\mathrm{H^+}]{k_7} \mathrm{V(^1O_2)} + \mathrm{HO_2^{\bullet}} \qquad (7)$$

Reaction between $\mathrm{HO_2^{\bullet}}$ and $\mathrm{V^V}$ will restore $\mathrm{V^V(O_2^{\bullet-})}$ [reaction (8), $k_8 = 10^5$ $\mathrm{M^{-1}\,s^{-1}}$ in $\mathrm{H_2O}$ solution].[5]

$$\mathrm{V^V} + \mathrm{HO_2^{\bullet}} \xrightarrow{k_8} \mathrm{V(O_2^{\bullet-})} + \mathrm{H^+} \qquad (8)$$

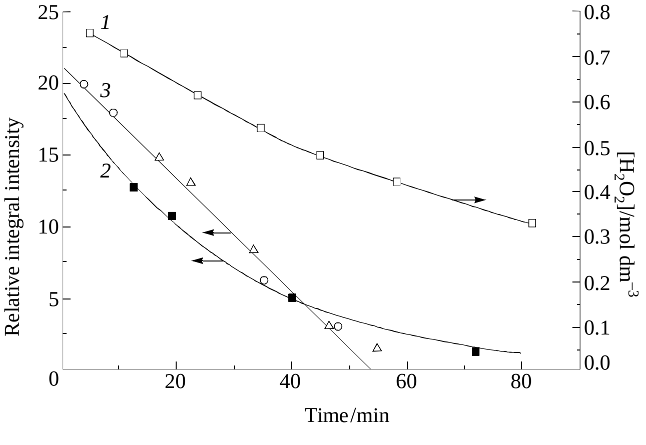

Figure 2 $\mathrm{H_2O_2}$ concentration (*1*) and relative integral intensity of the $\mathrm{V^V(O_2^{\bullet-})}$ EPR signal (*2* and *3*) *vs.* time. $[\mathrm{V^V}] = 10^{-2}$ M, $[\mathrm{H_2O_2}]_0 = 1$ M, 20 °C; (*2*) with Ar purging; (*3*) without any gas purging.

However, the $HO_2^{\bullet}$ radicals should undergo disproportionation according to reaction (9) more rapidly ($k_9 = 10^6$ M^{-1} s^{-1} in H_2O solution).[12]

$$2HO_2^{\bullet} \xrightarrow{k_9} H_2O_2 + O_2 \qquad (9)$$

The net result of the reactions (7), (8) and (9) is the dismutation of the complex with superoxide anion as a ligand. If this is the case, the system under question can be considered as the first example of $O_2^{\bullet-}$ dismutase not containing a Zn^{II}/Cu^{II} couple.

Grants from INTAS (grant no. 94/1515) and the Russian Foundation for Basic Research (grant no. 96-03-34101a) are gratefully acknowledged. We give our thanks to Dr. O. G. Poluectov and Professor V. Ya. Shlyapintokh of the N. N. Semenov Institute of Chemical Physics, RAS, for helpful discussions.

References

1 H. J. Guiraud and C. S. Foote, *J. Am. Chem. Soc.*, 1976, **98**, 1984.
2 A. P. Darmanyan, C. S. Foote and P. Jardon, *J. Phys. Chem.*, 1995, **99**, 11854.
3 A. P. Makarov, A. E. Gekhman, V. M. Nekipelov, E. P. Talsi, O. Ya. Polotnyuk, K. I. Zamaraev and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 765 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 694).
4 I. I. Moiseev, D. I. Shishkin and A. E. Gekhman, *New J. Chem.*, 1989, **13**, 683.
5 A. Samuni and G. Czapski, *Isr. J. Chem.*, 1969, **91**, 4673.
6 M. Setaka, Y. Kirino, T. Ozawa and T. Kwan, *J. Catal.*, 1969, **15**, 209.
7 V. M. Berdnikov and P. V. Schastnev, *Kinet. Katal.*, 1975, **16**, 83 (in Russian).
8 G. M. Larin, G. A. Zvereva, V. V. Minin and Yu. V. Rakitin, *Zh. Neorg. Khim.*, 1988, **33**, 2011 [*J. Inorg. Chem. USSR* (*Engl. Transl.*), 1988, **33**, 1146].
9 A. E. Gekhman, N. I. Moiseeva and I. I. Moiseev, *Dokl. Ross. Akad. Nauk*, 1996, **349**, 53 [*Dokl. Chem.* (*Engl. Transl.*), 1996, **349**, 165].
10 V. B. Ivanov, V. Ya. Shlyapintokh, O. M. Khvostach, A. B. Shapiro and E. G. Rozantsev, *J. Photochem.*, 1975, **4**, 313.
11 J. E. Wertz and J. R. Bolton, *Electron Spin Resonance Theory and Practical Applications*, McGraw Hill, New York, 1972.
12 E. T. Denisov, *Konstanty skorosti gomoliticheskikh zhidkofaznykh reaktsii* (*Rate Constants of Homolytic Liquid-phase Reactions*), Nauka, Moscow, 1971, p. 237 (in Russian).

Received: Moscow, 9th July 1997
Cambridge, 1st October 1997; Com. 7/05298G