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Electron Transfer Properties of Singlet Oxygen and Promoting Effects of Scandium Ion

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Electron-transfer kinetics from strong one-electron reductants such as decamethylferrocene and chromium(II) complexes to singlet oxygen ($^1O_2$: $^1\Delta_g$) were examined using laser flash photolysis in oxygen-saturated deuterated acetonitrile. The formation of decamethylferricenium ion in electron transfer from decamethylferrocene to $^1O_2$ was observed as a transient absorption band at $\lambda_{max} = 780$ nm, whereas the formation of $O_2^{\bullet -}$ is detected as a transient absorption spectrum of hexyl viologen radical cation ($\lambda_{max} = 600$ nm) which is formed by an electron transfer from $O_2^{\bullet -}$ to hexyl viologen. The reorganization energy of the electron-transfer reduction of $^1O_2$ in acetonitrile has been determined as 1.73 ± 0.14 eV from the analysis of the rate constants of electron transfer from the one-electron reductants to $^1O_2$ in light of the Marcus theory of electron transfer. The solvent-dependent reorganization energy of $^1O_2$ in acetonitrile is smaller than the corresponding value of ground-state oxygen in water (1.97 ± 0.03 eV), reflecting the longer O−O bond length in the excited state in reference to the ground state and the smaller solvation in acetonitrile. The reactivity of $^1O_2$ in an outer-sphere electron-transfer reaction from ferrocene to $^1O_2$ is enhanced by the addition of scandium triflate [$Sc(OTf)_3$]. This is ascribed to the strong binding of Sc^{3+} with the one-electron reduced species, i.e., $O_2^{\bullet -}$ rather than the excited state ($^1O_2$).

Introduction

Since direct concerted reactions between singlet organic molecules and triplet oxygen ($^3O_2$: $^3\Sigma_g^-$) are spin-forbidden, only electron transfer from organic donors to O_2 is allowed to occur. In contrast to $^3O_2$, the lowest excited state of oxygen, i.e., singlet oxygen ($^1O_2$: $^1\Delta_g$), can react directly with a number of organic and biochemical molecules to yield oxygenated products.[1−5] The electron-transfer reactivity of $^1O_2$ is also enhanced significantly as compared to $^3O_2$ because the one-electron reduction potential is shifted positively by the excitation energy of 0.98 eV.[3b,6] Thus, an electron-transfer mechanism has often been postulated in the interaction between $^1O_2$ and various types of electron donors.[7−12] A large number of rate constants have now been compiled for the reaction between $^1O_2$ and electron donors.[13−19] In these cases, however, the quenching of $^1O_2$ by electron donors generally occurs via formation of exciplexes, which involve only a partial charge-transfer rather than a full electron transfer.[13−19] A full electron transfer that is an exceptional case has only been reported by Foote et al. for the quenching of $^1O_2$ by *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD) in D_2O, in which formation of $TMPD^{\bullet +}$ was actually observed.[12a] The quenching of $^1O_2$ by TMPD has also been examined in a series of aprotic solvents, but in no other cases $TMPD^{\bullet +}$ has been observed.[14] Oxygen is known to be reduced more easily in water than in an aprotic solvent due to the effect of the stronger solvation of $O_2^{\bullet -}$ in water, as indicated by the large shift of −0.44 V for the $O_2/O_2^{\bullet -}$ couple on going from water to an aprotic solvent.[20] There has so far been no definitive report on outer-sphere electron-transfer reactions of $^1O_2$ in an aprotic solvent. Thus, the fundamental electron-transfer properties of $^1O_2$ such as the reorganization energy of electron transfer has yet to be evaluated in light of the Marcus theory of electron transfer.[21]

The electron acceptor ability of $^1O_2$ may be improved in the presence of metal ions, since a number of recent examples report on electron-transfer reactions, which reveal a significant acceleration in the presence of metal ions acting as a catalyst or promoter.[22,23] Scandium ion has recently been reported to be the most effective promoter among various metal ions in metal ion-promoted electron-transfer reduction of ground-state oxygen.[24] However, the reactivity of $^1O_2$ has never been controlled by the presence of metal ions.

We report herein the first kinetic data for outer-sphere electron-transfer reactions of $^1O_2$ with coordinately saturated inorganic complexes which can act as strong one-electron reductants to evaluate the reorganization energy for the reduction of $^1O_2$ in light of the Marcus theory of electron transfer.[21] The reorganization energy of the electron-transfer reduction of $^3O_2$ has previously been determined as 1.97 ± 0.03 eV from the direct rate measurements for the electron self-exchange between $^{36}O_2^{\bullet -}$ and $^{32}O_2$ utilizing ^{18}O as a probe.[25] Thus, the present study provides the first opportunity to compare the reorganization energies between the ground-state ($^3O_2$: $^3\Sigma_g^-$) and the excited-state oxygen ($^1O_2$: $^1\Delta_g$). We also report the promoting effects of scandium triflate [$Sc(OTf)_3$] on the outer-sphere electron-transfer reaction of $^1O_2$. The formation of $O_2^{\bullet -}-Sc^{3+}$ complex[26] produced in Sc^{3+}-promoted electron transfer from ferrocene to $^1O_2$ has been successfully detected by ESR. This

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may be the first case in which the reactivity of $^1O_2$ has been enhanced by the presence of metal ions.

Experimental Section

Materials. Decamethylferrocene $[Fe(Cp^*)_2]$ was obtained from Wako Pure Chemicals. Ferrocene $[Fe(Cp)_2]$ was obtained from Tokyo Kasei Organic Chemicals and purified by sublimation. $Cr(bpy)_3(PF_6)_2$ (bpy = 2,2′-bipyridine) and $Cr(phen)_3(PF_6)_2$ (phen = 1,10-phenanthroline) were prepared according to the literature.[27] 9,10-Dicyanoanthracene (DCA) was obtained from Tokyo Kasei Organic Chemicals. Scandium trifluoromethanesulfonate, $Sc(OTf)_3$ (99%, F.W. = 492.16) was obtained from Pacific Metals Co., Ltd. (Taiheiyo Kinzoku). 1,1-Dihexyl-4,4′-dipyridinium dibromide and the corresponding diperchlorate salt were prepared according to the procedure described elsewhere.[28] Tetrabutylammonium hexafluorophosphate used as a supporting electrolyte for the electrochemical measurements was also obtained commercially from Tokyo Kasei Organic Chemicals. 7-Amino-4-methylcoumarin (coumarin 120) for the laser dye was purchased from Lambda Physik. Acetonitrile (MeCN) and propionitrile (EtCN) as solvent were purified and dried by the standard procedure. Acetonitrile−d_3 (99.8%) was obtained from EURI SO-TOP, CEA, France and used as received.

$^1O_2$ Phosphorescence Measurements. An O_2-saturated acetonitrile-d_3 solution containing DCA (2.5×10^{-4} M) in a quartz cell (optical path length 10 mm) was excited at $\lambda = 422$ nm using a Cosmo System LVU-200S spectrometer. A photomultiplier (Hamamatsu Photonics, R5509-72) was used to detect emission in the near-infrared region (band path 2 mm). For the phosphorescence lifetime measurements, samples were excited by the frequency-tripled output of Q-switched Nd:YAG laser (Spectra Physics GCR-150-10) operating at 10 Hz. Typical pulse energies at sample were in the range 1−2 mJ. The emission was detected by a liquid nitrogen-cooled photomultiplier (Hamamatsu Photonics, R5509-72). The rise and the fall times of the instrument output waveform are 2.4 and 6.4 ns at $\lambda = 1300$ nm, respectively. The signal was captured and averaged by a digital storage oscilloscope (Tektronix TDS3032) and transferred to a PC for analysis. Typical decays were recorded as the average of 32 laser shots. Nanosecond pulse for sample excitation ($\lambda = 422$ nm) was obtained by the dye laser (Usho Optical Systems DL50) with the coumarin 120 in methanol (0.12 g/L). The decays were analyzed by nonlinear least-squares analysis of the observed time profile with a single-exponential function and in all cases gave good quality fits.

Phosphorescence lifetimes (τ) were measured for CD_3CN solutions containing DCA (2.5×10^{-4} M) with various electron donors in the absence and presence of $Sc(OTf)_3$. A CD_3CN solution of $Cr(bpy)_3(PF_6)_2$ and $Cr(phen)_3(PF_6)_2$ was first prepared under an atmospheric pressure of Ar, and an aliquot of the solution was added to an oxygen-saturated DCA solution just before the measurements to avoid the oxidation of $Cr(bpy)_3(PF_6)_2$ and $Cr(phen)_3(PF_6)_2$. There was no change in the shape of the phosphorescence spectra but there was a decrease of the phosphorescence lifetime by the addition of a quencher. The Stern−Volmer relationship (eq 1) was obtained for the ratio of the phosphorescence lifetimes in the absence and presence of

$$\tau_0/\tau = 1 + k_q\tau_0[D] \tag{1}$$

$Sc(OTf)_3$ and the concentrations of various electron donors [D] used as quenchers (τ_0 is the lifetime in the absence of a quencher).

Fluorescence Measurements. Quenching experiments of the fluorescence of DCA were carried out on a Shimadzu spectrofluorophotometer (RF-5000). The excitation wavelength of DCA was 422 nm in MeCN. The monitoring wavelength corresponds to the maxima of the emission band at $\lambda_{max} = 435$ nm. Typically, the MeCN solution was deaerated by argon purging for 8 min prior to the measurements. Relative fluorescence intensities were measured for MeCN solutions containing DCA (1.0×10^{-5} M) with various electron donors and O_2. There was no change in the shape but the fluorescence intensity decreased with the addition of a quencher. The Stern−Volmer relationship (eq 1′) was obtained for the ratio of the emission

$$I_0/I = 1 + K_{SV}[D] \tag{1′}$$

intensities and the concentrations of various electron donors and O_2 used as quenchers. The fluorescence lifetime of DCA was reported as $\tau_f = 19.6$ ns in deaerated MeCN solution at 298 K.[29] The observed quenching rate constants k_q ($= K_{SV}\tau_f^{-1}$) were obtained from the Stern−Volmer constants K_{SV} and the fluorescence lifetime τ_f.

Steady-State Photolysis. For steady-state photoirradiation experiments, a square quartz cuvette (10 mm i.d.) which contained an O_2-saturated MeCN (3.0 cm^3) of ferrocene (5.0×10^{-4} M), DCA (1.0×10^{-4} M), and $Sc(OTf)_3$ (5.0×10^{-3} M) was irradiated with a xenon lamp (Ushio Model V1-501C) through a cut-off filter (Toshiba UV-37) transmitting $\lambda > 380$ nm at 298 K for 15 min. The photochemical reaction was monitored using a Hewllet Packard 8453 diode array spectrophotometer.

Laser Flash Photolysis. The measurements of transient absorption spectra in photooxidation of decamethylferrocene were performed according to the following procedures. The acetonitrile solution was saturated with oxygen by flowing oxygen gas for 10 min prior to the measurement. The oxygen-saturated solution containing DCA (2.5×10^{-4} M) and decamethylferrocene (2.0×10^{-3} M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 420 nm with the power of 30 mJ. Similarly the oxygen-saturated solution containing DCA (2.5×10^{-4} M), decamethylferrocene (2.3×10^{-3} M) and hexyl viologen perchlorate (3.4×10^{-4} M) was excited by a Nd:YAG laser (Continuum, SLII-10, 4−6 ns fwhm) at 430 nm with the power of 30 mJ. A xenon flash lamp was used for the probe beam, which was detected with a Si−PIN module (Hamamatsu, S5343) after passing through the photochemical quartz vessel (10 mm × 10 mm) and a monochromator. The output from Si−PIN module was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 298 K. The measurements of transient absorption spectra in photooxidation of decamethylferrocene in the presence of hexyl viologen perchlorate were performed according to the procedure described elsewhere.[30]

Electrochemical Measurements. Electrochemical measurements of decamethylferrocene and $Cr(phen)_3(PF_6)_2$ were performed on a BAS 100B electrochemical analyzer in deaerated MeCN containing 0.10 M $Bu_4N^+PF_6^-$ ($TBAPF_6$) as a supporting electrolyte at 298 K. The platinum working electrode was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an $Ag/AgNO_3$ (0.01 M) reference electrode. The E^0_{red} values (vs $Ag/AgNO_3$) are converted into those versus SCE by adding 0.29 V.[31]

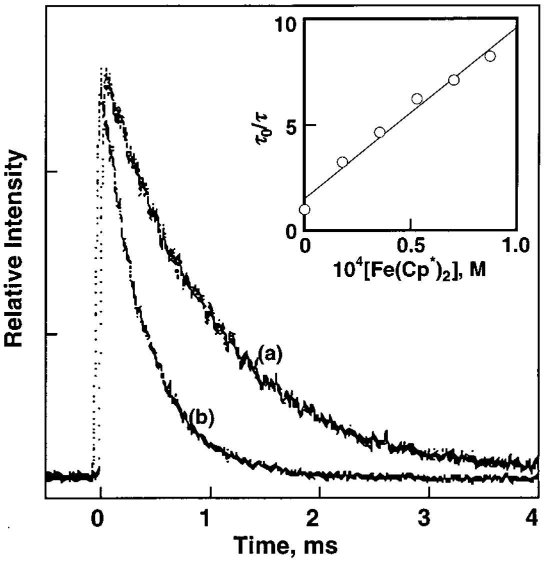

Figure 1. Decay curves of phosphorescence of $^1O_2$ at λ_{max} = 1270 nm in the absence and presence of Fe(Cp*)$_2$ (a, 0 M; b, 1.8 × 10^{-5} M) after laser flash of DCA (λ = 422 nm) in CD_3CN at 298 K. Inset: Stern−Volmer plot for the phosphorescence quenching of $^1O_2$ by Fe(Cp*)$_2$ in CD_3CN at 298 K.

ESR Measurements. The ESR spectra of O_2 radical anion ($O_2^{\bullet -}$) in the presence of Sc(OTf)$_3$ were measured at 193 K. The ESR spectrum of the Sc(OTf)$_3$ complex of $O_2^{\bullet -}$ was measured using a JEOL JES-FA100 with low-temperature cooling apparatus. The mixed solution of ferrocene (8.7 × 10^{-4} M), DCA (2.5 × 10^{-4} M), and Sc(OTf)$_3$ (1.0 × 10^{-2} M) in O_2-saturated propionitrile at 193 K was irradiated for 8 min with a high-pressure mercury lamp (USH-1005D) through a cutoff filter (Toshiba UV-37) transmitting λ > 380 nm focusing at the sample cell in the ESR cavity. The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra. The *g* values and hyperfine splitting constants (hfs) were calibrated using an Mn^{2+} marker.

Results and Discussion

Outer-Sphere Electron Transfer from Electron Donors to $^1O_2$ in CD_3CN. Singlet oxygen is produced using 9,10-dicyanoanthracene (DCA) as a sensitizer in oxygen-saturated CD_3CN[32] and detected by the $^1O_2$ phosphorescence at 1270 nm (see Experimental Section). The decay of $^1O_2$ phosphorescence obeys first-order kinetics, and the lifetime (1.0 ms) agreed with literature data.[13] The one-electron reduction potential of $^1O_2$ in acetonitrile is evaluated as (E^{0*}_{red} vs SCE = 0.11 V) by adding the excitation energy of $^1O_2$ (0.98 eV) to the E^0_{red} value of $^3O_2$ in the same solvent (−0.87 V).[33] Thus, one-electron reductants possessing the one-electron oxidation potential (E^0_{ox}) lower than 0.11 V are required to examine electron-transfer reactions with $^1O_2$. The first choice of an electron donor is decamethylferrocene [Fe(Cp*)$_2$], since the E^0_{ox} value is sufficiently negative (−0.14 V)[34] and the reorganization energy of outer-sphere electron transfer has well been established.[35] The addition of Fe(Cp*)$_2$ as a quencher results in a decrease in the $^1O_2$ lifetime, as shown in Figure 1. The Stern−Volmer plot (eq 1) gives a good linear correlation between τ_0/τ and the quencher concentration (inset of Figure 1). The quenching rate constant (k_q) is determined from the slope as 5.8 × 10^7 M^{-1} s^{-1}.

The transient formation and decay of [Fe(Cp*)$_2$]$^+$ at 780 nm in electron transfer from Fe(Cp*)$_2$ to $^1O_2$ and back electron transfer are successfully detected by the laser flash photolysis of an oxygen saturated CD_3CN solution containing DCA and Fe(Cp*)$_2$, as shown in Figure 2. The new absorption band appears at 780 nm upon the laser excitation, and this is a diagnostic absorption band due to [Fe(Cp*)$_2$]$^+$.[33] Under the present experimental conditions, the singlet excited state of DCA (^{1}DCA*) is mostly quenched by O_2 in O_2-saturated CD_3CN where the O_2 concentration (1.3 × 10^{-2} M)[36] is much higher than the Fe(Cp*)$_2$ concentration (Figure 2), since both rate constants of the energy transfer from ^{1}DCA* to O_2 and electron transfer from Fe(Cp*)$_2$ to ^{1}DCA* are expected to be close to the diffusion-controlled limit.[37] In such a case, the formation of Fe(Cp*)$_2^+$ via electron transfer from Fe(Cp*)$_2$ to ^{1}DCA* may be negligible. This is supported by the fact that there was no formation of Fe(Cp*)$_2^+$ detected in the absence of O_2 under otherwise the same experimental conditions. The absorption at 780 nm decays at 40 μs under the present experimental conditions probably due to the charge recombination reaction from $O_2^{\bullet -}$ to Fe(Cp*)$_2^+$ to produce the ground-state molecules (see inset of Figure 2).

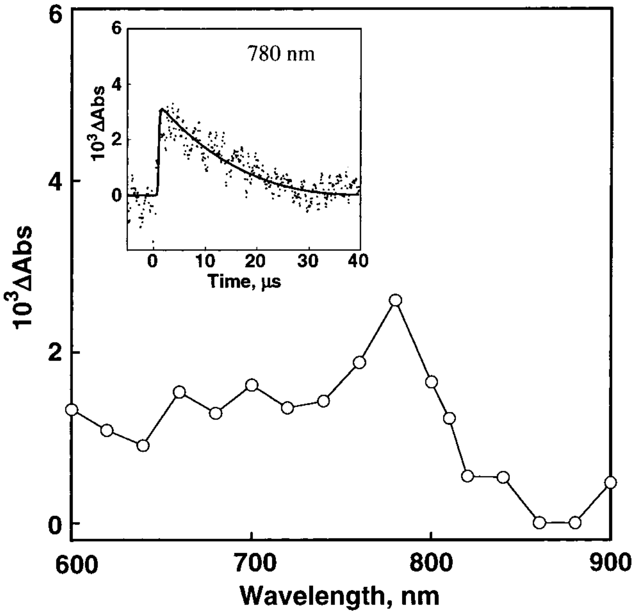

Figure 2. Transient absorption spectrum in the photooxidation of Fe(Cp*)$_2$ (2.0 × 10^{-3} M) at 1.5 μs after laser flash of DCA (2.5 × 10^{-4} M) in O_2-saturated CH_3CN at 298 K (laser excitation at λ = 420 nm). Inset: Time profile of the absorbance at 780 nm.

The transient formation of $O_2^{\bullet -}$ which should be formed together with [Fe(Cp*)$_2$]$^+$ observed in Figure 2 is also examined by employing hexyl viologen (HV^{2+}) to remove in turn an electron from $O_2^{\bullet -}$ formed in electron transfer from Fe(Cp*)$_2$ to $^1O_2$, as shown in Scheme 1. The transient formation of $HV^{\bullet +}$ formed in electron transfer from $O_2^{\bullet -}$ in Scheme 1 was detected by the laser flash photolysis of an O_2-saturated CD_3CN solution containing DCA (2.5 × 10^{-4} M), Fe(Cp*)$_2$ (2.3 × 10^{-3} M), and HV^{2+} (3.4 × 10^{-4} M) as shown in Figure 3. The appearance of the absorption at 600 nm is ascribed due to $HV^{\bullet +}$,[30] which decays over about 100 μs. The rate constant for the formation of $HV^{\bullet +}$ is determined as 6.1 × 10^7 M^{-1} s^{-1} by the curve fit shown in inset of Figure 3.[38] This value agrees well with the k_{et} value determined from the $^1O_2$ phosphorescence lifetime measurements (Figure 1). Such an agreement indicates that the rate-determining step for formation of $HV^{\bullet +}$ is the electron transfer from Fe(Cp*)$_2$ to $^1O_2$ and the subsequent electron transfer from $O_2^{\bullet -}$ to HV^{2+} is fast (Scheme 1).[39] Thus, the

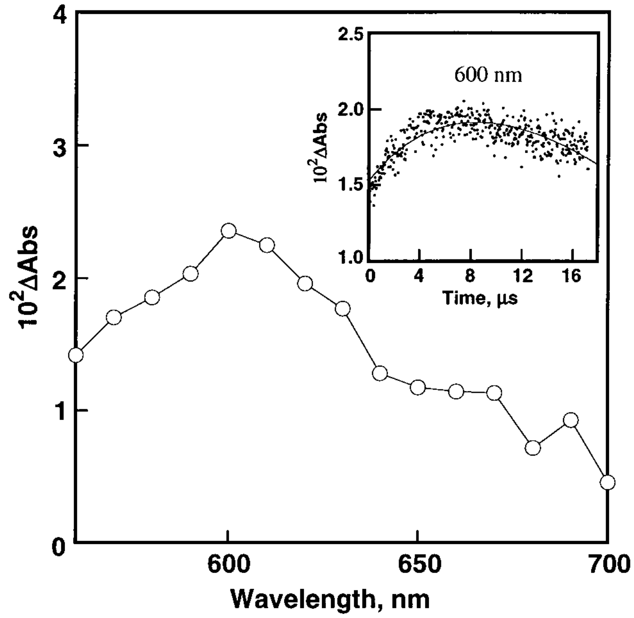

Figure 3. Transient absorption spectrum of hexyl viologen cation radical observed at 4 μs after laser flash of DCA (2.5×10^{-4} M) in the presence of Fe(Cp*)$_2$ (2.3×10^{-3} M) and hexyl viologen perchlorate (3.4×10^{-4} M) in O$_2$-saturated CD$_3$CN at 298 K (laser excitation at λ = 430 nm). Inset: Time profile of the absorbance at 600 nm.

SCHEME 1

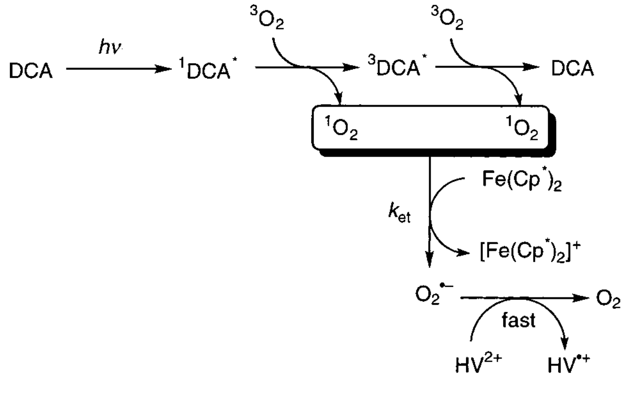

TABLE 1: Phosphorescence Quenching Rate Constants (k_{et}) of $^1O_2$ by Electron Donors in CD$_3$CN at 298 K, Redox Potentials (E^0_{ox}) of Electron Donors, and Reorganization Energies [λ(D$^+$/D)] for the Electron Self-Exchange Reactions

electron donor	E^0_{ox} (V)	ΔG^0_{et} (eV)	k_{et} ($M^{-1}\,s^{-1}$)	λ(D$^+$/D) (eV)	$\lambda(^1O_2/O_2^{\bullet-})$ (eV)
Cr(phen)$_3^{2+}$	−0.29	−0.40	3.4×10^8	0.70^b	1.81 ± 0.14
Cr(bpy)$_3^{2+}$	−0.26^a	−0.37	3.6×10^8	0.70^b	1.71 ± 0.14
Fe(Cp*)$_2$	−0.14	−0.25	5.8×10^7	0.80^c	1.61 ± 0.14

[a] Ref 27a. [b] Ref 27b. [c] Ref 34.

occurrence of electron transfer from an electron donor to $^1O_2$ in an aprotic solvent (CD$_3$CN) has well been confirmed for the first time.

The other choice of an electron donor is Cr(bpy)$_3^{2+}$, since the E^0_{ox} value is more negative (−0.26 V) and the reorganization energy of outer-sphere electron transfer has also been determined previously.[27a] Cr(phen)$_3^{2+}$, which has redox properties similar to those of Cr(bpy)$_3^{2+}$, was also used as an electron donor. As is the case of Fe(Cp*)$_2$, the rate constants (k_{et}) for electron transfer from Cr(bpy)$_3^{2+}$ and Cr(phen)$_3^{2+}$ to $^1O_2$ were determined from the $^1O_2$ phosphorescence lifetime measurements in the presence of these electron donors (see Experimental Section). The k_{et} values thus determined are listed in Table 1 together with the E^0_{red} values, the free energy changes of electron transfer (ΔG^0_{et}), and the reorganization energies [λ(D$^+$/D)] of electron self-exchange between the electron donor (D) and D$^+$.[27a,35] The use of stronger electron donors than Cr(bpy)$_3^{2+}$ or Cr(phen)$_3^{2+}$ would be much more difficult because of the instability in the presence of O$_2$.

Reorganization Energy of Electron Self-Exchange between $^1O_2$ and $O_2^{\bullet-}$. The dependence of k_{et} on the free energy change of electron transfer (ΔG^0_{et}) for outer-sphere electron transfer has been well established by Marcus as given by eq 2, where λ

$$k_{et} = Z\exp[-(\lambda/4)(1 + \Delta G^0_{et}/\lambda)^2/RT] \qquad (2)$$

is the reorganization energy of electron transfer and Z is the collision frequency taken as 1×10^{11} M^{-1} s^{-1}.[21,40] The λ value is determined from the k_{et} and ΔG^0_{et} values using eq 3, which is derived from eq 2. Since the λ value is considered as the

$$\lambda = 2[-RT\ln(k_{et}/Z)] - \Delta G^0_{et} + [(\Delta G^0_{et} - 2[-RT\ln(k_{et}/Z)])^2 - (\Delta G^0_{et})^2]^{1/2} \qquad (3)$$

average of the λ values of the electron self-exchange reactions of the donor (D$^+$/D) and acceptor ($^1O_2/O_2^{\bullet-}$), the $\lambda(^1O_2/O_2^{\bullet-})$ values are evaluated from the λ and the reported λ(D$^+$/D) values using eq 4. The $\lambda(^1O_2/O_2^{\bullet-})$ values thus derived from the k_{et} values using eqs 3

$$\lambda(^1O_2/O_2^{\bullet-}) = 2\lambda - \lambda(D^+/D) \qquad (4)$$

and 4 are also listed in Table 1.[40]

The $\lambda(^1O_2/O_2^{\bullet-})$ values in CD$_3$CN are eventually the same (1.73 ± 0.14 eV) irrespective of different electron donors in Table 1 as expected by the Marcus theory of electron transfer.[21] The $\lambda(^1O_2/O_2^{\bullet-})$ value in D$_2$O is also evaluated from the reported k_{et} value for electron transfer from TMPD to $^1O_2$, reported by Foote et al.[12a] as 1.69 eV.[41] These values for $^1O_2$ are smaller than the corresponding $\lambda(^3O_2/O_2^{\bullet-})$ value for the ground-state oxygen (1.97 ± 0.03 eV).[25] Such a smaller λ value for singlet oxygen may well be ascribed to the smaller inner reorganization energy due to the longer O−O bond length in the excited state (1.2155 Å) as compared to that in the ground state (1.2076 Å).[42,43]

Promoting Effects of Sc^{3+} on Electron-Transfer Reactions of $^1O_2$. When decamethylferrocene [Fe(Cp*)$_2$] is replaced by ferrocene [Fe(Cp)$_2$], the electron transfer from Fe(Cp)$_2$ to $^1O_2$ becomes endergonic ($\Delta G^0_{et} = 0.26$ eV > 0) due to the more positive E^0_{ox} value (0.37 V) than the value of Fe(Cp*)$_2$ (−0.14 V). Nevertheless, the quenching of $^1O_2$ by Fe(Cp)$_2$ occurs as shown in Figure 4a. From the slope of the Stern−Volmer plot in Figure 4a is obtained the k_q value as 4.9×10^6 M^{-1} s^{-1}. The rate constant of electron transfer from Fe(Cp)$_2$ to $^1O_2$ (k_{et}) is calculated as 7.3×10^2 M^{-1} s^{-1} from the ΔG^0_{et} value (0.26 eV) and λ value (1.34 eV)[44] using the Marcus equation (eq 2). The calculated k_{et} value is much smaller than the observed k_q value. Such a large discrepancy between the calculated and observed rate constants indicates that the quenching of $^1O_2$ by Fe(Cp)$_2$ occurs via an exciplex formation with a partial charge-transfer rather than a full electron transfer as reported for a number of $^1O_2$ quenching systems where no emission from the exciplex has been observed.[13−19,45] In fact, no transient formation of HV$^{\bullet+}$ was observed by the laser flash photolysis of an O$_2$-saturated CD$_3$CN solution containing DCA (2.5×10^{-4} M), Fe(Cp)$_2$ (2.3×10^{-3} M) and HV^{2+} (3.4×10^{-4} M), in contrast to the result in Figure 3.

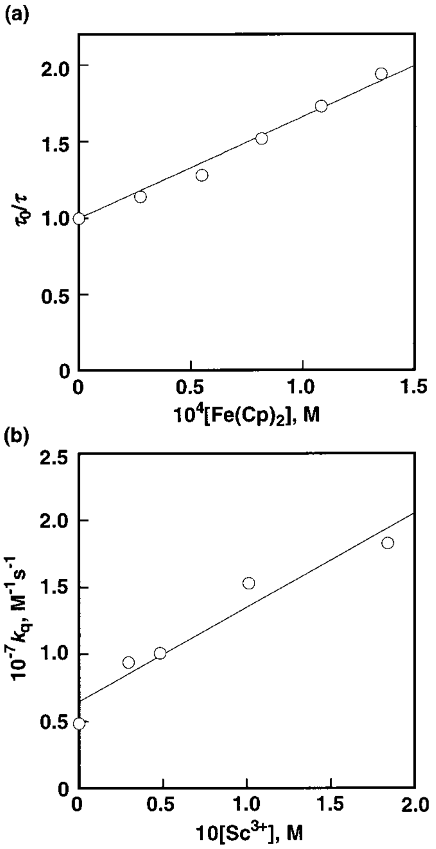

Figure 4. (a) Stern−Volmer plot for the phosphorescence quenching of $^1O_2$ by Fe(Cp)$_2$ in CD_3CN at 298 K. (b) Plot of the quenching rate constant (k_q) vs the Sc^{3+} concentration.

We have recently reported that a highly endergonic electron transfer from Co(TPP) (TPP^{2-} = dianion of tetraphenylporphyrin) to $^3O_2$ becomes possible in the presence of Sc(OTf)$_3$ in MeCN.[24] This is ascribed to the strong binding between $O_2^{\bullet -}$ and Sc^{3+}, which leads to the positive shift of the one-electron reduction potential of $^3O_2$. Such a binding between $O_2^{\bullet -}$ and the metal ion causes a split of the degenerate π* orbital level of $O_2^{\bullet -}$, and the splitting energy (ΔE) has been determined from the negative shift of the g_{zz} value of the ESR spectrum.[24] The ΔE values are linearly correlated to the rate constants of metal ion-promoted electron-transfer reactions (log k_{et}).[24] From the linear correlation, the binding energy between $O_2^{\bullet -}$ and Sc^{3+} has been evaluated as 0.56 eV.[24,46] The E^0_{red}* value of $^1O_2$ is expected to be shifted to the positive direction by the binding energy between $O_2^{\bullet -}$ and Sc^{3+} up to 0.68 V (vs SCE). In such a case, an electron transfer from Fe(Cp)$_2$ (E^0_{ox} vs SCE = 0.37 V) to $^1O_2$ becomes energetically feasible.

The quenching rate constant (k_q) for the $^1O_2$ quenching by Fe(Cp)$_2$ increases with increasing the Sc^{3+} concentration, as shown in Figure 4b. Such an enhancement of the quenching rate may be ascribed to the occurrence of electron transfer from Fe(Cp)$_2$ to $^1O_2$ in the presence of Sc^{3+}. In fact, a steady-state photoirradiation of an O_2-saturated CH_3CN solution containing DCA (1.0×10^{-4} M), Fe(Cp)$_2$ (5.0×10^{-4} M) and Sc(OTf)$_3$ (5.0×10^{-3} M) results in formation of Fe(Cp)$_2^+$, as indicated by appearance of the absorption band at λ_{max} = 618 nm. Fe(Cp)$_2$ was converted to Fe(Cp)$_2^+$ in the presence of Sc(OTf)$_3$ at prolonged irradiation time. The yield of Fe(Cp)$_2^+$ in the presence of 5.0×10^{-3} M Sc(OTf)$_3$ was 95%. However, no formation of Fe(Cp)$_2^+$ was observed without O_2 or Sc(OTf)$_3$ under otherwise the same experimental conditions. Thus, electron transfer from Fe(Cp)$_2$ to $^1O_2$ is made possible by the presence of Sc^{3+} to yield Fe(Cp)$_2^+$ and $O_2^{\bullet -}$ bound to Sc^{3+} ($O_2^{\bullet -}-Sc^{3+}$), as shown by eq 5. In contrast to the case of electron transfer from Fe(Cp*)$_2$ to $^1O_2$ without Sc^{3+} (Figure 3), there is no charge recombination reaction from $O_2^{\bullet -}$-Sc^{3+} to Fe(Cp)$_2^+$ to produce the ground-state molecules, and these are not intermediates but the final products (eq 5).

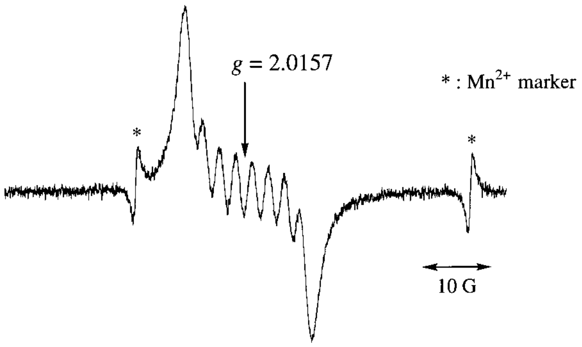

Figure 5. ESR spectrum of the $O_2^{\bullet -}-Sc^{3+}$ complex produced in photooxidation of Fe(Cp)$_2$ (8.7×10^{-4} M) by $^1O_2$ in the presence of DCA (2.5×10^{-4} M) and Sc^{3+} (1.0×10^{-2} M) in O_2 saturated EtCN at 193 K.

$$\mathrm{Fe(Cp)_2} + {}^1\mathrm{O_2} + \mathrm{Sc^{3+}} \rightarrow \mathrm{Fe(Cp)_2}^+ + \mathrm{O_2}^{\bullet -}-\mathrm{Sc^{3+}} \quad (5)$$

The formation of $O_2^{\bullet -}-Sc^{3+}$ is directly confirmed by the ESR measurements of an O_2-saturated propionitrile (EtCN) solution containing Fc(Cp)$_2$ (8.7×10^{-4} M) and DCA (2.5×10^{-4} M) at 193 K under photoirradiation with a xenon lamp. Figure 5 shows the observed ESR spectrum under the photoirradiation. The clear eight-line isotropic spectrum at the center is ascribed to the superhyperfine coupling of $O_2^{\bullet -}$ with the $^7/_2$ nuclear spin of the scandium nucleus (a_{Sc} = 4.21 G) in $O_2^{\bullet -}-Sc^{3+}$ as reported previously.[26] The isotropic g value (2.0157) is appreciably smaller than the corresponding value (2.030) of uncomplexed $O_2^{\bullet -}$ at 77 K, being consistent with the spin delocalization to the scandium nucleus as demonstrated by observation of superhyperfine.[26] Although the ESR spectrum of $O_2^{\bullet -}$ cannot be observed in solution due to the fast relaxation time, the binding of Sc^{3+} with $O_2^{\bullet -}$ makes it possible to observe the ESR spectrum in solution.[26] The $O_2^{\bullet -}-Sc^{3+}$ complex disappears at higher temperatures, e.g., 233 K due to the facile disproportionation reaction. This is the reason propionitrile is used instead of acetonitrile which is frozen at 229 K.

Effects of other metal ions on the $^1O_2$ quenching by Fe(Cp)$_2$ were also examined. However, there was no effects on the $^1O_2$ phosphorescence quenching by Fe(Cp)$_2$ when Sc(OTf)$_3$ was replaced by Mg(ClO$_4$)$_2$.

To examine a possible interaction between $^1O_2$ and Sc^{3+}, the $^1O_2$ phosphorescence spectra are compared in the absence and presence of Sc(OTf)$_3$ (2.3×10^{-3} M), as shown in Figure 6. The phosphorescence intensity is not affected by the presence of Sc^{3+}, and the lifetime is independent of the Sc^{3+} concentration (see inset of Figure 6). It was confirmed that the phosphorescence intensity and lifetime in the presence of large concentration of Sc^{3+} (0.18 M) were the same as those in the absence of Sc^{3+}. This indicates that the formation constant of the $^1O_2-Sc^{3+}$ complex formed prior to the electron transfer from Fe(Cp)$_2$ is too small to be detected in the $^1O_2$ phosphorescence spectra. Thus, the strong binding of Sc^{3+} occurs only to the one-electron reduced species, i.e., $O_2^{\bullet -}$, resulting in the occurrence of a full electron transfer which is faster than an exciplex formation with a partial electron transfer.

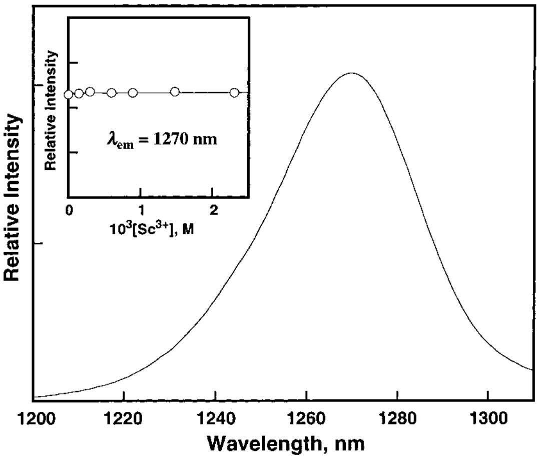

Figure 6. DCA-photosensitized phosphorescence spectrum of $^1O_2$ in CD_3CN at 298 K. Inset: Dependence of relative phosphorescence intensity of $^1O_2$ on $[Sc^{3+}]$ in CD_3CN at 298 K.

The k_q value (1.8×10^7 M^{-1} s^{-1}) in the presence of the largest $[Sc^{3+}] = 0.18$ M in Figure 4b is smaller than the k_q value (5.8×10^7 M^{-1} s^{-1}) for electron transfer from $Fc(Cp^*)_2$ to $^1O_2$. This indicates that the reorganization energy for reduction of $^1O_2$ in the presence of Sc^{3+} is significantly larger than the value in the absence of Sc^{3+} due to the strong binding of Sc^{3+} with $O_2^{\bullet -}$.

Summary and Conclusions

Occurrence of electron transfer from an electron donor to $^1O_2$ has been demonstrated for the first time in an aprotic solvent such as MeCN by detecting both the oxidized and reduced species using laser flash photolysis. Determination of the rate constants for electron transfer from one-electron reductants to $^1O_2$ has led to the first evaluation of the reorganization energy for electron-transfer reduction of $^1O_2$, which is compared with the value of $^3O_2$. The smaller reorganization energy of $^1O_2$ in reference to $^3O_2$ is ascribed to the longer O−O distance of the excited state than the ground state. Although there has been no example to attenuate the reactivity of $^1O_2$ by metal ions, it has been shown in this study that the electron-transfer reactivity of $^1O_2$ is enhanced by the strong binding of Sc^{3+} with $O_2^{\bullet -}$ produced in the electron transfer.

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(38) There was no change in the $^1O_2$ emission intensity upon addition of HV^{2+} to the DCA/Fc(Cp*)$_2$/O_2 system.

(39) The electron transfer from $O_2^{\bullet-}$ to $^1O_2$ to generate the ground-state moleucles may be negligible under the present experimental conditions such that the concentration of generated $^1O_2$ (ca. 10^{-5} M, see inset of Figure 3) is much smaller than the HV^{2+} concentration.

(40) A number of λ values have been determined using the Z value (1×10^{11} M^{-1} s^{-1}) which is most frequently used as the frequency factor for a bimolecular process. Thus, we used this value for evaluation of the λ value. See: Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987. However, a referee pointed out that the Z value may vary by more than a factor of 2. The difference in the Z value by a factor of 3 [3×10^{11} to $(^1/_3) \times 10^{11}$] in evaluating the λ and $\lambda(D^+/D)$ value results in uncertainty of ± 0.14 eV in $\lambda(^1O_2/O_2^{\bullet-})$, which is taken as the experimental error in Table 1.

(41) The λ value in D_2O is expected to be larger than the value in CD_3CN because of the larger solvation in D_2O. However, such a difference may be masked by the experimental errors (± 0.14 V) in determining the λ values in the two solvents.

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(44) The λ value is obtained as the average of the $\lambda(D^+/D)$ value of Fe(Cp)$_2$ (1.00 eV)[34] and $\lambda(O_2^{\bullet-}/O_2)$ value determined in this study (1.71 eV).

(45) There was no change in λ_{max}, but the $^1O_2$ emission intensity decreased in the presence of Fe(Cp)$_2$.

(46) The slope of the linear correlation between log k_{et} and ΔE is 14 which is somewhat smaller than the value (16.9) expected from the correlation between log k_{et} and the binding energies of $O_2^{\bullet-}$ with metal ions. By taking into account the ratio (14/16.9), the binding energy between $O_2^{\bullet-}$ and Sc^{3+} is determined as 0.56 eV from the ΔE value (0.68 eV).