Mechanisms and Rate Constants for the Quenching of Singlet Oxygen by Nickel Complexes

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An iterative numerical determination of the rate constants for both quenching of, k_q, and reaction with, k_r, singlet oxygen by dithiolato nickel complexes is developed. This numerical method gives accurate rate constants for a small number of kinetic runs. The substituent effects of these complexes on rate constants lead us to conclude that the complexes quench singlet oxygen by an energy-transfer mechanism. This numerical method developed for solution systems was applied to the estimation of the photofading rate of a cyanine dye on an epoxy resin plate.

The optical disc memory will be an increasingly important system for data storage, replacing the magnetic disc memory. In such systems, commercially available laser diodes, such as the Ga–As laser, emit in the wavelength range 780—840 nm.[1] Therefore, the dyes used in the optical disc memory need to have an absorption band in the near-infrared region. Cyanine dyes are typical for such use, however, the conventional cyanine dyes have poor light fastness. Several photostabilizers have been applied to improve the light fastness of the optical disc memory.[2,3]

It is well-known that some dyes undergo self-sensitized or dye-sensitized photooxidation via a singlet oxygen ($^1O_2$) mechanism. $^1O_2$ quenchers have been used to inhibit photooxidation of these dyes.[4]

The term "quenching of $^1O_2$" can be used to encompass both "physical" quenching, in which the interaction leads only to deactivation of $^1O_2$ to the ground state (reaction 5, rate constant k_q), and "chemical" quenching, in which $^1O_2$ reacts with a quencher to give an oxidation product of the quencher (reaction 6, rate constant k_r). In this paper, the former process will be called "quenching", the latter "reaction", and their sum (k_q+k_r) will be called "total quenching".

Rate constants for total quenching of $^1O_2$ by carotenes, amines, phenols, nickel complexes, sulfides, and others have been reported.[5] A few method for the separation of k_q from k_r have been reported,[5,6] however, the separation for β-carotene and dithiolato nickel complexes has not yet been carried out.

We report a numerical method used for separation of k_q and k_r. The substituent effect on these rate constants for dithiolato nickel complexes, which are known to be efficient $^1O_2$ quenchers,[7] is discussed. We also report an estimation for the photofading rate of a cyanine dye, with or without quencher, by the use of the numerical method.

Results and Discussion

Determination of Rate Constants. The kinetics of photooxidation reactions by $^1O_2$ have been studied in great detail. Rubrene, 2-methyl-2-pentene, or 1,3-diphenylisobenzofuran are often used as chemical traps for $^1O_2$, since these compounds react rapidly and cleanly with $^1O_2$.[5,8] When an aerated solution of rubrene and a $^1O_2$ quencher is irradiated, the following reactions occur:[8]

$$\mathrm{Ru} + h\nu \longrightarrow {}^1\mathrm{Ru} \longrightarrow {}^3\mathrm{Ru} \tag{1}$$

$$^3\mathrm{Ru} + \mathrm{O_2} \xrightarrow{k_t} \mathrm{Ru} + {}^1\mathrm{O_2} \tag{2}$$

$$^1\mathrm{O_2} \xrightarrow{k_d} {}^3\mathrm{O_2} \tag{3}$$

$$^1\mathrm{O_2} + \mathrm{Ru} \xrightarrow{k_o} \mathrm{RuO_2} \tag{4}$$

$$^1\mathrm{O_2} + \mathrm{Q} \xrightarrow{k_q} {}^3\mathrm{O_2} + \mathrm{Q} \tag{5}$$

$$^1\mathrm{O_2} + \mathrm{Q} \xrightarrow{k_r} \mathrm{QO_2} \tag{6}$$

Scheme 1.

where Ru is rubrene, ^{1}Ru and ^{3}Ru are the singlet rubrene and the triplet rubrene, respectively. RuO_2 is the rubrene photoperoxide. Q and QO_2 are the quencher and the oxidation product of the quencher, respectively.

The steady-state kinetic equation for the photofading rate of Ru and Q are given by;[5,6]

$$-\frac{\mathrm{d[Ru]}}{\mathrm{d}t} = \frac{I_0abc\, k_o[\mathrm{Ru}]}{k_d + k_o[\mathrm{Ru}] + (k_q + k_r)[\mathrm{Q}]} \tag{7}$$

$$-\frac{\mathrm{d[Q]}}{\mathrm{d}t} = \frac{I_0abc\, k_r[\mathrm{Q}]}{k_d + k_o[\mathrm{Ru}] + (k_q + k_r)[\mathrm{Q}]} \tag{8}$$

where I_0 is the incident light intensity, "a" is the fraction of light absorbed by rubrene, "b" is the fraction of singlet rubrenes which undergo intersystem crossing, and "c" is the fraction of triplet rubrenes which transfer energy to oxygen to give $^1O_2$. [Ru] and [Q] are the concentrations of rubrene and quencher, respectively. When the incident light is monochromatic, "a" is given by Eq. 9;[9]

$$a = 1/d\{1-\exp(-2.303(\kappa_{\mathrm{Ru}}[\mathrm{Ru}]+\kappa_{\mathrm{Q}}[\mathrm{Q}])d)\}$$
$$\frac{\kappa_{\mathrm{Ru}}[\mathrm{Ru}]}{(\kappa_{\mathrm{Ru}}[\mathrm{Ru}]+\kappa_{\mathrm{Q}}[\mathrm{Q}])} \qquad (9)$$

where "d" (=0.1 dm) is the light path in the reaction cell, κ_{Ru} and κ_{Q} are the molar absorptivity of rubrene and quencher at the incident light wavelength, respectively. Under the condition that [Q] is of the order of 10^{-5} mol dm^{-3}, quenching of ^{3}Ru or ^{1}Ru by Q is not significant, and thus I_0bc can be regarded as a constant.[10]

We determined k_q and k_r from the simultaneous differential equations, Eqs. 7—9, by using the Runge-Kutta technique and iterative calculations. The Runge-Kutta technique is a conventional numerical method for solving differential equations on a computer.[11] Our method is very convenient and gives accurate rate constants for a small number of kinetic runs. The validity of this method was confirmed by the following results: as shown in Fig. 1, the calculated concentrations of rubrene and quencher were in good agreements with those observed; no dependence of k_q and k_r for the concentration of quencher ($<2\times10^{-5}$ mol dm^{-3}) was detected.

Eq. 7 has been solved analytically, using the assumption that [Q] and I_0abc are constant, as follows;[8]

$$(k_q+k_r)=\frac{k_o([\mathrm{Ru}]_{\mathrm{F}}{}^{\mathrm{Q}}-[\mathrm{Ru}]_{\mathrm{F}}{}^{0})+k_d\ln([\mathrm{Ru}]_{\mathrm{F}}{}^{\mathrm{Q}}/[\mathrm{Ru}]_{\mathrm{F}}{}^{0})}{[\mathrm{Q}]\ln([\mathrm{Ru}]_{\mathrm{I}}/[\mathrm{Ru}]_{\mathrm{F}}{}^{\mathrm{Q}})} \qquad (10)$$

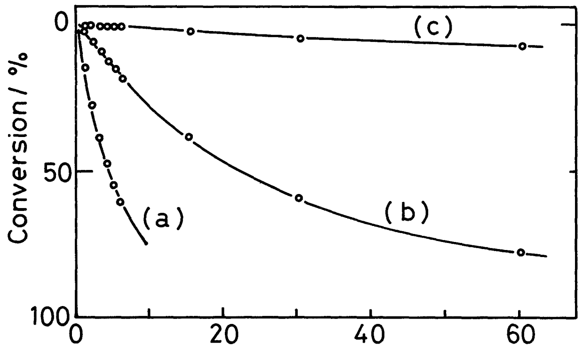
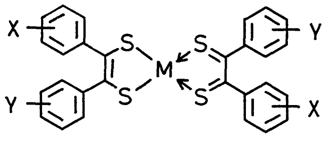
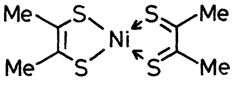


Fig. 1. Relative conversions in photofading of rubrene (1×10^{-4} mol dm^{-3}) with (b) and without (a) the complex **1c** (1×10^{-5} mol dm^{-3}) in aerated CH_3CN-C_6H_6 (4:1) (λ_{irr}=525 nm). (C): Relative conversions in photofading of the complex **1c** under the same condition as for (b). Circles and solid lines are the experimental and calculated results, respectively.

where $[\mathrm{Ru}]_{\mathrm{I}}$ is the initial concentration of rubrene, $[\mathrm{Ru}]_{\mathrm{F}}{}^{\mathrm{Q}}$ is the final concentration of rubrene in the quenched solution, and $[\mathrm{Ru}]_{\mathrm{F}}{}^{0}$ is the final concentration of rubrene in the unquenched solution. The rate constants determined by the two methods are shown in Table 1. The values of both (k_q+k_r) for the compounds **1a**, **8—10**, and **12—15** and of k_r for the compounds **12** and **13** agree well with those reported in the literature.[5,8]



1a: M=Ni, X=Y=H
1b: M=Ni, X=Y=4-OMe
1c: M=Ni, X=Y=4-CF_3
1d: M=Ni, X=Y=4-Cl
1e: M=Ni, X=Y=4-Et
1f: M=Ni, X=Y=3,4,5-$(OMe)_3$
1g: M=Ni, X=Y=3,4-Cl_2
1h: M=Ni, X=Y=2,4-Cl_2
1i: M=Ni, X=Y=2-Cl
1j: M=Ni, X=Y=2-Br
1k: M=Ni, X=H, Y=$N(Me)_2$
2a: M=Co, X=Y=4-Et
2b: M=Pt, X=Y=4-Et



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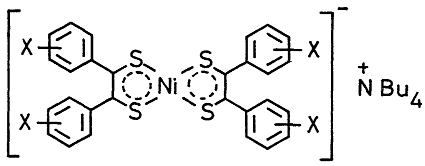
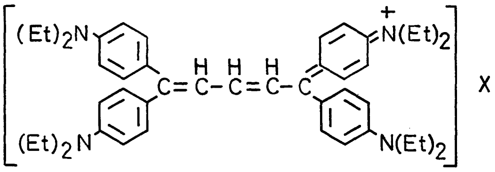


4a: X=H
4b: X=4-OMe
4c: X=4-CF_3
4d: X=3,4,5-$(OMe)_3$



5a: X=ClO_4^-
5b: X=[(3,4,5-$(OMe)_3$-$C_6H_2)_4S_4$Ni]$^-$

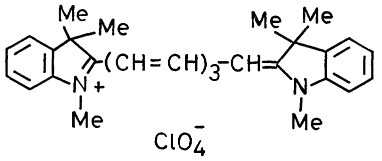


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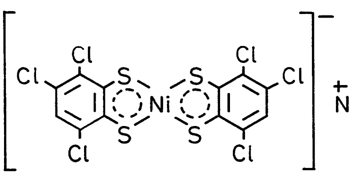
Table 1. Rate Constants[a] for $^1O_2$ Quenching by Various Compounds in CH_3CN-C_6H_6 (4:1)

Compound	$(k_q+k_r)/10^{10}$[b]	$k_q/10^{10}$	$k_r/10^6$
	$mol^{-1}\,dm^3\,s^{-1}$	$mol^{-1}\,dm^3\,s^{-1}$	$mol^{-1}\,dm^3\,s^{-1}$
1a	1.28±0.08	1.20±0.05	0.9±0.1
1b	1.03±0.13	1.01±0.01	0.4±0.1
1c	1.39±0.13	1.35±0.02	2.7±0.4
1d	1.17±0.12	1.17±0.01	1.1±0.2
1e[c]	0.78±0.11	0.71±0.05	0.1±0.01
1f	0.97±0.03	0.96±0.03	0.4±0.1
1g	1.17±0.06	1.23±0.03	2.4±0.3
1h	1.25±0.19	1.29±0.05	3.1±0.6
1i	1.13±0.09	1.20±0.05	1.0±0.2
1j	1.11±0.05	1.11±0.06	0.9±0.1
1k	0.98±0.02	0.98±0.01	0.3±0.1
2a[c]	0.55±0.05	0.54±0.01	1.6±0.1
2b[c]	0.85±0.05	0.80±0.02	0.2±0.1
3	1.30±0.11	1.39±0.03	0.9±0.1
4a	0.92±0.06	0.97±0.02	4.3±0.1
4b	0.86±0.08	0.89±0.02	8.4±0.2
4c	1.10±0.07	1.01±0.01	2.1±0.1
4d	0.70±0.10	0.76±0.06	4.9±0.3
5a	$(1.17\pm0.49)/10^2$	$(6.57\pm1.31)/10^3$	0.1±0.1
5b	0.56±0.04	0.51±0.08	0.5±0.1[d]
6	$(8.43\pm2.03)/10^3$	$(3.81\pm1.42)/10^3$	1.6±0.2
7	0.65±0.05	0.67±0.01	1.2±0.3
8	0.68±0.01	0.82±0.01	3.6±0.2
9[c]	0.57±0.13	0.52±0.05	—[g]
10[e]	$(9.18\pm0.89)/10^3$	$(8.90\pm0.19)/10^3$	—[g]
11[e]	$(1.35\pm0.40)/10^3$	$(3.29\pm0.76)/10^3$	—[g]
12[c]	$(1.31\pm0.10)/10^4$	$(0.77\pm0.02)/10^4$	0.4±0.04
13[c]	$(1.18\pm0.28)/10^2$	$(1.37\pm0.19)/10^2$	2.1±0.4
14[c]	1.27±0.08	1.22±0.03[f]	2.0±0.2[f]
15[c]	$(2.64\pm0.11)/10^2$	$(2.65\pm0.16)/10^2$	—[g]

a) These values were determined by using $k_o=4.2\times10^7\,mol^{-1}\,dm^3\,s^{-1}$ and $k_d=3.44\times10^4\,s^{-1}$ in CH_3CN-C_6H_6 (4:1) mixture.[16,20] b) These values were calculated by using Eq. 10.[8] c) Rate constants for these compounds were determined by using $k_o=4.2\times10^7\,mol^{-1}\,dm^3\,s^{-1}$ and $k_d=4.17\times10^4\,s^{-1}$ in benzene.[16,20] d) This value was calculated by using the absorption of cyanine moiety. e) Rate constants for these compounds were determined by using $k_o=3.25\times10^7\,mol^{-1}\,dm^3\,s^{-1}$ and $k_d=5.56\times10^4\,s^{-1}$ in benzene–ethanol (1:1) mixture.[16,20] f) These values were calculated by considering the dark reaction of β-carotene (first order rate constant=$3.2\times10^{-6}\,s^{-1}$). g) Not detected. h) Compounds **8**—**15** are as follows: **8**; bis(*O,O'*-diethylphosphorodithiolato)nickel, **9**; bis(dibutyldithiocarbamato)nickel, **10**; $NiCl_2\cdot6H_2O$, **11**; nickel bis(mesitylenesulfonate), **12**; 2,6-di-*t*-butyl-*p*-cresol, **13**; α-tocopherol, **14**; β-carotene, **15**; 1,4-diazabicyclo[2,2,2]octane.



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β-carotene faded slowly owing to a dark reaction in an aerated solution, and this reaction was observed to obey first-order kinetics. The rate constant for the dark reaction was first determined, and then k_q and k_r were determined from the solution of the differential equations, which included the term for the dark reaction.

Quenching of $^1O_2$ by Nickel Complexes. Although the mechanism of $^1O_2$ quenching by the dithiolato nickel complexes is not clear, two major mechanisms of quenching by other types of quenchers have been proposed.[5] The first is the energy-transfer quenching mechanism which is well-documented for β-carotene. The second is the charge-transfer quenching mechanism which involves interaction between the electron-poor $^1O_2$ molecule and an electron donor to give a charge-transfer complex. The energy-transfer mechanism appears to be more efficient in many cases, having a maximum rate of about $2\times10^{10}\,mol^{-1}\,dm^3\,s^{-1}$, whereas the rates for charge-transfer quenching are usually below $10^9\,mol^{-1}\,dm^3\,s^{-1}$, and often far lower.

Substituted *N,N*-dimethylanilines give a Hammett ρ of −1.71 for $^1O_2$ quenching,[12] since $^1O_2$ acts as an electron acceptor in the charge transfer mechanism. However, the neutral complexes **1a**—**1d** give a ρ or of 0.14 for k_q with a correlation coefficient of 0.929, and the reduced complexes **4a**—**4c** give a ρ of 0.06 for k_q with a correlation coefficient of 0.923. These small values of ρ show that substituent effect on k_q for these complexes is not significant. This insignificant substituent effect and the large value of k_q show that the charge-transfer mechanism does not play an important role in the $^1O_2$ quenching by the dithiolato nickel complexes.

The energy-transfer mechanism, which involves the formation of triplet quencher and ground state oxygen (Eq. 11), requires that the triplet state of the quencher lies very near or below the energy of $^1\Delta_g$ oxygen, 1270 nm.[5]

$$^1O_2 + Q \longrightarrow {}^3O_2 + {}^3Q \qquad (11)$$

Although the triplet energies of the complexes are not known, the quenching by the complexes is attributed to the energy-transfer mechanism because the substituent effect on k_q is not significant, the conjugated system is extensive, which would permit the triplet energy of the quencher to be below 1270 nm, and the values of k_q are very large.

The k_q of the cobalt complex **2a** was slightly smaller than that of the related nickel complex **1e**. This result is consistent with those of the metal complexes having other ligands.[7] The platinum derivative **2b** showed similar rate constants to that of the complex **1e**.

Although the nickel complexes **8** and **9** also quenched $^1O_2$ near the diffusion-controlled rate limit, the rates for the nickel salts **10** and **11** were below 10^8 mol^{-1} dm^3 s^{-1}. These results suggest that the mechanism for the quenching of $^1O_2$ by these salts is different from that for the dithiolato nickel complex.

Reaction of $^1O_2$ with Nickel Complexes. The Hammett ρ calculated for the k_r of the neutral complexes **1a**—**1d** is 0.98 with a correlation coefficient of 0.985. This positive value of ρ shows that the formation of a charge-transfer complex is not the rate-determining step of the reaction of $^1O_2$ with the complex **1**, and that the complex having electron-attracting substituents is rapidly decomposed by $^1O_2$.

It has been reported that the complex **1** is reducible to mono and dianion species, and that the reductions are reversible.[13,14] As shown in Fig. 2, complexes which show large values of k_r are easily reducible. This result suggests that the reduction reaction may be responsible for the decomposition of the neutral complexes. However, no participation of the reduction reaction in the decomposition was detected, since a large portion of rubrene in the photofading solution was consumed before any appreciable shift in the absorption maximum of the complex occurs.

In contrast to the neutral complex, the k_r of the reduced complexes **4a**—**4c** gave a Hammett ρ value of −0.72 with a correlation coefficient of 0.986. The negative value of ρ indicates that a charge-transfer complex may be involved in the reaction of $^1O_2$ with the complex **4**. It has been confirmed by XPS investigation that the electron densities in the Ni and S atoms of the complexes **4a**—**4c** are higher than those of the corresponding neutral complexes.[15] The reduced complex seems to give a negative value of ρ as a result of the higher electron density, which contributes to the formation of a charge-transfer complex.

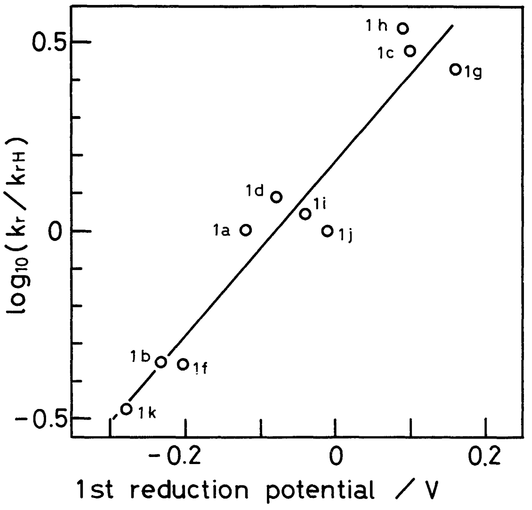

Fig. 2. Relationship between log (k_r) and first reduction potential of the complexes **1a**—**1k** (correlation coefficient=0.960). k_{rH} is the value of k_r for the complex **1a**.

Photofading of Cyanine Dye. The rate constants for the cyanine dyes **5a**, **5b**, and **6** were also measured. The ratio, k_q/k_r, may be considered as an indication of the stability of the compounds to photofading. The ratio for the complex **5b** is 15 times greater than that for the corresponding perchlorate **5a**. This implies that the counter anion moiety contributes remarkably to the stability of the complex **5b** against degradation by reaction with $^1O_2$. The fading curves, which were calculated from Eqs. 7 and 8 for the mixture of rubrene and cyanine dye **5b** or **6**, were in good agreement with the experimental observations. This fact suggests that these dyes were faded by $^1O_2$. The cyanine dye **5a** obeyed Eqs. 7 and 8 only for the initial period of the kinetic run.

In a previous paper,[2] we reported the light fastness of thin layers of the dye **6** with or without quenchers on an epoxy resin plate. The relative conversion in photofading of the dye **6** without quencher by visible light was observed to be 19.5%. In the present work we carried out a simulation of the photofading of dye **6** on an epoxy resin plate by the numerical method, using the assumptions that the dye **6** undergoes self-sensitized photooxidation via a $^1O_2$ mechanism and that the dye on an epoxy resin plate fades in a similar manner as in solution. Firstly, I_0bc was determined by the use of the numerical method from the experimental data, which was obtained from the photofading of the dye **6** in a solution of CH_3CN–C_6H_6 (4:1) without quencher by irradiation with light of 745 nm for 30 min. The calculation was carried out by using Eq.

12 with [Q]=0,

$$-\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t}=\frac{I_0abc\,k_\mathrm{r}[\mathrm{C}]}{k_\mathrm{d}+(k_\mathrm{q}+k_\mathrm{r})[\mathrm{C}]+(k'_\mathrm{q}+k'_\mathrm{r})[\mathrm{Q}]} \tag{12}$$

where [C] is the concentration of the dye, k_q and k_r are the rate constants associated with the dye **6**, and k'_q and k'_r are the rate constants associated with the quencher. Secondly, the time when 19.5% of the dye **6** without quencher will fade was calculated to be 35250 s by using the value calculated for I_0bc ($=1.46\times10^{-8}$ mol dm^{-2} s^{-1}) and Eq. 12. The relative conversions of the dye with quenchers after 35250 s irradiation were then calculated from Eqs. 12 and 13 by the numerical method. The observed and calculated relative conversion in photofading of the dye **6** are shown in Fig. 3.

$$-\frac{\mathrm{d}[\mathrm{Q}]}{\mathrm{d}t}=\frac{I_0abc\,k'_\mathrm{r}[\mathrm{Q}]}{k_\mathrm{d}+(k_\mathrm{q}+k_\mathrm{r})[\mathrm{C}]+(k'_\mathrm{q}+k'_\mathrm{r})[\mathrm{Q}]} \tag{13}$$

A good linear relationship is obtained between the calculated relative conversion of dye **6** and that observed from an epoxy resin plate, except for the dye with quencher **1h**. This linear relationship shows that our numerical method developed for a solution system can be applied to the estimation of the photofading rate of a dye in the solid state. However, this simulation has three deficiencies; namely, that the regression line in Fig. 3 does not intercept the origin, that the rate constants in solution were adopted for the calculation for the solid state, and that the light used for the photofading of the thin layer on an epoxy resin plate was not monochromatic. The photofading rate of the dye with a $^1O_2$ quencher is dependent on the balance between the numerator and the denominator of Eq. 12. The first deficiency can be attributed to the balance, which in the solid state is probably different from that in solition. In particular, value of k_d in solid state may significantly differ from that in solution because the solvent effect on k_d is very large.16) Therefore, k_d may contribute much to the first deficiency. For example, the regression line, obtained from the calculation assuming $k_d=2\times10^4$ s^{-1}, intercepts the origin.

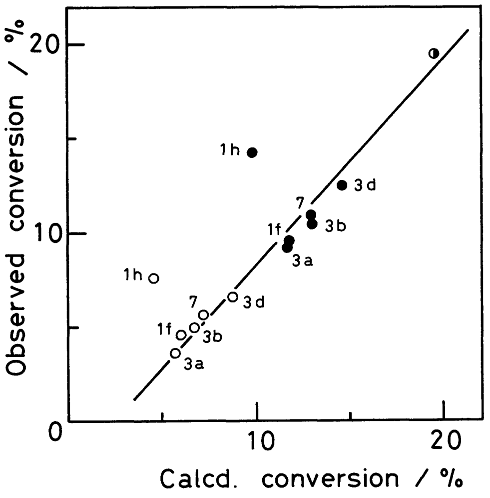

Fig. 3. Relationship between the observed and calculated relative conversion in photofading of cyanine dye **6** without (◑), with 5 wt% (●) or 15 wt% (○) quenchers. The observed conversion was determined from the absorbance of dye **6** on an epoxy resin plate. The calculated conversion was determined from the following values; $k_d=3.44\times10^4$ s^{-1}; $\lambda_{irr}=745$ nm; irradiation time=35250 s; concentration of the dye is 1×10^{-4} mol dm^{-3}.

We reported previously the value of k_r for the cyanine dye **6** in CH_3CN–C_6H_6 (4:1) estimated from the photofading data of the dye with quencher **1a** by visible light.17) The value of k_r is in quite agreement with the value shown in Table 1. This agreement provides an evidence for the validity of this simulation calculation.

Experimental

Materials. Rubrene (Aldrich) was used as received. Acetonitrile and benzene were of ultra guaranteed reagent grade (Kantokagaku Co.). The nickel complexes **1a**—**1j**, **3**, and **4a**—**4d** were prepared in our laboratory as described previously.2) Compounds **1k** was supplied by Nihonkankoshikiso Co. Cyanine dye **5a** was prepared according to the literature.18) Cyanine dye **6** was supplied by Kodak Co. Complex **7** (Mitsuitoatsu Co.) was purified by recrystallization from benzene. Complex **8** was supplied by Daihachikagaku Co. Complex **9** (Ouchi Shinko Co.) was purified by recrystallization from methanol. Compounds **10** and **12**—**15** were supplied by Tokyo Kasei Co. Nickel salt **11** was prepared according to the literature.19)

Bis[1,2-(4-ethylphenyl)-1,2-ethenedithiolato]cobalt (2a). To a solution of 4,4'-diethylbenzoin (1 g, 3.3 mmol) in dioxane (10 cm^3) was added P_2S_5 (1.6 g, 7.2 mmol) and ammonium sulfate (0.238 g, 1.8 mmol), and the mixture was refluxed for 2 h. To the cooled and filtered reaction solution was added $CoCl_2\cdot6H_2O$ (0.428 g, 1.8 mmol), and the mixture was refluxed for 3 h. Black crystals were collected by filtering the cooled solution. This product was recrystallized from benzene to give **2a** (464 mg, 38%); mp 297 °C (decomp); UV (CH_2Cl_2) 718 nm ($\varepsilon=13000$ mol^{-1} dm^3 cm^{-1}). Found: C, 65.16; H, 5.39%. Calcd for $C_{36}H_{36}S_4Co$: C, 65.92; H, 5.53%.

Bis[1,2-(4-ethylphenyl)-1,2-ethenedithiolato]platinum (2b). The product was obtained in a similar manner to that described above and recrystallized from $CHCl_3$–EtOH to give **2b** (145 mg, 7.8%); mp 305 °C (decomp); UV (CH_2Cl_2) 825 nm ($\varepsilon=54800$ mol^{-1} dm^3 cm^{-1}). Found: C, 54.69; H, 4.76%. Calcd for $C_{36}H_{36}S_4Pt$: C, 54.59; H, 4.58%.

Cyanine Dye (5b). Cyanine dye **5a** (100 mg, 0.13 mmol) and nickel complex **4d** (150 mg, 0.13 mmol) were dissolved in 15 cm^3 of *N*,*N*-dimethylformamide, and the mixture was stirred at 50 °C for 3 h. The reaction mixture was poured into 300 cm^3 of water. The precipitate was filtered, washed with water, and then dried in vacuo to give **5b** (148 mg, 72%); mp 187 °C (decomp); UV (CH_2Cl_2) 822 ($\varepsilon=181000$ mol^{-1} dm^3 cm^{-1}) and 944 nm ($\varepsilon=14800$ mol^{-1} dm^3 cm^{-1}). Found: C, 65.04; H, 6.79; N, 4.07%. Calcd for $C_{85}H_{103}N_4O_{12}S_4Ni$: C, 65.46; H, 6.66; N, 3.59%.

Kinetic Measurement. Mother solutions of rubrene (1×10^{-4} mol dm^{-3}) were prepared by dissolving weighed amounts of rubrene in measured volumes of acetonitrile–benzene (4:1). To assure the solutions with and without quencher had the same initial rubrene concentration, a weighed amount of quencher ($1-2\times 10^{-5}$ mol dm^{-3}) was dissolved in a measured volume of the mother solution. The volumetric flasks were wrapped in aluminum foil and much of the work was done in a dark room with orange light ($\lambda > 580$ nm). Solution of rubrene (3 cm^3), with and without quencher, were pipetted into UV cells. Six samples were irradiated as follows; two with no quencher, two with quencher (1×10^{-5} mol dm^{-3}), and two with quencher (2×10^{-5} mol dm^{-3}). The samples were placed in a Hitachi 650-10M fluorescence spectrophotometer, which was equipped with a 150 W Xenon lamp, UV cut-off filter, and were irradiated using 525 ± 10 nm light. The cell holder was the thermostated at 25 ± 0.5 °C during irradiation.

Without quencher, the half-life of rubrene was about 4 min. The concentrations of rubrene and quencher at given irradiation times were determined from the absorbance measured at 525 nm (rubrene) and at $\lambda_{\max}$ of the quencher, using a Shimadzu UV-260 or UV-3100 spectrophotometer. If the absorption bands of rubrene and the quencher were partially overlapped, the concentrations were determined from the difference spectra. The concentrations of the quenchers **12** and **13** were determined by a Shimadzu GC-15A gas chromatograph with a capillary column (25 m×0.33 mm) of Methyl Silicone OV-1. For quencher **12**, the column temperature was 210 °C, and *o*-dichlororbenzene was used as the internal standard. For quencher **13**, the column temperature was 270 °C, and squalane was used as the internal standard.

Numerical Calculation. In Eqs. 7 and 8, "*a*" was calculated by Eq. 9 with absorbances of rubrene and quencher, respectively, at 525 nm at each irradiation time.

In the absence of quencher, the value of I_0bc from Eq. 7 was determined by iterative calculations to give the best fit between the calculated concentrations of rubrene and those observed. The concentrations of rubrene at each irradiation time were calculated by using the Runge–Kutta method. The iterative calculations were repeated until deviations of the calculated concentrations of rubrene at each irradiation time from those observed converge below 0.2%.

The k_q and k_r were then converged into optimum values in a similar method uisng the value calculated for I_0bc and Eqs. 7 and 8 in the presence of rubrene and quencher. Final converged curves are shown in Fig. 1.

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10) Quenching of ^{1}Ru by Q should not be significant since [Q] is much less than that needed to significantly quench ^{1}Ru, of which lifetime is $13.4-16.4\times 10^{-9}$ s in solution.[8,21] Even if Q quenches ^{1}Ru near the diffusion-controlled rate limit, it would only quench abour 0.1% of ^{1}Ru.

As mentioned by Monroe,[8] quenching of ^{3}Ru by Q would be responsible for about 1% of the observed $^1O_2$ quenching;

$$^3\mathrm{Ru} + \mathrm{Q} \xrightarrow{k_{qt}} \mathrm{Ru} + \mathrm{Q} \qquad (14)$$

$$\frac{k_{qt}[\mathrm{Q}]}{k_t[\mathrm{O_2}]} = \frac{(4.7\times 10^9)\times(10^{-5})}{(3\times 10^9)\times(2\times 10^{-3})} = 0.008 \qquad (15)$$

where [O_2] is the concentration of oxygen in aerated $CH_3CN-C_6H_6$ (4:1),[22] k_{qt} and k_t are the values estimated.[8]

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