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Electron Transfer in the Quenching of Triplet States of Zinc Phthalocyanine and Methylene Blue by the Use of Fe(III), Co(III), and Organic Oxidants

Takeshi Ohno,* Shunji Kato, and Norman N. Lichtin†

Chemistry Department, College of General Education, Osaka University, Toyonaka, Osaka 560

† *Department of Chemistry, Boston University, Commonwealth Avenue, Boston, Massachusetts 02215, U. S. A.*

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The mechanism of the quenching of the triplet state of zinc phthalocyanine (ZnPc) and Methylene Blue (MB^+) by low-spin complexes of Fe(III) and Co(III) and aromatic oxidants was studied. The quenchers studied included $Fe^{III}(CN)_6^{3-}$, $Fe^{III}(CN)_4$(2,2-bipyridyl)$^-$, $Fe^{III}(CN)_2$(2,2-bipyridyl)$^+$, ferrocenium ion, Co^{III}(2,2′: 6′-2″-terpyridyl)$^{3+}$, Co^{III}(1,10-phenanthroline)$^{3+}$, dimethylviologen, 1,4-benzoquinone, and 2,4,7-trinitro-9-fluorenone (TNF). The rate constants of the quenching of ^{3}ZnPc varied from a diffusion-controlled one to 6×10^5 dm^3 mol^{-1} s^{-1} in the mixed solvent of dimethylacetamide (DMA) and water (7:3 by volume). The metal complexes quenched $^3MB^+$ and the triplet state of protonated MB^+ with a rate constant of more than 2×10^6 dm^3 mol^{-1} s^{-1} in an aqueous solution with 0.5 mol dm^{-3} of $MgCl_2$. The fractions of electron transfer yielding $ZnPc^{\dot{+}}$ in the quenching process (F_1) were high except for TNF and the iron(III) compounds. The F_1 fractions were also obtained in the quenching of $^3MB^+$ and the triplet state of the protonated MB^+. The absence of radical production in the quenching by the doublet iron(III) compounds can be explained in terms of spin-allowed reverse electron transfer in the life of the geminate radical pair. Fractions of the reverse electron transfer between the half-reduced quencher and $ZnPc^{\dot{+}}$ or $MB^{\dot{2+}}$ were also measured; they are very close to those of $1-F_1$. The data reported in this study are consistent with the following mechanistic features. (1) Every quenching encounter produces a geminated radical pair. (2) The geminated pair is common to the quenching of the triplet excited state by oxidants and to the reverse electron transfer between the free radicals formed in the quenching. The molar extinction coefficient of $ZnPc^{\dot{+}}$ was determined to be 2.9×10^4 dm^3 mol^{-1} cm^{-1} at 520 nm.

Electron transfer between an excited molecule and a quencher to produce redox products is a necessary step in the conversion of solar into chemical energy. Either the dissociation of the radicals or the reverse electron transfer may follow the electron-transfer quenching of the excited state within the lifetime of the geminate radical pair, the former of which yields redox products. The fraction of the radical formation in quenching has been called "the efficiency of electron transfer in the quenching process,"[1,2] which corresponds to "the cage-escape probability"[3,4] provided every quenching yields a geminate radical pair. Reverse electron transfer in a singlet radical pair reproducing the singlet reactant pair is spin-allowed,[5,6] so F_1 is nil unless the reverse electron transfer is unfavourable with respect to the free-energy change. On the other hand, reverse electron transfer in a triplet radical pair is spin-forbidden,[5–7] so F_1 is high except multiplicity restriction is broken by means of spin-orbit interaction.[2,8] The rate of the reverse electron transfer can be estimated by using Marcus' equation[9] or an empirical equation proposed by Rehm and Weller,[10] which is written in terms of the free-energy change and rearrangement energy involved in the electron transfer, provided the electron-transfer process is spin-allowed.

This paper will describe a study of electron-transfer quenching rates and the efficiency of electron transfer in the quenching of the triplet state of zinc phthalocyanine (ZnPc) and Methylene Blue (MB^+) by a substitution-inert coordination compound of iron(III) and cobalt(III) and some aromatic oxidants, such as 1,4-benzoquinone and dimethylviologen. The efficiency of the reverse electron transfer between the half-reduced quencher and half-oxidized ZnPc or MB^+ is also studied in order to make the quenching mechanism clear.

Metal phthalocyanine compounds are regarded as inert and stable metal complexes in which photoexcitation energy may not be dissipated before the conversion of solar to chemical energy. Since the phthalocyanine compounds resemble porphyrins in both geometrical and electronic structures, they have been studied by several workers. More recently, different results with respect to the efficiency of photo-electron transfer has been reported. Harriman and Richoux[11] reported F_1 to be less than 5% in the quenching of zinc phthalocyanine tetrasulfate by methylviologen in water. On the other hand, Tanno, Wöhrle, Kaneko, and Yamada[12] reported a high quantum yield of the production of the methylviologen radical on exciting magnesium phthalocyanine in a mixed solvent of dimethylsulfoxide and water.

MB^+ is a photosensitizer of the photogalvanic cell proposed by Rabinowitch[13] and developed by the present author (N. N. L.);[14] in the method, the reduction of MB^+ to $MBH^{\dot{+}}$ is coupled by the oxidation of Fe^{II} to Fe^{III}. Recently, $Fe^{III}(H_2O)_6^{3+}$ was reported to oxidize the singlet excited state of MB^+ with a very small yield.[15] The unfavorable process of MB^+-oxidation by iron(III) compound is worth examining.

Experimental

Materials. Water was purified by passage through a Millipore deionizer and a filter. Dimethylacetamide (DMA) was purified by vacuum distilation. The Puriss-grade $MB^+Cl^-\cdot3H_2O$ (Fluka), $HClO_4$ (Wako Junyaku), dimethylviologen** (Tokyo Kasei), 2,4,7-trinitro-9-fluorenone** (Tokyo Kasei), and 2,3,5,6-tetrachloro-1,4-benzoquinone** (Wako Junyaku) were used as supplied. The ZnPc (Tokyo Kasei), 1,4-benzoquinone** (Wako Junyaku), and 1,4-naphthoquinone (Wako Junyaku) were purified by vacuum sublimation immediately before use. The $Co^{III}(2,2':6'\text{-}2''\text{-terpyridyl}^{**})_2(ClO_4)_3$ and $Co^{III}(1,10\text{-phenanthroline}^{**})_3(ClO_4)_3$ were prepared by the method of Maki.[16] The ferrocenium ion was prepared immediately before use by the oxidation of ferrocene with iron(III) nitrate in 0.01 mol dm^{-3} of a $HClO_4$ aqueous solution. $Fe^{III}(2,2'\text{-bipyridyl}^{**})_2(CN)_2(NO_3)$ and $H[Fe^{III}(CN)_4(bpy)]$ were prepared by the method of Schilt.[17] The solvent for ZnPc was a mixture of DMA and water (7:3 by volume). The ionic strengths of the sample solution were kept to be 1—1.5 mol/dm^3 by using $MgCl_2$ or $NaClO_4$. All the test solutions were deaerated by purging nitrogen for 15—20 min.

Apparatus. A *NEC* ruby laser *SLG*-2018 with a *Q*-switch capable of providing up to 0.85 J per flash at 694.3 nm with a pulse width of 20 ns was used. The laser beam ($\phi=10$ mm) is vertically converged and longtudinally expanded by means of two cylindrical lenses to 6 mm × 12 mm on the photolysis cell (10 mm × 10 mm). The laser intensity was stabilized within a fluctuation of a few percent by controlling the temperature of the circulating water for the ruby rod. The absorption changes in the sample were measured by the use of the monitoring beam of a 150 W Xenon arc lamp, which was operated at 20 V (8 A) and which could be pulsed to 30—70 V by the use of a transistor-switched discharging circuit, made by Dr. N. Tatebe. The probe-beam is also focussed by a means of a convex lens on the sample cell with a pin hole ($\phi=1$ mm). A shutter driven by a pulse motor is put between the focusing lens and the sample cell to minimize photolysis. The intensity of the monitoring beam was measured by means of a Hamamatsu R955 photomultiplier tube and a Tektronix 456 synchroscope. Another ruby apparatus was used for the study of the MB^+-oxidation; it has been described in the literature.[18]

Measurements. The decay of ^3ZnPc was monitored at 450 or 490 nm. The decays of $^3MBH^{2+}$ and $^3MB^+$ were monitored at 710 and 820 nm respectively.[1] The yields of $ZnPc^{\ddagger}$ were measured at 520 nm ($\varepsilon_{520}=2.9\times10^4$ dm^3 mol^{-1} cm^{-1}). The yields of MB^{2+} were measured at 520 nm ($\varepsilon_{520}=5.7\times10^4$ dm^3 mol^{-1} cm^{-1} [19]). The rate of disappearance of $ZnPc^{\ddagger}$ were monitored through the decay of its absorbance at 835 nm. The rates of the disappearance of MB^{2+} were monitored through its absorbance at 520 nm or through its increase in absorbance due to MB^+.

Results and Discussion

T-T Absorption. On exposure to 694.3 nm light, the S_1-S_0 absorption of ZnPc was reduced and a transient species was observed with a lifetime of 200 μs. Its absorption spectrum, shown in Fig. 1, is very similar to the absorption spectrum of the triplet excited state of ZnPc in neutral 2-propanol previously reported.[20] The conversion of ZnPc to its triplet state can be estimated from the decrease in the peak absorbance of ZnPc at 672 nm almost completely disappeared for several hundred nano seconds on exposure to a laser beam intensified by means of a cyclindrical convex lens. The molar extinction coefficient of the triplet state at 490 nm can be calculated to be 3.25×10^4 mol^{-1} dm^3 cm^{-1}, which is very close to that reported in 2-propanol.

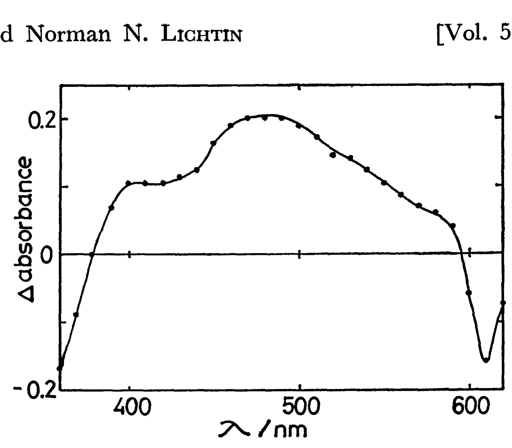

Fig. 1. Transient spectrum of ^3ZnPc in 70% DMA aqueous solution.
[ZnPc] = 5×10^{-6} mol/dm^3.

TABLE 1. QUENCHING-RATE CONSTANTS AND FRACTIONS OF ELECTRON TRANSFER IN THE QUENCHING OF ^3ZnPc IN DMA AQUEOUS SOLUTION

Quencher	$\frac{[HClO_4]}{\text{mol dm}^{-3}}$	$\frac{k_q}{10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}}$	F_1
Ferrocenium ion	0.01	1.0	0
$Fe^{III}(CN)_6^{3-}$	0.01	0.286	0
	0	0.019	0
TCBQ	0.01	1.3	0.27
	0	0.83	0.75
TNF	0.01	1.0	0
BQ	0.01	0.50	0.90
	0	0.50	0.78
1,4-Naphthoquinone	0.01	0.03	—
MV^{2+}	0.01	0.0005	0.43
	0	0.0036	1.0
$Co^{III}(tpy)_2^{3+}$	0.01	0.14	0.37
	0	0.53	0.70

The absorption spectra and molar extinction coefficients of $^3MB^+$ and the triplet state of protonated MB^+ ($^3MBH^{2+}$) have already been measured by the present authors, S.K.,[20] T.O., and N.N.L.[18] The decay-rate constants of $^3MBH^{2+}$ and $^3MB^+$ in the presence of a charged compound of iron(III) or cobalt(III) were measured in an aqueous solution with $MgCl_2$ of 0.5 mol/dm^3, where the electrostatic effect on the rate constant of the bimolecular process between $^3MBH^{2+}$ and the metal compound can be neglected.

Quenching Reactions of ^3ZnPc, $^3MBH^{2+}$, and $^3MB^+$. ^3ZnPc is quenched by an oxidant, such as the ferrocenium ion, $Fe^{III}(CN)_6^{3-}$, $Co^{III}(tpy)_2^{3+}$, BQ, 1,4-naphthoquinone, TNF, TCBQ, and MV^{2+}. The addition of the quencher did not change the ^3ZnPc

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** The following abbreviations are used; dimethylviologen:MV^{2+}, 2,4,7-trinitro-9-fluorenone:TNF, 2,3,5,6-tetrachloro-1,4-benzoquinone:TCBQ, 1,4-benzoquinone:BQ, 2,2':6'-2''-terpyridyl:tpy, 1,10-phenanthroline:phen, 2,2'-bipyridyl:bpy.

Table 2. Relevant properties of ZnPc, MB^+, and the quenchers

Species[a)]	pK_a	E°_{redox}, *vs.* NHE
ZnPc	—	1.02($ZnPc^+/ZnPc$)[c)]
^3ZnPc(1.13 eV[b)])	—	−0.11($ZnPc^+/^3ZnPc$)
MB^+	—	1.08(MB^{2+}/MB^+)[e)]
$^3MB^+$(1.44 eV[d)])	—	−0.36($MB^{2+}/^3MB^+$)
MBH^{2+}	0.0[g)]	1.06(MBH^{3+}/MBH^{2+})
$^3MBH^{2+}$(1.02 eV[f)])	7.2[f)]	0.04($MBH^{3+}/^3MBH^{2+}$)
$Fe^{III}(CN)_2(bpy)_2{}^+$	—	0.78[h)]
$Fe^{III}(H_2O)_6{}^{3+}$	—	0.77[k)]
$Fe^{III}(CN)_4(bpy)^-$	—	0.56[i)]
Ferrocenium ion	—	0.54[j)]
$Fe^{III}(CN)_6{}^{3-}$	—	0.36[k)]
$Co^{III}(phen)_3{}^{3+}$	—	0.40[l)]
$Co^{III}(tpy)_2{}^{3+}$	—	0.31[l)]
TCBQ	—	0.26[m)]
TNF	—	−0.08[n)]
BQ	—	−0.27[m)]
1,4-Naphthoquinone	—	−0.34[m)]
MV^{2+}	—	−0.22[o)]

a) S_0 state unless otherwise indicated. Excitation energy to the lowest triplet state is shown in parentheses. b) P. S. Vincent, E. M. Voigt, and K. E. Rieckhoff, *J. Chem. Phys.*, **55**, 4131 (1971). c) A. B. P. Lever and J. P. Wilshire, *Can. J. Chem.*, **54**, 2514 (1976). d) Ref. 23. e) T. Takizawa, T. Watanabe, and K. Honda, *J. Phys. Chem.*, **82**, 1391 (1978). f) Ref. 18. g) J. P. Keene, E. J. Land, and A. J. Swallow, "Pulse Radiolysis," ed by M. Evert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London (1965), p. 227. h) A. A. Schilt, *Anal. Chem.*, **35**, 1599, (1963). i) P. George, G. I. H. Hanavia, and D. H. Irvine, *J. Chem. Soc.*, **1959**, 2548. j) J. G. Mason and M. Rosenblum, *J. Am. Chem. Soc.*, **82**, 4216 (1960). k) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," 2nd ed, Prentice Hall, N. J. (1952). l) R. Farina and R. G. Wilkins, *Inorg. Chem.*, **7**, 514 (1968). m) C. K. Mann and K. K. Barness, "Electrochemical Reactions in Nonaqueous Systems," Marcell Deckker, N. Y. (1970). n) Estimated from the electron affinity (1.01 eV) by using this equation: $EA = -1.04E^\circ + 1.39$ (G. Briegleb, *Angew. Chem.*, **76**, 326 (1964)). o) S. Hunig, J. Gross, and W. Schenk, *Justus Liebigs Ann. Chem.*, **1973**, 324.

production immediately after flashing, but it did increase the decay rate of ^3ZnPc. However, TNF of more than 50 μmol/dm³ reduced both the fluorescence and the ^3ZnPc production; this effect is ascribed to complex formation in the ground state.[22)] An analysis of the pseudo-first order decay of ^3ZnPc in the presence of the oxidant gives the quenching-rate constant listed in Table 1. The quenching-rate constant with a charged quencher was changed in an acidic solution by $HClO_4$ of 0.01 mol/dm³; *i.e.*, that with a cation, MV^{2+} or $Co^{III}(tpy)_2{}^{3+}$, decreased and that with an anion, $Fe^{III}(CN)_6{}^{3-}$, increased compared to those in the neutral solution. No change in the quenching rate was observed with BQ in the $HClO_4$ solution. The dependence of the rate constants on the charge of the quencher suggests that ^3ZnPc in a 0.01 mol/dm³ $HClO_4$ solution takes a proton, so electrostatic interaction between the cation triplet state and the charged quencher modifies the quenching-rate constant.

The largest rate constant was obtained using TCBQ as a quencher; it is assumed to quench ^3ZnPc at the rate of the encounter. The decreasing order of the quenching rate constants is: TCBQ > TNF > BQ > 1,4-naphthoquinone > MV^{2+}, which agrees with the decreasing order of the redox potential ($E^\circ(Q/Q^{\cdot-})$ except for MV^{2+} (see Table 2). Since the free-energy change in the electron-transfer reaction between ^3ZnPc and the quencher (Q) is written by Eq. 1:

$$-\Delta G = F \times [E^\circ(Q/Q^{\cdot-}) - E^\circ(\mathrm{ZnPc}^{+\cdot}/\mathrm{ZnPc})], \tag{1}$$

where $E^\circ(\mathrm{ZnPc}^{+\cdot}/{}^3\mathrm{ZnPc})$ is the redox potential of ^3ZnPc and F is the Faraday constant, the quenching can be ascribed to electron transfer. The abnormally small rate constant with MV^{2+} can be explained by the large reorganization energy involved in electron transfer,[23)] which Marcus,[9)] Rehm and Weller[10)] have introduced in explanation of the rate of an adiabatic electron-transfer reaction. The quenching-rate constants with the metal compounds studied in this work were much slower than that expected from the free-energy change. The rate constant observed with $Co^{III}(tpy)_2{}^{3+}$ can be explained by the fairly large reorganization energy involved in the electron transfer:[24)] it is very close to the one estimated by using the equations of Marcus (Eq. 2) and Rehm and Weller (Eq. 3) to get the free energy of activation (ΔG^*_{12}) by using the self-exchange rate constants, electrostatically corrected, of 800 dm³ mol⁻¹ s⁻¹ for $Co^{III}(tpy)_2{}^{3+}$—$Co^{II}(tpy)_2{}^{2+}$ and of 1 × 10⁹ dm³ mol⁻¹ s⁻¹ for $\mathrm{ZnPc}^{+\cdot}$–^3ZnPc and by assuming that the electron-transfer rate constant (k) is written as in Eq. 4:

$$\Delta G^*_{12} = \frac{\Delta G^*_1(0) + \Delta G^*_2(0)}{4} + \frac{\Delta G_{12}}{2} + \frac{(\Delta G_{12})^2}{8 \times [\Delta G^*_1(0) + \Delta G^*_2(0)]}, \tag{2}$$

$$\Delta G^*_{12} = \frac{\Delta G_{12}}{2} + \left\{ \frac{(\Delta G_{12})^2}{4} + \frac{[\Delta G^*_1(0) + \Delta G^*_2(0)]^2}{4} \right\}^{1/2}, \tag{3}$$

where $\Delta G^*{}_1(0)$, $\Delta G^*{}_2(0)$, and ΔG_{12} are the free energies of activation for the self-exchange reaction of Reactants 1 and 2, and the free-energy change of the cross reaction between Reactants 1 and 2, and,

$$k = \kappa z \exp(-\Delta G^*_{12}/RT), \tag{4}$$

where κ and Z are the adiabatic parameter and the collision frequency (—10^{11} s⁻¹) respectively. The estimated rate constants are shown in Table 3. However, the estimated rate constant with $Fe^{III}(CN)_6{}^{3-}$ is still sixty times as large as the observed one, so some non-adiabaticity in the electron transfer may exist.

Spin restriction on any dynamic phenomenon of transition-metal compounds is still effective; for example, the rate constant of an exchange-type energy transfer between a triplet excited state of an organic compound

Table 3. Rate constants of electron-transfer processes (in $dm^3\,mol^{-1}\,s^{-1}$) observed and estimated by means of the Marcus equation and the Rehm and Weller equation

Reactants		$k_q^{ob}(k_{ret}) \times 10^{-8}$	$k_2^{EEa)} \times 10^{-8}$	$k^{cal}(RW)^{b)} \times 10^{-8}$	$k^{cal}(M)^{c)} \times 10^{-8}$	$k_q^{ob}/k^{cal}(RW)$
^3ZnPc	$^2Fe^{III}(CN)_6{}^{3-}$	0.19	3.5×10^{-4} d)	11	53	0.017
^3ZnPc	MV^{2+}	0.036	0.06e)	0.013	0.019	2.77
^3ZnPc	$Co^{III}(tpy)_2{}^{3+}$	5.3	8×10^{-6} f)	1.6	4.2	3.3
$^2ZnPc^{\cdot+}$	$^2Co^{II}(tpy)_2{}^{2+}$	4.6	8×10^{-6} f)	13.8	135	0.33
$^3MBH^{2+}$	$^2Fe^{III}(CN)_6{}^{3-}$	4.5	3.5×10^{-4} d)	11	32	0.42
$^3MBH^{2+}$	$Co^{III}(phen)_3{}^{2+}$	0.20	6.5×10^{-7} f)	0.38	0.066	0.53
$^3MBH^{2+}$	$Co^{III}(tpy)_2{}^{3+}$	0.05	8×10^{-6} f)	0.42	98	0.12
$^2MB^{2\cdot+}$	$^4Co^{II}(phen)_3{}^{2+}$	1.3	6.5×10^{-7} f)	8.2	0.66	0.16

a) The self-exchange electron-transfer rate constant of the second reactant is electrostatically corrected and normalized at 25 °C. b) Estimated by using Eqs. 3 and 4. c) Estimated by using Eqs. 2 and 4. d) Ref. 23. e) M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965). f) Ref. 24.

and a quartet ground state of the chromium(III) compound, yielding the singlet ground state of the organic compound and the doublet excited state of chromium(III), is limited to the spin-statistical factor of the process.[25] Therefore, it is reasonable to think that the spin non-conserved channel of electron transfer is still non-adiabatic ($\kappa<1$). In the quenching by the doublet $Fe^{III}(CN)_6{}^{3-}$, the formation of the encounter complex preceeds the electron transfer, which has the spin multiplicity of the doublet or quartet. The doublet complex is converted to $^2ZnPc^{\cdot+}$ and $^1Fe^{II}(CN)_6{}^{3-}$, but the quartet complex dissociates into the original reactants, ^3ZnPc and $^2Fe^{III}(CN)_6{}^{3-}$, without spin-inverted conversion into the redox products. Consequently, this kind of non-adiabaticity may reduce the quenching-rate constant to one quarter (the spin-statistical factor of the process), provided the spin restriction is firm. Another kind of non-adiabaticity may come from some specific hindrance to electron-exchange interaction between the reactants.

The decay rates of $^3MBH^{2+}$ and $^3MB^+$ increased in the presence of the oxidant; this did not, however, affect the triplet production immediately after flashing. The quenching rate constants of $^3MB^+$ in an ammonia alkaline aqueous solution by $Fe^{III}(CN)_6{}^{3-}$ and $Fe^{III}(CN)_4(bpy)^-$ are 4.3×10^9 and 4.5×10^9 $dm^3\,mol^{-1}\,s^{-1}$ respectively; these values are close to the diffusion-controlled rate constant of the bimolecular process in water. Each of the cobalt(III) compounds quenched $^3MB^+$ at a slower rate than did $Fe^{III}(CN)_6{}^{3-}$ as Table 4 shows. All the oxidants studied quenched $^3MBH^{2+}$ at a slower rate in an acidic solution than in the ammonia alkaline solution. It is reasonable to assume that $^3MB^+$, with the excitation energy of 1.44 eV,[26] is more susceptible to electron-transfer quenching than $^3MBH^{2+}$ with an excitation energy of 1.02 eV,[18] because $E°(MB^{\cdot+}/^3MB^+)$ is more positive than $E°(MBH^{3\cdot+}/^3MBH^{2+})$. The smaller quenching rate constant by the cobalt(III) compounds can not be explained without reference to the self-exchange rates being smaller than those with the iron(III) compounds (see Table 3). Though $Fe^{III}(H_2O)_6{}^{3+}$ of 0.04 mol/dm³ quenched MB^+ fluorescence, the decay of $^3MBH^{2+}$ was not effectively quenched, so the increase in the decay rate with $Fe^{III}(H_2O)_6{}^{3+}$ of 1 mmol/dm³ is one hundredth of the spontaneous decay rate of $^3MBH^{2+}$. This means that the $Fe^{III}(H_2O)_6{}^{3+}$ produced in the reduction of MB^+ has practically no effect on the photoreduction of MB^+ in the MB^+–$Fe^{II}(H_2O)_6{}^{2+}$ photogalvanic cell.

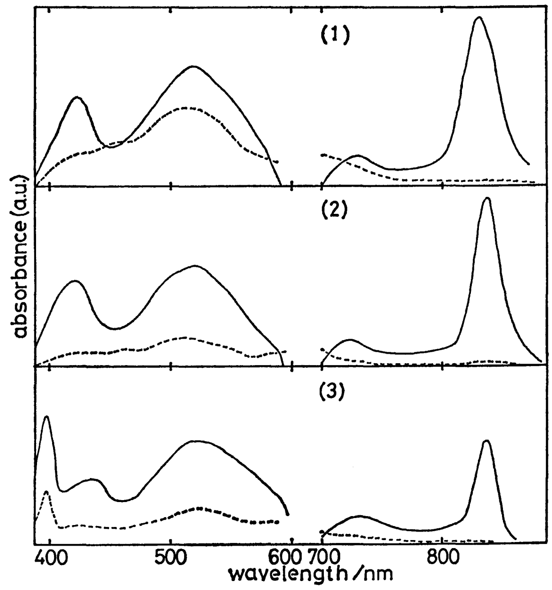


Fig. 2. Transient spectra of ZnPc solution containing an oxidant after the disappearance of ^3ZnPc. (1): $[ZnPc]=2\times10^{-5}$ mol/dm³ and $[Co^{III}(tpy)_2{}^{3+}]=2.4\times10^{-4}$ mol/dm³. ——: 10 μs after flashing, - - -: 1 ms after flashing. (2): $[ZnPc]=4\times10^{-6}$ mol/dm³ and $[BQ]=2\times10^{-3}$ mol/dm³. ——: 25 μs after flashing, - - -: 0.6 ms after flashing. (3): $[ZnPc]=2\times10^{-6}$ mol/dm³ and $[MV^{2+}]=1\times10^{-2}$ mol/dm³. ——: 300 μs after flashing, - - -: 2.5 ms after flashing.

Production of Half-oxidized ZnPc and MB^+. An intermediate was produced in the quenching of ^3ZnPc by TCBQ, BQ, 1,4-naphthoquinone, MV^{2+}, and $Co^{III}(tpy)_2{}^{3+}$. A transient absorption with maxima at 420, 530, 730, and 840 nm was observed immediately after the decay of ^3ZnPc, irrespective of the kind of oxidant, as Fig. 2 shows, so it can be identified as the half-oxidized form of ZnPc ($ZnPc^{\cdot+}$). In Fig. 2, the band at 394 nm can also be ascribed to the half-reduced form of MV^{2+}, which is well known to have absorp-

Table 4. QUENCHING-RATE CONSTANTS AND FRACTIONS OF ELECTRON TRANSFER IN THE QUENCHING OF ^{3}MBH^{2+} OR ^{3}MB$^+$ IN AN AQUEOUS SOLUTION WITH MgCl$_2$ OF 0.5 mol/dm^3

Quencher	[H$_2$SO$_4$]$^{a)}$	[NH$_4$OH]$^{a)}$	$k_q/10^9$ dm^3 mol^{-1} s^{-1}	F_1
$\mathrm{Fe^{III}(CN)_2(bpy)_2^+}$	5	0	2.0	0
$\mathrm{Fe^{III}(CN)_4(bpy)^-}$	5 0	0 5	2.1 4.5	0 0
$\mathrm{Fe^{III}(CN)_6^{3-}}$	5 0	0 5	0.45 4.3	0 0
$\mathrm{Co^{III}(phen)_3^{3+}}$	5 0	0 5	0.02 1.7	0.71 0.07
$\mathrm{Co^{III}(tpy)_2^{3+}}$	5 0	0 5	0.005 1.16	0.17 0
$\mathrm{Fe^{III}(H_2O)_6^{3+}}$	10$^{b)}$	0	0.005	—

a) The concentration of the acid or base is 10^{-3} mol/dm^3. b) H$_2$SO$_4$ is replaced by HNO$_3$.

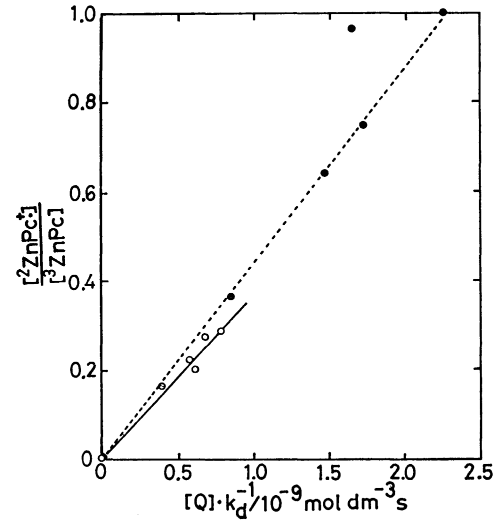


Fig. 3. Determination of k_{et} in the quenching of ^{3}ZnPc by BQ, ●, and by TCBQ, ○.
[ZnPc]$=2\times10^{-5}$ mol/dm^3 and [HClO$_4$]$=0.01$ mol/dm^3.

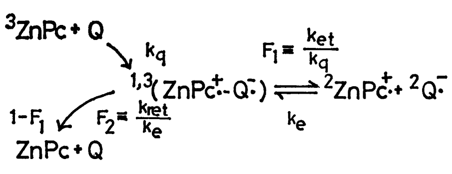


Fig. 4. Reaction scheme.

tion maxima at 394 and 604 nm in water.[27] The molar extinction coefficient of ZnPC$^{+\cdot}$ is calculated to be 2.9×10^4 dm^3 mol^{-1} cm^{-1} at 520 nm by assuming that MV$^{+\cdot}$ has the same molar extinction coefficient at 394 nm as that in water. Assuming that the conversion of ZnPc to ZnPc$^{+\cdot}$ can be estimated from the decrease in the strong absorbance of ZnPc ($\varepsilon_{672}=2.3\times10^5$ dm^3 mol^{-1} cm^{-1}), the same extinction coefficient of ZnPc$^{+\cdot}$ was obtained at 520 nm. The production of half-reduced quinone was not clearly observed, for the molar extinction coefficients are in the order of 10^3 dm^3 mol^{-1} cm^{-1}.[28] Since the extinction coefficient of $\mathrm{Co^{II}(tpy)_2^{2+}}$ is less than 1.6×10^3 dm^3 mol^{-1} cm^{-1} in the visible region,[29] the transient absorption spectrum observed with the cobalt complex can be fully ascribed to ZnPc$^{+\cdot}$. It is a little different from the spectra of either chemically oxidized forms of ZnPc in crystal[30] or of magnesium phthalocyanine in dichloromethane,[31] the former of which has been reported to exhibit three bands at 446, 550, and 730 nm.

The half-oxidized form of MB$^+$ (MB$^{2+\cdot}$) was also produced in the quenching of ^{3}MBH^{2+} and ^{3}MB$^+$ by the cobalt(III) compounds, which have an absorption maximum at 520 nm, like that observed in the self-quenching reaction of ^{3}MBH^{2+} [19] and in the electrolytic oxidation of MB$^+$.[32] The iron(III) compounds produced no MB$^{2+\cdot}$ in the quenching.

The production of ZnPc$^{+\cdot}$ in the quenching process can be written as Eq. 5;

$$[\mathrm{ZnPc}^{+\cdot}]_0 = [{}^3\mathrm{ZnPc}]_0\frac{k_{\mathrm{et}}[\mathrm{Q}]}{k_{\mathrm{d}}} \qquad (5)$$

where $[{}^3\mathrm{ZnPc}]_0$ and $[\mathrm{ZnPc}^{+\cdot}]_0$ are productions in mol/dm^3 per flash, k_{et} is the rate constant of overall electron transfer, and k_{d} is the decay-rate constant of ^{3}ZnPc in the presence of a quencher. As Fig. 3 shows, the ratio of $[\mathrm{ZnPc}^{+\cdot}]_0$ to $[{}^3\mathrm{ZnPc}]_0$ is proportional to $[\mathrm{Q}]/k_{\mathrm{d}}$ so the value of k_{et} can be obtained. The ratio of k_{et} to the quenching-rate constant can be regarded as the fraction of free-radical formation in the quenching, which is expressed as k_{et}/k_g and designated as F_1. F_1 can also be defined as a fraction dissociating to two free radicals, and the residue $(1-F_1)$, as a fraction performing a reverse electron-transfer reaction, as is shown in Fig. 4. F_1s are fairly high with BQ, MV^{2+}, TCBQ, and $\mathrm{Co^{III}(tpy)_2^{3+}}$. However, the iron(III) compounds did not yield ZnPc$^{+\cdot}$ in the quenching of ^{3}ZnPc, nor did TNF produced ZnPc$^{+\cdot}$ in the quenching of the excited singlet and the excited triplet states of ZnPc.

Two of the present authors (T.O. and N.N.L.) have previously demonstrated that the fraction, F_1, in a homogeneous solution can be explained in terms of the rate of reverse electron transfer in the life of cage complex with triplet multiplicity.[1,2] The rate of reverse electron transfer can be estimated from : (i) the breaking down of spin-conservation, (ii) the free energy change involved in electron transfer, and (iii) the reorganization energy of the reactants involved in electron transfer. If the spin-multiplicity restriction is firm for the reverse electron-transfer, F_1 is unity. However, intersystem crossing from the triplet complex to the singlet one occurs by means of two mechanisms, hyperfine interaction in a weakly interacting cage complex[33] and the spin-orbit interaction of the cage complex on the surrounding reaction surface, the latter of which may be strengthened by a heavy atom and σ-π and/or n-π interaction.

The small value of F_1 with TNF can be explained by means of the spin-orbit interaction of the cage complex on the surrounding reaction surface. The three nitro groups of TNF may induce intersystem crossing through charge transfer and/or σ-π interaction. It has also been reported that no nitro aromatic compound produces $Ru^{III}(bpy)_3^{3+}$ in the quenching of the excited state of $Ru^{II}(bpy)_3^{2+}$.[23] The high efficiencies with BQ, TCBQ, and MV^{2+} can be explained in terms of the spin-multiplicity restriction of reverse electron transfer within the life-time of the geminate pair. The dissociation rate of the geminate pair is too fast, compared to spin-inverted reverse electron transfer, to generate the free radicals in these cases. This is contrary to the fact that the radical yield in the quenching of excited $Ru^{II}(bpy)_3^{2+}$ depends on the charges of half-reduced oxidants; the yield of $Ru^{III}(bpy)_3^{3+}$ and $MV^{+\cdot}$ is 0.4, but that of $Ru^{III}(bpy)_3^{3+}$ and $BQ^{-\cdot}$ is only 0.05.[34] The much larger dependence on the reactant charge may be interpreted in terms of a faster spin-inverted geminate recombination which is caused by a heavy atom (ruthenium) of the reactant pair. The high F_1 of $MV^{+\cdot}$ formation in the ^3ZnPc quenching is consistent with a high yield of $MV^{+\cdot}$ with magnesium phthalocyanine in a 90% dimethyl sulfoxide aqueous solution containing of 10^{-3} mol/dm^3 of EDTA.[12]

The highly efficient production of $ZnPc^{+\cdot}$ and $MB^{2+\cdot}$ with the cobalt(III) compounds is attributable to the larger reorganization energy of the $Co^{III}(tpy)_2^{3+}$–$Co^{II}(tpy)_2^{2+}$ reaction or the $Co^{III}(phen)_3^{3+}$–$Co^{II}(phen)_3^{2+}$ reaction, since the large reorganization energy hinders the reverse electron transfer in the geminate radical pair, even though the free-energy change involved in the reverse process is so largely negative.

On the other hand, the reverse electron transfer from the iron(II) compounds to $ZnPc^{+\cdot}$ or $MB^{2+\cdot}$ in the geminate pair is a spin-allowed process, because both the total spin multiplicity of reactants and products are doublet;

$$^2[^2ZnPc^{+\cdot}\text{--}^1\text{ferrocene}] \rightarrow {}^2[^1ZnPc\text{--}^2\text{ferrocenium ion}]. \quad (6)$$

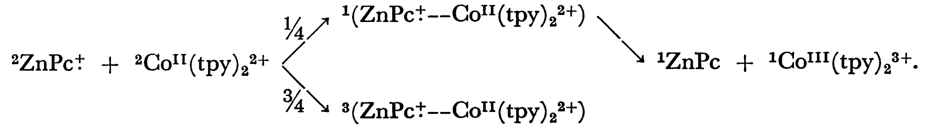
In this case, the rate of electron transfer can be estimated only from the free energy change and the reorganization energy. This situation is the same as that in the electron-transfer quenching of a singlet excited state. The singlet excited state of chlorophyll-a yields no cation radical in the quenching reaction by BQ.[5]

Decay of $ZnPc^{+\cdot}$ and $MB^{2+\cdot}$. The $ZnPc^{+\cdot}$ produced in the quenching of ^3ZnPc decayed in a complex way, resulting in a complete recovery of ZnPc within 0.1 s. The absorption spectrum of $ZnPc^{+\cdot}$ was changed to a broader one (shown in Fig. 2), which can be ascribed to a product in the decay of $ZnPc^{+\cdot}$, because the broad band around 700 nm appeared with the disappearance of the 835 nm band of $ZnPc^{+\cdot}$ in several milliseconds. The fact that both the disappearance rate of $ZnPc^{+\cdot}$ of the 700 nm band increased proportionally to the $ZnPc^{+\cdot}$ production suggests a bimolecular reaction of $ZnPc^{+\cdot}$, dimerization and/or disproportionation, although a single run of the decay of the absorbance at 835 nm could be analysed by means of the first-order kinetics. The recovery of ZnPc was accompanied by not only the disappearance of $ZnPc^{+\cdot}$, but also the decay of the second intermediate. An electron-transfer reaction may take place between oxidized species, $ZnPc^{+\cdot}$, and the second intermediate of ZnPc, and the reduced species of the oxidant. Actually, when $Co^{II}(tpy)_2^{2+}$ (1—5×10^{-5} mol/dm^3) was added to a sample solution containing ZnPc and $Co^{III}(tpy)_2^{3+}$, which is one of the products in the electron-transfer quencing, $ZnPc^{+\cdot}$ was completely converted to ZnPc without the appearance of the second intermediate. The rate constant of the electron-transfer reaction shown in Eq. 7 was obtained as 4.55×10^8 dm^3 mol^{-1} s^{-1} by analysing the pseudo-first-order decay of $ZnPc^{+\cdot}$ monitored at 835 nm:

$$^2ZnPc^{+\cdot} + {}^2Co^{II}(tpy)_2^{2+} \rightarrow ZnPc + Co^{III}(tpy)_2^{3+}. \quad (7)$$

The reverse electron transfer from the bulk proceeds via encounter complexes with either singlet or triplet multiplicity, the latter of which needs spin-inversion to the singlet complex on the surrounding reaction surface just as the reverse electron transfer in the geminate pair needs spin-inversion, triplet→singlet. Therefore, the second-order rate constant of the reverse reaction (k_{ret}) is expected to be correlated to the rate of the reverse electron transfer from the geminate pair in the forward process. It is conveinent to define the fraction of the reverse electron transfer (F_2) as the ratio of k_{ret} to the encounter-rate constant (k_e), which is assumed to be equal to the largest quenching-rate constant of ^3ZnPc (1.3×10^9 dm^3 mol^{-1} s^{-1}); *i.e.*, F_2 calculated as k_{ret}/k_e with $Co^{III}(tpy)_2^{3+}$ is 0.35, which is close to the fraction of geminate recombination ($1-F_1=0.30$). After $^3MBH^{2+}$ was converted to $MB^{2+\cdot}$ by $Co^{III}(phen)_3^{3+}$, $MB^{2+\cdot}$ disappeared *via* second-order kinetics with a rate constant of 1.3×10^9 dm^3 mol^{-1} s^{-1} in a solution with a high ionic strength: this process coincides with that of the product between $1-F_1$ (0.29) and the encounter-rate constant (k_e) of 4.5×10^9 dm^3 mol^{-1} s^{-1} in water.

The coincidence between the fractions of geminate recombination ($1-F_1$) and bulk recombination (F_2) supports mechanistic conclusions which have already been reached in the reductive quenching of $^3MBH^{2+}$ and $^3MB^+$ by iron(II) compounds[1] and aromatic compounds[2] and in the oxidative quenching of $^3Ru^{II}(bpy)_3^{2+}$ by $Cu^{II}(H_2O)_6^{2+}$.[35] On the basis of these studies, we can conclude that: (1) every quenching of the triplet state produces a geminate radical pair, unless the free energy change involved in electron transfer is largely positive and energy transfer to the quencher is possible; (2) the fraction of free-radical formation in the quenching is limited to the "cage escape probability," and (3) the fraction of geminate recombination, $1-F_1$, in the quenching process is close to k_{ret}/k_e. Consequently, we can predict F_1 from the rate constant of the thermal reverse electron-transfer process, which is itself possibly estimated from the free-energy change and the reorganization energy. Unfortunately, k_{ret} values estimated by using the equations of Marcus or Rehm and Weller are a little smaller than those observed for $^2ZnPc^{+\cdot}$–$^2Co^{II}(tpy)_2^{2+}$ and $^2MB^{2+\cdot}$–$^4Co^{II}(phen)_3^{2+}$. Though the estimated rate constants of the reverse process are considerably scattered (see Table 3), the smaller rate constants estimated are consistent with the spin-statistical factor of the reverse process, as may be seen in the following reaction scheme;



$$\begin{tikzcd}[column sep=small] & {}^1(\mathrm{ZnPc}^{\dot{+}}\text{--}\mathrm{Co^{II}(tpy)_2^{2+}}) \arrow[dr] & \\ {}^2\mathrm{ZnPc}^{\dot{+}} + {}^2\mathrm{Co^{II}(tpy)_2^{2+}} \arrow[ur, "1/4"] \arrow[dr, "3/4"'] & & {}^1\mathrm{ZnPc} + {}^1\mathrm{Co^{III}(tpy)_2^{3+}}. \\ & {}^3(\mathrm{ZnPc}^{\dot{+}}\text{--}\mathrm{Co^{II}(tpy)_2^{2+}}) & \end{tikzcd} \tag{8}$$

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References

1) T. Ohno and N. N. Lichtin, *J. Am. Chem. Soc.*, **102**, 4636 (1980).

2) T. Ohno and N. N. Lichtin, *J. Phys. Chem.*, **86**, 354 (1982).

3) H. Sana and M. Tachiya, *J. Chem. Phys.*, **71**, 1276 (1979).

4) S.-F. Chan, M. Chou, C. Creuts, T. Matsubara, and N. Sutin, *J. Am. Chem. Soc.*, **103**, 369 (1981).

5) D. Holten, M. Gouterman, W. W. Parson, M. W. Windsor, and M. G. Rockley, *Photochem. Photobiol.*, **23**, 415 (1976).

6) G. R. Seely, *Photochem. Photobiol.*, **27**, 639 (1978).

7) U. Steiner and G. Winter, *Chem. Phys. Lett.*, **55**, 364 (1978).

8) U. Steiner, M. Hafner, S. Schreiner, and H. E. A. Kramer, *Photochem. Photobiol.*, **9**, 119 (1974).

9) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

10) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

11) A. Harriman and M. -C. Richoux, *J. Chem. Soc., Faraday Trans. 2*, **76**, 1618 (1980).

12) T. Tanno, D. Wohrle, M. Kaneko, and A. Yamada, *Ber. Bunsenges. Phys. Chem.*, **84**, 1032 (1980).

13) E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940).

14) N. N. Lichtin, P. D. Wildes, T. L. Osif, and D. E. Hall, *Adv. Chem. Ser.*, **173**, 296 (1979).

15) T. Ohno and N. N. Lichtin, *J. Phys. Chem.*, **84**, 3485 (1980).

16) N. Maki, *Bull. Chem. Soc. Jpn.*, **42**, 2295 (1969).

17) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000 (1969).

18) T. Ohno, T. L. Osif, and N. N. Lichtin, *Photochem. Photobiol.*, **30**, 541 (1979).

19) P. Kamat and N. N. Lichtin, *J. Phys. Chem.*, **85**, 814 (1981).

20) M. P. Tuirko, V. V. Sapunov, and K. N. Salovev, *Opt. Spectrosk.*, **34**, 1094 (1973).

21) S. Kato, M. Morita, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **37**, 117 (1962).

22) P. J. McCartin, *J. Am. Chem. Soc.*, **85**, 2021 (1963).

23) C. R. Bock, J. A. Conner, A. R. Gutierrez, T. J. Meyer, D. G. Whitten, B. P. Sullivan, and J. K. Nagle, *J. Am. Chem. Soc.*, **101**, 4815 (1979).

24) T. Ohno and N. N. Lichtin, *J. Phys. Chem.*, **84**, 3019 (1980).

25) F. Wilkinson and C. Tsiamis, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1681 (1981).

26) K. Gollnick, *Ann. N. Y. Acad. Sci.*, **171**, 89 (1970).

27) J. A. Farrington, M. Evert, E. J. Land, and K. Fletcher, *Biochim. Biophys. Acta*, **314**, 372 (1973).

28) K. B. Patel and R. L. Willson, *Trans. Faraday Soc.*, **69**, 814 (1973).

29) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, **1962**, 341.

30) J. F. Meyers, G. W. R. Canham, and A. B. P. Lever, *Inorg. Chem.*, **14**, 461 (1975).

32) T. Watanabe, M. Kimura, and K. Honda, to be published.

31) D. Lexa and M. Reix, *J. Chim. Phys.*, **71**, 517 (1970).

33) K. Shulten, H. Staerk, A. Weller, H. -J. Werner, and B. Nickel, *Z. Phys. Chem. (Wiesbaden)*, **101**, 371 (1976).

34) J. R. Darwent and K. Kalyanasundaram, *J. Chem. Soc., Faraday Trans. 2*, **77**, 373 (1981).

35) H. A. Hoselton, C. -T. Lin, H. A. Schwarz, and N. Sutin, *J. Am. Chem. Soc.*, **100**, 2383 (1978).