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Yields of Electron Transfer Reactions in the Quenching of the Phosphorescent States (^{2}E) of Tris(2,2′-bipyridine)chromium(III) and Tris(4,7-diphenyl-1,10-phenanthroline)chromium(III) Compounds

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Molar absorption coefficients of the phosphorescent states (^{2}E) of $[\mathrm{Cr(2,2'\text{-}bipyridine)_3}]^{3+}$ and $[\mathrm{Cr(4,7\text{-}diphenyl\text{-}1,10\text{-}phenanthroline)_3}]^{3+}$ were determined. The ^{2}E state of $[\mathrm{Cr(2,2'\text{-}bipyridine)_3}]^{3+}$ was reduced to $[\mathrm{Cr(2,2'\text{-}bipyridine)_3}]^{2+}$ with the yield of less than 0.2 in the quenching by iron(II) compounds. The reduction yields of $[\mathrm{Cr(2,2'\text{-}bipyridine)_3}]^{3+}$ and $[\mathrm{Cr(4,7\text{-}diphenyl\text{-}1,10\text{-}phenanthroline)_3}]^{3+}$ in the quenching of ^{2}E by aromatic amines increase with the Gibbs energy change ($-\Delta G$) in the reverse electron-transfer process. The weak dependence of the yields on ΔG can not be interpreted in terms of adiabatic reverse electron transfer in the geminate pair, which is formed in the quenching process. The electron transfer from the chromium(II) compounds of triplet spin-multiplicity to the amine radical of doublet spin-multiplicity suffers from spin-restriction.

The bimolecular electron transfer reactions of photoexcited compounds are followed by two kinds of the reverse process. The one takes place in the lifetime of the geminate radical pair formed in the electron transfer quenching. The other can be observed to occur as the second order process with respect to the free radical formed in the bulk. Hoselton *et al.*[1] proposed that the small yield of the electron transfer products in the bulk was ascribed to the fast reverse electron transfer in the geminate pair. Ohno and Lichtin also found that the yield of free radical was reduced by the reverse electron transfer competing with the dissociation of the triplet geminate pair, though every bimolecular quenching of the phosphorescent state of a dye molecule, Methylene Blue, yielded the geminate radical pair.[2–4] Moreover, they found that the rates of the reverse electron transfer are slower than those estimated from the free energy changes and the rearrangement energies involved in the process. The slower rates of the reverse electron transfers were ascribed to the spin-restriction of the process.[4,5] In this work, the product yields in the electron transfer quenching of the phosphorescent states of $[\mathrm{Cr(2,2'\text{-}bipyridine^*)_3}]^{3+}$ and $[\mathrm{Cr(4,7\text{-}diphenyl\text{-}1,10\text{-}phenanthroline^*)_3}]^{3+}$ are investigated by means of laser photolysis kinetic spectroscopy. Nonadiabaticity due to spin-restriction on the electron transfer reactions will be discussed.

Experimental

Apparatus. An NEC SLG-2018 Q-switched ruby laser was used in most of the experiments. The second harmonics (347 nm) of the power less than 0.1 J was generated by using temperature matching nonlinear crystal of RDA supplied by Quantum Tecknology. The laser beam (ϕ=10 mm) is vertically converged and holizontally expanded to 3 mm ×12 mm on the sample cell (10 mm×10 mm) by using two cylindrical lenses. The monitoring beam from a 150 W xenon arc lamp was set in right angles to the laser beam. Increases in light intensity of 50—100 times can be obtained by the use of a transistor-switched discharging circuit. The converged monitoring beam passes through a small aperture on the sample cell, which is located at the depth of 1—2 mm from the cell window exposed to the laser. The laser intensity at 347 nm was attenuated by insertion of a filter solution of chromium alum. The details of the laser and the monitoring apparatuses have been described elsewhere.[4] The absoption change was recorded in a transient recorder, Kawasaki Electronica M-500T or a storagescope, Iwasaki-Tsushinki TS-8123, followed by computer analysis using a laboratory-constructed mini-computer.[6] A 5 cm long cell was used for an excitation by means of xenon flash apparatus. A Hitachi 323 Spectrophotometer was used for the measurement of absorption spectra and a Hitachi MPF-2A Spectrofluorophotometer was used for the measurement of phosphorescence.

Materials. $[\mathrm{Cr(bpy)_3](ClO_4)_3\cdot 1/2H_2O}$ was prepared by a similar method as that reported by Baker and Mehta.[7] The crude sample of $[\mathrm{Cr(bpy)_3](ClO_4)_3}$ was purified by repeated recrystalizations from the aqueous solution and the methanol solution. $[\mathrm{Cr(dp\text{-}phen)_3](ClO_4)_3\cdot H_2O}$ was prepared by a method of Kane-Maguire *et al.*[8] All the aromatic amines- diphenylamine(DPA), triphenylamine (TPA), 3,3′-dimethylbenzidine(DMB), 1,2-phenylenediamine (1,2-DP), 1,4-phenylenediamine (1,4-DP), *N,N,N′,N′*-tetramethylbenzidine(TMB), *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine(TMPD), supplied by Tokyo Kasei or Aldrich, were purified by vacuum sublimation. Ferrocene was recrystallized from the benzene solution and ferrocenecarboxylic acid was recrystallized from the ethanol solution. $\mathrm{Fe(NH_4)_2(SO_4)_2\cdot 6H_2O}$ and acetonitrile (AN) of Wako Pure Chemical Co. were used as supplied. Water was purified by the passage through a Millipore deionizer and filter.

Procedure. All the sample solutions were deaerated by purging with nitrogen of 99.99% purity for 15 min. All the measurements were done at 15±2 °C.

Molar Absorption Coefficients. The molar absorption coefficients of ^{2}E states were obtained on the assumption that all the $[\mathrm{Cr(bpy)_3}]^{3+}$ or $[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$ of 40—50 μM[†] were excited to the ^{2}E state by the laser light of 347 nm. The complete excitation of the compound to ^{2}E state was ascertained by a constant production of the transient absorbance due to ^{2}E with an attenuation of the laser intensity.

Quenching Rate Constants. Decays of the excited state absorptions of the chromium compounds were spectroscopically monitored with or without a quencher. In order not to excite the quenchers of TMPD and TMB which are photoionized on the exposure to 347 nm light, a xenon flash for the photolysis was used with a 375 nm cut-off-filter. The quenching rate constants of the excited state by TMPD

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* The following abbreviations will be used hereafter, 2,2′-bipyridine: bpy, and 4,7-diphenyl-1,10-phenanthroline: dp-phen.

[†] 1 M=1 mol dm^{-3}.

and TMB (k_q) were obtained from Stern-Volmer plots of the phosphorescence intensity of the chromium(III) chelate compounds ($[\mathrm{Cr(NN)_3}]^{3+}$).

Fractions of Electron-transfer-product Formation in the Quenching. The production of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ ($[\mathrm{Cr(N\text{-}N)_3}^{2+}]_0$) or the radical cation of amine in the quenching was calculated from the absorption change by using the molar absorption coefficients of $[\mathrm{Cr(bpy)_3}]^{2+}$ (4860 M^{-1}cm^{-1} at 560 nm[9]), $[\mathrm{Cr(dp\text{-}phen)_3}]^{2+}$(5500 M^{-1}cm^{-1} at 460 nm[10]), TPA$^{+\cdot}$ (30500 M^{-1}cm^{-1} at 660 nm in dichloromethane[11]), TMB$^{+\cdot}$ (41000 M^{-1} cm^{-1} at 474 nm in AN[12]), and TMPD$^{+\cdot}$ (12000 M^{-1}cm^{-1} in H_2O[13]). The production of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$, which decayed in several hundred microseconds, was measured after the fast disappearance of ^{2}E in a few microseconds. The production of ^{2}E state ($[^2\mathrm{Cr(N\text{-}N)_3}^{3+}]_0$) in the presence of the quencher was monitored to be constant. The fractions of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production in the quenching, denoted by F_1, were calculated as a ratio of the reaction rate constant of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production (k_{et}) to the quenching rate constant (k_q) or a ratio of $[\mathrm{Cr(N\text{-}N)_3}^{2+}]_0$ to $[^2\mathrm{Cr(N\text{-}N)_3}^{3+}]_0$ with the complete quenching. The rate constants of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production (k_{et}) were determined by using a following equation,

$$\frac{[\mathrm{Cr(N\text{-}N)_3}^{2+}]_0}{[^2\mathrm{Cr(N\text{-}N)_3}^{3+}]_0} = k_{et}\frac{[\mathrm{Q}]}{k_d}, \qquad (1)$$

where [Q] is the quencher concentration and k_d is the observed decay rate constant of $^2[\mathrm{Cr(N\text{-}N)_3}]^{3+}$ in the presence of the quencher.

Results

Absorption Spectrum of Excited State of $[Cr(N\text{-}N)_3]^{3+}$. A transient species observed after laser excitation of $[\mathrm{Cr(N\text{-}N)_3}]^{3+}$ exhibits an absorption spectrum as in Figs. 1 and 2. The lifetimes of the excited state were 60 μs for $[\mathrm{Cr(bpy)_3}]^{3+}$ and 200 μs for $[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$. The transient absorbances of $^2[\mathrm{Cr(bpy)_3}]^{3+}$ at 390 nm and of $^2[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$ at 520 nm were measured with attenuation of the laser intensity (see Fig. 3).

Electron Transfer Quenching of ^2E by Iron(II) Compounds. Ferrocene and ferrocenecarboxylic acid of less than 0.5 mM quenched the ^{2}E state of $[\mathrm{Cr(bpy)_3}]^{3+}$ in a 70% AN aqueous solution. Iron(II) ions in a 1 M HCl or a 1 M $HClO_4$ aqueous solution also quenched the ^{2}E. The quenching were more effective in 1 M HCl than in 1 M $HClO_4$. The quenching rate constants are shown in Table 1. As the ^{2}E state decayed in the presence of ferrocene, another transient species was produced, whose absorption spectrum consists of bands at 480 and 560 nm as is shown in Fig. 4. This transient spectrum is almost identical to that of $[\mathrm{Cr(bpy)_3}]^{2+}$ reported by König and Herzog,[9] and by Serpone *et al.*[10] The iron(III) compound formed, ferro-

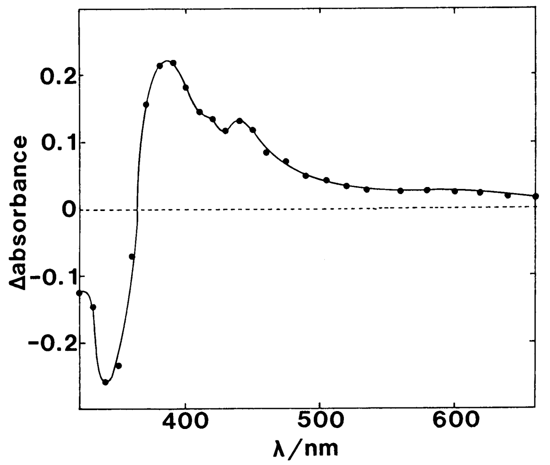

Fig. 1. Difference absorption spectrum of the photolyzed solution of $[\mathrm{Cr(bpy)_3}]^{3+}$ (100 μM) in AN-water (1:1 by volume) just after laser excitation.

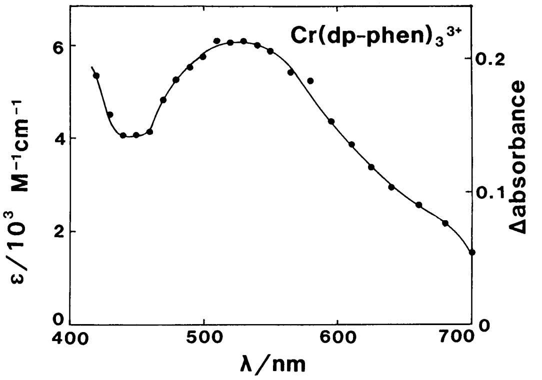

Fig. 2. Difference absorption spectrum of the photolyzed solution of $[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$ (40 μM) in AN-water (1:1 by volume) just after laser excitation.

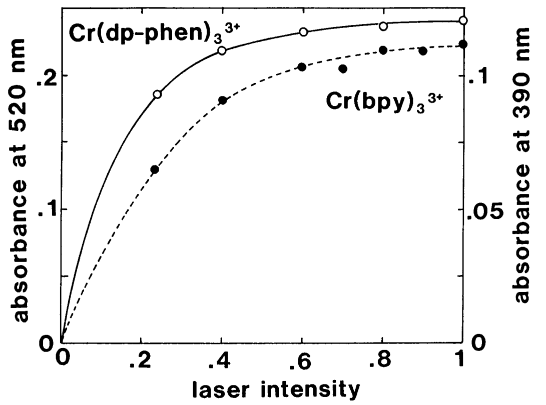

Fig. 3. Transient absorbance with attenuation of laser intensity. The closed circle: at 390 nm for $[\mathrm{Cr(bpy)_3}]^{3+}$ of 50 μM, and the open circle: at 520 nm for $[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$ of 40 μM.

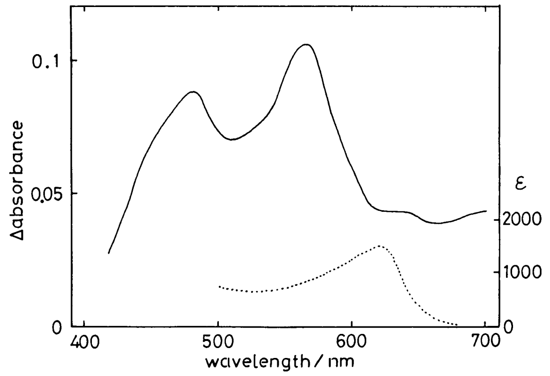

Fig. 4. Absorption spectra of the reaction intermediates. Solid line; the photolyzed solution of $[\mathrm{Cr(bpy)_3}]^{3+}$ with ferrocene of 1.1×10^{-4} M in AN-water (7:3 by volume), dotted line; ferrocenium oxidized by $Fe(ClO_4)_3$ in 1 M $HClO_4$.

TABLE 1. RATE CONSTANTS OF QUENCHING, ELECTRON TRANSFER, AND REVERSE ELECTRON TRANSFER AND REDOX POTENTIALS.

Compound	$E°$	k_q	k_{et}	k_{ret}	F_l
	V	$10^9\ M^{-1}\ s^{-1}$	$10^9\ M^{-1}\ s^{-1}$	$10^9\ M^{-1}\ s^{-1}$	
Fe^{2+}	0.77[a)]	0.007	1.2×10^{-3}	1.0	0.17
$Fe^{2+}Cl_x$		0.04	3.2×10^{-3}	1.4	0.081
Ferrocene	0.54[b)]	6.2	1.1	—	0.18
Ferrocene-COOH	0.79[b)]	7.3	0.50	—	0.069

a) W. M. Latimer, "Oxidation Potentials", 2nd ed, Prentice- Hall N. Y. (1952). b) H. Hemming and O. Grurtler, *J. Organomet. Chem.*, **11**, 307(1968).

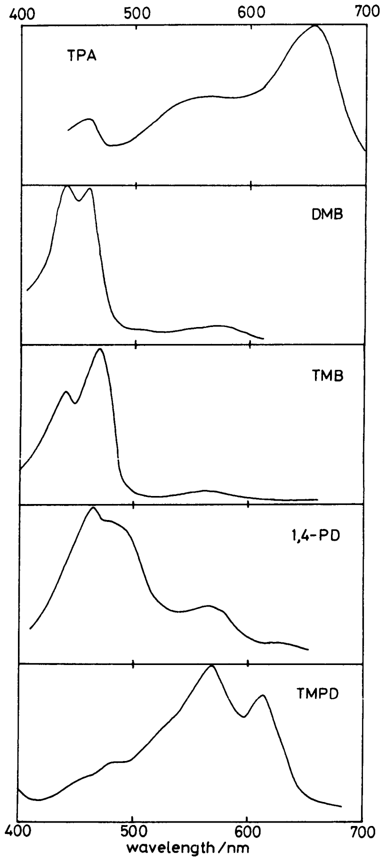

Fig. 5. Difference absorption spectra of the photolyzed solution of $[Cr(bpy)_3]^{3+}$ and the amine after the decay of ^2E. The intensity is arbitary.
a) triphenylamine, b) 3,3′-dimethylbenzidine, c) *N,N,N′,N′*-tetramethylbenzidine, d) 1,4-phenylenediamine, e) *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine.

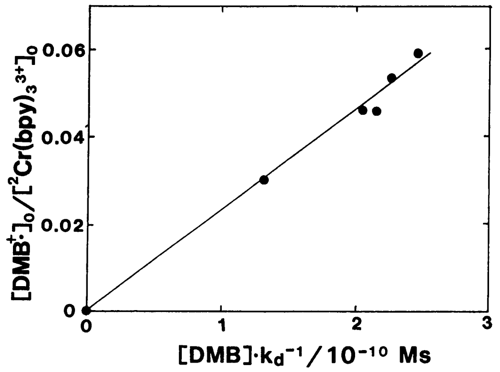

Fig. 6. Determination of k_{et} in the quenching of $^2[Cr(bpy)_3]^{3+}$ by DMB. $[DMB^{+\cdot}]_0$ is the production of one-electron oxidized 3,3-dimethylbenzidine in the quenching.

cenium ion, has a minor contribution to the transient spectrum, because ferrocenium ion which was obtained by the oxidation of ferrocene in a 1 M $HClO_4$ 70% AN aqueous solution with iron(III) ion, has a broad and weak absorption (the molar absorption coefficient is $800\ M^{-1}\ cm^{-1}$ at 560 nm).

The fraction of $[Cr(bpy)_3]^{2+}$ production in the quenching by the iron(II) compounds examined are less than 0.18 of the ^2E production. The values of k_{et} and F_l are shown in Table 1.

Electron Transfer Quenching of ^2E by Aromatic Amines. Aromatic amines of DPA, TPA, DMB, 1,2-PD, 1,4-PD, TMB, and TMPD, quenched the ^2E of $[Cr(N\text{-}N)_3]^{3+}$ with the rate contants close to the diffusion-controlled one (see Table 2). The quenching processes resulted in the production of the second transient species of $[Cr(N\text{-}N)_3]^{2+}$ and the radical cation of the amine. As Fig. 5 shows, transient absorption spectra were observed after the disappearance of ^2E except for the quenching by DPA. They are composed of the bands at 560 nm due to $[Cr(N\text{-}N)_3]^{2+}$ and the more intense band(s) which can be ascribed to the radical cation of the quencher, because these intense bands are in agreement with those of the radical cation reported[11—13]; the band at 660 nm is ascribed to $TPA^{+\cdot}$, the bands at 440 and 460 nm to $DMB^{+\cdot}$, the band at 465 nm to $1,4\text{-}PD^{+\cdot}$, the band at 470 nm to $TMB^{+\cdot}$, and the bands at 580 and 615 nm to $TMPD^{+\cdot}$. The rate constants of the electron transfer reactions (k_{et}) are obtained by plotting Eq. 1 as is shown in Fig. 6. Most of the fractions of $[Cr(N\text{-}N)_3]^{2+}$ production measured in the quenching of $^2[Cr(bpy)_3]^{3+}$ were obtained as the ratio of k_{et} to k_q. As for $^2[Cr(dp\text{-}phen)_3]^{3+}$, all the fractions were obtained as the ratio of $[Cr(dp\text{-}phen)_3]^{2+}$ production to $^2[Cr(dp\text{-}phen)_3]^{3+}$ production with complete quenching of $^2[Cr(dp\text{-}phen)_3]^{3+}$. They are tabulated in Table 2. All the radical and $[Cr(bpy)_3]^{2+}$ formed in the quenching reactions were returned to the parent compounds via the second-order reaction, *e.g.* the reverse electron transfer.

Discussion

^2E States of $[Cr(N\text{-}N)_3]^{3+}$. The difference absorption spectra of photolyzed solution of $[Cr(N\text{-}N)_3]^{2+}$ are ascribed to the production of the excited state of $[Cr(N\text{-}N)_3]^{3+}$, ^2E which are identical to those reported by Maestri *et al.*[14] and by Serpone *et al.*[10]

TABLE 2. REDOX POTENTIALS OF AROMATIC AMINES AND RATE CONSTANTS OF ^{2}E WITH AROMATIC AMINES

Compound	$E°/\mathrm{V}$	$\mathrm{Cr(bpy)_3}^{3+}$		$\mathrm{Cr(dp\text{-}phen)_3}^{3+}$	
		$\frac{k_q}{10^9\mathrm{M^{-1}s^{-1}}}$	F_1	$\frac{k_q}{10^9\mathrm{M^{-1}s^{-1}}}$	F_1
TPA	1.10$^{a)}$	2.4	0.006	9.2	0.019
DPA	1.06$^{a)}$	3.8	0	—	—
DMB	0.69$^{a)}$	3.2	0.068	6.6	0.11
1, 2-PD	(0.67)$^{b)}$	3.6	0.05	15	0.14
TMB	0.56$^{a)}$	3.5	0.115	6.7	0.21
1, 4-PD	0.41$^{a)}$	4.6	0.22	6.6	0.50
TMPD	0.25$^{a)}$	5.6	0.29	2.0	0.73

a) C. K. Mann and K. K. Barnes, "Electrochemical Reactions In Nonaqueous Systems," Marcel Deckker, N. Y. (1970). b) The value is estimated from the redox potential of 1, 4-PD assuming the difference in the redox potential between 1, 2-PD and 1, 4-PD to be equal to the difference in the redox potential between *N, N, N', N'*,-tetramethyl-1, 2-phenylenediamine and *N, N, N', N'*,-tetramethyl-1, 4-phenylenediamine.$^{c)}$ c) A. Zweig, J. E. Lancaster, N. T. Neghia, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 4130(1964).

The complete conversion of $\mathrm{Cr(N\text{-}N)_3}^{3+}$ to the ^{2}E state (see Fig. 3) allowed us to calculate the molar absorption coefficients of the excited states to be $3.1\times10^3\ \mathrm{M^{-1}\,cm^{-1}}$ at 390 nm and to be $200\ \mathrm{M^{-1}\,cm^{-1}}$ at 600 nm for $^2[\mathrm{Cr(bpy)_3}]^{3+}$ and to be $6.0\times10^3\ \mathrm{M^{-1}\,cm^{-1}}$ at 520 nm for $^2[\mathrm{Cr(dp\text{-}phen)_3}]^{3+}$ after the correction due to the depression of absorbance of the ground state. They agree in the order with the molar absorption coefficients of $^2[\mathrm{Cr(bpy)_3}]^{3+}$ calcuated from the light absorption, which was roughly estimated from the absorbance of the sample solution in the wide wavelength region and the light intensity of non-monochromatic pumping xenon flash.[14] Since the absorption bands of ^{2}E except for the broad band of $^2[\mathrm{Cr(bpy)_3}]^{3+}$ at 600 nm are too strong to be assigned as a d-d band,[15] they can be assigned to the transitions from ^{2}E at 13700 cm^{-1} to the doublet CT state. This assignment is in agreement with that proposed by Serpone *et al.*,[10] who studied the band shift in the absorption spectra of excited chromium(III) compounds of substituted 2,2′-bipyridine or 1,10-phenanthroline. Since strong CT transitions of ^{2}E states were also observed in the visible region for chromium(III) compounds, such as $[\mathrm{Cr(NCS)_6}]^{3-}$, $[\mathrm{Cr(NCS)_4(NH_3)_2}]^{-}$, Cr(acetylacetonato)$_3$, and so on,[16] an appearance of strong CT band in the visible region can be expected for the excited states of most chromium(III) compounds. Meanwhile, the weak and broad band in the visible region can be assigned to a d-d transition ($^2\mathrm{E}\rightarrow{}^2\mathrm{A}_2$).

The strong absorption bands of ^{2}E are useful to estimate the production of ^{2}E and to calculate the fractions (F_1) of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production in the quenching process. It is parenthetically noted that a larger molar absorption coefficient of $^2[\mathrm{Cr(bpy)_3}]^{3+}$ (7000 M^{-1} cm^{-1}) has been reported by Lilie and Waltz.[17] They obtained the value on an assumption made by Ferraudi *et al.*[18] that the production of $[\mathrm{Cr(bpy)_3}]^{2+}$ in the complete quenching by $\mathrm{Fe^{2+}_{aq}}$ in 0.1 M $\mathrm{HClO_4}$ might be equal to the production of $^2[\mathrm{Cr(bpy)_3}]^{3+}$. However, since the efficiency of $[\mathrm{Cr(bpy)_3}]^{2+}$ production in the quenching may not be unity (0.18 in 1 M $\mathrm{HClO_4}$), this value of the molar absorption coefficient is assumed to be the possible maximum.

Electron Transfer Reaction of ^{2}E with Amines. The productions of $[\mathrm{Cr(bpy)_3}]^{2+}$ and the radical cation of the aromatic amine indicate the quenching of ^{2}E *via* electron transfer mechanism by the amine, as has been reported by Ballardini *et al.*[19] The efficiencies (F_1) of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production in the quenching reaction can be expressed as $F_1=k_{et}/k_q$ using the rate constants of electron transfer reaction (k_{et}) and quenching reaction (k_q). As Table 2 shows, the values of the F_1 increase with the decrease of the redox potential of the amine; F_1 is the largest with TMPD (0.25 V) and the smallest with DPA (1.08 V) or TPA (1.1 V). This trend in the change of F_1 can be understood by assuming the following reaction mechanism, in which a reaction intermediate, a geminate pair or a cage complex, is postulated.

$$^2[\mathrm{Cr(N\text{-}N)_3}]^{3+}+\mathrm{D}\longrightarrow{}^2(^3[\mathrm{Cr(N\text{-}N)_3}]^{2+}-{}^2\mathrm{D}^{\cdot+}),\quad k_f \tag{2}$$

$$^2(^3[\mathrm{Cr(N\text{-}N)_3}]^{2+}-{}^2\mathrm{D}^{\cdot+})\longrightarrow{}^3[\mathrm{Cr(N\text{-}N)_3}]^{2+}+{}^2\mathrm{D}^{\cdot+},\ k_{dis} \tag{3}$$

$$^2(^3[\mathrm{Cr(N\text{-}N)_3}]^{2+}-{}^2\mathrm{D}^{\cdot+})\longrightarrow{}^4[\mathrm{Cr(N\text{-}N)_3}]^{3+}+\mathrm{D}.\quad k_r \tag{4}$$

The fraction of $[\mathrm{Cr(N\text{-}N)_3}]^{2+}$ production in the quenching can be rewritten as,

$$F_1 = k_{dis}/(k_{dis}+k_r), \tag{5}$$

using the rate constants of elementary processes of the geminate pair. The dependence of k_r on the free energy change (ΔG) involved in the process is apparently reflected on the ratio of k_r to k_{dis}, which is expressed as the observable quantity, $1/F_1-1$, because the rate of electron transfer can be written as follows, provided that the electron transfer process is adiabatic,

$$k_r = (k_1k_2f_{12})^{1/2}\exp(-\Delta G/2RT), \tag{6}$$

where k_1 and k_2 are the rate constants of the self exchange electron transfer of reactants 1 and 2, respectively, and f_{12} is nearly constant.[20] Then, the final expression is as follows,

$$\ln(k_r/k_{dis}) = \ln(1/F_1-1) = -\Delta G/2RT + A', \tag{7}$$

for the adiabatic process on assuming the free energy change for the dissociation of the geminate pair to be constant. As shown in Figs. 7 and 8, the values of ln $(1/F_1-1)$ nearly fit the expected relation of Eq. 7, provided that the difference in the solvation energy and the electrostatic energy between the initial and the final states is neglected and ΔG is expressed as $E°(\mathrm{Cr^{III}/Cr^{II}})-E°(\mathrm{D^{\cdot+}/D})$, where $E°(\mathrm{Cr^{III}/Cr^{II}})$ and $E°(\mathrm{D^{\cdot+}/D})$ are the redox potentials of $[\mathrm{Cr(N\text{-}N)_3}]^{3+}$

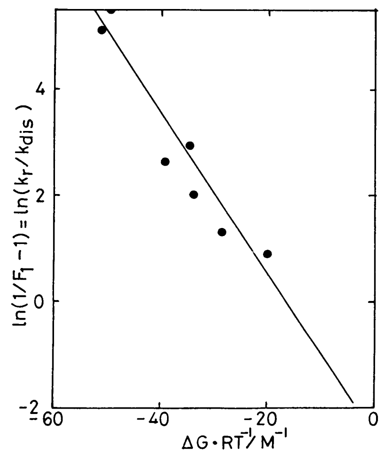

Fig. 7. The dependence of the fraction of $[Cr(bpy)_3]^{2+}$ production in the quenching reaction on the free energy change involved in the reverse electron transfer.

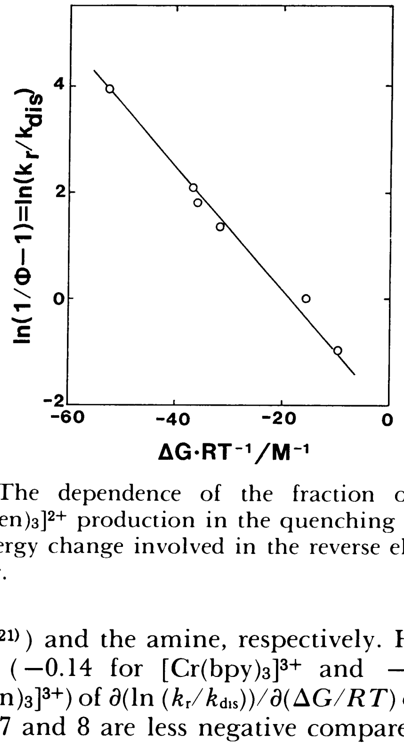

Fig. 8. The dependence of the fraction of $[Cr(dp\text{-}phen)_3]^{2+}$ production in the quenching on the free energy change involved in the reverse electron transfer.

($-0.26\,V$[10,21]) and the amine, respectively. However, the values (-0.14 for $[Cr(bpy)_3]^{3+}$ and -0.12 for $[Cr(dp\text{-}phen)_3]^{3+}$) of $\partial(\ln(k_r/k_{dis}))/\partial(\Delta G/RT)$ obtained from Figs. 7 and 8 are less negative compared to the ideal value (-0.5) estimated for an adiabatic electron transfer process. Since the reverse electron transfer is accompanied by spin conversion (doublet→quartet) as shown in Eq. 4, the nonadiabaticity in the process may retards the reaction rate. Actually, a less negative value(-0.07) of $\partial(\ln(k_r/k_{dis}))/\partial(\Delta G/RT)$ was obtained for the spin-inverted electron transfer between doublet organic radicals containing no heavy atom.[3,5] The larger dependence of k_r on ΔG was reported for the spin-inverted electron transfer reactions between doublet iron(III) compounds and the doublet radical of Methylene Blue,[3] and between the triplet excited state of $[Ru(bpy)_3]^{2+}$ and doublet $Cu^{+2}{}_{aq}$.[1]

An alternative explanation is that a part of the geminate pair may be converted to an exciplex in which the spin conversion more likely occurs and the reverse electron transfer occurs as a radiationless transition of the exciplex. Since the dependence of radiationless transition rate in the exciplex on ΔG is positive according to Mataga *et al.*,[22] $\partial(\ln k_r/k_{dis})/\partial(\Delta G/RT)$ is expected to be positive. This kind of switchover mechanism has been proposed to explain the radical yield in the bimolecular quenching of singlet excited state.[23]

Electron Transfer Reaction of ^2E with Iron(II) Compounds. Efficiencies of $[Cr(bpy)_3]^{2+}$ formation in the quenching by the iron(II) compounds are calculated to be 0.069—0.18 as shown in Table 1. The smaller values of the efficiencies with iron(II) ion in the 1 M hydrochloric acid than in the 1 M perchloric acid are essentially ascribed to the faster reverse electron transfer in the geminate pair because the reverse electron transfer from the bulk in the hydrochloric acid ($1.4\times10^9\,M^{-1}\,s^{-1}$) is faster than that in the perchloric acid ($1.0\times10^9\,M^{-1}\,s^{-1}$). However, since the efficiencies of net electron transfer in the quenching are much smaller than the fraction of collision complex undergoing no electron transfer in the bulk reverse process (0.53—0.67), which can be obtained from the rate constants of the reverse electron transfer (k_{ret}) and the collision complex formation (k_e) as $(k_e-k_{ret})/k_e$, other types of quenching, paramagnetic ion-induced intersystem crossing and energy transfer must be accompanied with electron transfer. It is probable that the iron(II) quenching of ^2E takes place *via* quintet iron-induced intersystem crossing,[15b] which was proposed in the iron(II) quenching of triplet excited molecule.[24] Meanwhile, the ΔG-dependence of k_q in the iron(II) quenching of ^2E led to conclusion that the principal process was not energy transfer but electron transfer.[25]

The larger rate of reverse electron transfer in the 1 M hydrochloric acid indicates the formation of $Fe^{III}Cl_{6-n}(H_2O)_n{}^{(3-n)+}(n=1-6)$. The larger quenching rate constant in 1 M HCl than in 1 M $HClO_4$ may sugggest the formation of the chloride complex of iron(II), which is responsible for the faster rate of reverse electron transfer in the geminate pair.

F_I in the quenching by ferrocenecarboxylic acid is less than a half of the value by ferrocene. This reduction is ascribed to the fast reverse electron transfer in the geminate pair compared to ferrocene because $-\Delta G$ of the reverse process with ferrocenecarboxylic acid (1.06 ev) is larger than that (0.81 ev) with ferrocene.

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