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Electron transfer reduction of cobalt tetraphenylporphyrin by hydroquinone dianions and alkylation with alkyl halides

Shunichi Fukuzumi *, Junichi Maruta
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

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Abstract

The electron transfer reduction of cobalt(III) tetraphenylporphyrin ($CoTPP^+$) by hydroquinone dianions occurs via stepwise electron transfer from hydroquinone dianions to produce cobalt(I) tetraphenylporphyrin anion ($CoTPP^-$) in acetonitrile. The rates of electron transfer from hydroquinone dianions to CoTPP are discussed in light of the Marcus theory of electron transfer to distinguish between outer-sphere and inner-sphere electron transfer processes. The self-exchange rate of the planar diamagnetic $CoTPP^-$ and the low-spin CoTPP complex is somewhat smaller than that of the $CoTPP^+$–CoTPP couple, showing a sharp contrast with the fast exchange rate of the couple of an octahedral high-spin d^8 cobalt(I) complex and the corresponding high-spin d^7 cobalt(II) complex. $CoTPP^-$ formed by the electron transfer reduction of $CoTPP^+$ by hydroquinone dianions reacts with various alkyl halides (RX) to yield the corresponding alkylcobalt(III) tetraphenylporphyrins (RCoTPP). The rate constants are determined directly by following the formation of RCoTPP in MeCN at 298 K. The contribution of both an S_N2 and an outer-sphere electron mechanism is discussed in light of the Marcus theory of electron transfer.

Keywords: Electron transfer; Reduction; Cobalt complexes; Porphyrin complexes; Kinetics and mechanism

1. Introduction

Electron transfer reactions of metalloporphyrins have been extensively studied in relation to their pivotal role in biological redox processes [1–4]. However, the formation of low valent metalloporphyrins has so far required the use of strong heterogeneous reductants such as sodium amalgam and thereby it has been difficult to carry out a direct kinetic study on the formation of metal(I) porphyrins [5]. Thus, little is known about the electron transfer reactivities of metal(I) porphyrins as compared with those of metal(III) and metal(II) porphyrins [1–4]. On the other hand, the metal(I) porphyrins are known to react with alkyl halides to produce metal-σ-alkyl derivatives of metalloporphyrins [5,6]. Savéant and others have reported kinetic studies on the reactions of metal(I) porphyrins with alkyl halides by applying electrochemical methods [7–10]. Based on the electrochemical studies, an S_N2 mechanism has been generally suggested to occur for the reactions of metal(I) porphyrins with alkyl halides, but in some cases an outer-sphere electron transfer mechanism has also been reported to be invoked depending on the substrate [7–10]. Thus, it seems of interest to perform a direct kinetic study on the reactions of metal(I) porphyrins with alkyl halides in order to gain further insight into the distinction between an S_N2 and an outer-sphere electron transfer mechanism.

We have recently reported that hydroquinone dianions produced by the reactions of hydroquinones with tetramethylammonium hydroxide in acetonitrile act as strong electron transfer reductants in the homogeneous system [11]. We report herein detailed kinetic studies on the electron transfer reduction of cobalt(III) tetraphenylporphyrin ($CoTPP^+$) to cobalt(II) tetraphenylporphyrin (CoTPP) and cobalt(I) tetraphenylporphyrin ($CoTPP^-$) by hydroquinone dianions as well as the reactions of $CoTPP^-$ with various alkyl halides (RX) to yield alkylcobalt(III) tetraphenylporphyrins (RCoTPP). The distinction between an outer-sphere electron transfer and an S_N2 mechanism is discussed in light of the Marcus theory of electron transfer [12].

2. Experimental

2.1. Materials

Cobalt(II) tetraphenylporphyrin (CoTPP) was prepared as described in the literature [13]. CoTPP was

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* Corresponding author.

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oxidized by oxygen in the presence of HCl in ethanol to obtain (tetraphenylporphinato)cobalt(III) chloride [14], which was purified by recrystallization from methanol. The perchlorate salt was obtained by the metathesis of the chloride salt with $AgClO_4$ and recrystallized from toluene [15]. Hydroquinones and alkyl halides used in this study were obtained commercially and purified by the standard methods. Tetramethylammonium hydroxide ($Me_4N^+OH^-$) was obtained from Sigma. A stock acetonitrile solution of hydroquinone dianions (0.10 mol dm^{-3}) was prepared by adding an aliquot of a methanol solution of $Me_4N^+OH^-$ (2.0 mol dm^{-3}) to a deaerated acetonitrile solution containing hydroquinones (0.111 mol dm^{-3}). Acetonitrile used as a solvent was purified and dried by the standard procedure [16].

2.2. Product analysis

Typically, an acetonitrile solution (200 cm^3) containing CoTPPCl or $CoTPPClO_4$ (2.0×10^{-4} mol dm^{-3}) was deaerated by bubbling with argon gas through a stainless steel needle for 1 h, and an appropriate aliquot of 2,3-dimethylhydroquinone dianion (0.10 M) and alkyl halide were added sequentially in 5 min interval to the solution by means of a microsyringe and mixed under an atmospheric pressure of argon. After the reaction was complete, the resulting solution was concentrated under vacuum. The alkylcobalt(III) tetraphenylporphyrin (RCoTPP) was isolated by filtration. The ^1H NMR spectra of RCoTPP showed the characteristic signals in the high-field regions due to the alkyl group bound to cobalt and they were identical with those prepared independently [16]. A typical example: ^1H NMR ($CDCl_3$) $\delta(Me_4Si)$ of coordinated alkyl ligand (ppm): EtCoTPP, −4.04 (t, 3H), −3.46 (q, 2H). The porphyrin ligand proton resonances were found at 7.65–7.80 (m, 12H), 8.03–8.20 (m, 8H), 8.80 (s, 8H).

2.3. Kinetic measurements

Kinetic measurements were performed under deaerated conditions using a Hewlett Packard 8452A diode array spectrophotometer, which was thermostated at 233 or 298 K. Rates of electron transfer from hydroquinone dianions to $CoTPP^+$ and CoTPP in acetonitrile at 233 K were followed by an increase in absorbance due to $CoTPP^-$ ($\lambda_{max} = 360$ nm) [17] under the pseudo-first-order conditions where the concentrations of hydroquinone dianions were maintained at >10-fold excess of the CoTPP concentration (5.0×10^{-6} mol dm^{-3}). Rates of the reactions of $CoTPP^-$ with alkyl halides in acetonitrile at 298 K were followed by an increase in absorbance due to RCoTPP ($\lambda_{max} = 406$ nm) [18] under the pseudo-first-order conditions where the concentrations of alkyl halides were maintained at >20-fold excess of the $CoTPP^-$ concentration (5.0×10^{-6} mol dm^{-3}). Pseudo-first-order rate constants were determined by a least-squares curve fit using a microcomputer. The pseudo-first-order plots were linear for three or more half-lives with the correlation coefficient $\rho > 0.999$.

2.4. Cyclic voltammetry

The one-electron reduction potential ($E_{red}°$) of CoTPP and the one-electron oxidation potentials ($E_{ox}°$) of hydroquinone dianions ($X–Q^{2-}$) were determined by cyclic voltammetry, which was performed on a Hokuto Denko model HA-301 potentiostat–galvanostat at 298 K in MeCN containing 0.10 mol dm^{-3} Bu_4NClO_4 as supporting electrolyte using a saturated calomel electrode (SCE) as a reference under deaerated conditions. The cyclic voltammograms of the $CoTPP/CoTPP^-$ and $X–Q^{\bullet -}–X–Q^{2-}$ couples showed reversible waves from which the $E_{red}°$ and $E_{ox}°$ values were obtained.

3. Results and discussion

3.1. Electron transfer from hydroquinone dianions to $CoTPP^+$ and CoTPP

Addition of 2,3-dimethylhydroquinone dianion (Me_2Q^{2-}: 2.5×10^{-6} mol dm^{-3}), formed by the reaction of 2,3-dimethylhydroquinone (Me_2QH_2) with tetramethylammonium hydroxide ($Me_4N^+OH^-$), to an MeCN solution of CoTPPCl or $CoTPPClO_4$ (5.0×10^{-6} mol dm^{-3}) at 233 K results in an instant formation of CoTPP ($\lambda_{max} = 412$ nm), followed by an increase in absorbance due to $CoTPP^-$ ($\lambda_{max} = 360$ and 424 nm) and the corresponding semiquinone radical anions $Me_2Q^{\bullet -}$ ($\lambda_{max} = 324$ nm) with isosbestic points as shown in Fig. 1. The stepwise electron transfer reduction of $CoTPP^+$ to CoTPP and then $CoTPP^-$ (Scheme 1) is also observed in the reaction of CoTPPCl with other hydroquinone dianions ($X–Q^{2-}$); trimethylhydroqui-

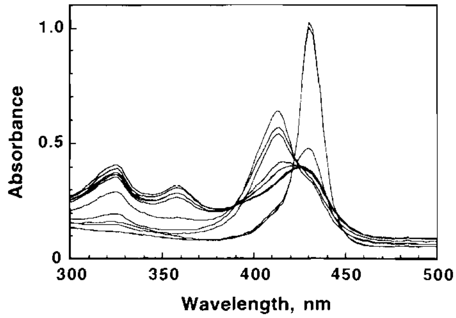
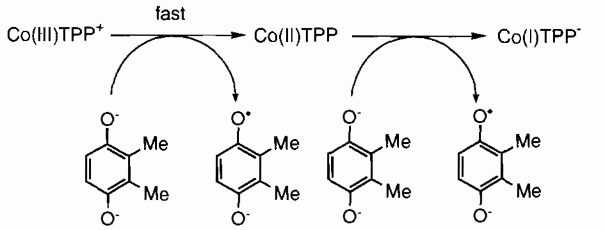


Fig. 1. Electronic spectra observed in the electron transfer reduction of $CoTPP^+$ (5.0×10^{-6} mol dm^{-3}) by 2,3-dimethylhydroquinone dianion (2.5×10^{-5} mol dm^{-3}) in deaerated MeCN at 233 K; 1 s interval.



Scheme 1. Stepwise electron transfer from Me_2Q^{2-} to $CoTPP^+$.

Table 1

Observed rate constants (k_{obs}) of electron transfer from hydroquinone dianions ($X–Q^{2-}$) to CoTPP in MeCN at 233 K, the one-electron oxidation potentials ($E_{ox}°$) of $X–Q^{2-}$ and the calculated rate constants (k_{out}) of outer-sphere electron transfer

$X–Q^{2-}$	$E_{ox}°$ vs. SCE (V)	k_{obs} [a] ($dm^3\ mol^{-1}\ s^{-1}$)	k_{out} [b] ($dm^3\ mol^{-1}\ s^{-1}$)
Me_3Q^{2-}	−1.16	1.5×10^4	8.7×10^4
Me_2Q^{2-}	−1.12	1.1×10^4	3.8×10^4
MeQ^{2-}	−1.07	1.2×10^4	1.3×10^4
$MeOQ^{2-}$	−1.02	1.4×10^4	4.4×10^3
Q^{2-}	−0.98	1.1×10^4	1.8×10^3
ClQ^{2-}	−0.88	7.5×10^3 [c]	3.9×10^2
Cl_4Q^{2-}	−0.71	[d]	
$(CN)_2Q^{2-}$	0.00	[d]	

[a] The experimental errors are within ±10%.

[b] Calculated based on the Marcus theory, see text.

[c] At 253 K.

[d] No reaction.

none dianion (Me_3Q^{2-}), methylhydroquinone dianion (MeQ^{2-}), methoxyhydroquinone dianion ($MeOQ^{2-}$), hydroquinone dianion (Q^{2-}) and chloro-hydroquinone dianion (ClQ^{2-}). When the tetrachlorohydroquinone dianion (Cl_4Q^{2-}) or 2,3-dicyanohydroquinone dianion ($(CN)_2Q^{2-}$) is employed, however, no further reduction of CoTPP to $CoTPP^-$ following the initial electron transfer from the hydroquinone dianion to $CoTPP^+$ has been observed.

Rates of electron transfer from $X–Q^{2-}$ to CoTPP were followed by the increase in absorbance due to $CoTPP^-$ ($\lambda_{max} = 360$ nm) in Fig. 1, obeying pseudo-first-order kinetics in the presence of a large excess of $X–Q^{2-}$ (see Section 2). The pseudo-first-order rate constants were proportional to the $X–Q^{2-}$ concentrations, and thereby the rate of electron transfer obeys the ordinary second-order kinetics, showing a first-order dependence on the concentration of each reactant. The second-order rate constants of electron transfer (k_{et}) in MeCN at 233 or 253 K are listed in Table 1.

The one-electron oxidation potentials ($E_{ox}°$) of $X–Q^{2-}$ determined by the cyclic voltammograms of $X–Q^{2-}$ (see Section 2) in MeCN are also listed in Table 1. On the other hand, the one-electron reduction potential of CoTPP in MeCN is determined as −0.85 V from the cyclic voltammogram of CoTPP (see Section 2). The free energy change of electron transfer ($\Delta G_{et}°$) is given from the difference of the $E_{ox}°$ and $E_{red}°$ values (Eq. (1)), where F is the Faraday constant. As shown

$$\Delta G_{et}° = F(E_{ox}° - E_{red}°) \quad (1)$$

in Table 1 the electron transfer from $X–Q^{2-}$ to CoTPP occurs when $\Delta G_{et}° < 0$ (X = Me_3, Me_2, Me, MeO, H and Cl), while no electron transfer occurs when $\Delta G_{et}° > 0$ (X = Cl_4 and $(CN)_2$).

The k_{et} values of electron transfer reduction of CoTPP in Table 1 are significantly smaller than the reported exchange rate constant for the couple of bpy (2,2′-bipyridine) complexes of Co(II) and Co(I); $Co(bpy)_3^{2+}$–$Co(bpy)_3^+$ couple (1×10^9 $dm^3\ mol^{-1}\ s^{-1}$ at 298 K) [19]. On the other hand, the exchange rate constant for the $Co(bpy)_3^{3+}$–$Co(bpy)_3^{2+}$ couple (18 $dm^3\ mol^{-1}\ s^{-1}$) is much smaller than that for the $Co(bpy)_3^{2+}$–$Co(bpy)_3^+$ couple [20]. Co(I) in an octahedral tris(2,2′-bipyridine) ligand field is known to be in a high-spin d^8 triplet configuration because of the small energy gap of the z^2 and x^2–y^2 orbitals [20]. Co(II) is also in a high-spin d^7 quartet configuration, but Co(III) is in a low-spin singlet configuration [21]. The difference in the spin state is reflected in the Co–N bond length difference (Δd_0); the Δd_0 value for the Co(III)–Co(II) couple (0.19 Å) is much larger than that for the Co(II)–Co(I) couple (−0.02 Å) [20]. Such a difference in the inner-sphere reorganization is suggested to cause the significant difference in the electron-exchange barriers for the $Co(bpy)_3^{3+}$–$Co(bpy)_3^{2+}$ couple and the $Co(bpy)_3^{2+}$–$Co(bpy)_3^+$ couple [20]. However, in the case of a planar cobalt(I) complex, $CoTPP^-$ for example, the gap of the z^2 and x^2–y^2 orbitals in a strong planar ligand field of $CoTPP^-$ is appreciably large, and thereby the ground state configuration of Co(I) almost at the center of the planar ligand field becomes diamagnetic, $(d\pi)^6(z^2)^2$ [22]. The formations of other planar diamagnetic Co(I) species have been well established [23]. Thus, in contrast to the case of octahedral cobalt complexes, the electron-exchange barrier for the couple of a low-spin doublet CoTPP ($S = 1/2$) [24] and a diamagnetic $CoTPP^-$ ($S = 0$) may be as large as that for the couple of a diamagnetic $CoTPP^+$ ($S = 0$) [14] and a doublet CoTPP. The exchange barriers for the low-spin Co(III)–Co(II) couples are known to be generally high because of the large variations of cobalt–axial ligand bond lengths [25].

The activation parameters of the exchange rate constant for the $CoTPP^+$–CoTPP couple have been reported to be $\Delta H^{\neq} = 8.4$ kcal mol^{-1} and $\Delta S^{\neq} = -34$ e.u. [2]. Assuming the activation parameters are the same as those for the CoTPP–$CoTPP^-$ couple, the activation free energy ($\Delta G_{11}^{\neq}$) of the exchange rate constant for the CoTPP–$CoTPP^-$ couple at 233 and 253 K is 16.3 and 17.0 kcal mol^{-1}, respectively. Although the exchange rate constant for the $Q^{\bullet-}$–Q^{2-} couple is not known, the value may be similar to the reported value for the Q–$Q^{\cdot-}$ couple (3.8×10^8 dm^3 mol^{-1} s^{-1}) [26]. Assuming that the activation enthalpy is the same as the reported value (2.3 kcal mol^{-1}) for the TCNE–$TCNE^{\cdot-}$ (tetracyanoethylene) couple [27], the activation free energy ($\Delta G_{22}^{\neq}$) for the $Q^{\cdot-}$–Q^{2-} couple at 233 and 253 K is obtained as 3.1 and 3.2 kcal mol^{-1}, respectively. According to the Marcus theory of outer-sphere electron transfer [12], the intrinsic activation free energy ($\Delta G_0^{\neq}$) of the electron transfer at $\Delta G_{et}^\circ = 0$ is given as the average of the activation free energy for each couple ($\Delta G_{11}^{\neq}$ and $\Delta G_{22}^{\neq}$) by Eq. (2).

$$\Delta G_0^{\neq} = (\Delta G_{11}^{\neq} + \Delta G_{22}^{\neq})/2 \quad (2)$$

The activation free energy of electron transfer is then evaluated from the $\Delta G_0^{\neq}$ and ΔG_{et}° values according to Eq. (3). The rate constants of electron transfer (k_{out})

$$\Delta G_{et}^{\neq} = \Delta G_0^{\neq}[1 + (\Delta G_{et}^\circ/4\Delta G_0^{\neq})]^2 \quad (3)$$

are then calculated by using Eq. (4), where Z is the the frequency factor, taken as 1.0×10^{11} dm^3 mol^{-1} s^{-1}

$$k_{out} = Z\ \exp(-\Delta G_{et}^{\neq}/RT) \quad (4)$$

[12]. The calculated rate constants (k_{out}) of outer-sphere electron transfer are also listed in Table 1, where k_{obs} values of electron transfer from X–Q^{2-} to CoTPP are approximately the same order of magnitude as the corresponding k_{out} values, indicating that the electron transfer from the hydroquinone dianions to CoTPP occurs via an outer-sphere pathway and the exchange barrier for the CoTPP–$CoTPP^-$ couple is about the same as that for the $CoTPP^+$–CoTPP couple. Some difference between the k_{obs} and k_{out} values in Table 1 may be caused by the possible contribution of an inner-sphere electron transfer pathway as well as error in estimation of the $\Delta G_{11}^{\neq}$ and $\Delta G_{22}^{\neq}$ values. In such a case, the activation free energy ($\Delta G_{11}^{\neq}$) of the exchange rate constant for the CoTPP–$CoTPP^-$ couple estimated above gives the minimum value. In any case, the results in Table 1 have clearly established the much slower exchange rate for the planar CoTPP–$CoTPP^-$ couple than that for the couple of octahedral Co(II) and Co(I) complexes.

3.2. Alkylation of $CoTPP^-$ with alkyl halides

$CoTPP^-$ formed by the electron transfer reduction of $CoTPP^+$ by X–Q^{2-} reacts with alkyl halides (RX) to yield the corresponding alkylcobalt(III) tetraphenylporphyrin (RCoTPP) as shown in Eq. (5). A typical spectral change in the alkylation of $CoTPP^-$ with RX

$$CoTPP^- + RX \longrightarrow RCoTPP + X^- \quad (5)$$

is shown in Fig. 2, where the disappearance of absorbance due to $CoTPP^-$ ($\lambda_{max} = 360$ and 424 nm) is accompanied by the rise of absorbance due to EtCoTPP ($\lambda_{max} = 406$ nm) in the reaction of $CoTPP^-$ with EtBr.

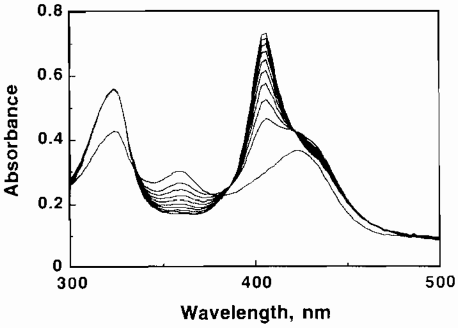


Fig. 2. Electronic spectra observed in the reaction of $CoTPP^-$ (5.0×10^{-6} mol dm^{-3}) with EtBr (5.0×10^{-3} mol dm^{-3}) in deaerated MeCN at 298 K; 5 s interval.

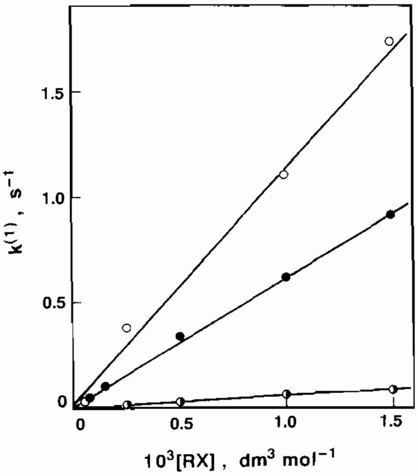


Fig. 3. Plots of pseudo-first-order rate constants (k^1) vs. [RX] for the reactions of $CoTPP^-$ (5.0×10^{-6} mol dm^{-3}) with n-BuI (○), EtI (●), n-BuBr (◑) in deaerated MeCN at 298 K.

A similar spectral change is observed in the reactions of $CoTPP^-$ with $PhCH_2Br$, MeI, n-BuI, n-PrI, $PhCH_2Cl$, EtI, n-BuBr, s-BuI and n-PrBr. In the case of n-BuCl, n-PrCl, i-PrBr and PhI, however, the disappearance of absorbance due to $CoTPP^-$ is accompanied by the rise of absorbance due to CoTPP ($\lambda_{max} = 412$ nm) and no RCoTPP has been formed. The rates of formation of RCoTPP in the reaction of $CoTPP^-$ with a large excess of RX obeyed pseudo-first-order kinetics. The pseudo-first-order rate constants k^1 are strictly proportional to the RX concentration as shown in Fig. 3. Thus, the rate of formation of RCoTPP obeys the second-order kinetics, showing a first-order dependence on the concentration of each reactant. The observed second-order rate constants (k_{obs}) are listed in Table 2.

Savéant [7] reported the approximate value of the second-order rate constant (3.0×10 dm^3 mol^{-1} s^{-1}) for the reaction of $CoTPP^-$ with n-BuBr in DMF from the experimental variations of the anodic-to-cathodic peak current ratio of the first wave with sweep rate and the n-BuBr concentration. The k_{obs} value for the reaction of $CoTPP^-$ with n-BuBr in MeCN at 298 K

Table 2
Observed rate constants (k_{obs}) for the reactions $CoTPP^-$ with alkyl halides (RX) in MeCN at 298 K and the calculated rate constants (k_{et}) of outer-sphere electron transfer from $CoTPP^-$ to RX

RX	$E_{red}°$ vs. SCE [a] (V)	$\Delta G_{22}^{\neq}$ [a] (kcal mol^{-1})	k_{obs} [b] (dm^3 mol^{-1} s^{-1})	k_{et} [c] (dm^3 mol^{-1} s^{-1})
$PhCH_2Br$	-0.70	31.7	8.1×10^4	6.9×10^{-7}
MeI	-1.31	25.3	3.8×10^4	6.5×10^{-10}
n-BuI	-1.21	25.3	1.1×10^3	5.6×10^{-9}
n-PrI			1.1×10^3	
$PhCH_2Cl$	-0.89	32.9	7.0×10^2	1.5×10^{-8}
EtI	-1.16	25.3	6.1×10^2	1.6×10^{-8}
n-BuBr	-1.22	31.8	5.3×10	2.0×10^{-11}
EtBr	-1.14	31.7	4.1×10	1.1×10^{-10}
s-BuI	-0.93	30.2	3.6×10	2.9×10^{-8}
n-PrBr	-1.17	31.7	2.0×10	6.1×10^{-11}
n-BuCl			[d]	
n-PrCl			[d]	
i-PrBr			[d]	
PhI			[d]	

[a] Ref. [28].

[b] The experimental errors are within ±10%.

[c] Calculated based on the Marcus theory, see text.

[d] No RCoTPP has been formed.

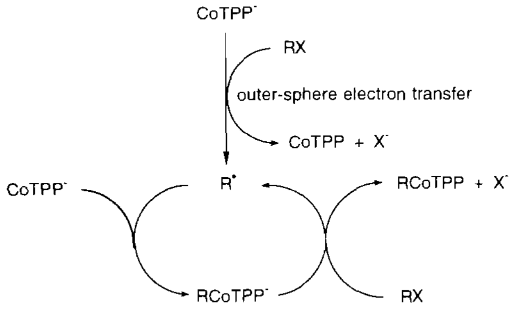
determined directly by following the formation of n-BuCoTPP (5.3×10 dm^3 mol^{-1} s^{-1}) agrees well with the reported value in DMF. Kadish and co-workers [9] also reported the second-order rate constants (k_{obs}) for the reactions of $CoTPP^-$ with various alkyl halides in THF by applying the electrochemical method. The reported k_{obs} values in THF at 295 K are an order of magnitude smaller than those determined directly in MeCN at 298 K (Table 2). The k_{obs} value is the largest in the case of $PhCH_2Br$ (8.1×10^4 dm^3 mol^{-1} s^{-1}) and decreases in the order: $PhCH_2Br > MeI > n\text{-}BuI = n\text{-}PrI > PhCH_2Cl > EtI > n\text{-}BuBr > EtBr > s\text{-}BuI > n\text{-}PrBr \gg n\text{-}BuCl$, n-PrCl, PhI (the corresponding RCoTPP is not formed). Within a series of alkyl halides with the same R group, the k_{obs} values decrease in the order: $I > Br \gg Cl$, consistent with an increase in the R–X bond strength [29], as noted by Kadish and co-workers [9]. The effect of the alkyl group having the same X is not straightforward; $Me \gg n\text{-}Bu = n\text{-}Pr > Et > s\text{-}Bu$. Kadish and co-workers [9] suggested that the large rate constant of MeI as compared with the other alkyl iodides is ascribed to the contribution of an electron transfer pathway (Scheme 2) in addition to an S_N2-type reaction.

The distinction between an outer-sphere electron transfer and an S_N2 pathway may be made by comparing the calculated rate constants of outer-sphere electron transfer based on the Marcus theory with the observed values. We have previously reported that the rate constants of photoinduced electron transfer from the singlet excited state of 10-methyl-9,10-dihydroacridine ($^1AcrH_2{}^*$) to various alkyl and phenyl halides agree well with the calculated rate constants of outer-sphere electron transfer by using the Marcus equation (Eq. (3)) [28]. With regard to the intrinsic barrier for the one-electron reduction of RX, the activation free energies for the $RX\text{–}RX^{\bullet-}$ couple ($\Delta G_{22}^{\neq}$) have been reported [28,30]. Since the minimum $\Delta G_{11}^{\neq}$ value for the $CoTPP\text{–}CoTPP^-$ couple (18.5 kcal mol^{-1} at 298 K) is obtained as the $\Delta G_{11}^{\neq}$ value for the $CoTPP^+\text{–}CoTPP$ couple (vide supra), the minimum intrinsic activation free energy ($\Delta G_0^{\neq}$) of the electron transfer from $CoTPP^-$ to RX at $\Delta G_{et}° = 0$ is given as the average of the activation free energy for each couple ($\Delta G_{11}^{\neq}$ and $\Delta G_{22}^{\neq}$) by using Eq. (2). The activation free energy of electron transfer is evaluated from the $\Delta G_0^{\neq}$ and $\Delta G_{et}°$ values by using the Marcus equation (Eq. (3)). The rate constants of electron transfer (k_{et}) are then calculated by using Eq. (4). The calculated rate constants (k_{et}) of outer-sphere electron transfer from $CoTPP^-$ to RX, which can be regarded as the maximum values are also listed in Table 2 together with the $E_{red}°$ and $\Delta G_{22}^{\neq}$ values for the $RX\text{–}RX^{\bullet-}$ couple. The k_{et} values are 10^{10}–10^{13} times smaller than the k_{obs} values in Table 2.

$$\mathrm{CoTPP^- + RX \xrightarrow[\text{electron transfer}]{\text{outer-sphere}} (CoTPP\ R^\bullet\ X^-) \xrightarrow{\text{fast}} RCoTPP + X^-}$$

Scheme 2. Outer-sphere electron transfer pathway.

The extremely larger reactivity than expected from an outer-sphere electron transfer pathway could be explained by the amplification due to the chain reaction as shown in Scheme 3. The radical $R^\bullet$ produced in the initial outer-sphere electron transfer from $CoTPP^-$ to RX may add to $CoTPP^-$ to give $RCoTPP^-$, which



Scheme 3. Chain reaction initiated by outer-sphere electron transfer.

then transfers an electron to RX to yield RCoTPP, accompanied by the regeneration of R$^{\bullet}$. In such a case the overall reactivity may be amplified by a factor of the chain length. However, the overall rate of the chain reactions (Scheme 3) involving an additional rate-determining step besides the initial electron transfer step would not obey simple second-order kinetics showing a first-order dependence on the concentration of each reactant as observed in Fig. 3. Thus, the 10^9–10^{13} times larger k_{obs} values than the corresponding k_{et} values in Table 2 strongly indicate that the reaction of CoTPP$^-$ with each RX (including MeI) proceeds via an S$_N$2 pathway, which involves significant interaction between CoTPP$^-$ and RX, rather than an outer-sphere electron transfer pathway.

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