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Activationless Electron Self-Exchange of High-Valent Oxo and Imido Complexes of Chromium Corroles

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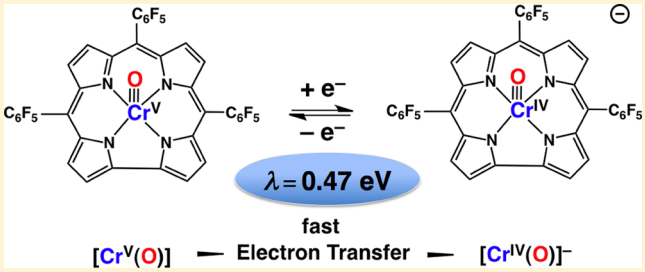
Supporting Information

ABSTRACT: Rate constants of electron self-exchange of high-valent oxo and imido complexes of chromium(V/IV) corrole have been determined in acetonitrile and toluene at various temperatures by electron paramagnetic resonance (EPR) line width variation of the EPR spectra. The observed activation enthalpies ($\Delta H_{obs}^{\ddagger}$) of electron self-exchange of chromium(V)−oxo and −imido corrole with the corresponding chromium(IV) complexes are zero in toluene, whereas the $\Delta H_{obs}^{\ddagger}$ values are slightly positive in acetonitrile. Such activationless electron self-exchange transfer resulted in extremely fast electron-transfer reactions of chromium(V)−oxo and −imido corrole in sharp contrast with slow electron-transfer reactions of other high-valent metal−oxo and −imido complexes.



INTRODUCTION

High-valent metal−oxo complexes are the key oxidizing intermediates in various oxidation reactions of heme and non-heme metal enzymes.[1−3] Extensive effort has been devoted to examining the biomimetic reactivities of high-valent metal−oxo complexes in relation to their enzymatic counterparts.[4−8] Electron-transfer properties of high-valent metal−oxo complexes are the most fundamental to understanding their reactivity.[9−11] In general, electron-transfer reactions of high-valent metal−oxo complexes are slow because of the large reorganization energies (λ) associated with the elongation of the metal−oxygen multiple bond upon reduction.[9−11] λ reflects the nuclear rearrangement of the redox partners and their environment associated with the reactions according to the Marcus theory of electron transfer.[12] In the case of vanadium(V)−oxo complexes, such as $[V^{V}O(salen)]^{+}$ [salen = *N*,*N*′-ethylenebis(salicylideneiminate)(2−)][13] and $Ph_4P[V^{V}O(hybeb)]$ [$hybeb^{4-}$ = a tetradentate diamidodiphenolate(4−) ligand],[14] the rate constants of the eletron self-exchange for the $[V^{V}O(salen)]^{+}/[V^{IV}O(salen)]$ and $[V^{V}O(hybeb)]^{-}/[V^{IV}O(hybeb)]^{2-}$ couples were reported to be 7.4×10^9 and 3.9×10^9 M^{-1} s^{-1}, respectively. The high reactivity and yet totally reversible characteristics of the vanadium(V/IV)−oxo redox couple have been utilized as redox mediators in dye-sensitized solar cells (DSSCs) to accomplish excellent photovoltaic performance.[13,14] In the case of a mononuclear Cr(V)−oxo complex,[15] $[Cr^{V}(O)(6\text{-}COO^{-}\text{-}tpa)](BF_4)_2$ [6-COO^{-}-tpa = *N*,*N*-bis(2-pyridylmethyl)-*N*-(6-carboxylato-2-pyridylmethyl)-amine], the λ value of electron-transfer reactions of the $Cr^{V}(O)$ complex was determined to be 1.03 eV, which is significantly smaller than the values reported for $Fe^{IV}(O)$ and $Mn^{IV}(O)$ complexes (e.g., λ = 2.5 eV),[9] but much larger than the values for the $V^{V}(O)$ complexes ($\lambda \sim 0.5$ eV).[13,14] So far, there has been no report of fast electron-transfer reactions of $Cr^{V}(O)$ complexes with small λ values.

We report herein fast electron self-exchange of a high-valent oxo of chromium corrole as well as the isoelectronic imido complex.[16] The rate constants of electron self-exchange were determined by electron paramagnetic resonance (EPR) line width variation of the EPR spectra of high-valent oxo and imido complexes of chromium(V) corroles in the presence of the chromium(IV) complexes. The activation enthalpies ($\Delta H_{obs}^{\ddagger}$) of electron self-exchange of chromium(V)−oxo corrole with the corresponding chromium(IV) complexes were determined to be close to zero in toluene. The reason for these unusual activationless electron-transfer reactions of chromium(V)−oxo and −imido corrole is discussed in comparison with slow electron-transfer reactions of other high-valent metal−oxo complexes.

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EXPERIMENTAL SECTION

Materials. All solvents and chemicals were of reagent-grade quality, obtained commercially, and used without further purification, unless otherwise noted. Acetonitrile (MeCN) was dried according to published procedures and distilled under Ar prior to being used.[17] Octamethylferrocene (Me_8Fc) was purchased from Aldrich and used as received. 2-(*tert*-Butylsulfonyl)(*p*-toluenesulfonyliminoiodo)-benzene (PhINTs) and iodosylbenzene (PhIO) were prepared from iodobenzene diacetate according to a literature procedure.[18] Chromium oxo corrole [(tfpc)Cr(O)] and chromium imido corrole [(tpfc)Cr(NTs)] were prepared by literature methods.[18,19] Chromium(V)−oxo and −imido complexes of 5,10,15-tris-(pentafluorophenyl)corrole (tpfc)Cr^{V}(O) (**1**) and (tpfc)Cr^{V}(NTs) (**2**), where Ts = *p*-toluenesulfonate, have been synthesized and characterized as reported previously.[20,21]

Spectroscopic and Kinetic Measurements. Electron transfer (ET) from Me_8Fc (1.0×10^{-5} M) to (tpfc)Cr^{V}(O) (1.0×10^{-5} M) was examined at 298 K using a Hewlett-Packard 8453 photodiode-array spectrophotometer with a quartz cuvette (path length of 1.0 cm). Typically, a deaerated MeCN solution of Me_8Fc was added with a microsyringe to a deaerated MeCN solution containing Cr^{V}(O) complexes in a quartz cell (total volume of 2.0 mL).

Kinetic measurements for electron transfer from Me_8Fc and (TPP)Mn^{II} to (tpfc)Cr^{V}(O) were measured by using a UNISOKU RSP-601 stopped-flow spectrophotometer with an MOS-type highly selective photodiode array at 298 K. The rates of oxidation of Me_8Fc as well as (TPP)Mn^{II} to give [(tpfc)Cr^{IV}(O)]$^-$ in deaerated MeCN were monitored by the increase in the intensity of the absorption band due to (TPP)Mn^{III} (λ_{max} = 477 nm).

Nanosecond transient absorption spectral measurements were taken according to the following by a Panther OPO pumped Nd: YAG laser (Continuum, SLII-10, 4−6 ns fwhm) at 355 nm. The resulting time-resolved transient absorption spectra were measured by using a continuous Xe lamp (150 W) and a photodiode (Hamamatsu 2949) as the probe light and detector, respectively. The output from the photodiode and the photomultiplier tube was recorded using a digitizing instrument for 10 min prior to measurements. Rates of photoinduced electron-transfer reactions were monitored, and constants were determined by a least-squares curve fit. All experiments were performed at 298 K.

EPR Measurements. The electron self-exchange of chromium(V/IV) was monitored by EPR, in the presence of (tpfc)Cr^{V}(O) (5.0×10^{-4} M) and [(tpfc)Cr^{IV}(O)]$^-$ (2.0, 5.0, 10, or 20×10^{-3} M) in the quartz EPR tube (3.0 mm inside diameter) from 285 to 308 K. [(tpfc)Cr^{IV}(O)]$^-$ was generated by simply adding a varying amount of the Me_8Fc solution to the (tpfc)Cr^{V}(O) solution. The EPR spectrum was recorded on a JEOL X-band spectrometer (JES-RE1XE) under nonsaturating microwave power conditions (1.0 mW) operating at 9.2025 GHz. The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio (S/N) of the observed spectrum (modulation width, 0.5 G; modulation frequency, 100 kHz).

Theoretical Calculations. Theoretical calculations of the properties of molecules were performed using density functional theory (DFT) with the CAM-B3LYP density functional[22] and the 6-311G(d) basis set. All calculations were performed using Gaussian 03.[23] Graphical outputs of the computational results were generated with GaussView (version 3.09) developed by Semichem, Inc.[24]

RESULTS AND DISCUSSION

Electron Transfer from Me_8Fc to (tpfc)Cr^{V}(E), where E = O or NTs. The one-electron reduction of chromium(V)−oxo and −imido complexes of 5,10,15-tris(pentafluorophenyl)-corrole (tpfc)Cr^{V}(O) (**1**) and (tpfc)Cr^{V}(NTs) (**2**) (Ts = *p*-toluenesulfonate) by 1 equiv of Me_8Fc (octamethylferrocene) resulted in quantitative formation of [(tpfc)Cr^{IV}(O)]$^-$ and [(tpfc)Cr^{IV}(NTs)]$^-$, respectively. The electron transfer from Me_8Fc (E_{ox} = −0.04 V vs SCE)[25] to **1** (E_{red} = 0.16 V vs SCE) and **2** (E_{red} = 0.12 V vs SCE)[13] occurred exergonically in acetonitrile to produce [(tpfc)Cr^{IV}(O)]$^-$ and [(tpfc)-Cr^{IV}(NTs)]$^-$, as shown in eq 1.

$$(tpfc)Cr^{V}(E) + Me_8Fc \rightarrow [(tpfc)Cr^{IV}(E)]^- + Me_8Fc^+ \quad (1)$$

Addition of Me_8Fc (1.0×10^{-5} M) to a deaerated MeCN solution containing (tpfc)Cr^{V}(O) (1.0×10^{-5} M) resulted in a decrease in the intensity of the absorbance band at 400 nm together with an increase in the intensity of the new absorption bands at 420 and 577 nm as shown in Figure 1. These data are consistent with the formation of [(tpfc)Cr^{IV}(O)]$^-$ by electron transfer from Me_8Fc to (tpfc)Cr^{V}(O), and a similar spectral change was observed for (tpfc)Cr^{V}(NTs) (see Figure S1 of the Supporting Information).

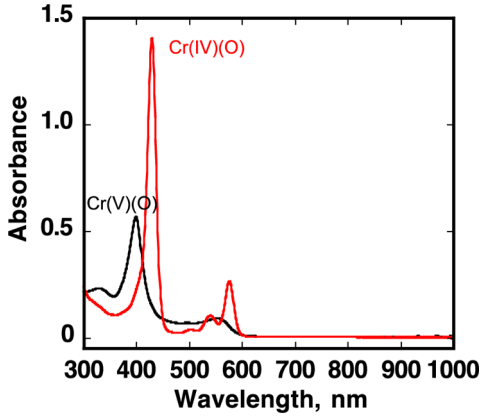

Figure 1. Absorption spectral change of [(tpfc)Cr^{V}(O)] (1.0×10^{-5} M) upon addition of Me_8Fc in N_2-saturated MeCN at 298 K.

Electron Self-Exchange. The EPR spectrum of (tpfc)-Cr^{V}(O) in acetonitrile at 298 K is shown in Figure 1, agreeing with the simulated spectrum with hyperfine splitting due to four equivalent nitrogens (a_N = 3.0 G) and a maximal slope line width (ΔH_{msl} = 0.80 G). In the wider magnetic field region, the hyperfine splitting due to ^{53}Cr was observed and the $a(^{53}Cr)$ value was determined to be 16.3 G. The large $a(^{53}Cr)$ value and the *g* value (1.9854), which is significantly smaller than the free spin value (2.0023), are indicative of a $3d_{xy}^1$ ground-state electronic configuration.[20,21,26] The hyperfine splitting due to four equivalent pyrrole nitrogens results from the spin polarization of the nitrogen ps orbitals with the $3d_{xy}$ orbital. DFT calculations of the spin densities of (tpfc)Cr^{V}(O) agree well with the observed a_N and $a(^{53}Cr)$ values (Figure S2 of the Supporting Information).

In the presence of 10 equiv of [(tpfc)Cr^{IV}(O)]$^-$ in acetonitrile, the line width is significantly broadened (Figure 2c,d) because of fast electron self-exchange between (tpfc)-Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^-$ (eq 2). To our surprise, the line width of the EPR signal of (tpfc)Cr^{V}(O) in toluene remains unchanged as the temperature is decreased from 318 to 288 K (Figure 2e,f). This observation indicates that the electron self-exchange reaction is temperature-independent with zero activation barrier. The rate constants (k_{ex}) of the electron self-exchange reactions between (tpfc)Cr^{V}(O) and [(tpfc)-Cr^{IV}(O)]$^-$ were determined using eq 2

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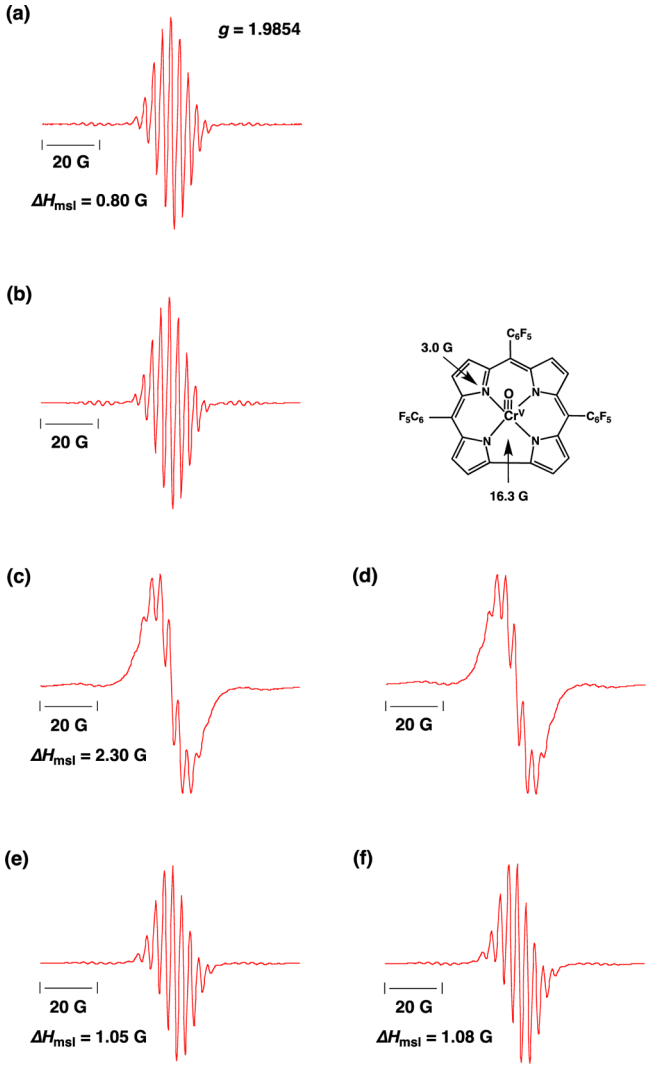

Figure 2. (a) EPR spectrum of (tpfc)Cr^{V}(O) (5.0×10^{-4} M) in acetonitrile at 298 K and (b) computer-simulated spectrum (ΔH_{msl} = 0.80 G). (c) EPR spectrum of (tpfc)Cr^{V}(O) in the presence of [(tpfc)Cr^{IV}(O)]$^-$ (5.0×10^{-3} M) in acetonitrile at 298 K and (d) computer-simulated spectrum (ΔH_{msl} = 2.30 G). EPR spectra of (tpfc)Cr^{V}(O) in the presence of [(tpfc)Cr^{IV}(O)]$^-$ (5.0×10^{-3} M) in toluene at (e) 288 K and (f) at 318 K. The inset shows hyperfine coupling constants obtained by the EPR simulation.

$$(\text{tpfc})\text{Cr}^{V}(\text{O}) + [(\text{tpfc})\text{Cr}^{IV}(\text{O})]^- \overset{k_{ex}}{\rightleftharpoons} [(\text{tpfc})\text{Cr}^{IV}(\text{O})]^- + (\text{tpfc})\text{Cr}^{V}(\text{O}) \quad (2)$$

$$k_{ex} = 1.52 \times 10^7(\Delta H_{msl} - \Delta H^{\circ}_{msl}) / \{(1 - P_i)[[(\text{tpfc})\text{Cr}^{IV}(\text{O})]^-]\} \quad (3)$$

where ΔH_{msl} and ΔH°_{msl} are the maximal slope line widths of the EPR spectra in the presence and absence of [(tpfc)-Cr^{IV}(O)]$^-$, respectively, and P_i is a statistical factor, which can be taken to be nearly zero.[27] The electron self-exchange rate constants (k_{ex}) in toluene and acetonitrile at various temperatures were also determined from the slopes of the linear plots of ΔH_{msl} and [[(tpfc)Cr^{IV}(O)]$^-$] (Figure S3 of the Supporting Information), which are listed in Table 1. The reorganization energy (λ) of the electron exchange between (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^-$ was determined to be 0.47 V by eq 4

$$k_{ex}^{-1} - k_{diff}^{-1} = Z^{-1} \exp(\lambda/4RT) \quad (4)$$

where k_{diff} is the diffusion rate constant (2.0×10^{10} M^{-1} s^{-1}) and Z is the collision frequency (1.0×10^{11} M^{-1} s^{-1}) in MeCN (Figure S4 of the Supporting Information).[12,28−30]

Virtually similar results were obtained for electron self-exchange between (tpfc)Cr^{V}(NTs) (**2**) and [(tpfc)-Cr^{IV}(NTs)]$^-$ (Figure S5 of the Supporting Information). The activation parameters were determined from the Eyring plots in Figure 3. The $\Delta H_{obs}^{\ddagger}$ and $\Delta S_{obs}^{\ddagger}$ values are listed in Table 2.

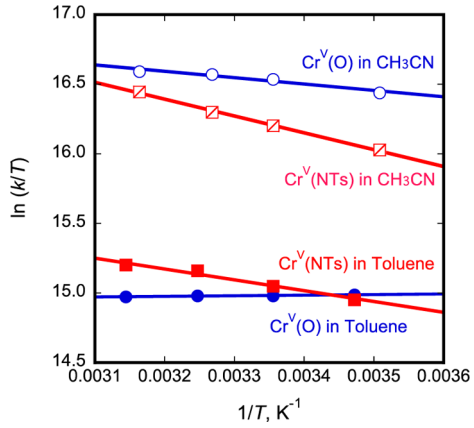

Figure 3. Eyring plots of rate constants of electron self-exchange reaction between (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^-$ and between (tpfc)Cr^{V}(NTs) and [(tpfc)Cr^{IV}(NTs)]$^-$ in toluene and acetonitrile.

The $\Delta H_{obs}^{\ddagger}$ values of electron self-exchange of (tpfc)Cr^{V}(O)/[(tpfc)Cr^{IV}(O)]$^-$ and (tpfc)Cr^{V}(NTs)/[(tpfc)Cr^{IV}(NTs)]$^-$ in toluene are smaller than the values in the more polar solvent acetonitrile. The small activation enthalpies indicate that electron self-exchange reactions proceed via an intermediate, the energy of which is lower than that of the reactant pair, and the energy difference between the reactant pair and the

Table 1. Electron Self-Exchange Rate Constants (k_{ex}) of (tpfc)Cr^{V}(O)/[(tpfc)Cr^{IV}(O)]$^-$ and (tpfc)Cr^{V}(NTs)/[(tpfc)Cr^{IV}(NTs)]$^-$ in Acetonitrile and Toluene

		k_{exp}[b] ($\times 10^9$ M^{-1} s^{-1})			
		285 K	298 K	306 K	316 K
(tpfc)Cr^{V}(O)	acetonitrile	3.92 ± 0.27	4.52 ± 0.35	4.80 ± 0.55	5.08 ± 0.76
	toluene[a]	0.93 ± 0.10	0.96 ± 0.12	0.98 ± 0.10	1.01 ± 0.08
(tpfc)Cr^{V}(NTs)	acetonitrile	2.61 ± 0.02	3.24 ± 0.07	3.68 ± 0.07	4.39 ± 0.15
	toluene[a]	0.90 ± 0.01	1.03 ± 0.11	1.19 ± 0.14	1.27 ± 0.19

[a]The temperatures were slightly different: 288, 298, 308, and 318 K. [b]Experimental error of ±10%.

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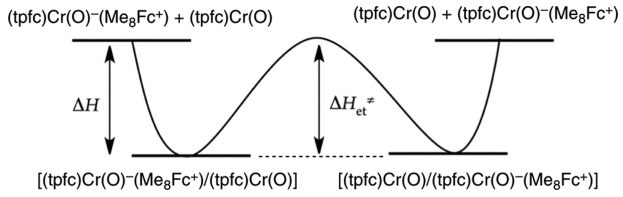
Table 2. Activation Parameters of Electron Self-Exchange between (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^{-}$ and between (tpfc)Cr^{V}(NTs) and [(tpfc)Cr^{IV}(NTs)]$^{-}$ in Toluene and Acetonitrile[a]

	$\Delta H_{obs}^{\ddagger}$ (kcal mol^{-1})		$\Delta S_{obs}^{\ddagger}$ (cal mol^{-1} K^{-1})	
acceptor/donor	CH_3CN	toluene	CH_3CN	toluene
(tpfc)Cr^{V}(O)/[(tpfc)Cr^{IV}(O)]$^{-}$	0.91 ± 0.14	−0.12 ± 0.02	−11.3 ± 0.5	−17.8 ± 0.1
(tpfc)Cr^{V}(NTs)/[(tpfc)Cr^{IV}(NTs)]$^{-}$	2.38 ± 0.09	1.60 ± 0.22	−7.0 ± 0.3	−12.0 ± 0.7

[a]Experimental errors were calculated from the least-squares method using linear fittings in Figure 3.

intermediate is larger than the activation energy from the intermediate as shown in Scheme 1, in which the case of electron self-exchange between (tpfc)Cr^{V}(O) and [(tpfc)-Cr^{IV}(O)]$^{-}$ is illustrated with the countercation (Me_8Fc^{+}).

Scheme 1



In general, an electron-transfer reaction proceeds via a precursor complex formed between an electron donor and an acceptor.[31] In the case of electron self-exchange between zinc porphyrin and the radical cation, zinc porphyrin forms a strong charge-transfer π complex with zinc porphyrin radical cation because of overlap of the π-orbitals of two planar porphyrin rings.[32] In the case of electron self-exchange between (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^{-}$, as well, (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^{-}$ may form a strong charge-transfer π-complex prior to electron transfer. In such a case, the observed activation enthalpy ($\Delta H_{obs}^{\ddagger}$) is given by the sum of the heat of formation of the π-complex ($\Delta H < 0$) and the activation enthalpy of electron transfer in the π-complex ($\Delta H_{et}^{\ddagger} > 0$) as shown in eq 5.[32,33]

$$\Delta H_{obs}^{\ddagger} = \Delta H + \Delta H_{et}^{\ddagger} \quad (5)$$

In toluene, the absolute ΔH value may be the same as $\Delta H_{et}^{\ddagger}$, resulting in activationless electron transfer. In acetonitrile, which is much more polar than toluene, the solvent reorganization energy of electron transfer increases, resulting in the overall positive $\Delta H_{obs}^{\ddagger}$ value. The negative $\Delta S_{obs}^{\ddagger}$ values listed in Table 1 are consistent with the organized complex formation prior to electron transfer in Scheme 1.

Reorganization Energy for the Electron-Transfer Reduction of (tpfc)Cr^{V}(O). The activationless electron self-exchanges between [(tpfc)Cr^{IV}(O)]$^{-}$ and **1** and between [(tpfc)Cr^{IV}(NTs)]$^{-}$ and **2** indicate small a reorganization energy of electron transfer. This is in sharp contrast to the large reorganization energies associated with electron-transfer reduction of other high-valent metal−oxo complexes such as Fe^{IV}(O) and Mn^{IV}(O) complexes (e.g., λ = 2.5 eV).[9,34,35] The small λ value of electron-transfer reduction of (tpfc)Cr^{V}(O) was examined by estimating rates of electron transfer by using Me_8Fc as well as (TPP)Mn^{II} (E_{ox} = −0.15 V vs SCE),[36] where TPP = tetraphenylporphyrin, as electron donors to (tpfc)-Cr^{V}(O) in acetonitrile at 298 K (Figure S6a of the Supporting Information). Rates of electron transfer from Me_8Fc and (TPP)Mn^{II} to (tpfc)Cr^{V}(O) were too fast to follow not only at room temperature but also at −40 °C. The electron-transfer reactions were complete during the mixing time of stopped-flow measurements (Figure S6b,c of the Supporting Information). The rate constant is estimated to be larger than 10^7 M^{-1} s^{-1}. The rate constant of the intermolecular electron-transfer rate constant (k_{et}) was evaluated using the Marcus cross relationship from electron donor Me_8Fc or (TPP)Mn^{II} to Cr^{V}(O) by eq 6

$$k_{et} = (k_{11}k_{22}K_{12}f)^{1/2} \quad (6)$$

where k_{11} and k_{22} are the rate constants for self-exchange reactions of the electron donor and the electron acceptor, respectively, K_{12} is the electron-transfer equilibrium constant, which is obtained from the one-electron oxidation potential of the electron donor and one-electron reduction potential of the electron acceptor, and f is a function of k_{11}, k_{22}, and K_{12}, being close to unity.[12] According to the Marcus cross relationship eq 6, the rate constants of intermolecular electron transfer from Me_8Fc and (TPP)Mn^{II} to (tpfc)Cr^{V}(O) were estimated to be 1.1 × 10^{10} and 1.1 × 10^{8} M^{-1} s^{-1}, respectively, using the k_{11} values (5.3 × 10^{6} and 3.2 × 10^{3} M^{-1} s^{-1}),[37,38] k_{22} value (4.5 × 10^{9} M^{-1} s^{-1} in Table 1), and K_{12} values (5.1 × 10^{3} and 8.4 × 10^{2}). The estimated electron-transfer rate constants are consistent with the fact that the ET process could not be monitored by stopped-flow methods.

The rate constant of electron transfer from the excited state of $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) to **1** was determined by nanosecond laser flash photolysis measurements of a deaerated MeCN solution of **1** and $[Ru^{II}(bpy)_3]^{2+}$ at 298 K (Figure S7a). The second-order rate constant (k_{et}) of electron transfer from $[Ru(bpy)_3]^{2+*}$ (the asterisk denotes the excited state) to **1** was determined to be 5.4 × 10^{9} M^{-1} s^{-1} (Figure S7b). The driving force of electron transfer from $[Ru(bpy)_3]^{2+*}$ to **1** is evaluated from the one-electron oxidation potential of $[Ru(bpy)_3]^{2+*}$ (−0.81 V vs SCE)[39] and the one-electron reduction potential of **1** (0.16 V vs SCE) to be 0.97 eV, which is approximately twice the λ value of **1** (0.48 eV). In such a case, the k_{et} value is expected to be approximately the same as the k_{ex} value of **1** according to the Marcus theory of electron transfer.[12] Indeed, the k_{et} value is approximately the same as the k_{ex} value of **1** (4.5 × 10^{9} M^{-1} s^{-1}).

The reorganization energy for the one-electron reduction of (tpfc)Cr^{V}(O) was evaluated theoretically by using density functional theory (DFT) calculations at the CAM-B3LYP/6-31G(d) level of theory (see the Experimental Section of the Supporting Information). The difference between the energy of (tpfc)Cr^{V}(O) with the same structure as [(tpfc)Cr^{IV}(O)]$^{-}$ and the energy with the optimized structure of [(tpfc)Cr^{IV}(O)]$^{-}$ can be regarded as the reorganization energy of the inner coordination spheres (λ_i) associated with the structural change upon the electron-transfer reduction of (tpfc)Cr^{V}(O) in the gas phase. The λ_i value thus obtained is 7.89 kcal mol^{-1} (0.30 eV). This value is slightly larger than that of the zinc tetraphenylporphyrin (ZnTPP)/$ZnTPP^{\bullet+}$ system. The differ-

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ence from the observed λ value (0.47 eV) corresponds to the solvent reorganization energy (0.17 eV).

The observed small λ value of (tpfc)Cr^{V}(O) may result from the no or little change in the $Cr^{V}\equiv O$ bond distance (1.57 Å) in (tpfc)Cr^{V}(O) as compared with the $Cr^{IV}\equiv O$ bond distance (1.57 Å), as reported by Czernuszewicz et al.[40] The triple bond is maintained in the reduced form $Cr^{IV}\equiv O$ as indicated by even a higher Raman frequency of ν(CrO) of $Cr^{IV}\equiv O$ as compared with that of $Cr^{V}\equiv O$.[40] The Cr−N distances are 1.521 for the $Cr^{V}O$ complex and 1.528 Å for the $Cr^{IV}O$ complex calculated by DFT (Figure S8 of the Supporting Information). Such small bond length changes also support the fast electron exchange of Cr^{V}(O)/Cr^{IV}(O). This is quite different from the cases of other high-valent metal−oxo complexes such as Fe^{IV}=O and Mn^{IV}=O complexes in which the double bonds become single bonds upon the one-electron reduction.[34,35]

CONCLUSIONS

In conclusion, activationless electron self-exchange transfer occurs between (tpfc)Cr^{V}(O) and [(tpfc)Cr^{IV}(O)]$^{-}$ and between (tpfc)Cr^{V}(NTs) and [(tpfc)Cr^{IV}(NTs)]$^{-}$ in toluene because of the small reorganization energies of electron transfer with no or little change between the $Cr^{V}\equiv E$ and $Cr^{IV}\equiv E$ bond distances and formation of π-complexes prior to electron transfer, exhibiting a sharp contrast to the commonly encountered cases of other high-valent metal−oxo species such as Fe^{IV}=O and Mn^{IV}=O complexes. Facile electron-transfer reactions of (tpfc)Cr^{V}(O) with small reorganization energies were estimated by DFT calculation. The unique electron-transfer properties of (tpfc)Cr^{V}(O) and (tpfc)-Cr^{V}(NTs) with much smaller reorganization energies as compared with those of other high-valent metal−oxo complexes may pave a new way to utilize them as efficient electron-transfer catalysts, which are now under investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01777.

Experimental kinetics and DFT computational details (PDF)

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Notes

The authors declare no competing financial interest.

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