Nature of Intermediates in the Peroxyoxalate Chemiluminescent Reactions

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Recently, Givens *et al.* have proposed for the first time that at least two intermediates are involved in the chemiluminescence(CL) reaction of bis(2,4,6-trichlorophenyl) oxalate(TCPO) with H_2O_2, triethylamine, and 9,10-diphenylanthracene(DPA) in ethyl acetate.[1] The intermediates encompass those in earlier reports,[2,3] but contrast with the assertion that 1,2-dioxetanedione is the key intermediate[4] or that the key intermediate should not contain an aromatic ring.[5]

The present study has been conducted to verify whether key intermediate may vary with starting oxalic ester using TCPO and bis(2,4-dinitrophenyl)oxalate (DNPO).

The reactions of the key intermediate, X, may be represented by[2-5]

$$X + F \xrightarrow{k_c} XF \qquad (1)$$

$$X \xrightarrow{k_d} \text{non-chemiluminescent decay} \qquad (2)$$
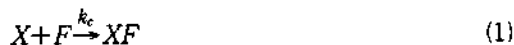
where F stands for a fluorescer. Under the condition of an excess oxalic ester, the CL intensity extrapolated to $t = 0$, I_o, can be given by[2]

$$I_o = C \frac{k_c [F]}{k_c [F] + k_d} \qquad (3)$$

where C is an experimental constant independent of fluorescer concentration. Thus, a plot of I_o^{-1} *vs.* $[F]^{-1}$ will give a straight line. The ratio of k_c/k_d is then available as the quotient of intercept/slope. If a common key intermediate should be involved, the k_c/k_d ratio is expected to be equal regardless of oxalic esters.

Experimental details are described elsewhere.[6] The CL internsity *vs.* time showed an apparent single exponential decay, indicating a key intermediate is important.

A typical plot of I_o^{-1} *vs.* $[F]^{-1}$ for perylene is shown in Figure 1. Satisfactory straight lines are obtained both for two different solvents and oxalic esters. The slope/intercept values calculated from similar plots are summarized in Table 1, and show that the k_c/k_d ratios are essentially constant with an average value of $(2.1 \pm 0.1) \times 10^3 M^{-1}$ in ethyl acetate, which compares favorably with that of $(1.3 \pm 0.1) \times 10^3 M^{-1}$ in more viscous dibutylphthalate(DBP). The high ratios confirm earlier experiments that fluorescers act as catalysts for the decomposition of key intermediates.[2,3]

It is noted, however, that the k_c/k_d ratios for TCPO and DNPO under identical conditions are $(2.2 \pm 0.1) \times 10^3 M^{-1}$ and $(6.5 \pm 0.2) \times 10^3 M^{-1}$, respectively. This discrepancy contrary to the expectation from Eq. (3) was considered to arise either from the reaction between the key intermediate and a byproduct phenol, or from different type of intermediate. The former possibility was examined by adding a constant amount of 2,4-dinitrophenol(DNP) and carring out the iden-
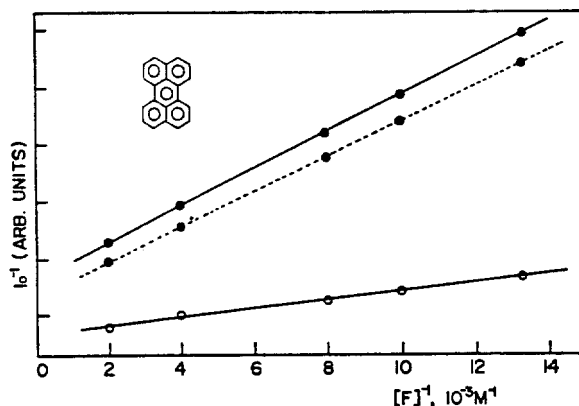

Figure 1. Typical plots of I_o^{-1} *vs.* $[F]^{-1}$ for perylene with TCPO(●) or DNPO(○) in ethylacetate(——) or DBP(----).

Table 1. k_c/k_d Values in an Excess of Aryloxalic Ester[a]

fluorescer	solvent[b]	aryloxalic ester	k_c/k_d, $10^3 M^{-1}$
anthracene	ethyl acetate	TCPO	2.1
DPA	ethyl acetate	TCPO	2.0
perylene	ethyl acetate	TCPO	2.2
anthracene	DBP	TCPD	1.3
DPA	DBP	TCPD	1.3
perylene	DBP	TCPO	1.4
perylene	ethyl acetate	DNPO	6.5
perylene + DNP	ethyl acetate	DNPO	6.5

[a]Concentration: aryloxalic ester, $2.0 \times 10^{-3} M$: sodium salicylate, $1.2 \times 10^{-4} M$. Concentration range of fluorescers; 0.75×10^{-4}–$5.0 \times 10^{-4} M$. [b]Contained 5%, *t*-butyl alcohol.

tical measurement. The addition of $1.0 \times 10^{-4} M$ DNP caused the CL intensity to decrease by about 20%, but did not change the k_c/k_d ratio(Table 1). Thus another competing reaction of the intermediate with the phenol appears to be excluded. Incidently the corresponding ratio[2] with bis-(pentachlorophenyl)oxalate in chlorobenzene was obtained to be $4.8 \times 10^3 M^{-1}$. The results appear to support that key intermediates vary withstarting oxalic ester. Further investigations should be necessary to elucidate the complex nature of the intermediates.

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