

Communication

Water-Induced Regeneration of a 2,2-Diphenyl-1-picrylhydrazyl Radical after Its Scandium Ion-Promoted Electron-Transfer Disproportionation in an Aprotic Medium

Ikuo Nakanishi ^{1,*}, Yoshimi Shoji ¹, Kei Ohkubo ^{1,2,*}, Hiromu Ito ¹ and Shunichi Fukuzumi ^{3,4,*}

- ¹ Quantum RedOx Chemistry Team, Institute for Quantum Life Science (iQLS), Quantum Life and Medical Science Directorate, National Institutes for Quantum Science and Technology (QST), Inage-ku, Chiba 263-8555, Japan; shoji.yoshimi@qst.go.jp (Y.S.); ito.hiromu@qst.go.jp (H.I.)
 - ² Institute for Advanced Co-Creation Studies, Open and Transdisciplinary Research Initiatives, Osaka University, Suita 565-0871, Japan
 - ³ Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Republic of Korea
 - ⁴ Department of Chemistry, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan
- * Correspondence: nakanishi.ikuo@qst.go.jp (I.N.); ohkubo@irdd.osaka-u.ac.jp (K.O.); fukuzumi@chem.eng.osaka-u.ac.jp (S.F.)

Abstract: A neutral, stable radical, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH[•]), has been frequently used to estimate the activity of antioxidants for more than 60 years. However, the number of reports about the effect of metal ions on the reactivity of DPPH[•] is quite limited. We have recently reported a unique electron-transfer disproportionation of DPPH[•] to produce the DPPH cations (DPPH⁺) and anions (DPPH[−]) upon the addition of scandium triflate [Sc(OTf)₃ (OTf = OSO₂CF₃)] to an acetonitrile (MeCN) solution of DPPH[•]. The driving force of this reaction is suggested to be an interaction between DPPH[−] and Sc³⁺. In this study, it is demonstrated that the addition of H₂O to the DPPH[•]–Sc(OTf)₃ system in MeCN resulted in an increase in the absorption band at 519 nm due to DPPH[•]. This indicated that an electron-transfer comproportionation occurred to regenerate DPPH[•]. The regeneration of DPPH[•] was also confirmed by electron paramagnetic resonance (EPR) spectroscopy. The amount of DPPH[•] increased with an increasing amount of added H₂O to reach a constant value. The detailed mechanism of regeneration of DPPH[•] was proposed based on the detailed spectroscopic and kinetic analyses, in which the reaction of DPPH⁺ with [(DPPH)₂Sc(H₂O)₃]⁺ generated upon the addition of H₂O to [(DPPH)₂Sc]⁺ is the rate-determining step.

Keywords: radical; electron transfer; disproportionation; scandium ion; Lewis acid; comproportionation; EPR; kinetics; reaction mechanism



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1. Introduction

2,2-Diphenyl-1-picrylhydrazyl radical (DPPH[•]) is a neutral, stable radical that has been frequently used to estimate the activity of antioxidants for more than 60 years [1–4]. It is known that the radical-scavenging reactivity of antioxidants is significantly affected by the reaction environments, such as solvents [5,6], pH [7,8], the presence of metal ions [9–18], and so on. However, the number of reports about the reactivity of DPPH[•] in the presence of metal ions is quite limited. We have demonstrated that the DPPH[•]-scavenging reactivity of phenolic compounds, such as a vitamin E model, flavonoids, and hydroquinones, is significantly enhanced in the presence of redox-inactive metal ions with a moderate Lewis acidity, such as Mg²⁺ [10] and Al³⁺ [9]. The coordination of the metal ion to the one-electron reduced species of DPPH[•] (DPPH[−]) may stabilize the product, resulting in the acceleration of the electron transfer. On the other hand, DPPH[•] is known to undergo reversible one-electron reduction and oxidation to produce DPPH[−] and the corresponding cation (DPPH⁺),

respectively, in organic solvents (Figure 1A) [19–22]. We have also reported that an electron-transfer disproportionation of $\text{DPPH}^\bullet$ to produce DPPH^+ and DPPH^- occurs upon the addition of scandium triflate [$\text{Sc}(\text{OTf})_3$ ($\text{OTf} = \text{OSO}_2\text{CF}_3$)] to an acetonitrile (MeCN) solution of $\text{DPPH}^\bullet$ [23]. Since there is no proton source in this reaction system, DPPH^- does not undergo protonation to produce DPPH-H . Then, DPPH^- may significantly be stabilized by the strong Lewis acidity of Sc^{3+} with a formation constant of $2.3 \times 10^3 \text{ M}^{-1}$. Recently, Denzo et al. have reported the reactivity of $\text{DPPH}^\bullet$ in the presence of metal cations (Cu^{2+} and Zn^{2+}) and acids (HClO_4 and HNO_3) in MeCN [24]. A strong Brønsted acid, such as HClO_4 , is required for the disproportionation of $\text{DPPH}^\bullet$ to occur. We report herein that the addition of water to the MeCN solution containing DPPH^+ , DPPH^- and $\text{Sc}(\text{OTf})_3$ resulted in the electron-transfer comproportionation between DPPH^+ and DPPH^- to regenerate $\text{DPPH}^\bullet$, demonstrating the reversibility of the Sc^{3+} -catalyzed electron-transfer disproportionation of $\text{DPPH}^\bullet$. The reversible redox reactivity of $\text{DPPH}^\bullet$ in the presence of the redox-inactive metal ion with strong Lewis acidity shows a unique electron-transfer redox reaction of radical species in aprotic media.

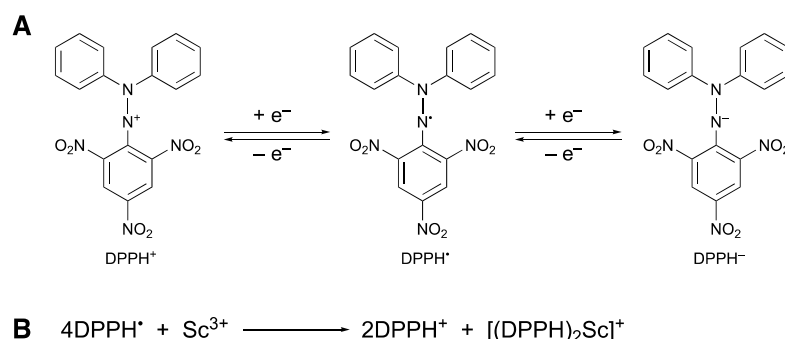


Figure 1. (A) Redox behavior of $\text{DPPH}^\bullet$. (B) Sc^{3+} -induced disproportionation of $\text{DPPH}^\bullet$.

2. Results and Discussion

When $\text{Sc}(\text{OTf})_3$ was added to an MeCN solution of $\text{DPPH}^\bullet$, a decrease in the absorption band of $\text{DPPH}^\bullet$ at 519 nm was observed, accompanied by an increase in the absorption band at 380 nm due to the electron-transfer disproportionation [23]. The band at 380 nm is characteristic of DPPH^+ . The spectral titration conducted in this study shows the $\text{Sc}(\text{OTf})_3/\text{DPPH}^\bullet$ molar ratio being 1:4 (Figure 2). Thus, two molecules of DPPH^- are suggested to be stabilized by one Sc^{3+} , as shown in Figure 1B, although the $[(\text{DPPH})_2\text{Sc}]^+$ complex has yet to be detected.

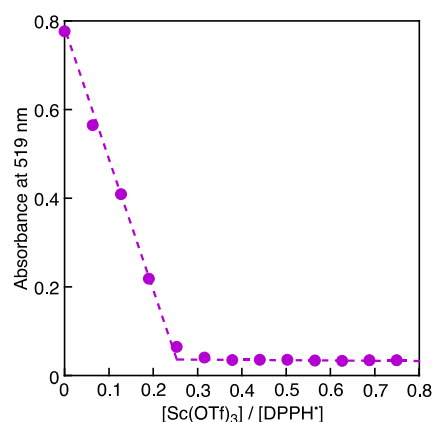


Figure 2. Plot of the absorbance at 519 nm vs. $[\text{Sc}(\text{OTf})_3]/[\text{DPPH}^\bullet]$ in MeCN. $[\text{DPPH}^\bullet]$ and $[\text{Sc}(\text{OTf})_3]$ are concentrations of $\text{DPPH}^\bullet$ ($6.6 \times 10^{-5} \text{ M}$) and $\text{Sc}(\text{OTf})_3$ ($4.2 \times 10^{-6} \text{ M}$, each), respectively.

Upon the addition of H_2O to this solution, the absorption band at 519 nm due to $\text{DPPH}^\bullet$ increased. The time course changes in the absorbance at 519 nm after the addition of several amounts of H_2O are shown in Figure 3A,B. At all the concentrations of H_2O , the

reaction has completed after 1500 s. Figure 4 shows the overlapped absorption spectra at 1500 s after the addition of varying amounts of H₂O. The absorption band at 380 nm due to DPPH⁺ decreased, accompanied by an increase in the absorption band at 519 nm due to DPPH[•] with clear isosbestic points at 344 and 449 nm.

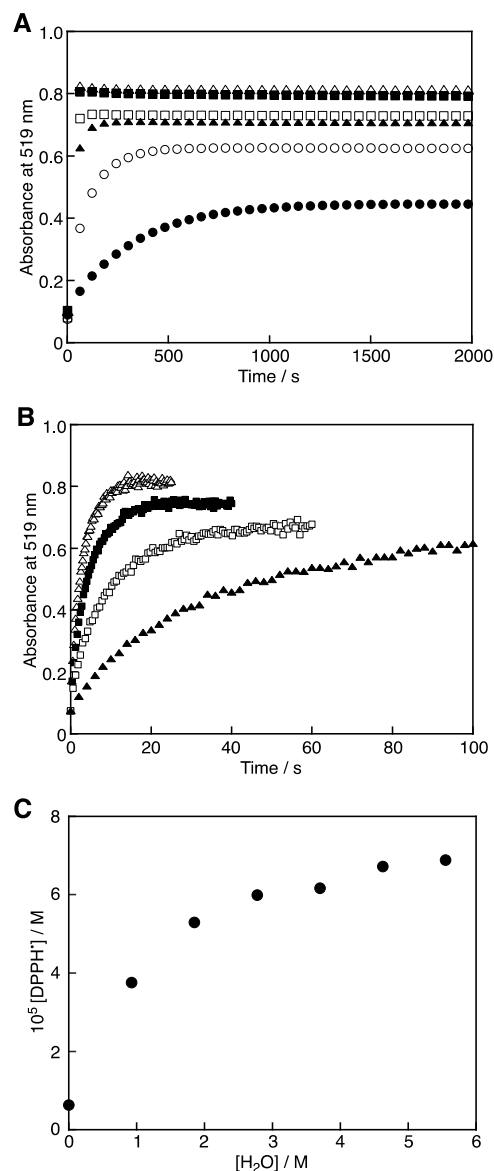


Figure 3. (A) Time course change monitored by the Agilent 8453 photodiode array spectrophotometer in the absorbance at 519 nm after the addition of H₂O (closed circles 50 μL (9.3×10^{-1} M), open circles 100 μL (1.9 M), closed triangles 150 μL (2.8 M), open squares 200 μL (3.7 M), closed squares 250 μL (4.2 M), and open triangles 300 μL (5.6 M)) to the MeCN solution containing DPPH[•] and Sc(OTf)₃ at 298 K. The final concentrations of DPPH[•] and Sc(OTf)₃ are 7.1×10^{-5} M and 2.0×10^{-5} M, respectively, in 3 mL MeCN–H₂O. (B) Time course change monitored by the stopped-flow spectrophotometer in the absorbance at 519 nm after addition of H₂O (closed triangles 150 μL (2.8 M), open squares 200 μL (3.7 M), closed squares 250 μL (4.2 M), and open triangles 300 μL (5.6 M)) to the MeCN solution containing DPPH[•] and Sc(OTf)₃ at 298 K. The final concentrations of DPPH[•] and Sc(OTf)₃ are 7.1×10^{-5} M and 2.0×10^{-5} M, respectively, in 3 mL MeCN–H₂O. (C) Plot of [DPPH[•]] vs. [H₂O] at 1500 s after the addition of H₂O to the MeCN solution containing DPPH[•] and Sc(OTf)₃. The final concentrations of DPPH[•] and Sc(OTf)₃ are 7.1×10^{-5} M and 2.0×10^{-5} M, respectively, in 3 mL MeCN–H₂O.

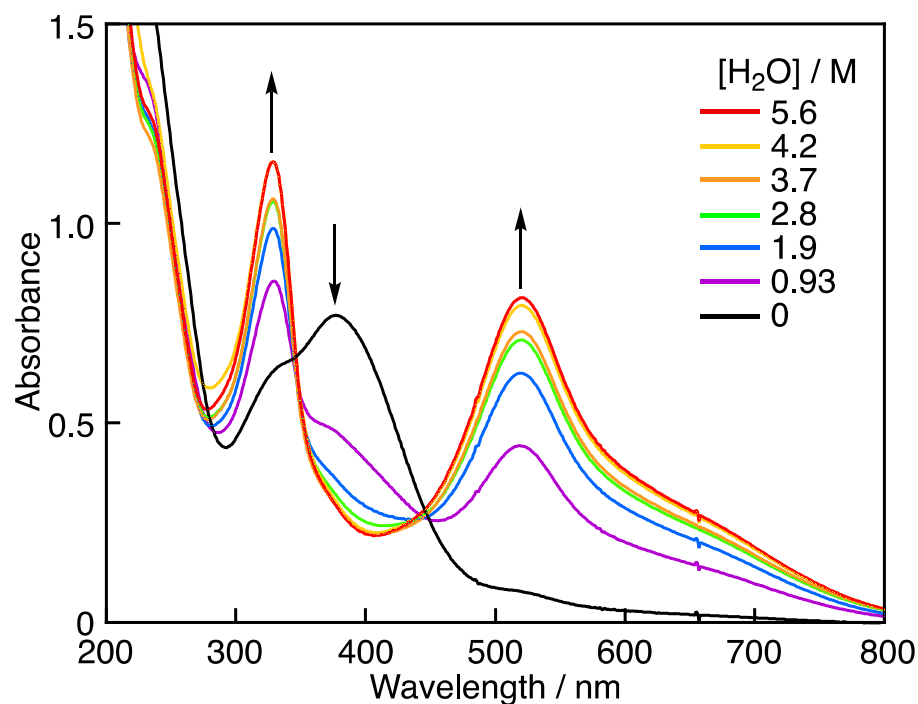


Figure 4. Spectral change observed 1500 s after the addition of H_2O (9.3×10^{-1} , 1.9, 2.8, 3.7, 4.2, and 5.6 M) to the MeCN solution containing $\text{DPPH}^\bullet$ and $\text{Sc}(\text{OTf})_3$. The final concentrations of $\text{DPPH}^\bullet$ and $\text{Sc}(\text{OTf})_3$ are 7.1×10^{-5} M and 2.0×10^{-5} M, respectively, in 3 mL MeCN– H_2O .

The regeneration of $\text{DPPH}^\bullet$ upon the addition of H_2O to the $\text{DPPH}^\bullet$ – $\text{Sc}(\text{OTf})_3$ system in MeCN was also confirmed by the electron paramagnetic resonance (EPR) spectroscopy. The well-resolved five lines having a g value of 2.0036 were observed in the EPR spectrum of $\text{DPPH}^\bullet$ in MeCN (Figure 5A). Upon addition of $\text{Sc}(\text{OTf})_3$ to the MeCN solution of $\text{DPPH}^\bullet$, the signal intensity was significantly decreased, as shown in Figure 5B. The addition of H_2O to this reaction system resulted in the regeneration of $\text{DPPH}^\bullet$, which was confirmed by the increase in the EPR signal intensity due to $\text{DPPH}^\bullet$ (Figure 5C).

Figure 3C shows $[\text{DPPH}^\bullet]$ vs. $[\text{H}_2\text{O}]$ at 1500 s after the addition of H_2O to the 3 mL MeCN solution containing $\text{DPPH}^\bullet$ (7.1×10^{-5} M) and $\text{Sc}(\text{OTf})_3$ (2.0×10^{-5} M). The $[\text{DPPH}^\bullet]$ values were calculated using the extinction coefficient (ϵ) of $1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 519 nm [2] and increased with increasing $[\text{H}_2\text{O}]$ to reach a constant value. It is suggested that the complex formation of Sc^{3+} with H_2O may weaken the interaction between DPPH^- and Sc^{3+} , leading to the electron-transfer comproportionation to produce $\text{DPPH}^\bullet$. In fact, a hexaaqua complex, $\text{Sc}(\text{H}_2\text{O})_6^{3+}$, has been reported for the Sc^{3+} hydration in aqueous perchlorate solution [25].

The rise of the absorbance at 519 nm due to $\text{DPPH}^\bullet$ shown in Figure 3A,B obeyed pseudo-first-order kinetics. Figure 6 shows a double logarithmic plot of the pseudo-first-order rate constants (k_{obs}) vs. $[\text{H}_2\text{O}]$. The slope of this plot (dashed line in Figure 6), except for the k_{obs} value at 9.3×10^{-1} M H_2O , is about three, suggesting that a triaqua complex, $[(\text{DPPH})_2\text{Sc}(\text{H}_2\text{O})_3]^+$, may be formed by the addition of H_2O to $[\text{Sc}(\text{DPPH})_2]^+$ as shown in Figure 7A. Then, the reaction B (Figure 7) occurs to produce two molecules of $\text{DPPH}^\bullet$, DPPH^- , and $[\text{Sc}(\text{H}_2\text{O})_3]$ as the rate-determining step followed by a rapid reaction between DPPH^- and DPPH^+ to produce two molecules of $\text{DPPH}^\bullet$ (Figure 7C).

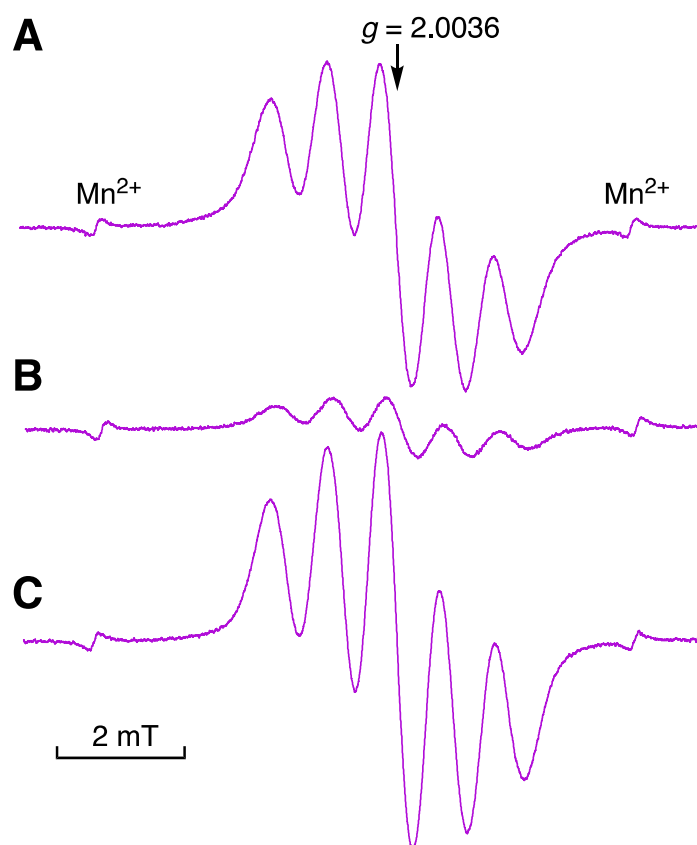


Figure 5. EPR spectra of (A) DPPH• (7.1×10^{-5} M) in MeCN, (B) DPPH• (7.1×10^{-5} M) in the presence of $\text{Sc}(\text{OTf})_3$ (2.0×10^{-5} M) in MeCN, and (C) DPPH• (7.1×10^{-5} M) in the presence of $\text{Sc}(\text{OTf})_3$ (1.8×10^{-5} M) and H_2O (5.6 M) in MeCN.

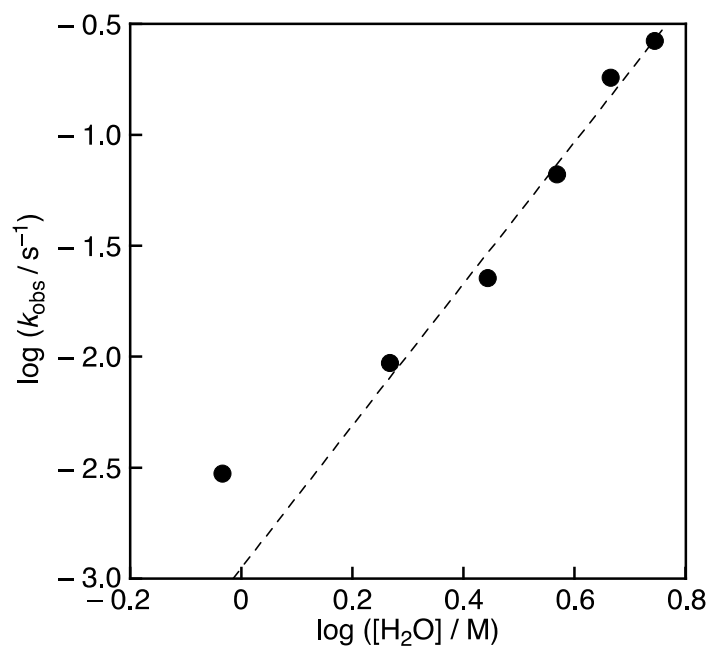


Figure 6. Plot of $\log k_{\text{obs}}$ vs. $\log[\text{H}_2\text{O}]$.

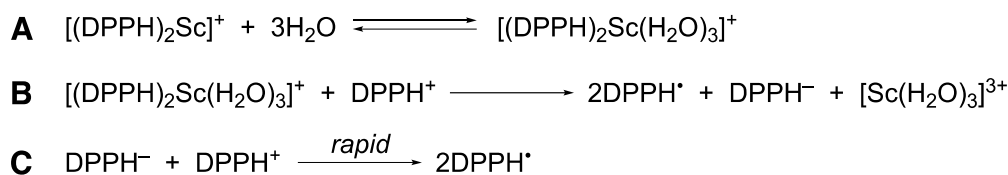


Figure 7. Proposed mechanism of the DPPH[•] regeneration. (A) Addition of H₂O to form [(\text{DPPH})₂Sc(\text{H}_2\text{O})₃]⁺. (B) Rate-determining electron transfer from [(\text{DPPH})₂Sc(\text{H}_2\text{O})₃]⁺ to DPPH⁺. (C) Rapid comproportionation between DPPH[−] and DPPH⁺.

3. Materials and Methods

3.1. Materials

DPPH[•] was commercially obtained from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan. Sc(OTf)₃ was purchased from Sigma–Aldrich, St. Louis, MO, USA. MeCN (spectral grade) used as a solvent was commercially obtained from Nacalai Tesque, Inc., Kyoto, Japan, and used as received. The water used in this study was freshly prepared with a Milli-Q system (Millipore Direct-Q UV3) (Merck Millipore, Burlington, MA, USA).

3.2. Spectral Measurements

Typically, a 10 µL aliquot of Sc(OTf)₃ (6.1×10^{-3} M) in MeCN was added to a quartz cuvette (10 mm i.d.) which contained DPPH[•] in MeCN (2.95, 2.90, 2.85, 2.80, 2.75 or 2.70 mL). This led to an electron-transfer disproportionation of DPPH[•] to produce DPPH⁺ and [(\text{DPPH})₂Sc]⁺. After 1 h, water (50, 100, 150, 200, 250, or 300 µL) was added to this MeCN solution (2.95, 2.90, 2.85, 2.80, 2.75, or 2.70 mL, respectively). The molar concentrations of 50, 100, 150, 200, 250, and 300 µL H₂O in 3 mL MeCN–H₂O are 9.3×10^{-1} , 1.9, 2.8, 3.7, 4.2, 5.6 M, respectively. The final concentrations of DPPH[•] and Sc(OTf)₃ were 7.1×10^{-5} M and 2.0×10^{-5} M, respectively, in 3 mL MeCN–H₂O. UV-vis spectral changes associated with the reaction were monitored using an Agilent 8453 photodiode array spectrophotometer thermostated with a Peltier temperature control at 298 K (Agilent Technologies, Santa Clara, CA, USA). The regeneration rates of DPPH[•] were followed by monitoring the absorbance change at 519 nm due to DPPH[•] on the Agilent 8453 photodiode array spectrophotometer ([H₂O] = 9.3×10^{-1} and 1.9 M) or on a UNISOKU RSP-1000-02NM stopped-flow spectrophotometer (UNISOKU Co., Ltd., Osaka, Japan), which was thermostated with a Thermo Scientific NESLAB RTE-7 Circulating Bath (Thermo Fisher Scientific, Inc., Waltham, MA, USA) at 298 K ([H₂O] = 2.8, 3.7, 4.2, and 5.6 M). The k_{obs} values were obtained by a least-square curve fit using an Apple MacBook Pro personal computer (Apple Inc., Cupertino, CA, USA). The first-order plots of $\ln(A_\infty - A)$ vs. time (A and A_∞ are the absorbance at the reaction time and the final absorbance, respectively) were linear until three or more half-lives, with a correlation coefficient $\rho > 0.999$. In each case, it was confirmed that the k_{obs} values derived from at least three independent measurements agreed within experimental error of $\pm 5\%$. In all cases, solutions were normally equilibrated with air.

3.3. EPR Measurements

The EPR spectra of DPPH[•] (7.1×10^{-5} M) in the presence or absence of Sc(OTf)₃ (2.0×10^{-5} M) and/or H₂O (5.6 M) in MeCN were taken using an LLC-04B ESR sample tube (LABOTEC Co., Ltd., Tokyo, Japan) on a JEOL X-band spectrometer (JES-RE1X) (JEOL Ltd., Tokyo, Japan) at room temperature under the following conditions: microwave frequency 9.43 GHz, microwave power 8 mW, center field 338 mT, sweep width 15 mT, sweep rate 3 mT min^{−1}, modulation frequency 100 kHz, modulation amplitude 0.2 mT, and time constant 0.1 s. EPR data acquisition was controlled by the WIN-RAD ESR Sata Analyzer System (Radical Research, Inc., Tokyo, Japan). The g values were calibrated with an Mn²⁺ marker. In all cases, solutions were normally equilibrated with air.

4. Conclusions

The addition of H₂O to the MeCN solution containing DPPH⁺ and [(DPPH)₂Sc]⁺ resulted in the regeneration of DPPH[•]. It is suggested that the complex formation of Sc³⁺ with H₂O may weaken the interaction between DPPH[−] and Sc³⁺, leading to the electron-transfer comproportionation to produce DPPH[•]. The detailed mechanism of regeneration of DPPH[•] was proposed based on the detailed spectroscopic and kinetic analyses, in which the reaction of DPPH⁺ with [(DPPH)₂Sc(H₂O)₃]⁺ generated upon the addition of H₂O to [(DPPH)₂Sc]⁺ is the rate-determining step.

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