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Activation of Electron-Transfer Reduction of Oxygen by Hydrogen Bond Formation of Superoxide Anion with Ammonium Ion

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A hydrogen bond formed between the superoxide anion and the ammonium ion (NH_4^+) accelerates electron transfer from the C_{60} radical anion to oxygen significantly, whereas the tetra-*n*-butylammonium ion has no ability to form a hydrogen bond with the superoxidie anion, exhibiting no acceleration of the electron-transfer reduction of oxygen. The second-order rate constant of electron transfer from $C_{60}^{\bullet-}$ to O_2 increases linearly with increasing concentration of NH_4^+. This indicates that $O_2^{\bullet-}$ produced in the electron transfer from C_{60} to O_2 is stabilized by 1:1 complex formation between $O_2^{\bullet-}$ and NH_4^+. The 1:1 complex formed between $O_2^{\bullet-}$ and NH_4^+ was detected by ESR. The binding of $O_2^{\bullet-}$ with NH_4^+ results in a positive shift of the reduction potential of O_2 with increasing concentration of NH_4^+, leading to the acceleration of electron transfer from $C_{60}^{\bullet-}$ to O_2.

Introduction

Dioxygen (O_2) is an ideal oxidant for the chemical industry as well as for biological systems, because O_2 is abundant and environmentally benign. Because direct oxidation of substrates with the triplet O_2 is spin-forbidden, nature has developed numerous metalloprotein systems for the reductive activation of O_2, which is finely controlled by hydrogen bonding between the reduced O_2 and an amino acid residue of the metalloproteins.[1,2] In general, hydrogen bonding is a specific recognition motif which can selectively stabilize or destabilize different oxidation states of substrates, thus modulating the electron-transfer processes.[3−5] In photosynthesis, for example, two *p*-benzoquinones termed Q_a and Q_b act in concert to enable efficient charge separation to take place.[6,7] Q_a and Q_b are often identical quinones: plastoquinone in higher plants and ubiquinone in bacterial systems.[8] Specific hydrogen bonds to nearby amino acid residues are able to tailor the quinone to perform a specific function.[9] Hydrogen bonding is expected to be more favorable in the one-electron reduced state such as the semiquinone radical anion, because of the negative charge present in the oxygen atom of the radical anion. The strong hydrogen bond formation of the semiquinone radical anion with hydrogen bond donors, which can modulate the electron-transfer reduction of *p*-benzoquinone, has been reported.[10−12] However, the effects of hydrogen bond formation between the superoxide anion ($O_2^{\bullet-}$) and hydrogen bond donors on the reduction potential of O_2 and electron-transfer reactions from electron donors to O_2 have yet to be examined.[13]

We report herein hydrogen bond formation between $O_2^{\bullet-}$ and the ammonium ion in a polar solvent, which can promote the electron-transfer reduction of O_2. The fullerene radical anion ($C_{60}^{\bullet-}$), which can be produced by the photoinduced electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] to C_{60},[14] was used to examine electron-transfer reduction of O_2 in the presence of NH_4^+. The effect of NH_4^+ on the one-electron reduction potential of O_2 and the detection of the NH_4^+ complex of $O_2^{\bullet-}$ by ESR provide valuable insight into the mechanism of the NH_4^+-promoted electron-transfer reduction of O_2.

Experimental Section

Materials. Fullerene (C_{60}) was purchased from Tokyo Kasei Organic Chemicals, Japan. The dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] was prepared according to the literature.[14,15] 9,10-Dihydro-10-methylacridine ($AcrH_2$) was prepared from 10-methylacridinium iodide ($AcrH^+I^-$) by reduction with $NaBH_4$ in methanol and purified by recrystallization from ethanol.[16,17] Ammonium hexafluorophosphate (NH_4PF_6) was purchased from Aldrich and used as received without further purification. Tetra-*n*-butylammonium hexafluorophosphate (Bu_4NPF_6) was obtained from Tokyo Kasei Organic Chemicals, Japan, purified using standard methods,[18] and dried under vacuum at 40 °C for at least 1 week prior to use. Dimethyl sulfoxide (DMSO) and chlorobenzene (PhCl) was purchased from Aldrich Co. and used as received without further purification.

Kinetic Measurements. $C_{60}^{\bullet-}$ was prepared by photoirradiation (>290 nm) of a deaerated DMSO/PhCl (1:1 v/v) solution containing C_{60} (1.0×10^{-3} M) and $(BNA)_2$ (4.5×10^{-4} M) with a 500 W xenon lamp (Ushio Optical ModelX SX-UID 500XAMQ) through a UV cutoff glass filter (Asahi Techno Glass UV-29). The concentration of $C_{60}^{\bullet-}$ thus formed was determined from the absorbance at $\lambda_{max} = 1080$ nm ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}). Kinetic measurements of electron-transfer reactions from $C_{60}^{\bullet-}$ (5.0×10^{-5} M) to O_2 in the presence and absence of NH_4PF_6 [$(0-5.0) \times 10^{-3}$ M] were performed using a Shimadzu 3100 spectrophotometer. All the kinetic measurements were carried out under pseudo-first-order conditions, where the concentrations of NH_4PF_6 were maintained at >10-fold excess of concentrations of $C_{60}^{\bullet-}$ at 298 K. Pseudo-first-order rate constants were determined by least-squares curve fits using a personal computer.

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Determination of O_2 Concentrations in DMSO/PhCl (1:1 v/v). A square quartz cuvette (10 mm i.d.) was filled with a aerated solution of dimethyl sulfoxide and chlorobenzene [DMSO/PhCl (1:1 v/v)] (5.5 cm^3) containing 10-methyl-9,10-dihydroacridine ($AcrH_2$, 3.0×10^{-2} M) and acetic acid (1.6×10^{-3} M). When the solution was irradiated with a 500 W xenon lamp, the absorption band due to $AcrH^+$ ($\lambda = 360$ nm, $\epsilon = 1.8 \times 10^4$ M^{-1} cm^{-1}) appeared and the absorbance reached a limiting value after prolonged photoirradiation. Because $AcrH_2$ is oxidized by an equivalent amount of oxygen to produce $AcrH^+$ in the presence of an acid under photoirradiation,[19,20] the concentration of oxygen in air-saturated DMSO/PhCl was determined as 2.4×10^{-3} M from the limiting value of the absorbance and the ϵ value of $AcrH^+$. The O_2 concentration in the O_2-saturated DMSO/PhCl was estimated as 5-fold of that in air-saturated DMSO/PhCl.

ESR Measurements. The ESR spectra were recorded at low temperature on a JEOL X-band ESR spectrometer (JES-ME-LX). A quartz ESR tube (internal diameter: 5.5 mm) containing an oxygen-saturated solution of $(BNA)_2$ containing NH_4PF_6 or Bu_4NPF_6 at 143 K was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000-W high-pressure Hg lamp (Ushio-USH1005D) through an aqueous filter. The ESR spectra were measured under nonsaturating microwave power conditions. The amplitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S*/*N*) ratio of the observed spectra. The *g* values were calibrated with a Mn^{2+} marker.

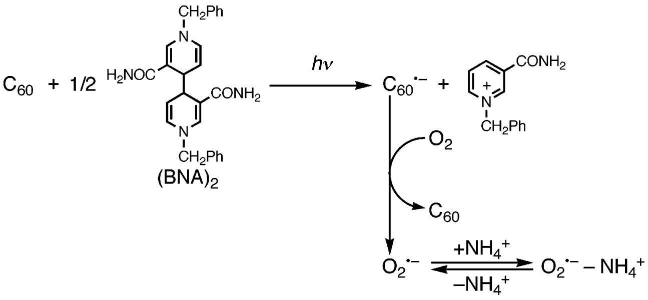
Cyclic Voltammetry. Cyclic voltammetry measurements were performed at 298 K on a BAS 630B electrochemical analyzer in oxygen-saturated DMSO/PhCl (1:1 v/v) solution containing 0.10 M NH_4PF_6 or 0.10 M Bu_4NPF_6 as the supporting electrolyte at 298 K. A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with a BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/$AgNO_3$ (0.01 M) reference electrode. All potentials (vs Ag/Ag^+) were converted to values vs SCE by adding 0.29 V.[21]

Theoretical Calculations. Density-functional theory (DFT) calculations were performed on a 8CPU workstation (PQS, Quantum Cube QS8-2400C-064). Geometry optimizations were carried out using the Becke3LYP functional and 6-31G basis set[22−24] with the unrestricted Hartree−Fock (UHF) formalism and as implemented in the Gaussian 03 program Revision C.02. Graphical outputs of the computational results were generated with the Gauss View software program (ver. 3.09) developed by Semichem, Inc.

Results and Discussion

Acceleration Effect of NH_4^+ on Rates of Electron-Transfer Reduction of O_2. The dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$], which can act as a unique two electron donor,[14] is used as electron sources to reduce C_{60} to $C_{60}^{\bullet-}$ photochemically. The photoinduced electron transfer from the singlet excited state of $(BNA)_2$ to C_{60} affords $(BNA)_2^{\bullet+}$ and $C_{60}^{\bullet-}$, followed by a fast cleavage of the C−C bond of $(BNA)_2^{\bullet+}$ to produce 1-benzylnicotinamide radical ($BNA^\bullet$) and BNA^+.[14] The subsequent second electron transfer from $BNA^\bullet$ to C_{60} occurs rapidly judging from the lower oxidation potential of $BNA^\bullet$ (E_{ox} vs SCE $= -1.08$ V)[25] than the reduction potential of C_{60} ($E_{red} = -0.45$ V vs SCE).[26] Thus, once photoinduced electron transfer from $(BNA)_2$ to C_{60} occurs, two equivalents of $C_{60}^{\bullet-}$ molecules are produced (Scheme 1).

SCHEME 1



The formation of $C_{60}^{\bullet-}$ can be readily monitored by the NIR absorption band at 1080 nm, which is diagnostic of $C_{60}^{\bullet-}$.[14,27] The $C_{60}^{\bullet-}$ reacts with O_2 slowly in an air-saturated mixed solution of dimethyl sulfoxide and chlorobenzene [DMSO/PhCl (1:1 v/v)] as shown in Figure 1A. Addition of NH_4PF_6 to an air-saturated DMSO/PhCl solution of $C_{60}^{\bullet-}$ results in remarkable acceleration of the decay of $C_{60}^{\bullet-}$. The mixed solvent of DMSO and PhCl (1:1 v/v) is used to dissolve both NH_4PF_6 and C_{60}. The decay of $C_{60}^{\bullet-}$ obeys pseudo first-order kinetics (see the first-order plot in Figure 1B). The pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of NH_4PF_6. The slope of the linear plot of k_{obs} vs [NH_4PF_6] becomes 5 times larger when an O_2-saturated DMSO/PhCl solution is employed instead of an air-saturated solution (Figure 2). This indicates that the decay rate of $C_{60}^{\bullet-}$ is proportional to concentration of O_2. Thus, an intermolecular electron transfer from $C_{60}^{\bullet-}$ to O_2 is accelerated by the presence of NH_4PF_6. The second-order rate constant (k_{et}) of electron transfer from $C_{60}^{\bullet-}$ to O_2 in the presence of NH_4^+ (2.0×10^{-3} M) is determined from the k_{obs} value (2.4×10^{-1} s^{-1}) under air ([O_2] $= 2.4 \times 10^{-3}$ M) as 1.0×10^2 M^{-1} s^{-1}. The first-order dependence of the electron-

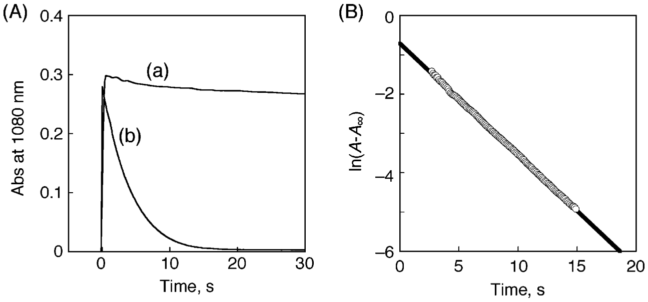


Figure 1. (A) Decay time profile of absorbance at 1080 nm due to $C_{60}^{\bullet-}$ (a) in the absence and (b) in the presence of NH_4PF_6 (1.0×10^{-3} M) in air-saturated DMSO/PhCl (1:1 v/v) at 298 K. (B) First-order plot for the decay of absorbance at $\lambda = 1080$ nm in the presence of NH_4PF_6 (1.0×10^{-3} M).

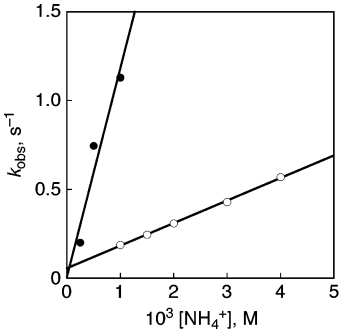


Figure 2. Plot of k_{obs} vs [NH_4^+] for electron transfer from $C_{60}^{\bullet-}$ (5.0×10^{-5} M) to O_2 in air-saturated (○) and O_2-saturated (●) DMSO/PhCl (1:1 v/v) at 298 K.

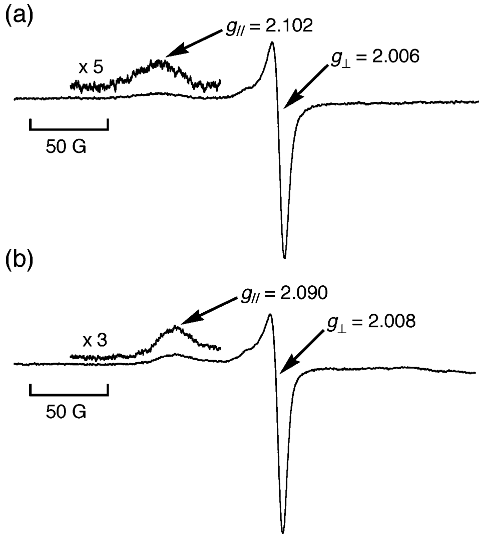


Figure 3. ESR spectra observed in photoirradiation of an O_2-saturated DMSO/PhCl (1:1 v/v) solution containing $(BNA)_2$ (1.0×10^{-2} M) and (a) Bu_4NPF_6 (0.10 M) and (b) NH_4PF_6 (0.10 M) with a high-pressure mercury lamp at −130 °C.

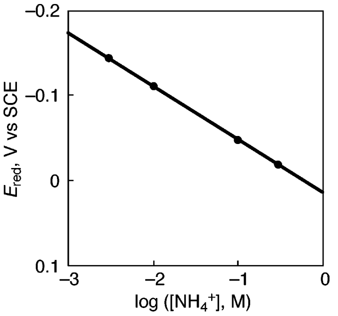


Figure 4. Nernst plot of E_{red} for O_2 against $\log[NH_4^+]$ in O_2-saturated DMSO/PhCl (1:1 v/v) at 298 K.

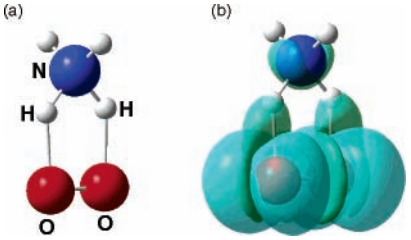


Figure 5. (a) Optimized structure and (b) spin distribution of the $O_2^{\bullet -}-NH_4^+$ complex calculated at B3LYP/6-31G level.

transfer rate on concentration of NH_4PF_6 (Figure 2) indicates formation of a 1:1 complex between $O_2^{\bullet -}$ and NH_4PF_6. In contrast to the case of NH_4PF_6, addition of Bu_4NPF_6 resulted in no acceleration of electron transfer from $C_{60}^{\bullet -}$ to O_2.

ESR Detection of NH_4^+ Complex with $O_2^{\bullet -}$. The complex formation of $O_2^{\bullet -}$ with NH_4^+ is confirmed by ESR (vide infra). When an O_2-saturated DMSO/PhCl solution containing $(BNA)_2$ (1.0×10^{-2} M) and Bu_4NPF_6 (0.10 M) is irradiated with a high-pressure mercury lamp, $O_2^{\bullet -}$ formed photochemically is detected by the ESR spectrum in frozen DMSO/PhCl at −130 °C which shows a well-known anisotropic ESR signal with $g_{\parallel} = 2.102$ and $g_{\perp} = 2.006$ due to $O_2^{\bullet -}$ as shown in Figure 3a.[28,29]

The ESR signal of $O_2^{\bullet -}$ is significantly changed by addition of NH_4PF_6 (0.10 M) to the $(BNA)_2/O_2$ system, which shows an ESR signal with $g_{\parallel} = 2.090$ and $g_{\perp} = 2.008$, as shown in Figure 3b. The deviation of the $g_{\parallel}$-value from the free spin value ($g_e = 2.0023$) is known to be caused by the spin−orbit interaction, as given by eq 1, where λ is the spin−orbit coupling constant

$$g_{\parallel} = g_e + 2[\lambda^2/(\lambda^2 + \Delta E^2)]^{1/2} \quad (1)$$

(0.014 eV) and ΔE is the energy splitting of π_g levels due to the complex formation between $O_2^{\bullet -}$ and cations.[29−31] Under the conditions that $\Delta E \gg l$, eq 1 is reduced to a simple relation, $g_{\parallel} = g_e + 2\lambda/\Delta E$. The small $g_{\parallel}$ value (2.090) in the presence of NH_4PF_6 as compared with the $g_{\parallel}$ value in the presence of Bu_4NPF_6 (2.102) is thereby attributed to the binding of $O_2^{\bullet -}$ with NH_4^+, which results in the larger ΔE value. However, the binding of NH_4^+ with $O_2^{\bullet -}$ is much weaker that that of metal ions acting as a strong Lewis acid such as Sc^{3+}.[29,32] The strong binding of Sc^{3+} with $O_2^{\bullet -}$ results in a large energy splitting of π_g levels, when the ESR signal of the $O_2^{\bullet -}/Sc^{3+}$ complex can be observed in solution due to the elongation of the relaxation time.[32] In contrast to the case of the $O_2^{\bullet -}/Sc^{3+}$ complex, the ESR signal of the $O_2^{\bullet -}/NH_4^+$ complex could only be observed in a frozen medium.

Effect of NH_4^+ on One-Electron Reduction Potentials of O_2. The binding of $O_2^{\bullet -}$ with NH_4^+ is expected to shift the reduction potential of O_2 to a positive direction in the presence of NH_4PF_6. This is confirmed by the cyclic voltammograms (see Experimental Section). The E_{red} value for $O_2/O_2^{\bullet -}$ (−0.95 V vs SCE) in the presence of Bu_4NPF_6 (0.10 M) in DMSO/PhCl is shifted significantly to −0.05 V vs SCE in the presence of NH_4PF_6 (0.10 M). This is shown in Figure 4, where the E_{red} values determined from the cyclic voltammetry measurements in DMSO/PhCl are plotted against $\log[NH_4PF_6]$. The slope of the plot of E_{red} for $O_2/O_2^{\bullet -}$ vs $\log[NH_4PF_6]$ is 0.059. This is the expected slope ($2.3RT/F = 0.057$ at 298 K) by the Nernst equation (eq 2) for the 1:1 complex formation between $O_2^{\bullet -}$

$$E_{red} = E^0_{red} + (2.3RT/F)\log\{(1 + K_{red}[NH_4PF_6])/(1 + K_{ox}[NH_4PF_6])\} \quad (2)$$

and NH_4^+, where E^0_{red} is the one-electron reduction potential in the absence of NH_4PF_6, K_{red} is the formation constant of the $O_2^{\bullet -}/NH_4^+$ complex, and K_{ox} is the formation constant of the O_2/NH_4^+ complex.[33]

In the case of the E_{red} value of *p*-benzoquinone (Q) in the presence of NH_4^+, the slope of Nernst plot was reported as 0.12, indicating a 1:2 complex, $Q^{\bullet -}/(NH_4^+)_2$.[12] The 1:2 complex between $Q^{\bullet -}$ and NH_4^+ was detected by ESR.[12] In the case of $O_2^{\bullet -}$, however, only a 1:1 complex is formed between $O_2^{\bullet -}$ and NH_4^+.

The binding mode of $O_2^{\bullet -}$ with NH_4^+ is examined by the DFT calculation at the B3LYP/6-31G level (see Experimental Section). The computed optimized structure and spin distribution of the $O_2^{\bullet -}-NH_4^+$ complex are shown in Figure 5. The side-on binding of two hydrogens of NH_4^+ with $O_2^{\bullet -}$ is most stabilized as compared with the end-on binding of one hydrogen of NH_4^+ with $O_2^{\bullet -}$. This shows sharp contrast with the case of $O_2^{\bullet -}-Sc^{3+}$ complex in which Sc^{3+} has been reported to bind with $O_2^{\bullet -}$ in an end-on fashion.[32]

Reorganization Energy of Electron Self-Exchange between O_2 and the $O_2^{\bullet -}-NH_4^+$ Complex. According to the Marcus theory of electron transfer, the k_{et} value is given as a function of the free energy change of electron transfer (ΔG_{et}) for adiabatic outer-sphere electron transfer as given by eq 3, where λ is the

$$k_{et} = Z \exp[-(\lambda/4)(1 + \Delta G_{et}/\lambda)^2/RT] \quad (3)$$

reorganization energy of electron transfer and Z is the collision frequency taken as 1×10^{11} M^{-1} s^{-1}.[34] The λ value of electron transfer from $C_{60}^{\bullet-}$ to O_2 in the presence of NH_4^+ (2.0×10^{-3} M) is determined as 67 ± 2 kcal mol^{-1} from the k_{et} value (vide supra) and the ΔG_{et} value using eq 4, which is derived from eq

$$\lambda = 2[-RT\ln(k_{et}/Z)] - \Delta G_{et} - [(\Delta G_{et} - 2[-RT\ln(k_{et}/Z)])^2 - (\Delta G_{et})^2]^{1/2} \quad (4)$$

3. The ΔG_{et} value is obtained from the E_{ox} value of $C_{60}^{\bullet-}$, which is equivalent to the E_{red} value of C_{60} (−0.45 V vs SCE) and the E_{red} value of O_2 in the presence of 2.0×10^{-3} M NH_4^+ (−0.15 V vs SCE) using eq 5, where F is the Faraday constant. The

$$\Delta G_{et} = F(E_{ox} - E_{red}) \quad (5)$$

reorganization energy of electron transfer between D and A (λ_{DA}) is obtained as the average of the reorganization energy for the electron self-exchange between D and $D^{\bullet+}$ (λ_D) and that between A and $A^{\bullet-}$ (λ_A), eq 6.[34] Thus, the $\lambda(O_2/O_2^{\bullet-}-NH_4^+)$

$$\lambda_{DA} = (\lambda_D + \lambda_A)/2 \quad (6)$$

value is determined as 126 ± 4 kcal mol^{-1} from the observed λ value of electron transfer from $C_{60}^{\bullet-}$ to O_2 in the presence of NH_4^+ (2.0×10^{-3} M) and the $\lambda(C_{60}^{\bullet-}/C_{60})$ value (8.3 kcal mol^{-1})[36] by eq 7. The $\lambda(O_2/O_2^{\bullet-}-NH_4^+)$ value is much larger

$$\lambda(O_2/O_2^{\bullet-}-NH_4^{+}) = 2\lambda - \lambda(C_{60}^{\bullet-}/C_{60}) \quad (7)$$

than the $\lambda(^3O_2/O_2^{\bullet-})$ value (45.5 ± 0.7 kcal mol^{-1})[37] and the $\lambda(^1O_2/O_2^{\bullet-})$ value (40 ± 2 kcal mol^{-1}).[38] Such a large λ value for the electron exchange between O_2 and $O_2^{\bullet-}$ in the presence of NH_4^+ is attributed to the strong binding of $O_2^{\bullet-}$ with NH_4^+ associated with the electron-transfer reduction of O_2 in the presence of NH_4^+. A large λ value (104 kcal mol^{-1}) was also reported for the intramolecular electron transfer from ferrocene to naphthoquinone moiety in a ferrocene-naphthoquinone dyad in the presence of Sc^{3+} (5.0×10^{-4} M) because of strong binding of Sc^{3+} with naphthoquinone radical anion upon electron transfer.[39]

In conclusion, the ammonium ion (NH_4^+) forms a strong hydrogen bond with $O_2^{\bullet-}$, which results in the small $g_{\parallel}$ value of the ESR spectrum of $O_2^{\bullet-}$, significant acceleration of the rate of electron transfer from $C_{60}^{\bullet-}$ to O_2, and a large positive shift of the one-electron reduction potential of O_2.[40]

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(40) Protonation of His-516 has been reported to result in a reduction of the activation energy barrier by 6.0 kcal mol^{-1} due to a decrease in the reorganization energy rather than an enhancement of the driving force by electrostatic stabilization for $O_2^{\bullet-}$ during activation of O_2 by the flavoprotein glucose oxidase; see: Roth, J. P.; Klinman, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 62. In contrast, the acceleration of electron-transfer reduction of O_2 by NH_4^+ in solution results from a large positive shift of the one-electron reduction potential of O_2 due to the strong hydrogen bond of NH_4^+ with $O_2^{\bullet-}$, when the reorganization energy of electron-transfer becomes much larger than the value in the absence of NH_4^+.