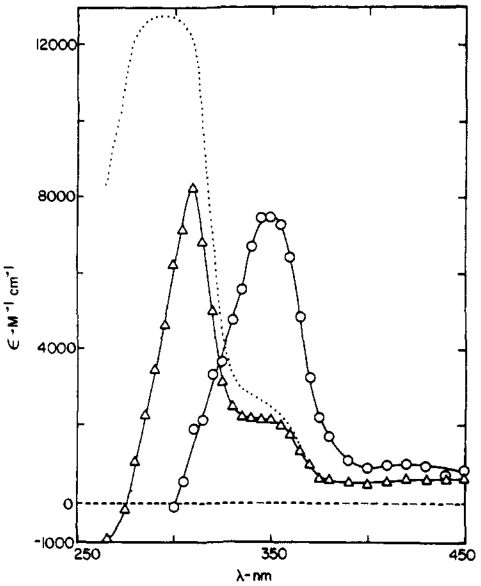

Figure 4. Absorption spectra of the radicals produced by reaction of $(CH_3)_2\dot{C}OH$ with *p*-nitrobenzyl bromide at pH 2. The solution contained 1×10^{-4} M substrate and 0.7 M *i*-PrOH and was bubbled with N_2O. The spectra were recorded 10 μs after the pulse (Δ) and 150 μs later (○). The dotted line is the initial spectrum corrected for the bleaching of the parent compound.

of *i*-PrOH which scavenges both OH and H to produce $(CH_3)_2\dot{C}OH$ (reaction 4), which then reduces the nitro compound (reaction 5). The rate constant of this one-electron reduction of *p*-nitrobenzyl bromide was determined to be $2.6 \times 10^9 M^{-1} s^{-1}$, i.e., in the same range as those of several other nitro aromatic compounds.[20] The spectra observed with this system at pH 2 are shown in Figure 4. The initial spectrum is mostly that of the protonated radical $BrCH_2Ph\dot{N}O_2H$, with some contribution from the anion $BrCH_2Ph\dot{N}O_2^-$. The pK_a for such a radical (eq 7) is

$$\mathrm{XCH_2Ph\dot{N}O_2H \rightleftarrows XCH_2Ph\dot{N}O_2^- + H^+} \tag{7}$$

expected to be ~3.[21] The spectrum observed at later times is that of the nitrobenzyl radical (eq 8).

$$\mathrm{XCH_2Ph\dot{N}O_2H \rightarrow X^- + \dot{C}H_2PhNO_2 + H^+} \tag{8}$$

The rate of the intramolecular transfer at pH 2 was only $2 \times 10^4 s^{-1}$, as compared with $1.7 \times 10^5 s^{-1}$ in neutral solution. This decrease must be due to the protonation of the nitro group. From the rates observed at pH 2.3, 1.9, 1.6, 1.4, 1.2, 0.9, and 0.6 (3.3, 2.0, 1.3, 1.0, 0.7, 0.6, and 0.3 $\times 10^4 s^{-1}$, respectively) the pK_a of the nitro group is determined to be 2.8 ± 0.1 and the rate of intramolecular electron transfer in the protonated radical is estimated as $(3 \pm 1) \times 10^3 s^1$. It was difficult to determine the kinetics of the latter process accurately at high acidities because second-order decay of the radicals overlapped the slow intramolecular reaction. The decrease in rate upon protonation of the nitro group is by a factor of 56, comparable to the ratio of 42 found for the (*o*-nitrobenzoato)cobalt(III) complex.[3] This trend may be rationalized by the lack of negative charge in the protonated form or by changes in redox potentials,[22] i.e., that the nitro anion radical is a stronger reductant than its protonated form.

Conclusion

It has been demonstrated that anion radicals of nitrobenzyl halides undergo intramolecular electron transfer and decompose into halide ions and nitrobenzyl radicals. This process takes place with rates varying from 0 to $10^6 s^{-1}$ and is governed by the nature of the halide and the relative position of the nitro to the CH_2X group on the ring. The relative rates for the ortho and para derivatives are 1:40:140 for Cl:Br:I. The ortho decompose twice as rapidly as the para, while the meta decompose much more slowly. Protonation of the nitro group in the radical slows down the electron transfer and decomposition considerably.

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[19] Whillans, D. W. *Radiat. Phys. Chem.* **1977**, *10*, 335.
[20] Asmus, K. D.; Wigger, A.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 862. Adams, G. E.; Willson, R. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 719. Neta, P.; Meisel, D. *J. Phys. Chem.* **1976**, *80*, 519.
[21] See review by: Neta, P. *Adv. Phys. Org. Chem.* **1976**, *12*, 223 and references therein.
[22] Meisel, D.; Neta, P. *J. Am. Chem. Soc.* **1975**, *97*, 5198.

Fluorescer-Enhanced Chemiluminescence of a Cyclic Peroxalate via Electron Exchange

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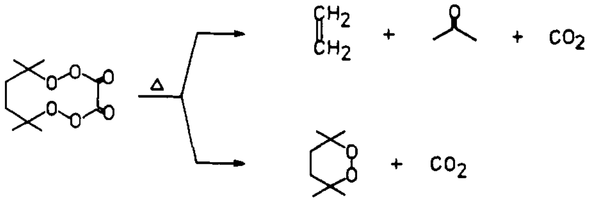
Abstract: The direct and fluorescer-enhanced chemiluminescence of the cyclic peroxalate 7,7,10,10-tetramethyl-1,2,5,6-tetroxecane-3,4-dione is reported. That enhancement by 9,10-diphenylanthracene was much less effective than that by 9,10-dibromoanthracene and that triplet quenchers such as O_2 and piperylene did not alter significantly the rubrene-enhanced emission intensities suggested that the enhanced chemiluminescence was not derived via energy transfer from triplet-state products. At high fluorescer concentration the fluorescer catalyzes the decomposition of the cyclic peroxalate, but this catalysis is chemiluminescent. The logarithmic dependence between the enhanced chemiluminescence intensity and the oxidation potential of the fluorescer confirms that the dominant mechanism of light enhancement is via electron exchange.

The cyclic peroxalate in eq 1 was shown[3] to decarboxylate thermally into ethylene and acetone (major products) and into 3,3,6,6-tetramethyl-1,2-dioxane (minor product). The interesting observation about this cyclic peroxalate was its significantly higher activation energy ($\Delta H^{\ddagger}$ = 30 ± 1 kcal/mol) toward decarboxylation than its acyclic congener di-*tert*-butyl peroxalate ($\Delta H^{\ddagger}$ = 22 ± 1 kcal/mol). This was surprising, especially since thermochemical measurements revealed that the cyclic peroxalate



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[2] Graduate Research Fellows in the Support for Biomedical Education (SUBE) Program sponsored by NIH-MBS.
[3] Adam, W.; Sanabia, J. *J. Chem. Soc., Chem. Commun.* **1972**, 74.

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possessed a significantly more negative heat of reaction ($\Delta H° = -99 \pm 2$ kcal/mol) than the corresponding acyclic peroxalate ($\Delta H° = -57 \pm 2$ kcal/mol).

Since the sum of the activation enthalpy and reaction enthalpy is ca. 130 kcal/mol for the cyclic peroxalate, sufficient energy is released at its transition state to expect electronically excited products. Indeed, preliminary observations confirmed that electronic excitation was formed in the thermal decarboxylation of the cyclic peroxalate, but fluorescers such as rubrene had to be added to visualize the chemiluminescence. From the acyclic peroxalate, however, no light emission could be elicited even with efficient fluorescers such as rubrene. We report in this paper our results on the cyclic peroxalate–rubrene chemiluminescence.

Experimental Section

Materials. The cyclic peroxalate was prepared in 11% yield (mp 108–109 °C dec (lit.[4] mp 110–111 °C dec)) from 2,5-bis(hydroperoxy)-2,5-dimethylhexane (Lucidol Corp.) and oxalyl chloride (Eastman), according to the literature procedure.[4] *Caution*! A highly explosive peroxidic polymer is formed as the major product. After careful trituration of the crude product with pure *n*-pentane to remove the desired cyclic peroxalate, the polymeric residue should be disposed of without delay by treatment with excess KI solution. On one occasion the polymer was accidentally allowed to air-dry and the sample violently detonated. In our hands, the cyclic peroxalate did not exhibit such temperamental behavior; but all safety measures should be excercised. The cyclic peroxalate was stored in the freezer in the form of *o*-xylene stock solutions.

Tetramethyl-1,2-diazetidine 1,2-dioxide (mp 180 °C dec (lit.[5] 177–177.5 °C)) was prepared and purified as described.[5] Piperylene (Aldrich) was freshly distilled prior to use: bp 44–45 °C (760 mmHg), $n^{20}{}_{D}$ 1.4300 (lit.[6] bp 42 °C (760 mmHg), $n^{20}{}_{D}$ 1.4301).

9,10-Dibromoanthracene (Aldrich) was recrystallized as yellow needles several times from ethanol (mp 226 °C (lit.[7] mp 226 °C)), 9,10-diphenylanthracene (Eastman) was recrystallized as yellow needles several times from benzene (mp 249–251 °C (lit.[8] mp 248–250 °C)), and naphthacene (Aldrich) was recrystallized as orange needles several times from xylene (mp 338 °C (lit.[9] mp 341 °C)). Rubrene and perylene (Aldrich, Gold Label) were used without further purification. All fluorescers exhibited the reported fluorescence characteristics.[10] Analytical reagent *o*-xylene (Aldrich) was employed as solvent.

Apparatus. Total chemiluminescence intensities were measured with a Mitchell-Hastings photometer,[11] equipped with an RCA PF-1006 or a Hamamatsu RP 28A photomultiplier tube, which were powered by a Hewlett-Packard Model Harrison 6515 dc power supply. The photomultiplier output signal was amplified by means of a Keithley 427 current amplifier and monitored with a Hewlett-Packard Model 17501A recorder. A constant temperature in the photometer cell compartment was maintained within 0.5 °C of the desired temperature with the help of a Haake Model FJ circulating thermostat. The temperature of the cell compartment was determined by means of a thermocouple.

Measurements. The Packard scintillation glass vial was charged with 3.0 mL of an *o*-xylene solution of the cyclic peroxalate and fluorescer at the desired concentration, placed into the cell compartment, and allowed to equilibrate thermally (ca. 10 min). The chemiluminescence signal (in volts) was recorded vs. time, usually beyond 2–3 half-lives. The voltage outputs were converted to luminescence units (einstein/(s·L)) by using the experimentally established conversion factor ($(1.87 \pm 0.02) \times 10^{-12}$ einstein/(s·L·V). The latter was determined by means of a calibrated POPOP–PPO scintillation cocktail, kindly supplied by Professor, J. W. Hastings, Harvard University.[12]

The total intensity emissions of the enhanced chemiluminescence were corrected for relative spectral response of the phototube.[13] Furthermore, in view of the high fluorescer concentrations that were employed, it was necessary to correct for reabsorption.[13] This was achieved by measuring the chemiluminescence intensity (I_0) as a function of sample volume (V) (respectively, 4.0, 3.0, and 1.5 mL) and extrapolating a ln I_0/V vs. V plot to zero volume. This correction was most appreciable for rubrene (ca. 20%) and negligible for DPA.

Table I. Enhanced Chemiluminescence Intensities ($I_0{}^{EC}$) and Rate Constants ($k_{obsd}{}^{EC}$) for the Cyclic Peroxalate-Rubrene System in *o*-Xylene at 399 K[a]

run	10^4[rubrene], M	$10^{12}I_0{}^{EC}$,[b] einstein/(L·s)	$10^4k_{obsd}{}^{EC}$, s^{-1}
1	2.78	3.52 ± 0.31	3.15 ± 0.16
2	5.05	5.88 ± 0.48	3.12 ± 0.28
3	10.1	10.7 ± 0.95	3.00 ± 0.24
4	15.3	14.6 ± 1.5	3.08 ± 0.19
5	17.4	15.9 ± 1.4	3.60 ± 0.31

[a] $[\text{Peroxalate}]_0 = 3.36 \times 10^{-3}$ M. [b] Corrected for relative spectral response of phototube.

From the intensity vs. time plots the total chemiluminescence intensities were extrapolated to zero time (t_0), affording the initial intensities (I_0). A first-order rate analysis of the intensity decay with time afforded the observed rate constants (k_{obsd}). The reproducibility of the data is ca. 10%.

Results and Discussion

Direct Chemiluminescence. Under optimal conditions of high peroxalate concentrations (ca. 0.1 M) in xylene and high decomposition temperatures (ca. 120 °C), it was possible to observe direct chemiluminescence with our Mitchell-Hastings photometer setup. However, the emission intensities were too weak to be recorded as a fluorescence spectrum on a Perkin-Elmer Model MPF-3B spectrofluorimeter. Thus, it was not possible to determine which species was emitting.

The direct initial emission intensities were $I_0{}^{DC} = (0.90 \pm 0.17) \times 10^{-14}$ einstein/(L·s) at 385 K and $[\text{peroxalate}]_0 = 0.070$ M in *o*-xylene. I_0 decayed exponentially with time, indicating first-order kinetics with $k_{obsd}{}^{DC} = (3.4 \pm 0.5) \times 10^{-4}$ s^{-1}. In fact, it is important to point out that the cyclic peroxalate decomposition rate, followed by the disappearance of its characteristic 1812-cm^{-1} carbonyl band (quantitative infrared spectroscopy), was, within the experimental error ($k_{obsd}{}^{IR} = (4.2 \pm 0.4) \times 10^{-4}$ s^{-1}), identical with that by direct chemiluminescence under comparable conditions. From these data we calculate a direct chemiluminescence quantum yield $\phi^{DC} = (3.8 \pm 0.3) \times 10^{-10}$ einstein/mol, using the formula given in eq 2.[13] Indeed, the cyclic peroxalate is a very

$$\phi^{DC} = I_0{}^{DC}/k_{obsd}{}^{DC}[\text{peroxalate}]_0 = \phi^S\phi^f \qquad (2)$$

inefficient chemiluminescent system. Moreover, since we could not measure a fluorescence spectrum of the direct chemiluminescence, we do not know the emitter, and the singlet excitation yield (ϕ^S) could not be estimated by means of the formula[12] given in eq 2 since the fluorescence quantum yield (ϕ^f) is not known.

Enhanced Chemiluminescence. On the addition of fluorescers such as 9,10-diphenylanthracene (DPA), 9,10-dibromoanthracene (DBA), and rubrene, the weak direct chemiluminescence was enhanced enormously, the relative ordering being rubrene ($\sim 10^5$) > DPA ($\sim 10^2$) > DBA (~ 10) > direct (1.0). The numbers in parentheses represent the approximate enhancement factors of the enhanced emission intensities (I^{EC}) relative to the direct emission intensity (I^{DC}) under similar conditions. For each fluorescer, we confirmed that the chemiluminescence spectrum matched its fluorescence spectrum.

The fact that the relative I^{EC} of DPA was ca. tenfold greater than that for DBA immediately revealed that the light enhancement was not derived from intercepting triplet excited states, produced in the thermolysis of the cyclic peroxalate. Had this been the case, then the effective triplet counter DBA should have resulted in a higher enhanced emission intensity than the effective singlet counter DPA.[14] Control experiments confirmed that

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[4] Adam, W.; Sanabia, J. *J. Am. Chem. Soc.* **1977**, *99*, 2735.

[5] Singh, P.; Boocock, D.; Ullman, E. F. *Tetrahedron Lett.* **1971**, 3935.

[6] Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967.

[7] Heilbrou, J. M.; Heaton, J. S. "Organic Syntheses"; Wiley, New York, 1941; Collect. Vol. I, p 207.

[8] Ingold, C. K.; Marshall, P. G. *J. Am. Chem. Soc.* **1926**, *48*, 3081.

[9] Davis, W. W.; Krahl, M. E.; Cloves, G. H. A. *J. Am. Chem. Soc.* **1940**, *62*, 3080.

[10] Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970.

[11] Mitchell, G. W.; Hastings, J. W. *Anal. Biochem.* **1971**, *39*, 243.

[12] Hastings, J. W.; Weber, G. *J. Opt. Soc. Am.* **1963**, *53*, 1410.

[13] Adam, W.; Simpson, G. A.; Yany, F. *J. Phys. Chem.* **1974**, *78*, 2559.

[14] Turro, N. J.; Lechtken, P.; Schuster, G.; Orell, J.; Steinmetzer, H.-C.; Adam, W. *J. Am. Chem. Soc.* **1974**, *96*, 1627.

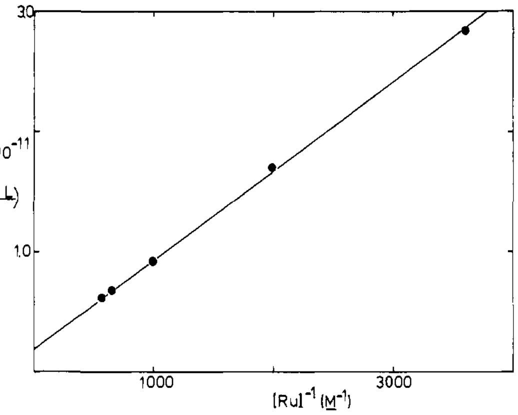


Figure 1. Double-reciprocal plot of the enhanced chemiluminescence intensity (I_0^{EC}) vs. rubrene concentration for the cyclic peroxalate–rubrene system in o-xylene at 399 K and peroxalate concentration 3.36 × 10^{-3} M.

typical triplet quenchers such as oxygen and piperylene did not significantly alter (reduction by less than threefold) the I^{EC} values for rubrene, the most effective enhancing fluorescer (enhancement by more than 10^5-fold).

Next we proceeded to evaluate the enhanced chemiluminescence efficiency of the cyclic peroxalate–rubrene system. The pertinent data are summarized in Table I and the double-reciprocal plot is shown in Figure 1. From this plot we extrapolate the limiting enhanced emission intensity at infinite membrane concentration I^{EC} = (4.70 ± 0.2) × 10^{-11} einstein/(L·s). Using eq 3, we calculate an enhanced chemiluminescence yield of ϕ^{EC} = (4.38 ± 0.3) ×

$$\phi_{Fl}^{EC} = I^{EC}/k_{obsd}^{EC}[\text{peroxalate}]_0 = \phi^S\phi_{ET}^{SS}\phi_{Fl}^{f} \qquad (3)$$

10^{-5} einstein/mol for the cyclic peroxalate–rubrene system at infinite rubrene concentration.

Normally one would proceed to calculate by eq 3[13] the singlet excitation efficiency (ϕ^S) for the enhanced chemiluminescent system in question, by assuming that the chemienergization is derived from singlet–singlet energy transfer. At infinite rubrene concentration the energy-transfer parameter ϕ_{ET}^{SS} is unity; i.e., all singlets generated by the cyclic peroxalate are intercepted by the fluorescer. However, at high rubrene concentration ([rubrene] > 10^{-3} M) we observed a catalytic decomposition of the cyclic peroxalate. More significantly, the enhanced chemiluminescence yileds (ϕ^{EC}) also continued to increase. In other words, the higher the rubrene concentration, the faster the decomposition of the cyclic peroxalate and the higher the light yield. Although at very high rubrene concentrations there was a leveling effect, this was in part due to reabsorption by the fluorescer and a dark-induced decomposition of the peroxalate by the excited fluorescer. Both effects could be confirmed by means of control experiments. In the latter case, selective photophysical excitation of the fluorescer by direct irradiation of a solution of the cyclic peroxalate and fluorescer at room temperature showed appreciable destruction of the cyclic peroxalate as monitored by quantitative infrared spectroscopy. In the absence of the fluorescer the cyclic peroxalate was photostable under the irradiation conditions.

In view of this catalytic chemiluminescent decomposition of the cyclic peroxalate at high rubrene concentration, determination of an excitation yield from the enhanced chemiluminescence quantum yield ϕ^{EC} at infinite rubrene concentration according to eq 3 is meaningless. It was therefore essential to understand the nature of the catalytic chemiluminescent process operating in the cyclic peroxalate–rubrene system. Therefore, the rubrene-enhanced chemiluminescence of the cyclic peroxalate was examined at [rubrene] > 10^{-3} M and at three different temperatures. The pertinent data are summarized in Table II. In Figure 2 k_{obsd} is plotted vs. [rubrene] for the three temperatures. The linear dependence between k_{obsd}^{EC} and [rubrene] follows the relationship shown in eq 4, where k_{dir} represents the rate constant

$$k_{obsd}^{EC} = k_{dir} + k_{cat}[\text{rubrene}] \qquad (4)$$

for the direct decomposition and k_{cat} that for the rubrene-catalyzed one. From these slopes we calculate that k_{cat} ($s^{-1}\cdot M^{-1}$) is (3.17 ± 0.28) × 10^{-2}, (12.0 ± 1.1) × 10^{-2}, and (12.8 ± 1.2) × 10^{-2}, respectively, for 364, 385, and 392 K. At a particular temperature, the intercept extrapolates to a k_{dir} value which is, within the experimental error, equal to the k_{obsd}^{DC} value of the direct chemiluminescence (absence of rubrene); e.g., at 385 K the respective values are k_{dir} = (5.0 ± 1.2) × 10^{-4} s^{-1} and k_{obsd}^{DC} = (3.40 ± 0.5) × 10^{-4} s^{-1}. From the temperature dependence of the catalytic process k_{cat}, we estimate that $\Delta H^{\ddagger}$ = 15 ± 2 kcal/mol and $\Delta S^{\ddagger}$ = −26 ± 3 eu. Clearly, the relatively low activation barrier but very negative entropy for the catalytic process point to an activated complex composed of fluorescer and substrate.

Table II. Rubrene-Catalyzed Decomposition of the Cyclic Peroxalate as a Function of Rubrene Concentration and Temperature in o-Xylene[a]

run	T, K	10^4[rubrene], M	$10^4k_{obsd}^{EC}$, s^{-1}
1	364[a]	86.0	2.33 ± 0.17
2		143	3.85 ± 0.22
3		170	4.67 ± 0.24
4		225	6.75 ± 0.36
5	385[b]	33.8	9.23 ± 0.67
6		65.7	12.8 ± 0.8
7		102	17.4 ± 1.1
8	392[c]	27.9	20.6 ± 1.2
9		47.1	23.0 ± 1.1
10		83.3	27.2 ± 1.3
11		100	30.1 ± 2.1

[a] At $[\text{peroxalate}]_0$ = 6.97 × 10^{-4} M. [b] At $[\text{peroxalate}]_0$ = 13.3 × 10^{-4} M. [c] At $[\text{peroxalate}]_0$ = 2.98 × 10^{-4} M.

Table III. Enhanced Chemiluminescence Intensities (I_0^{EC}) of the Cyclic Peroxalate–Fluorescer System and Oxidation Potentials (E_{Ox}) of the Fluorescers in o-Xylene at 367 K[a]

fluorescer	I_0^{EC},[b] einstein/(L·s)	E_{Ox},[c] V
rubrene	(17.1 ± 1.6) × 10^{-12}	0.82
naphthacene	(0.51 ± 0.04) × 10^{-12}	0.95
perylene	(0.73 ± 0.06) × 10^{-12}	1.06
DPA	(4.05 ± 0.5) × 10^{-3}	1.22

[a] $[\text{Peroxalate}]_0$ = 6.72 × 10^{-4} M, [Fl] = 1.07 × 10^{-2} M. [b] Corrected for relative spectral response of phototube, for reabsorption, and for fluorescence efficiency. [c] Vs. SCE. Taken from: Mann, C. K.; Barnes, K. K. "Electrochemical Reactions in Non-Aqueous Systems"; Marcel Dekker: New York, 1970. Parker, V. D. J. Am. Chem. Soc. 1976, 98, 98.

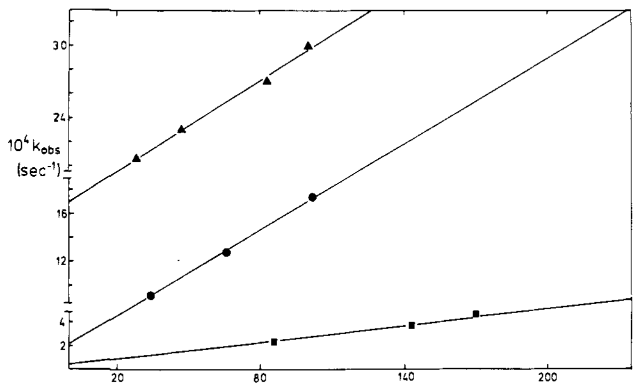


Figure 2. Rubrene-catalyzed decomposition of the cyclic peroxalate in o-xylene as a function of rubrene concentration at 364 (■), 385 (●), and 392 K (▲) and peroxalate concentration of 6.97 × 10^{-4}, 13.3 × 10^{-4} and 2.98 × 10^{-4} M, respectively.

These experimental data obviously hint at the recently discovered electron-exchange chemiluminescence, evidently a general mechanism operating between readily reduced peroxides and readily oxidized fluorescers.[15] Indeed, when we examined the

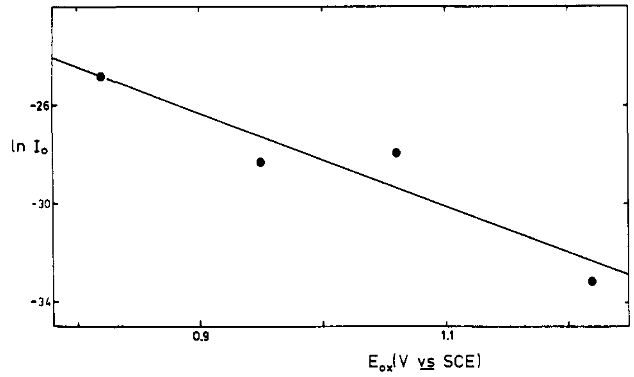
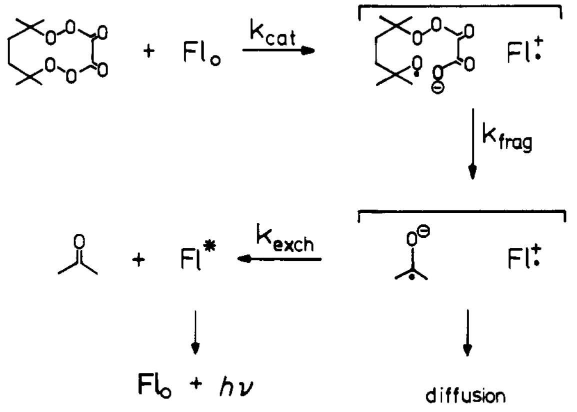


Figure 3. Logarithmic dependence of fluorescer-enhanced chemiluminescence intensity (I_0^{EC}) vs. oxidation potential (E_{Ox}) for the cyclic peroxalate–fluorescer system in *o*-xylene at 367 K and 6.72×10^{-4} M peroxalate concentration. The ln I_0^{EC} values are directly proportional to k_{obsd} since corrections for fluorescence quantum yields of Fl have been made (cf. footnote *b* in Table III).

light efficiency of this enhanced chemiluminescence as a function of catalyst structure (Table III), employing DPA, perylene, naphthacene, and rubrene as catalyzing fluorescers, a reasonable linear dependence between ln I_0^{EC} and the oxidation potential (E_{Ox}) was observed (Figure 3). The large scatter of points was due to experimental problems in view of the high temperatures employed. Nevertheless, the fluorescer-catalyzed chemiluminescence exhibited by the cyclic peroxalate operates through electron exchange as portrayed in eq 5. Although the exact mechanistic



(5)

details are uncertain in eq 5, after the electron-transfer step (k_{cat}) a fraction of the peroxalate radical anion fragments into two molecules of CO_2 and one molecule each of ethylene, acetone, and ketyl radical (k_{frag}). Finally, electron back-exchange (k_{exch}) between the ketyl radical and the fluorescer radical cation produces the latter electronically excited. Apparently this sequence of events is sufficiently exothermic for chemienergization.

Since the rubrene-enhanced chemiluminescence is considerably more efficient than the direct chemiluminescence of the cyclic peroxalate, the contribution to the enhanced emission intensity (I^{EC}) by the direct process via singlet–singlet energy transfer (eq 3) is negligible. Therefore, we can safely consider that the observed enhanced emission intensity is completely electron exchange derived. The enhanced chemiluminescence efficiency is then given by eq 6. For example, at the particular set of experimental

$$\phi^{EC} = \frac{I^{EC}}{k_{cat}[\mathrm{Fl}][\mathrm{peroxalate}]} = \phi^{CIEEL}\phi^{f} \tag{6}$$

conditions employed (Table I), i.e., [peroxalate] = 33.6×10^{-4} M and [rubrene] = 15.3×10^{-4} M, at which the observed enhanced emission intensity is $I_{EC} = (14.6 \pm 1.5) \times 10^{-12}$ einstein/(L·s) and $k_{cat} = (1.28 \pm 0.12) \times 10^{-1}$ M^{-1}·s^{-1} at 392 K, we calculate $\phi^{EC} = (2.25 \pm 0.3) \times 10^{-5}$ einstein/mol. Furthermore, the light yield for the electron exchange process can be calculated from eq 6, in which ϕ^{CIEEL} is the efficiency of electron-exchange luminescence. At the temperature employed, the fluorescence yield of rubrene[16] is $\phi^f = 0.85$, affording $\phi^{CIEEL} = (2.64 \pm 0.3) \times 10^{-5}$ as the experimentally observed electron-exchange luminescence for the cyclic peroxalate–rubrene system. Although the ϕ^{CIEEL} value is considerably smaller than that for other electron-exchange luminescence systems that have been reported,[15] the rubrene-catalyzed enhanced chemiluminescence of the cyclic peroxalate is by magnitudes more efficient than its direct chemiluminescence.

A final point concerns the slope of the ln I_0^{EC} vs. E_{Ox} plot (Figure 3). According to the Weller rate law for electron exchange[17] (eq 7), the slope should be $-1/RT$ or -1.67 at 300 K

$$k_{cat} = (k_BT/Nh)e^{\Delta S^*/R}e^{-(E_{Ox}-E_{Red}-e^2/\epsilon R_0)/RT} \tag{7}$$

for full electron transfer. From Figure 3 we calculate a slope of -0.84 ± 0.10, i.e., ca. 50% of the expected theoretical value. Apparently only a small fraction of the available reaction free energy is channeled into the electron-transfer mode in the transition state.[15]

In conclusion, it appears that the chemically initiated electron exchange chemiluminescence (CIEEL mechanism) is quite general for readily oxidized fluorescers and readily reduced peroxides. Besides the cyclic peroxalate reported here, others include the diphenoyl peroxide,[15] α-peroxylactones,[15,18] *o*-xylylene peroxides,[15] α-pyrone endoperoxides,[19] and peroxyacetate.[15] Such chemiluminescence systems are among the most efficient that are known to date. It is likely that other CIEEL-active peroxides will be discovered in the near future. Our research for such peroxides continues.

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(15) (a) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. (b) *J. Am. Chem. Soc.* **1979**, *101*, 5851.

(16) Abbot, S. R.; Ness, S.; Hercules, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 1128.

(17) Weller, A.; Zachariasse, K. "Molecular Luminescence"; E. C. Lim, Ed.; W. A. Benjamin, New York, 1969.

(18) (a) Adam, W.; Cueto, O.; Yany, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. (b) Adam, W.; Cueto, O. *J. Am. Chem. Soc.* **1979**, *101*, 6511.

(19) Adam, W.; Erden, I. *J. Am. Chem. Soc.* **1979**, *101*, 5693.