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AN ENERGY TRANSFER CHEMILUMINESCENT REACTION OF LOPHINE PEROXIDES

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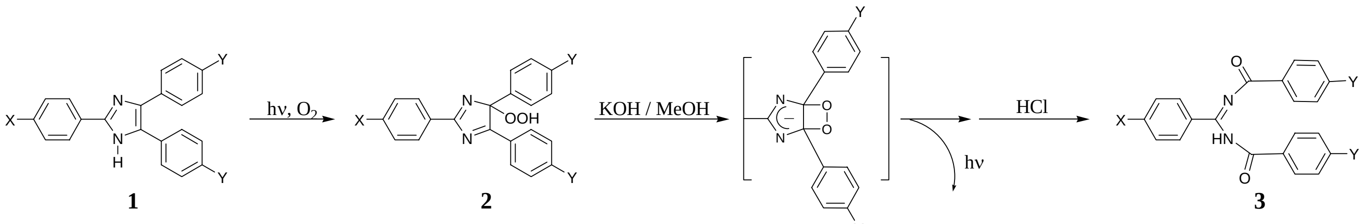
Abstract – A linear correlation existed between the absorption energy of activators ($E_{o\text{-}o}$'s) and the sensitized chemiluminescence (CL) yields (ϕ_{SCL}'s) for the CL reaction of lophine peroxides (**2a** and **2b**), whereas a linear correlation did not exist between their oxidation potentials (E_{ox}'s) and ϕ_{SCL}'s. Based on the finding, an energy transfer mechanism is likely rather than an electron transfer mechanism like the CIEEL mechanism.

INTRODUCTION

The chemiluminescent (CL) reactions, in which the chemical energy was utilized to promote organic substances to an excited state, have attracted chemists. It is the most important question for understanding the CL reaction what is the chemical excitation mechanism. Since the chemically initiated electron exchange luminescence (CIEEL) mechanism was suggested by Schuster,[1] the CL reaction of a dioxetane system has been believed to obey the CIEEL mechanism. We have been examined the CL reaction of a lophine system which is believed to involve a dioxetane intermediate, for which there is no proof.[2,3,4] We thought that if the dioxetane intermediate involves in the CL reaction, chemical excitation may obey the CIEEL mechanism. On this line, we started to tested the effect of sensitizers (S`s) on the CL reaction of 2-*p*-X-phenyl-4-hydroperoxy-4,5- dipheny-4H-isoimidazoles (lophine peroxide) (**2a**) (X = H, Y = H) and (**2b**) [X = N(Me)$_2$, Y = F].[5,6] When bis-(phenylethynyl)naphthacene (BPEN), rubrene, bis- (phenylethynyl)anthracene (BPEA), and perylene were used as S`s, the quantum yields of the sensitized CL (ϕ_{SCL}) were increased as the absorption energy ($E_{0\text{-}0}$) of S decreased.



1a, X = H, Y = H
1b, X = N(Me)$_2$, Y = F

2a, X = H, Y = H
2b, X = N(Me)$_2$, Y = F

Dioxetane intermediate

3a, X = H, Y = H
3b, X = N(Me)$_2$, Y = F

Scheme 1

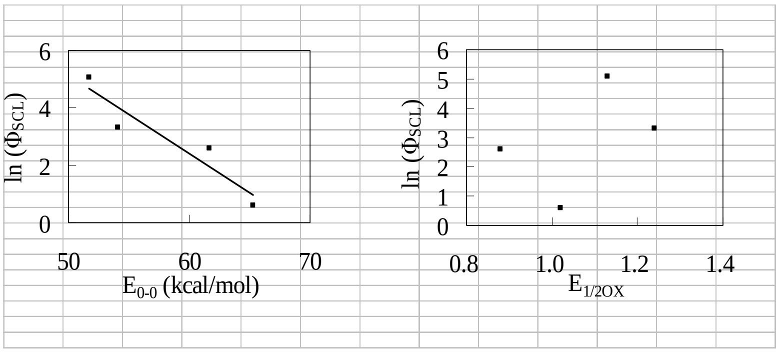


Figure 1. The correlation diagrams. a: ln (ϕ_{SCL}) vs E_{0-0} (kcal/mol) and b: ln (ϕ_{SCL}) vs $E_{1/2OX}$

EXPERIMENTAL

General procedures: The CL spectra were recorded on a HAMAMATSU PHOTONICS model C-2491 photonic multi-channel analyzer. The fluorescent spectra were recorded on a HITACHI MPF-4 fluorescent spectrophotometer. The UV spectra were measured with a HITACHI 228 spectrophotometer. E_{ox}'s for activators were measured by ALS/H CH Instrument Electrochemical Analyzer. Lophine peroxides **2a** and **2b** were prepared by the method of Kimura *et al.*[5,6]

RESULTS AND DISCUSSION

The oxidation of imidazoles (**1a**) and (**1b**) with $^1O_2$ (generated by methylene blue photosensitization at -78 °C) gave the corresponding hydroperoxides **2a** and **2b** in good yields (Scheme 1).[3,4] CL emissions were measured by means of a photodiode array which recorded integrated light yields in terms of the number of photons. The CL light emission was counted by PMA upon addition of 0.2 mL of the KOH solution into a solution (1 mL) of the hydroperoxides (10^{-3} M) in CH_2Cl_2. The CL of **2a** and **2b** were detected around 550 nm and 480 nm, respectively. After usual work up, the corresponding amidines (**3a**) and (**3b**) were isolated in 81% yield and ~100% yield, respectively (Scheme 1). Amidine **3a** was nonfluorecent, while **3b** was fluorescent, under the CL reaction conditions. The CL efficiency (ϕ_{CL}) was determined by comparing the total amount of CL light emitted with that of light from the 3-(2'-spiroadamantane)-4-methoxy-4-(3"-hydroxy) phenyl-1, 2-dioxetane standard ($\phi_{CL} = 0.25$).[7] The CL quantum efficiency for **2a** was 7.2×10^{-6} and that for **2b** was 8.4×10^{-4}.

In the presence of an activator (1×10^{-3} M), ϕ_{SCL}'s were observed both from **2a** and from **2b**. We used the fluorescent S`s, BPEN, rubrene, BPEA, and perylene to confirm whether $\phi_{SCL}$ obeys the CIEEL mechanism or not. The oxidation potential ($E_{ox}$'s), the absorption energies ($E_{o\text{-}o}$'s), and $\phi_{SCL}$'s for S`s are summarized in Table 1. A linear correlation existed between the $E_{o\text{-}o}$'s and ϕ_{SCL}'s, whereas a linear correlation did not exist between the E_{ox}'s and ϕ_{SCL}'s as illustrated in Fig. 1. The CL intensity from S`s increases as the extent of overlap between absorption o-o bands of activators and the CL band of lophine peroxide increases. This finding is consistent with an energy transfer mechanism rather than an electron transfer mechanism like CIEEL.

The energy cascade from lophine peroxides to S as an emitter is presented in Eqs. (1) ~ (4).

$$\begin{array}{lll} & \text{Rate} & \\ \text{Lophine peroxide (LP)} \xrightarrow{\text{Base (B)}} \text{Amidine* (AM*)} & k_1[LP][B] & (1) \\ AM^* \longrightarrow AM + h\nu & k_2[AM^*] & (2) \\ AM^* \longrightarrow AM & k_3[AM^*] & (3) \\ AM^* + S \longrightarrow AM + S^* & k_4[AM^*][S] & (4) \end{array}$$

Assume the mechanism of Eqs. (1) ~ (4) where the rate of formation of the amidine* (AM*) is constant; k_3 represents the sum of the rate constants for decay of AM* by all other processes except CL and sensitized CL by sensitizers, for which fluorescence efficiencies are as shown in Table 1.

The rate of change of [AM*] is given by

$$d[AM^*]/dt = k_1[LP][B] - k_2[AM^*] - k_3[AM^*] - k_4[AM^*][S] \qquad (5)$$

So that applying the steady state approximation gives

$$k_1[LP][B] = k_2[AM^*] + k_3[AM^*] + k_4[S] \qquad (6)$$

The sensitized CL quantum yield in the presence of S is

$$\phi_{SCL} = k_q[S]/ (k_2 + k_3 + k_4[S]) \qquad (7)$$

The reciprocal of the quantum yield for production of S* is given by Eq. (8)

$$1/\phi_{SCL} = (k_2 + k_3)/ k_4[S] + 1 \qquad (8)$$

A plot of 1/ϕ_{SCL} versus 1/ [BPEN] gives a straight line with a slope (k_2 + k_3)/ k_4. For **2a** and **2b**, slopes are 3.54 and 0.0779, respectively. The more efficient **2b** has a slower deactivation process, while the less efficient **2a** does a faster deactivation process.

Table 1. The sensitized efficiencies (ϕ_{SCL}’s) for **2a** and **2b**, the oxidationpotential(E_{ox}'s), the absorption energies ($E_{o\text{-}o}$'s), and the sensitized efficiencies (ϕ_{SCL})for S`s

	BPEN	Rubrene	BPEA	Perylene
_ scl:**2a**	76_10^{-6}	20_10^{-6}	9.4_10^{-6}	1.3_10^{-6}
_ scl:**2b**	13_10^{-4}	5.5_10^{-4}	_	_
_ FL	0.66^{a}	_ 1.00^{b}	0.96^{a}	0.99^{c}
_abs (nm)	553	528	464	438
$E_{0\text{-}0}$ (kcal/mol)	51.7	54.1	61.7	65.3
$E_{1/2ox}$ (V)	1.02	0.88	1.24	1.13

a:reference8. b:reference9. c:reference10.

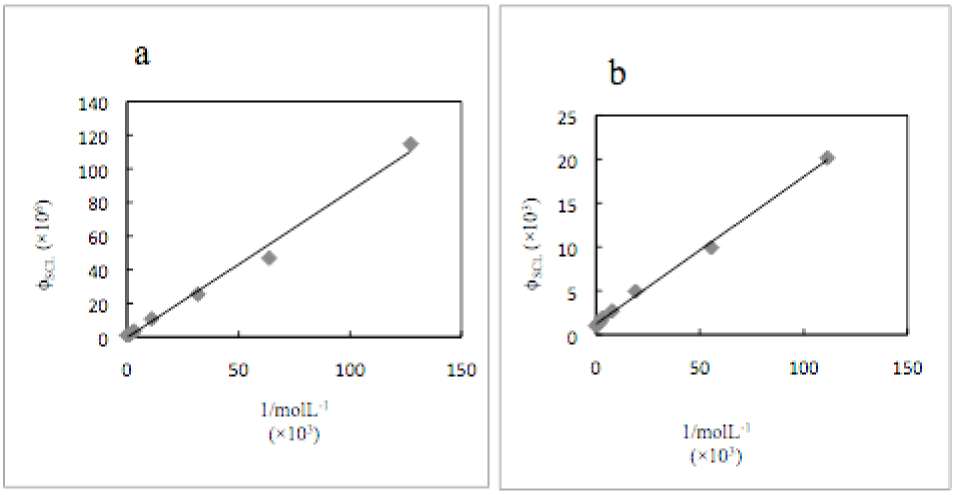


Figure 2. The plot of 1/f_{SCL} versus 1/$f_{[BPEN]}$: a is the case of **2a** b is the case of **2b**

CONCLUSION

A linear correlation existed between the $E_{o\text{-}o}$'s and ϕ_{SCL}'s, whereas a linear correlation did not exist between the E_{ox}'s and ϕ_{SCL}'s. Based on the finding, an energy transfer mechanism is likely rather than an electron transfer mechanism like the CIEEL mechanism. This finding means that the dioxetane intermediate does not involve in the chemi-excitation step. The more efficient **2b** has a slower deactivation process, while the less efficient **2a** does a faster deactivation process.

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REFERENCES

1. G. B. Schuster, *Acc. Chem. Res.*, 1979, **12**, 366.
2. M. Tsunenaga, H. Iga, and M. Kimura, *Tetrahedron Lett*., 2005, **46**, 1877.
3. K. Nakashima, *Biomed*. *Chromatoger*., 2003, **17**, 83.
4. M. Kimura, M. Tsunenaga, S. Takami, and Y. Ohbayashi, *Bull*. *Chem*. *Soc*. *Jpn*., 2005, **78**, 929.
5. M. Kimura, H. Nishikawa, H. Kura, H. Lim, and E. H. White, *Chem. Lett*., 1993, **3**, 505.
6. M. Kimura, G. H. Lu, H. Nishigawa, Z. Q. Zhang, and Z. Z. Hu, *Luminescence*, 2007, **22**, 72.
7. M. Matsumoto, N. Arai, and N. Watanabe, *Tetrahedron Lett*., 1996, **37**, 8535.
8. D. R. Maulding and B. G. Roberts, *J*. *Org*. *Chem*., 1969, **34**, 1734.
9. K. C. Wu and A. M. Trozzolo, *J*. *Phys*. *Chem*., 1979, **83**, 3180.
10. W. R. Dawson and M. W. Windsor, *J*. *Phyz*. *Chem*., 1965, **72**, 3251.

Supplemental Data

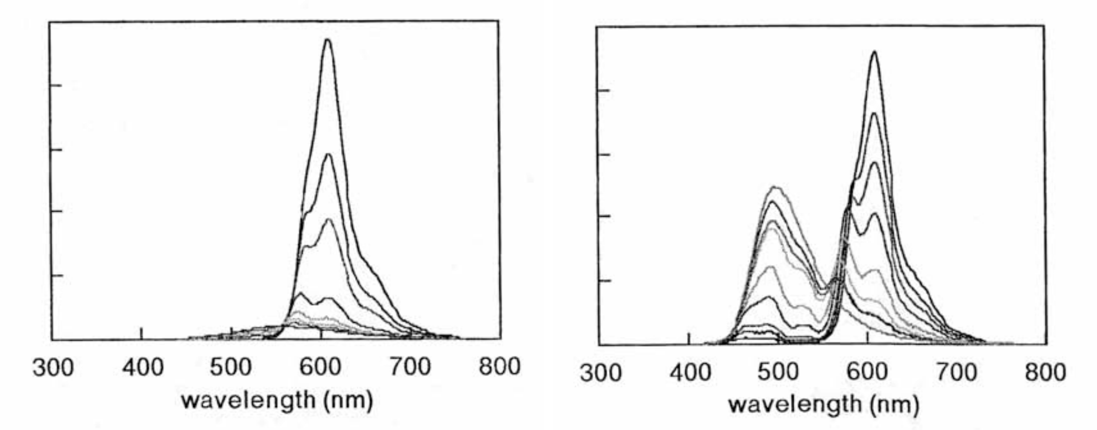
2a **2b**

Figure The Chemiluminescence Spectra for **2a** and **2b** sensitized with gradient concentration of BPEN in CH_2Cl_2