A Kinetic Study of the Chemiluminescent Reactions of Bis(2,4-dinitrophenyl)Oxalate, Hydrogen Peroxide, and Fluorescent Polycyclic Aromatic Hydrocarbons

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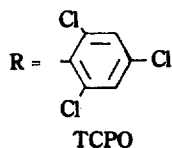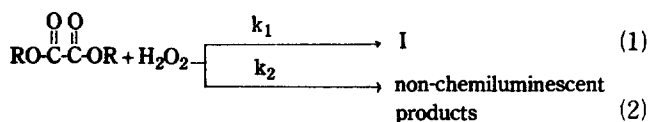*Department of Chemistry, Korea University, Seoul 136-701. Received January 13, 1989*

A kinetic study on the chemiluminescence resulting from the reaction between bis(2,4-dinitrophenyl) oxalate(DNPO) and hydrogen peroxide in the presence of fluorescent polycyclic aromatic hydrocarbons in a viscous phthalate medium has been conducted. The resultant data confirm that the reaction between DNPO and H_2O_2 is the rate determining step. Higher rate constants are obtained with DNPO than those with bis(2,4,6-trichlorophenyl) oxalate (TCPO).

Introduction

The chemilumenescence(CL) from a chemical reaction of oxalic ester and hydrogen peroxide in the presence of fluorescent compounds, classified as peroxyoxalate CL, are important for practical CL devices[1] and for utilization to detect fluorescent compounds with a better signal-to-noise ratio than direct excitation.[2-5]

Since investigation of the mechanism, however, by which light is produced in peroxyoxalate CL reactions has proved to be difficult due to the complex multistep processes involved, only a limited number of mechanistic studies have been performed.[6-11] In particular, the identification of key intermediate and its role responsible for the CL has not been established unequivocally.[12]

Catherall *et al.*[8] proposed a mechanism based on a base-catalized reaction between bis(pentachlorophenyl)oxalate and hydrogen peroxide. If it is applicable to the present system, the rate determining step should be the reaction between DNPO and H_2O_2 and may be represented by

$$RO-\overset{O}{\underset{\parallel}{C}}-\overset{O}{\underset{\parallel}{C}}-OR + H_2O_2 \begin{array}{c} \xrightarrow{k_1} \\ \xrightarrow{k_2} \end{array} \begin{array}{l} I \qquad\qquad (1) \\ \text{non-chemiluminescent} \\ \text{products} \qquad (2) \end{array}$$

R = (structures for TCPO and DNPO)

TCPO   DNPO

where I stands for a single key intermediate, and k_1 and k_2 are the second order rate constants. The key intermediate the reacts and forms a complex with a fluorescer, followed by the emission of light. Assuming that all the lifetimes of the key intermediate, of the complex, and of the excited state of fluorescer are short and that their steady-state concentrations are small, the intensity of CL emission at a time t, I_t, should be propotional to the product of DNPO and H_2O_2 concentration at t,

$$I_t \propto k_1 [DNPO] [H_2O_2] \qquad (3)$$

However, Givens *et al.* have reported an experimental evidence of at least two intermediates for a reaction of TCPO with H_2O_2 and triethylamine.[9] This possibility was suggested
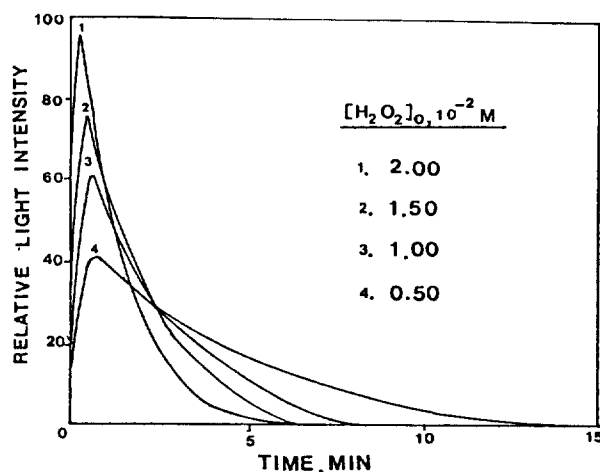

Figure 1. Relative light intensity of CL *vs.* time for 5.0×10^{-4}M DNPO, 1.0×10^{-4}M perylene, 4.0×10^{-5}M sodium salicylate and various concentration of H_2O_2.

previously.[12] Therefore, the mechanism awaits further studies.

To help understand the complex nature of the peroxyoxalate CL, a study has been attempted with DNPO and H_2O_2 using perylene, rubrene, and 9,10-diphenylanthrance(DPA) as fluorescers in phthalate media and the results are compared with those of TCPO.

Experimental

DNPO was prepared and recrystallized by the method of Mohan and Turro.[13] H_2O_2 purchased from Riedl-de Haën was vacuum distilled to obtain 94% by weight. Perylene, rubrene, and 9,10-diphenylanthracene(DPA) of reagent grade from Aldrich were used without purification. Dimethylphthalate and dibutylphthalate of reagent grade from Junsei were selected as the solvent, but tert-butylalcohol from Junsei was dehydrated with sodium and fractional distilled.

The CL reaction was carried out in a 1.0 cm fluorescence cell inserted in a thermostated housing of a Hitachi 650-60 spectrofluorimeter. A 1.5 m*l* solution of DNPO and a fluorescer in dibutylphthalate was added to the cell. The cell was purged with nitrogen. The reaction was initiated by injecting 0.5 m*l* solution of H_2O_2 and sodium salicylate in 4:1 dimethylphthalate/ *t*-butylalcohol (by volume) purged previously with

Table 1. Effect of H_2O_2 on the CL Decay Rate Constants(k_d) in 10^{-3}sec^{-1} and Relative Quantum Efficiencies(q_r) at Various Excess Concentrations of H_2O_2[a]

[H$_2$O$_2$]$_0$ (/10^{-2}M)	perylene		rubrene		DPA	
	k_d	q_r	k_d	q_r	k_d	q_r
2.00	10.2	1.00	9.7	0.54	9.2	0.32
1.75	9.3	0.96	8.5	0.53	7.3	0.31
1.50	8.8	0.98	7.1	0.52	6.8	0.31
1.25	6.6	0.97	6.7	0.53	6.5	0.30
1.00	5.3	0.98	5.0	0.54	4.7	0.32
0.50	3.1	0.91	1.9	—	2.4	—

[a]reactant condition: DNPO; $5.0 \times 10^{-4}M$, sodium salicylate; $4.0 \times 10^{-5}M$, fluorescer; $1.0 \times 10^{-4}M$.
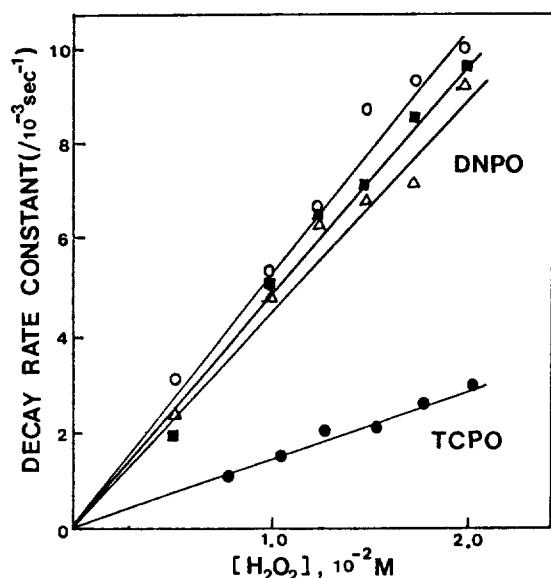
Figure 2. Decay constants of perylene(o), DPA($\triangle$), and rubrene($\blacksquare$) vs. H_2O_2 concentration at $5.0 \times 10^{-4}M$ DNPO, $4.0 \times 10^{-5}M$ sodium salicylate, and $1.0 \times 10^{-4}M$ fluorescers. Decay rate constants for TCPO($\bullet$) are the average of perylene, rubrene, and DPA under similar conditions.

nitrogen. The decay of CL intensity with time was monitored by the spectrofluorimeter with the lamp turned off at wavelengths such that the reabsorption of emission was negligible. An IBM-4341 computer was used to determine the decay rate constant of the CL intensity and the area under the intensity-time curve.

Results and Discussion

CL Reaction in an Excess of H_2O_2. Figure 1 shows typically the concentration dependence of H_2O_2 in excess over DNPO on the relative CL intensity vs. time in a solution of $5.0 \times 10^{-4}M$ DNPO, $1.0 \times 10^{-4}M$ perylene and $4.0 \times 10^{-5}M$ sodium salicylate. The decay beyond a maximum has an apparent single exponential behavior. The data presented in Table 1 show the effect of varying the hydrogen peroxide concentration on the CL decay rate constants and on the relative quantum efficiencies when concentrations of oxalic esters, sodium salicylate, and fluorescers were held constant. The

Table 2. Comparison of Second-Order Rate Constants in an Excess of H_2O_2

fluorescer	$k_1 + k_2$[a]		a[oxalic ester]$_o + b$	
	TCPO[b]	DNPO	TCPO[b]	DNPO
perylene	0.16	0.49	0.17	0.47
rubrene	0.14	0.50	0.12	0.45
DPA	0.11	0.42	0.11	0.45

[a]from Figure 2. [b]from ref. 11.
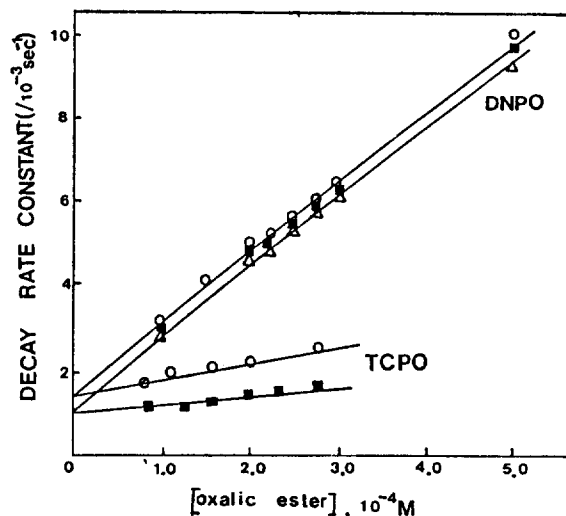
Figure 3. Decay rate constants of perylene(o), rubrene($\blacksquare$), and DPA($\triangle$) vs. oxalic ester concentration at 2.0×10^{-2}M H_2O_2.

relative quantum efficiency is the ratio of the area under the CL intensity-vs-time curve to the [H_2O_2]. The decay rate constants as plotted in Figure 2 show a linear relationship and pass through the origin. The removal of DNPO by Eqs.(1) and (2) can be written as

$$-d[\text{DNPO}]/dt = (k_1 + k_2) \, [\text{DNPO}] \, [\text{H}_2\text{O}_2] \qquad (4)$$

Under in an excess of H_2O_2, the concentration of DNPO at t is given by

$$[\text{DNPO}]_t = [\text{DNPO}]_0 \exp \{- (k_1 + k_2) \, [\text{H}_2\text{O}_2]_o t\} \qquad (5)$$

where the concentration with subscript "0" implies the initial concentration. From Eqs.(3) and (5), the decay rate constant is expected to be $(k_1 + k_2)[\text{H}_2\text{O}_2]_0$ and experimental results in Figure 2 agree well with the prediction.

The values of $k_1 + k_2$ obtained from the slopes in Figure 2 are summarized in Table 2. On consideration of experimental uncertainties, essentially no significant differences in the slopes of three fluorescers were considered to exist and consequently the fluorescer was not taking part in the rate determining step, which agrees with the previous work.[8] Included are the decay rate constant averaged for perylene, rubrene, and DPA under similar conditions with TCPO.[11]

Now, the concentration of oxalic esters in an excess of [H_2O_2] were varied. Figure 3 shows those data for the effect of TCPO and DNPO concentrations on the CL decay rates of exponential curves obtained at constant concentrations of sodium salicylate, H_2O_2, and fluorescers. The decay rate constants again showed a linear dependence on the initial oxalic ester concentrations, but did not pass through the origin,

Table 3. Effect of H_2O_2 and Fluorescer Concentrations on the CL Decay Rate Constants in 10^{-4} sec^{-1} in an Excess of DNPO (1.0×10^{-3} M)[a]

[fluorescer]	[H_2O_2], $1.0 \times 10^{-4}M$			[H_2O_2], $2.0 \times 10^{-4}M$		
(/ $10^{-5}M$)	perylene	rubrene	DPA	perylene	rubrene	DPA
100	9.0	9.0	9.0	9.1	9.4	9.5
10.0	8.9	8.8	8.9	—	9.2	8.4
1.0	8.3	8.9	—	8.6	—	—

[a]sodium salicylate; $4.0 \times 10^{-5}M$.

Table 4. Effect of H_2O_2 Concentration on the CL Decay Rate Constants in $10^{-4}s^{-1}$ in an Excess of DNPO[a]

[H_2O_2](/ 10^{-5}M)	perylene	rubrene	DPA
2.5	6.7	6.9	6.5
5.0	6.9	7.0	6.9
10	6.5	7.4	6.6

[a]DNPO; $8.0 \times 10^{-4}M$, sodium salicylate; $4.0 \times 10^{-5}M$, fluorescer; $1.0 \times 10^{-4}M$.

which suggests that the CL intensity with time in an excess of H_2O_2 should follow a relation as in connection with that of

$$I_t \propto \exp\{-(a[DNPO]_0 + b)[H_2O_2]_0 t\} \quad (6)$$

Figure 2. The slope and intercept correspond to $a[H_2O_2]_0$ and $b[H_2O_2]_0$, respectively, from which a and b were calculated using $[H_2O_2]_0 = 2.0 \times 10^{-2}M$. Since Eq.(6) describes the same system in a different way, therefore $a[DNPO]_0 + b = k_1 + k_2$.

The values computed with the slopes and the intercepts in Figure 3 are listed in Table 2 and are in excellent agreement with $k_1 + k_2$ directly obtained from Figure 2, and are essentially independent of fluorescers. The total number of photons emitted(Q_t) is the integral of I_t of Eq.(6) from $t = 0$ to $t = \infty$ and a calculation of the relative quantum efficiency should, however, be dependent on the type of fluorescers because of differences in their yields of excitation and fluorescence. It may be concluded that under conditions of an excess H_2O_2 the rate determining step of CL emission is confirmed to be the reaction between oxalic ester and H_2O_2.[8]

CL Reaction in an Excess of DNPO. When oxalic ester is in excess over H_2O_2, the CL intensity at t is given by a similar equation as Eq.(5), from which H_2O_2 is replaced by DNPO in the exponential term. That is, the CL decay is expected to be independent of H_2O_2 and fluorescers. The data in Table 3 and 4 agree well with such expectation. Even when fluorescer concentration was varied by a factor of 10^2 at two different concentrations of H_2O_2 (Table 3), the decay rate constants remained essentially a constant. In another experiment (Table 4), H_2O_2 concentration was varied from $1.0 \times 10^{-4}M$ to $2.5 \times 10^{-5}M$ and the decay rate constants were fairly unvariant within experimental error.

From these results in Table (3) and (4) and the respective [DNPO] the average value of the second-order rate constant were calculated to be $k_1 + k_2 = 0.86 \pm 0.04M^{-1}sec^{-1}$. However, the value is approximately twice as large as that obtained in an excess H_2O_2. A very much similar investigation with TCPO yielded the second-order rate constant, $k_1 + k_2 =$
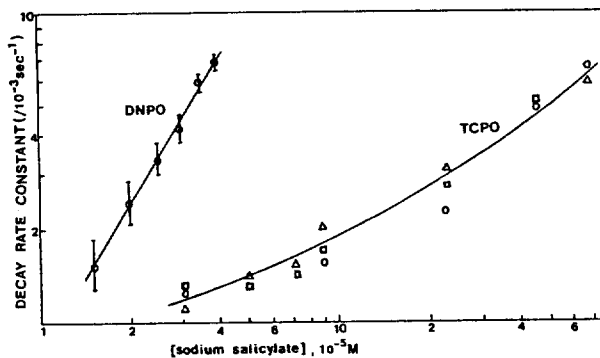
Figure 4. Average decay rate constants of perylene, rubrene, and DPA vs. sodium salicylate concentration at $4.0 \times 10^{-4}M$ DNPO, $2.0 \times 10^{-2}M$ H_2O_2, and $5.0 \times 10^{-4}M$ fluorescers. Data of perylene (○), rubrene(□), and DPA(△) for TCPO are from ref. 11.

$0.42 \pm 0.04M^{-1}s^{-1}$ under the condition of excess TCPO,[11] and the value is higher than that obtained in excess of H_2O_2 by about a factor of three. These discrepancies in the second-order rate constant may arise from the acid-base equilibria involved with salicylic acid and H_2O_2 as proposed by Catherall *et al.*[8] The real species to lead a necleophilic reaction with oxalic ester is OOH^- whose concentration may be assumed constant by the equibria above under the condition of an excess H_2O_2. Accordingly, Eq.(6) should be modified to $\exp\{-(a[DNPO]_0 + b)[OOH^-]t\}$ under the conditions of an excess H_2O_2. Apparently the effective concentration of OOH^- should be maintained to about 1/2 of $[H_2O_2]_0$ under the condition of excess H_2O_2. Higher decay rate constants and second-order rate constants for DNPO than those for TCPO are attributed to the more electron attracting power by nitro groups than by chloro groups.

The magnitude of $k_1 + k_2$ is about 20 times smaller than that obtained with bis(pentachlorophenyl)oxalate in chlorobenzene-ethylacetate solvents.[8] This probably indicates that the CL reaction was retarded considerably in a viscous medium ($\eta = 17$ cp) employed here.

Effect of Sodium Salicylate as Base Catalyst. As the concentration of sodium salicylate increased, the time to reach the maximum intensity became slightly shorter and the decay rate turned out to be faster. Figure 4 presents quantitatively the effect of sodium salicylate on the CL decay rate constants for perylene, rubrene, and DPA. It is noted that the decay rate constants were essentially independent of the concentration and type of fluorescers, but increased with increasing the concentration of sodium salicylate regardless of the fluorescers for both TCPO and DNPO, which disagrees with the result by Catherall *et al.*[8] This discrepancy was examined in a previous study[11] with TCPO by the absorption spectroscopy over the region of 200-400 nm. Since no reaction between TCPO and sodium salicylate was found to occur and the decay rate constants are increasing with the increase of sodium salicylate concentration under the experimental conditions, the sodium salicylate seems to mainly enhance the relative ionization of H_2O_2 instead of forming a more effective base catalyst with oxalic esters.

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Adsorption of Some Aliphatic Dimercaptans on the Silver Surface Investigated by Raman Spectroscopy

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Adsorption of 1,3-propanedithiol, 1,4-butanedithiol, 1,5-pentanedithiol, and 1,6-hexanedithiol on silver surface has been investigated by surface-enhanced Raman spectroscopy. It has been found that the conformations of the adsorbates were mainly affected by steric interaction of the adsorbates with the surface. As the alkyl chain length separating the thiol groups increased, surface stacking efficiency became increasingly important in determining conformation of the adsorbate on the surface.

Introduction

When a molecule adsorbs on metal surfaces such as Ag, Cu, and Au, its Raman scattering intensity can be tremendously enhanced. This plenomenon, so-called surface-enhanced Raman scattering (SERS)[1-7] has been utilized to obtain vibrational spectra of the adsorbates forming monolayer on the surfaces. The SER spectra thus obtained have proved useful for the investigation of the chemical nature of the adsorbates[8], their orientations with respect to the surface[9-11], and the metal-adsorbate interaction[12,13].

Recently, we have carried out SERS investigation of several aliphatic mercaptans adsorbed on silver surface [11,14-18]. It has been found that these mercaptans adsorbed on the surface dissociatively, namely after losing the thiol protons and that the resulting thiolate anions adsorbed through their sulfur atoms. In addition, the SER spectra provided information on the conformational isomerism of the adsorbed thiolate anions. When the surface was sparsely populated with the adsorbates, various conformational isomers with respect to the C-C bonds adjacent to the sulfur atoms were found. On the other hand, only the trans conformers existed when the adsorbates formed a full monolayer coverage on the surface. This was explained in terms of surface stacking efficiency of the trans conformers.

A similar investigation has been performed on the surface adsorption of 1,2-ethanedithiol. This molecule adsorbed as a bidentate dithiolate dianion after losing two protons. In contrast to the cases of monomercaptans, gauche form was dominant on the surface regardless of surface coverage. This was attributed to less steric interaction of the adsorbed

gauche form with the surface than that of the trans form.

In the present paper, the SERS investigation on longer chain dithiols, namely 1,3-propanedithiol (1,3-PDT), 1,4-butanedithiol(1,4-BDT) 1,5-pentanedithiol(1,5-PDT), and 1,6-hexanedithiol(1,6-HDT) is reported. The major purpose of the present work is to investigate further the factors affecting the conformation of the adsorbates.

Experimental

The method of preparation of silver sol and details of Raman scattering measurement have been reported elsewhere[19]. The 514.5 nm line of an Ar^+ laser(Spectra physics model 164-06) was used as an exciting source. In a typical experiment, the laser power and spectral slit width were 200-300 mW and 5-10 cm^{-1} respectively.

Methanol solutions of dithiols were diluted with water to final concentrations of 10^{-2} M or less. Around 10 μl of dithiol solution was injected into 1 ml silver sol solution and aqueous polyvinylpyrrolidone (2%, 10-20 μl) was added to stabilize the solution. Dithiolate dianion solutions were prepared by mixing neat dithiols with 3 M NaOH aqueous solution in 1:10 volume rations.

To prepare a silver dithiolate salt, a methanolic solution of 0.5 M dithiol and 1 M silver nitrate solution were mixed in 1:1 volume ratio with vigorous stirring. The yellow precipitate of a silver dithiolate salt was then filtered, and rinsed thoroughly with methanol and water successively. A pellet of silver dithiolate salt was spun at 3000 rpm during the Raman scattering measurment to minimize laser-induced damage.

All the chemicals used were reagent grade and triply