

ESR Spectra of Superoxide Anion–Scandium Complexes Detectable in Fluid Solution

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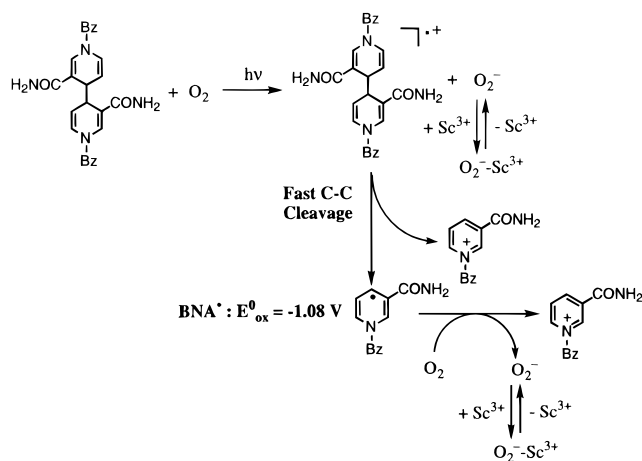
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The most definitive detection of superoxide anion O_2^- , which is of considerable importance in living systems,¹ has been made by the ESR spectrum which gives a characteristic two-line highly anisotropic signal due to the large spin–orbit coupling of oxygen in frozen media containing aprotic solvents or on various solid oxide surfaces at 77 K.^{2–4} However, the disadvantage of the ESR detection of O_2^- is the significant line broadening resulting from fast relaxation because of the quenching of the orbital angular momentum by fluctuating solvent interactions or orbital degeneracy which has precluded the detection in fluid solution particularly at higher temperatures.^{5,6} Thus, no ESR spectra of O_2^- have so far been reported in fluid solution at room temperature.⁷

We report herein that the isotropic ESR spectra of O_2^- can be obtained successfully in solution at temperatures much higher than the melting point of aprotic solvents even at 60 °C when O_2^- forms a 1:1 complex with scandium ion. The superhyperfine splitting due to the scandium nucleus and the hyperfine coupling of oxygen enriched in ^{17}O provide valuable information about the structure of the $O_2^-Sc^{3+}$ complex in solution.

The dimeric 1-benzyl-1,4-dihydropyridinamide [(BNA)₂], which can act as a unique two-electron donor,⁸ is used as an electron source to reduce O_2 to O_2^- photochemically. As shown in Scheme

Scheme 1



1, the photoinduced electron transfer from the singlet excited state of (BNA)₂ to O₂ gives (BNA)₂^{•+} and O₂^{•-}, followed by a fast cleavage of the C–C bond of the dimer to produce *N*-benzyl-nicotinamide radical (BNA[•]) and BNA⁺.^{8,9} The subsequent second electron transfer from BNA[•] to O₂ occurs rapidly, judging from the oxidation potential of BNA[•] (E_{ox}^0 vs SCE = -1.08 V)¹⁰ lower than the reduction potential of O₂ (E_{red}^0 = -0.8 V).¹¹ Thus, once photoinduced electron transfer from (BNA)₂ to O₂ occurs, 2 equiv of O₂^{•-} molecules are produced.¹²

When an oxygen-saturated propionitrile solution containing (BNA)₂ (1.7×10^{-3} M) is irradiated with a high-pressure mercury lamp, O₂^{•-} formed photochemically is detected by the ESR spectrum in frozen propionitrile at 77 K which shows a well-known signal with $g_{||} = 2.072$ and $g_{\perp} = 2.009$.⁵ When the temperature is raised above the frozen temperature (e.g., -60 °C), no ESR signal can be detected due to the line-broadening resulting from the fast relaxation, although the signal appears clearly again by lowering the temperature to 77 K.

Addition of scandium triflate (Sc(OTf)₃) and 3 equiv of hexamethylphosphoric triamide (HMPA) ligand to the (BNA)₂–O₂ system, however, results in the appearance of the sharp isotropic ESR signal under irradiation of the light in fluid solution at 25 °C as shown in Figure 1, where oxygen is enriched in ^{17}O to provide valuable information about the inequivalency of oxygen nuclei in the O₂^{•-} complex.^{13,14} The clear eight-line isotropic spectrum at the center is ascribed to the superhyperfine coupling of O₂^{•-} with the $^{7/2}$ nuclear spin of the scandium nucleus ($a_{Sc} = 3.82$ G). The isotropic g value (2.0165) is appreciably smaller than the average value (2.030)^{5,15} of the principal three g

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(15) Because of the broad line of the $g_{||}$ component, only four significant figures can be determined accurately.

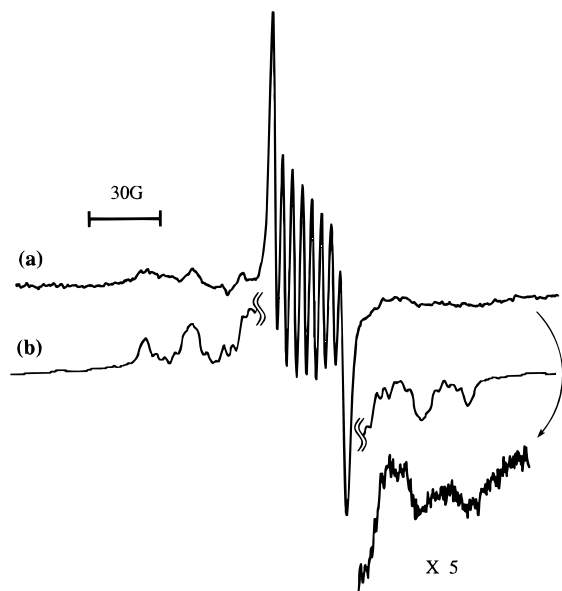


Figure 1. (a) ESR spectrum observed after irradiation of an ^{17}O (40%) oxygen-saturated propionitrile solution containing $(\text{BNA})_2$ (6.9×10^{-3} M), $\text{Sc}(\text{OTf})_3$ (8.1×10^{-2} M), and HMPA (2.5×10^{-1} M) with a high-pressure mercury lamp at room temperature. (b) Computer simulation spectrum with $g = 2.0165$, $a_{\text{Sc}} = 3.82$ G, $a(^{17}\text{O}^1) = 21$ G, $a(^{17}\text{O}^2) = 14$ G, $\Delta H_{\text{msl}} = 3.5$ G. The center lines are omitted for clarity.

components of O_2^- at 77 K, being consistent with the spin delocalization to the scandium nucleus as demonstrated by observation of superhyperfine coupling.¹⁶ The O_2^- complex is stable in the presence of HMPA and only a 30% decrease in the signal intensity is observed in 1 h after cutting off the irradiation

(16) Although the g value is similar to that of HO_2^* and the metal ion complex,⁴ the absence of hyperfine splitting due to hydrogen and the much higher stability of the signal indicates strongly that the observed radical is the $\text{O}_2^- - \text{Sc}^{3+}$ complex rather than $\text{HO}_2^* - \text{Sc}^{3+}$ complex, see: ref 4; Samuni, A.; Czapski, G. *J. Phys. Chem.* **1970**, *74*, 4592.

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(19) The signal at the magnetic field higher than the center eight-line signal is magnified by a factor of 5, since the ^{17}O hyperfine line intensities at the higher magnetic field are much smaller than those at the lower magnetic field probably due to different relaxation time depending on I_z of ^{17}O . Although the simulation result is a rather preliminary one, the two inequivalent $a(^{17}\text{O})$ values are determined accurately.

(20) The O_2^- acts as a nucleophile in the reaction with Sc^{3+} to yield $^{\circ}\text{OO}^- - \text{Sc}^{3+}$ (HMPA) as in the reaction with RX to yield ROO° ; see ref 1a.

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light at room temperature.¹⁷ Thus, the ESR spectrum of the $\text{O}_2^- - \text{Sc}^{3+}$ -HMPA complex can be detected even at 60 °C under irradiation of the light, although it disappeared completely in 20 min after cutting off the light. The g value increases with the decrease in the temperature from 2.0163 (60 °C) to 2.0168 (−30 °C), when the a_{Sc} value decreases from 3.88 (60 °C) to 3.77 G (−30 °C). Such a change in the g and a_{Sc} values with temperature may be attributed to the stronger coordination of HMPA to Sc^{3+} , which results in the weaker coordination of O_2^- to Sc^{3+} at the lower temperature. The weaker the coordination of O_2^- to Sc^{3+} , the closer to free O_2^- , and then the larger the g value, but the smaller the a_{Sc} value.

There are two sets of six lines due to the hyperfine splitting of two different ^{17}O atoms ($I = 5/2$) in Figure 1,¹⁸ although the center lines are masked by the strong eight-line signal of $^{16}\text{O}_2^- - \text{Sc}^{3+}$ -HMPA complex with $g = 2.0165$ and $a_{\text{Sc}} = 3.82$ G. The two inequivalent $a(^{17}\text{O})$ values are determined as 21 and 14 G by comparison between the observed signal (Figure 1a) and the computer simulation lines (Figure 1b).¹⁹ Such inequivalent $a(^{17}\text{O})$ values are fully consistent with an “end-on” coordination form of $^{\circ}\text{O}-\text{O}^- - \text{Sc}^{3+}$ (HMPA) in which the electron spin is more localized at the terminal oxygen.²⁰ With respect to alkali-metal superoxide complexes a number of ab initio calculations have been reported, and there is good agreement for the 6-31G basis set calculation of O_2^- , $\text{O}_2^- - \text{Li}^+$, and $\text{O}_2^- - \text{Na}^+$ with the experimental geometries.²¹ Thus, the optimized geometry of $\text{O}_2^- - \text{Sc}^{3+}$ was calculated from an unrestricted Hartree-Fock (UHF) SCF optimization using the 6-311++G** basis set.²² In contrast with the C_{2v} symmetry of alkali-metal superoxide complexes,²¹ the linear end-on coordination of O_2^- is most stable in $\text{O}_2^- - \text{Sc}^{3+}$. Such an end-on coordination of O_2^- to Sc^{3+} results in the removal of degeneracy of the SOMO orbital, decreasing the relaxation time significantly to make it possible to observe the ESR spectrum in fluid solution at temperatures even higher than room temperature. This is the first definitive detection of O_2^- -metal ion complex which is responsible for catalysis of metal ions in electron-transfer reduction of oxygen.²³

Without the HMPA ligand, the $\text{O}_2^- - \text{Sc}^{3+}$ complex becomes unstable because of the much faster disproportionation of the $\text{O}_2^- - \text{Sc}^{3+}$ complex, when the ESR spectrum can be observed during the photoirradiation below −30 °C. The a_{Sc} value (4.26 G) without HMPA is larger than that with HMPA (3.82 G) because of the stronger interaction between O_2^- and Sc^{3+} without the HMPA ligand.

The clear eight-line isotropic ESR spectrum ($g = 2.0218$) was also observed for the $\text{O}_2^- - \text{Lu}^{3+}$ -HMPA complex due to the superhyperfine coupling of O_2^- with the $7/2$ nuclear spin of the Lu nucleus ($a_{\text{Lu}} = 8.58$ G) during photoirradiation of an O_2 -saturated propionitrile solution of $(\text{BNA})_2$ (6.3×10^{-3} M), $\text{Lu}(\text{OTf})_3$ (7.7×10^{-2} M), and HMPA (7.7×10^{-1} M) at room temperature. Similarly, the ESR spectrum of $\text{O}_2^- - \text{Y}^{3+}$ -HMPA complex ($g = 2.0202$, $\Delta H_{\text{msl}} = 5.0$ G) was also observed at room temperature, although the superhyperfine due to the $1/2$ nuclear spin of the Y nucleus was not resolved because of the relatively large line width and the smaller isotropic hyperfine constant of the Y nucleus as compared with those of the Sc and Lu nuclei.²⁴

Thus, the present study provides a unique and useful way for the ESR detection of superoxide ion in fluid solution.

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