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# Convenient Determination of Rate Constants of Quenching of Singlet Oxygen and Its Reaction with Dithiolene Nickel Complexes

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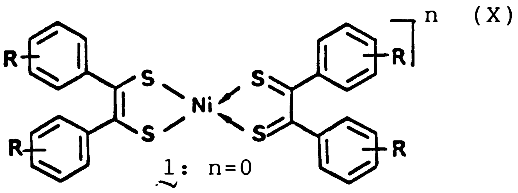
The rate constants of quenching of singlet oxygen ($k_q$) and its reaction ($k_r$) with bis(dithiobenzil)nickel complexes have been determined by a simulation method from photo-irradiation of rubrene in the presence of oxygen, and the substituent effects in these complexes on $k_r$ and $k_q$ values have been discussed.

Dithiolene nickel complexes are known to be effective as a quencher of singlet oxygen. Recently, these complexes are applied to an optical data storage system together with cyanine dyes.[1,2] We have examined substituent effects for bis(dithiobenzil)nickel complexes on their absorption spectra and solubilities,[3,4] and the influence of these nickel complexes on inhibiting the photofading of a cyanine-thin layer[5] to apply to the optical data storage system. The rate constants of singlet oxygen quenching for various nickel complexes have been measured by using rubrene and 2,5-dimethylfuran which react with singlet oxygen to form peroxides.[6] When an aerated solution of rubrene and a singlet oxygen quencher is irradiated, the following reactions occur:[7]

$$
\begin{aligned}
\mathrm{Ru} &\xrightarrow{h\nu} \mathrm{Ru}^{*} \\
\mathrm{Ru}^{*} + {}^{3}\mathrm{O}_2 &\xrightarrow{\qquad} \mathrm{Ru} + {}^{1}\mathrm{O}_2 \\
{}^{1}\mathrm{O}_2 &\xrightarrow{k_d} {}^{3}\mathrm{O}_2 \\
{}^{1}\mathrm{O}_2 + \mathrm{Ru} &\xrightarrow{k_o} \mathrm{RuO}_2 \\
{}^{1}\mathrm{O}_2 + \mathrm{Q} &\xrightarrow{k_q} {}^{3}\mathrm{O}_2 + \mathrm{Q} \\
{}^{1}\mathrm{O}_2 + \mathrm{Q} &\xrightarrow{k_r} \mathrm{QO}_2
\end{aligned}
$$

where Ru is rubrene, Ru* is the rubrene excited species, $RuO_2$ is the rubrene peroxide, Q is the quencher and $QO_2$ is the oxidation product of the quencher.

In this paper, we report the convenient determination of rate constants $k_r$ of singlet oxygen with bis(dithiolene)nickel complexes (**1**-**2**) and substituent effects



**1**: n=0
**2**: n=-1

**1a**: R=H
**1b**: R=4-OMe
**1c**: R=4-Cl
**1d**: R=4-$CF_3$
**1e**: R=3,4-dichloro-
**1f**: R=2,4-dichloro-
**1g**: R=3,4,5-trimethoxy-
**2a**: R=H, X=$\overset{+}{N}Bu_4$
**2b**: R=4-$CF_3$, X=$\overset{+}{N}Bu_4$

on $k_r$ and $k_q$ in this reaction. Rates of singlet oxygen quenching for nickel complexes have been observed under the conditions of near diffusion controlled rate limit and only the rate constants for total quenching ($k_q$ + $k_r$) were reported.$^{6-8)}$ To determine each of them, $k_r$ (or $k_q$) or their ratio must be measured independently. Though various techniques can be used to separate $k_q$ and $k_r$ in experiments, the rate constant $k_r$ for nickel complexes has been unknown yet.

We separate them by simulation calculations$^{9)}$ using the Runge-Kutta method of Eqs. 1 and 2$^{10)}$ at a given irradiation time (Fig. 1):

$$-\frac{d[Ru]}{dt} = \frac{I_0abck_o[Ru]}{k_d + k_o[Ru] + (k_q + k_r)[Q]} \qquad (1)$$

$$-\frac{d[Q]}{dt} = \frac{I_0abck_r[Q]}{k_d + k_o[Ru] + (k_q + k_r)[Q]} \qquad (2)$$

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, c is the fraction of triplet rubrenes which transfer energy to oxygen to give singlet oxygen, and [Ru] and [Q] are concentrations of rubrene and quencher, respectively.

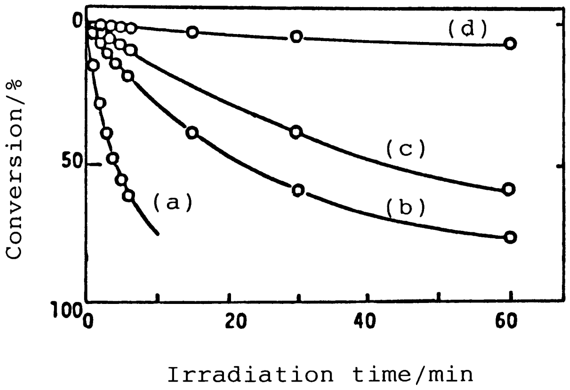


Fig. 1. Photofading of rubrene ($1x10^{-4}$mol $dm^{-3}$) with and without nickel complex **1d** in $CH_3CN$-$C_6H_6$ (4:1) mixture ($\lambda_{irr}$=525 nm). Concentration of nickel complex is (a) 0, (b) $1x10^{-5}$ and (c) $2x10^{-5}$mol $dm^{-3}$. (d):Photofading of nickel complex in a mixture of rubrene and nickel complex ($2x10^{-5}$mol $dm^{-3}$). Curves are drawn by the R-K method.

The results for the rate constants $k_q$ and $k_r$ together with the evaluation from Eq. 3$^{7)}$ are summarized in Table 1.

$$(k_q + k_r)=(k_o([Ru]_f -[Ru]_f^{\circ}) + k_d\ln([Ru]_f/[Ru]_f^{\circ}))/[Q]\ln([Ru]_i/[Ru]_f) \qquad (3)$$

where $[Ru]_i$ is the initial concentration of rubrene, $[Ru]_f$ the final concentration of rubrene in the quenched solution, $[Ru]_f^{\circ}$ the final concentration of rubrene in the unquenched solution, and [Q] the quencher concentration.

Though the ($k_q$ + $k_r$) for **1a** derived from the Monroe's method using our experimental data was good agreement with published data ($1.1x10^{10}$ $dm^3$ $mol^{-1}s^{-1}$), no

Table 1. Rate constants[a)] $k_q$ and $k_r$ for singlet oxygen quenching of nickel complexes **1**-**2**

| Complex | $(k_q+k_r)^{b)}\times10^{-10}$ / $dm^3mol^{-1}s^{-1}$ | $k_q\times10^{-10}$ / $dm^3mol^{-1}s^{-1}$ | $k_r\times10^{-6}$ / $dm^3mol^{-1}s^{-1}$ | Conversion[c)] of Nickel Complex/% | 1st Reduction[d)] potential/V |
|---|---|---|---|---|---|
| **1a** | 1.28±0.08 | 1.20±0.05 | 0.9±0.1 | 4.7 | -0.12 |
| **1b** | 1.03±0.13 | 1.05±0.01 | 0.5±0.1 | 2.7 | -0.23 |
| **1c** | 1.17±0.12 | 1.17±0.01 | 1.1±0.2 | 4.4 | -0.08 |
| **1d** | 1.39±0.13 | 1.35±0.02 | 2.7±0.4 | 11.9 | 0.10 |
| **1e** | 1.17±0.06 | 1.23±0.03 | 2.4±0.3 | 11.3 | 0.16 |
| **1f** | 1.25±0.19 | 1.29±0.05 | 3.1±0.6 | 17.3 | 0.09 |
| **1g** | 0.97±0.03 | 1.02±0.03 | 0.7±0.1 | 3.9 | -0.20 |
| **2a** | 1.33±0.17 | 1.12±0.05 | 3.0±0.1 | 16.5 | - |
| **2b** | 1.10±0.07 | 1.00±0.02 | 1.9±0.1 | 7.4 | - |

a)These values were determined by Eqs. 1 and 2 using $k_d=3.44\times10^4$ $s^{-1}$ and $k_o=4.2\times10^7$ $dm^3mol^{-1}s^{-1}$ in $CH_3CN-C_6H_6$ (4:1) mixture.[12,13)] The initial concentration of rubrene was $1.0\times10^{-4}$ mol $dm^{-3}$. b)These values were calculated by using Monroe's method.[7)] c)Conversion of nickel complexes in a mixture of rubrene and nickel complex ($2\times10^{-5}$ mol $dm^{-3}$) after irradiation for 90 min. d)The reduction potentials of the nickel complex were measured in $CH_2Cl_2$ by cyclic voltammetry using an Ag/AgCl reference electrode.[5)]

substituent effects on total quenching rate ($k_q$ + $k_r$) for nickel complexes were observed (Table 1). There was little difference between $k_q$ and ($k_q$ + $k_r$) and, however, the absolute values of standard deviations are smaller for $k_q$ than ($k_q$ + $k_r$) obtained by the known method.[7)] The values of $k_r$ for these complexes are nearly same to the values of $k_r$ which were determined separately for phenols and sulfides[7)] and the values of $k_r$ for **1f** is larger by 6 times than that for **1b**. There is a good correlation between conversion of nickel complexes and $k_r$. Obviously the substituent effect of neutral complex **1** on $k_r$ was observed, whereas only a little substituent effect of reduced complex **2** was shown. Though the mechanism of singlet oxygen quenching by nickel complexes is not clear, some mechanisms of quenching by other quenchers have been proposed as follows. 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 the interaction of the electron-poor singlet oxygen molecule with electron donor to give a charge-transfer complex. Substituted dimethylanilines[11)] give Hammett ρ of -1.71 for singlet oxygen quenching, since singlet oxygen acts as an electron accepter in the charge transfer mechanism. However, ρ is 0.89 for $k_r$ of neutral nickel complex **1** (correlation coefficient; 0.982, n=4) and is clearly different from that of dimethylanilines. Complex **1** gives a linear correlation of log($k_r$) with the first reduction potentials (correlation coefficient; 0.969, n=7). These results suggest that the formation of a charge-transfer complex of complex **1** with singlet oxygen is not the rate determining step, since the sign of $\rho$ is positive. The $k_r \ll k_q$ means that the amount of nickel complex which reacts is very small relative to the amount of singlet oxygen quenched in solution and only little nickel complex is consumed for singlet oxygen quenching under the conditions.

In conclusion, the singlet oxygen quenching mechanism of nickel complexes **1** and **2** may be mainly the energy-transfer mechanism, since very high $k_q$ values for nickel complexes, as well as $\beta$-carotene, are obtained and no substituent effect on $k_q$ is observed. This result suggests that nickel complex **1** with smaller $k_r$ is more efficient photostabilizer with a long lifetime in an optical data storage system using a cyanine dye due to its photostability.

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9) The $k_q$ and $k_r$ were determined from the following calculations. In Eqs. 1 and 2, a was calculated from absorbances of rubrene and nickel complexes, respectively, at 525 nm at each irradiation time. The concentrations of rubrene and nickel complex ([Ru] and [Q]) were measured at 525 nm of rubrene and at $\lambda_{max}$ of nickel complex (780-890 nm), respectively. First, the $I_0bc$ value from Eq. 1 was determined by the Runge-Kutta method, which is a conventional method for numerical integration with computer. The calculations were repeated until deviations of the calculated concentrations of rubrene at each irradiation time from observed concentrations converge below 0.002. Then, the $k_q$ and $k_r$ were converged into optimum values in a similar method using Eqs. 1 and 2 at each irradiation time in the presence of rubrene and nickel complexes. Final simulation curves are shown in Fig. 1.
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