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Abnormal Broadening of Free Radical EPR Lines: A New Test Probe for Singlet Dioxygen in Solution[§]

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Introduction

Singlet dioxygen is known as an active oxidant in both synthetic chemistry and biological systems.[1,2] Quenching of ${}^1O_2$ by oxygen- and sulfur-centered radicals is well-known.[3−6] This paper reports evidence for an interaction between ${}^1O_2$ molecule and free radical species based on EPR spectra.

Experimental Section

EPR spectra were recorded using a Radiopan SE/X-2542 radiospectrometer (9.450 MHz, 0.5 G modulation amplitude) at 255−293 K. DPPH, $g = 2.0036$, was used as the internal field marker. The methods of treatment and simulation of EPR data were described elsewhere.[7] The intensities of free radical signals were determined using the third and fourth components of the EPR signal of Mn/MgO as the external standard. Solutions of 10^{-2} M Na_2MoO_4 (Aldrich, 99+%, ACS grade) in phosphate buffer (pH = 10.5) and $VO(acac)_2$ (Aldrich, 95%) in AcOH were used as the catalyst precursors for the H_2O_2 decomposition. EPR experiments showed that the V(IV) signal of $VO(acac)_2$ disappears after the first H_2O_2 drop is added to the solution, indicating the oxidation of V(IV) to V(V).[8−11]

In a typical experiment, 1 mL (9.7 mmol) of an aqueous solution of H_2O_2 (9.67 M) was added to 9 mL of glacial AcOH containing 10^{-2} M $VO(acac)_2$. The solution obtained was put into the 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 purging gases, O_2, Ar, or CO_2.

Results and Discussion

Several systems containing metal complexes and H_2O_2 to generate singlet dioxygen are known (see eq 1),[8−13]

$$2H_2O_2 \xrightarrow{\text{catalyst}} {}^1O_2 + 2H_2O \qquad (1)$$

where catalyst is $Ca(OH)_2$, H_2TiO_3, $NaVO_3$, Na_2MoO_4, Na_2WO_4, etc. in alkaline media.[12]

V(V) compounds have been shown to catalyze H_2O_2 decomposition in AcOH solution, giving rise to high yields of ${}^1O_2$, detected by both chemical reactions and characteristic phosphorescence at 1275 nm.[8−13] As hydrogen peroxide was decomposed, the phosphorescence intensity at 1275 nm decreased exponentially ($\tau_{1/2} = 17 \pm 3$ min at 15 °C and $[V(V)] = 10^{-4}$ M).

According to our phosphorescence data, the lifetime of ${}^1O_2$ generated photochemically by porphyrin sensitization[14] is equal to 23 ± 1 μs in AcOH solution at room temperature. Correspondingly, the peak concentration of ${}^1O_2$ at $[H_2O_2]_{init} = 1$ M did not exceed $\sim 3 \times 10^{-9}$ M.

In the present work, V(V)/H_2O_2/AcOH (system A) and Mo(VI)/H_2O_2/H_2O (system B) were used as the sources of ${}^1O_2$. 3-Carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy (**1**) and 4-(1-methylethyl)-2,2,5,5-tetramethyl-3-imidazolinium-1-yloxy (**2**) stable radicals and a V(V) complex containing the superoxide anion radical, $V(V)(O_2^{\bullet -})$ (**3**), were chosen as spin labels.

Well-resolved EPR signals of the free radicals (line widths of ca. 1−1.3 G) were observed in systems A and B in an inert gas (Ar or CO_2) flow only. Thus, the EPR spectrum of **1** (10^{-4} M) in an aqueous solution of MoO_4^{2-} (10^{-2} M) and H_2O_2 (1 M) showed a triplet ($g = 2.0049$, hfs = 15.49 G) with $\delta = 1.52$ G under Ar purging. Under ${}^3O_2$ purging, δ was broadened up to ca. 2.50 G due to dipole−dipole interaction.[15] In the absence of any gas purging, δ was dramatically broadened in ca. 0.5 min. The value of ca. 8.3 G was reached in about 10 min after addition of H_2O_2. When Ar purging was resumed, δ narrowed up to the original value. Such a broadening and narrowing of the EPR lines of the free radical can be observed repeatedly (by switching on and off Ar purging) until complete H_2O_2 consumption.

An octet with $g = 2.011\,25 \pm 0.000\,05$ G and $a_V = 0.000\,44$ cm^{-1} parameters coinciding with those for the known vanadium complex **3**[16−18] was detected in system A in the course of the H_2O_2 decomposition.[8−13] The strong and well-resolved octet of **3** was only observed when the EPR cell was purged with Ar or CO_2. Under ${}^3O_2$ flow, the lines of the octet were broadened up to ca. 1.5 G. Without any gas purging, under conditions of ${}^1O_2$ accumulation, the lines of the **3** spectrum were broadened to such an extend that hfs became practically unresolved.

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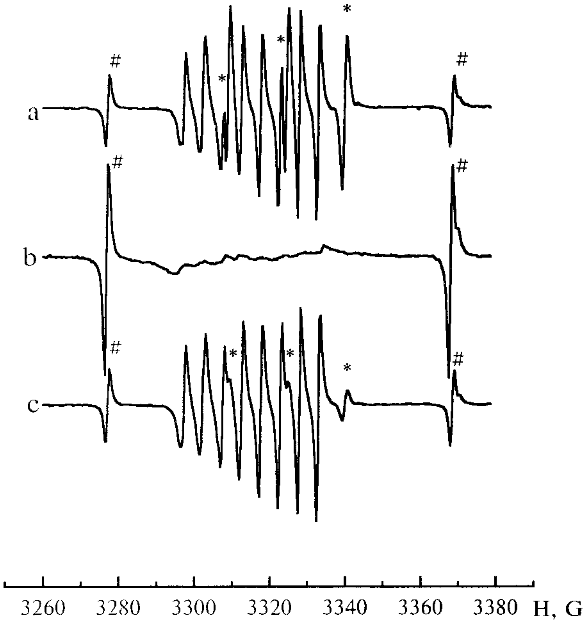

Figure 1. EPR spectra of the solution of radical **2** and $V(V)(O_2^{\bullet-})$ in the $H_2O_2/V(V)/AcOH$ system. $[V(V)] = 10^{-2}$ M, $[H_2O_2]_0 = 1$ M, $[\mathbf{2}] = 2 \times 10^{-5}$ M, 20 °C. (a) Upon Ar purging. The components of the EPR spectrum corresponding to the triplet of **2** are marked by asterisks. (b) Without any gas purging after the decomposition of H_2O_2 was started, e.g., under the conditions of the $^1O_2$ accumulation in the solution. (c) After Ar purging was restarted. The EPR components corresponding to the triplet of **2** are marked by asterisks. The two lines edging the spectra at the high- and low-frequency fields marked by # are the third and fourth components of the Mn/MgO EPR signal, correspondingly.

Nitroxyl radical **2** was found to be consumed rather slowly in system A. This allowed one to monitor EPR spectra of the radical during the H_2O_2 decomposition. Superposition of two well-resolved EPR signals, the octet of **3** and the triplet of **2**, was observed only under Ar purging (see Figure 1a). When Ar purging was stopped, the spectral lines of both radicals were broadened up to ca. 10 G in 5−10 min (see Figure 1b). After resumption of the Ar purging, the line widths became narrow again (see Figure 1c). This effect can be observed repeatedly as long as H_2O_2 and nitroxyl radical **2** are still present.

The nature of the evolving or bubbling gas was found not to influence the values of *g*, hfs, and integral intensities of EPR spectra, suggesting that one radical species is responsible for both the narrow and broad signals.

All data obtained showed that the EPR spectral lines of such dissimilar paramagnetic species as complex **3** and nitroxyl radicals **1** and **2** are broadened to nearly the same value in two different catalytic systems A and B. In all cases, the broadening was due to the absence of the inert gas purging, and the EPR lines were narrowed by switching Ar or CO_2 purging on. These facts imply that the broadening of EPR lines owes its origin to a common factor.

The spectral lines of all radicals under study in both A and B catalytic systems became broadened in 1−5 min after the Ar flow was stopped. This suggests the formation of a volatile, very effective relaxant agent accumulating rapidly during the H_2O_2 decomposition in the absence of an inert gas flow. Minor side products of the H_2O_2/AcOH decomposition like CO_2, CH_3OH, and CH_3OOAc cannot serve as the relaxants insofar as the addition of these compounds was proved to have no effect on the shape of the spectra. Moreover, no such products could be expected to form in the system B.

The observed EPR signal broadening (ca. 5−10 G) is much more pronounced than that normally observed for the $^3O_2$ dipole−dipole interaction, which was usually close to ca. 1.5 G. For instance, we observed that the spectrum of 2,2,6,6-tetramethyl-4-hydropiperidine-1-yloxy was broadened up to ca. 1 G under $^3O_2$ purging. On condition that $^3O_2$ is formed only, e.g., in the $Fe(II)/Fe(III)/H_2O_2/H_2O$ system,[12] a broadening of the EPR signal similar to that caused by the $^3O_2$ dipole−dipole interaction was observed. Thus, EPR spectra of an aqueous solution of **1** (10^{-4} M) and $FeSO_4$ (10^{-2} M) revealed a well-resolved triplet of **1** with a line width of ca. 0.8 G before H_2O_2 addition and 2.24 G in the course of H_2O_2 decomposition.

Both A and B systems are known as chemical sources of $^1O_2$.[8−13] Under an inert gas flow, the concentration of $^1O_2$ dissolved should be lower than that without purging. So, the observed changes in the line width can be attributed to the $^1O_2$/$RO^\bullet$ interaction, where $RO^\bullet$ is an oxygen-centered free radical species, e.g., $V(V)(O_2^{\bullet-})$ radical anion and/or nitroxyl radicals **1** and **2**.

The mechanism of free radical/$^1O_2$ molecule interaction leading to the observed phenomenon is still unclear. Mechanistic schemes involving spin- or electron-exchange reactions between the paramagnetic species and the $^1O_2$ molecule yielding the radical spin conversion and $^1O_2$ quenching and mechanistic schemes assuming addition/elimination steps involving radical species $RO^\bullet$ and $^1O_2$ molecule are under consideration and experimental examination.

The only direct technique to detect singlet dioxygen is chemiluminescence.[19] A new very sensitive test probe for singlet dioxygen in solution can be proposed.

In conclusion, a new phenomenon in singlet dioxygen chemistry was observed: the EPR signals of organic and inorganic paramagnetic species were found to be dramatically broadened as a result of an interaction between the species and $^1O_2$ molecule in aqueous[20] and AcOH solution.

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Supporting Information Available: Phosphorescence spectrum of $^1O_2$ as recorded in the course of H_2O_2 decomposition in the $V(V)/H_2O_2/AcOH$ system, pictures showing the behavior of radicals **1**−**3** in the $V(V)/H_2O_2/AcOH$ and $Mo(VI)/H_2O_2/H_2O$ systems, a table collecting EPR spectral parameters of the $V(V)(O_2^{\bullet-})$ complex in the $H_2O_2/V(V)/AcOH$ system, and EPR spectra of the solution of radicals **2** and $V(V)(O_2^{\bullet-})$ in the $H_2O_2/V(V)/AcOH$ system and radical **1** in the $Fe(II)/Fe(III)/H_2O_2/H_2O$ system under different conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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