Fluorescer-Enhanced Chemiluminescence of α-Peroxylactones via Electron Exchange[1]

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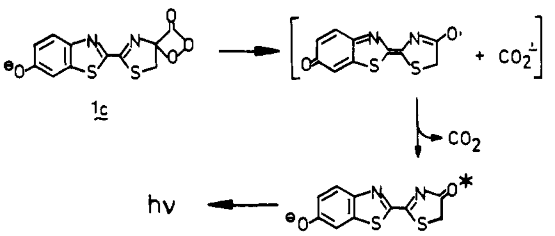
Abstract: Fluorescence of polycyclic aromatic hydrocarbons such as rubrene (Ru), naphthacene (Naph), perylene (Per), and 9,10-diphenylanthracene (DPA) is chemienergized by the dimethyl α-peroxylactone. Two modes of chemienergization operate concurrently, namely, the classical energy transfer process, involving rate-determining unimolecular decomposition of the α-peroxylactone, and the more efficient (ca. 50-fold) novel electron exchange luminescence process, involving a rate-determining bimolecular reaction between the fluorescers and α-peroxylactone. In the latter case the fluorescers enhance the chemiluminescence by catalyzing the decomposition of the α-peroxylactone. The catalysis is in the order of the oxidation potentials of the fluorescers, i.e., Ru $>$ Naph $>$ Per $>$ DPA, as evidenced by a linear dependence of the catalytic rate constants (k_{cat}) and activation energies (E_a) on the fluorescer oxidation potentials (E_{ox}). The β-peroxylactones are ineffective as electron exchange substrates.

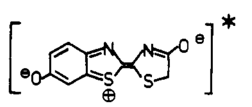
The involvement of α-peroxylactones as energizers of bioluminescence has been clearly established.[4] Although there existed conflict of opinion as to whether these "high-energy" molecules intervened in the firefly bioluminescence,[5a] recently it has been established beyond any reasonable doubt that α-peroxylactones are indeed reaction intermediates in luciferin-type bioluminescence, leading to the observed light emission.[5b,c] However, while the efficiency of light emission by the firefly is essentially quantitative,[6] for chemical model systems, e.g., α-dimethyl and α-*tert*-butyl derivatives, the yield of direct chemiluminescence is very low (ca. 0.1%);[7] i.e., out of 1000 α-peroxylactone molecules that decompose only one lights up.

A plausible rationalization of these apparently divergent results was recently made[8] in terms of the chemically initiated electron exchange luminescence (CIEEL) mechanism.[9] Thus, homolytic cleavage of the firefly α-peroxylactone to afford a solvent caged radical pair and back transfer of an electron from the carbon dioxide radical anion to the enol radical partner are postulated to produce a singlet excited oxyluciferin enolate which efficiently deexcites via fluorescence (eq 1). A key feature in this mechanism is the phenolate ion moiety because blocking of the phenoxyl group to prevent ionization extinguishes essentially completely the firefly bioluminescence.[10]


(eq 1)

1c

Alternatively, it has been suggested[11] that the charge-transfer structure of the singlet excited oxyluciferin enolate (shown below) is formed directly which efficiently deexcites after charge annihilation. A detailed theoretical analysis[12] supports this suggestion since the fluorescence of the oxyluciferin enolate is derived from a low-lying π,π^* singlet with substantial charge transfer from the benzenethiazolyl moiety to the oxythiazoline chromophore. In this context it is interesting and significant to mention that phosphorescence should also be π,π^* triplet derived, but with no significant charge transfer between the chromophores.



If such an intramolecular electron exchange luminescence mechanism indeed applies in the firefly bioluminescence, then it must be demonstrable intermolecularly between simple model compounds such as the α-peroxylactone and readily oxidizable fluorescers. In fact, an early foreboding of this expectation was observed in the fluorescein-enhanced chemiluminescence accompanying the base-catalyzed decomposition of α-hydroperoxy esters which involve the α-peroxylactones.[13] Furthermore, the electron exchange luminescence mechanism could recently be substantiated with the α-peroxylactones directly using polycyclic aromatic hydrocarbons such as rubrene, naphthacene, perylene, and DPA.[14] We now give a more complete and detailed account of our investigation on this problem.

Experimental Section

Materials. The dimethyl α-peroxylactone was prepared as a CH_2Cl_2 stock solution according to reported procedures.[15] The concentrations of these stock solutions, usually 0.01–0.05 M in α-peroxylactone, were determined by quantitative infrared analysis.

Methylene chloride (Baker) was purified according to standard procedures.[16] The metal-free solvent was prepared by stirring the purified CH_2Cl_2 with 50 g/L EDTA for 4 h prior to distillation.

The fluorescers 9,10-diphenylanthracene (Eastman), naphthacene (Aldrich), perylene (Aldrich), and rubrene (Eastman) were used without further purification.

The Packard scintillation glass vials as well as all other glassware were rinsed thoroughly prior to use with aqueous EDTA and dried in a vacuum oven.

Apparatus. Total chemiluminescence intensities were measured with a Mitchell-Hastings photometer,[17] equipped with a RCA PF-1006 or a Hamamatsu Type RP 28 HA photomultiplier tube and a Hewlett-Packard Model 17501 A recorder. Constant temperature in the photometer cell compartment was maintained within 0.5 °C of the desired temperature by means of a Colora variable temperature circulating bath.

Measurements. The Packard scintillation glass vial was charged with 3.0 mL of the fluorescer solution (enhanced chemiluminescence) or CH_2Cl_2 (direct chemiluminescence), placed into the cell compartment, and allowed to equilibrate thermally (ca. 10 min). The required amount of the α-peroxylactone was injected directly into the fluorescer solution and the chemiluminescence signal (in volts) recorded vs. time, usually beyond 2–3 half-lives. The voltage signals were converted to luminescence units (einstein/s·L) using the experimentally established conversion factor $1.87 \pm 0.02 \times 10^{-12}$ einstein/s·L·V. The latter was determined with the help of a calibrated POPOP-PPO scintillation cocktail,[7] kindly supplied by Professor J. W. Hastings, Harvard University.[18] The total intensity emissions of the enhanced chemiluminescence were corrected for relative spectral response of the phototube;[7] however, this was not necessary for the direct chemiluminescence emissions since the acetone fluorescence was within

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Table I. Rate Constants (k_{obsd}, k_{cal}, and k_{dir}) of the Fluorescer-Catalyzed Decomposition of Dimethyl α-Peroxylactone[a] in CH_2Cl_2

entry	temp, K	fluorescer	10^4 Fl, M	$I_0 \times 10^{12}$, einstein/s·L[c]	$10^4 k_{obsd}$, s^{-1} [b]	k_{cal}, $M^{-1} s^{-1}$ [e]	$10^4 k_{dir}$, s^{-1} [f]
1			1.0		5.15 ± 0.12		
2	293	rubrene	4.0		11.6 ± 0.6	2.150 ± 0.055	3.00 ± 0.29
3			8.0		20.2 ± 0.1		
4			1.0	29.4	12.0 ± 0.3		
5	300	rubrene	4.0	190	23.7 ± 0.2	3.915 ± 0.087	8.07 ± 0.45
6			8.0	390	39.4 ± 0.9		
7			1.0		27.2 ± 1.0		
8	308	rubrene	4.0		50.9 ± 0.8	7.915 ± 0.131	19.3 ± 0.7
9			8.0		82.6 ± 0.7		
10			2.0		4.72 ± 0.4		
11	293	naphthacene	5.0		5.77 ± 0.03	0.347 ± 0.032	4.03 ± 0.21
12			10.0		7.50 ± 0.40		
13			2.0	23.0	11.4 ± 0.1		
14	300	naphthacene	5.0	59.3	13.6 ± 0.2	0.711 ± 0.036	10.0 ± 0.2
15			10.0	114	17.1 ± 0.4		
16			2.0		27.4 ± 0.1		
17	308	naphthacene	5.0		31.9 ± 0.4	1.513 ± 0.057	24.4 ± 0.4
18			10.0		39.5 ± 0.6		
19			10.0		4.65 ± 0.04		
20	293	perylene	25.0		5.78 ± 0.20	0.0837 ± 0.0053	3.76 ± 0.17
21			50.0		7.98 ± 0.25		
22			10.0	65.1	10.7 ± 0.2		
23	300	perylene	25.0	163	11.9 ± 0.03	0.247 ± 0.030	7.26 ± 0.03
24			50.0	245	20.2 ± 0.1		
25			10.0		24.7 ± 0.4		
26	308	perylene	25.0		27.4 ± 0.3	0.429 ± 0.046	19.0 ± 1.5
27			50.0		41.3 ± 0.4		
28			15.0		4.16 ± 0.02		
29	293	DPA	30.0		4.26 ± 0.04	0.00667 ± 0.00083	4.06 ± 0.03
30			60.0		4.46 ± 0.04		
31			15.0	47	9.28 ± 0.08		
32	300	DPA	30.0	87	9.55 ± 0.03	0.0182 ± 0.0018	9.00 ± 0.07
33			60.0	183	10.1 ± 0.1		
34			15.0		23.2 ± 0.1		
35	308	DPA	30.0		24.0 ± 0.1	0.0390 ± 0.0074	22.7 ± 0.3
36			60.0		25.0 ± 0.5		
37	300	none[d]		0.0422	10.2 ± 0.1		

[a] At 1.0×10^{-4} M in α-peroxylactone. [b] Calculated from the exponential time profiles of the chemiluminescence decay. [c] Total chemiluminescence emissions extrapolated at t_0 from intensity vs. time plots. [d] Direct chemiluminescence. [e] Slope of k_{obsd} vs. [Fl] plot. [f] Intercept of k_{obsd} vs. [Fl] plot.

2% of that of the POPOP-PPO scintillation cocktail. At the concentrations of fluorescers used, reabsorption was less than 20%.[7] Under the experimental conditions oxygen quenching of the rubrene fluorescence was less than 10%, as confirmed by measuring its photoenergized fluorescence in nitrogen, oxygen, and air purged solutions.

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}). These experimental data are summarized in Table I.

Results

On comparison of the direct chemiluminescence (DC), e.g., run 37 in Table I, with the rubrene-enhanced chemiluminescence (EC), e.g., runs 4-6 in Table I, it is clearly evident that already at [Ru] ca. 10^{-4} M the decomposition of the α-peroxylactone is faster.[19] This catalytic effect holds true for the other fluorescers, but it is less pronounced. Figure 1, in which k_{obsd} for the dimethyl system is plotted against fluorescer concentration [Fl], brings out the catalysis more obviously. Significant is the fact that the fluorescer effect not only increases the rate of decomposition of the α-peroxylactone, but also the light intensity is enhanced, i.e., the catalysis is a chemiluminescent process. In fact, since the k_{obsd} vs. [Fl] plots (Figure 1) are linear for each fluorescer, the rate equation governing the catalysis is that shown in eq 2. Here I is the

$$I = -dP/dt = k_{obsd}[P] \qquad (2)$$

$$\text{where } k_{obsd} = k_{dir} + k_{cal}[Fl]$$

chemiluminescence intensity, which is equal to the rate of α-peroxylactone consumption (dP/dt), and k_{obsd} is the observed first-order rate constant, made up of the direct chemiluminescence contribution characterized by k_{dir} and the enhanced chemiluminescence contribution characterized by k_{cat}. Therefore, from the k_{obsd} vs. [Fl] linear plots (Figure 1) we can extrapolate the k_{dir} values as the intercepts and k_{cal} values as the slopes. These data are summarized in Table I for the α-peroxylactone at the specified conditions. An excellent check on these data is the fact that the k_{dir} values (Table I) extrapolated from the fluorescer-catalyzed plots (Figure 1) match the k_{obsd} values (Table I) measured in the direct chemiluminescence, i.e., no fluorescer present.

Table II. Catalytic Rate Constant (k_{cat}) and Activation Parameters for the Fluorescer-Catalyzed Decomposition of Dimethyl α-Peroxylactone[a] in CH_2Cl_2

fluorescer	temp, K[b]	$10^2 k_{cat}$, $M^{-1}\,s^{-1}$	E_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta G^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, Gibbs/mol	E_{ox}, V vs. SCE
rubrene	293	215 ± 6	15.6 ± 0.3	15.0 ± 0.4	16.7	−5.7 ± 1.2	0.82[c]
	300	392 ± 9					
	308	792 ± 13					
naphthacene	293	34.7 ± 3.2	17.6 ± 0.9	17.0 ± 0.9	17.7	−2.4 ± 2.9	0.95[d]
	300	71.1 ± 3.6					
	308	151 ± 6					
perylene	293	8.37 ± 0.53	19.4 ± 2.2	18.8 ± 2.2	18.5	1.0 ± 2.0	1.06[d]
	300	24.7 ± 3					
	308	42.9 ± 4.6					
DPA	293	0.667 ± 0.083	21.0 ± 2.1	20.3 ± 3.0	20.0	1.1 ± 2.5	1.22[c]
	300	1.82 ± 0.18					
	308	3.90 ± 0.74					
none[e]	293	0.0458 ± 0.0008[f]	19.8 ± 0.2	19.2 ± 0.2	21.7	−8.2 ± 0.5	
	300	0.102 ± 0.001					
	308	0.240 ± 0.001					

[a] At 1.0×10^{-4} M in α-peroxylactone. [b] Within 0.5 K. [c] In CH_2Cl_2, ref 32. [d] Reference 33. [e] Direct chemiluminescence. [f] These values are k_{dir}.

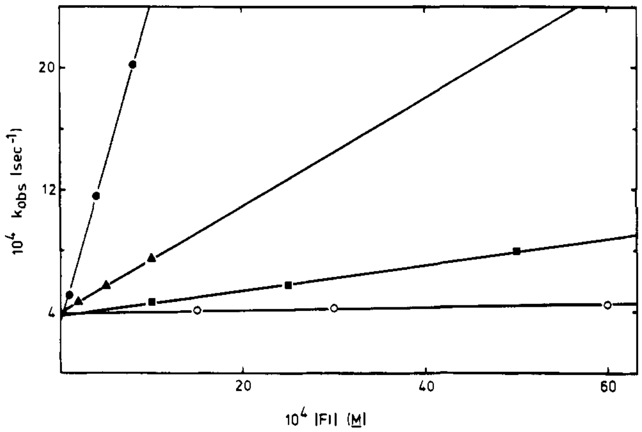


Figure 1. Rubrene- (●), naphthacene- (▲), perylene- (■), and DPA- (○) enhanced chemiluminescence of dimethyl α-peroxylactone in CH_2Cl_2 at 300 K.

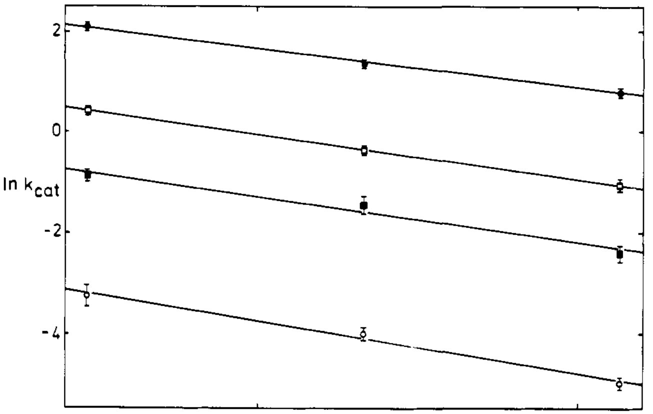


Figure 2. Arrhenius plots of rubrene- (●), naphthacene- (□), perylene- (■), and DPA- (○) enhanced chemiluminescence of dimethyl α-peroxylactone in CH_2Cl_2.

Next the temperature dependence of the fluorescer-catalyzed chemiluminescence was examined. The k_{cat} values and activation parameters are summarized in Table II. Typical Arrhenius plots are exhibited in Figure 2. For comparison the k_{dir} values derived from the direct chemiluminescence as a function of temperature and their activation parameters are also listed in Table II.

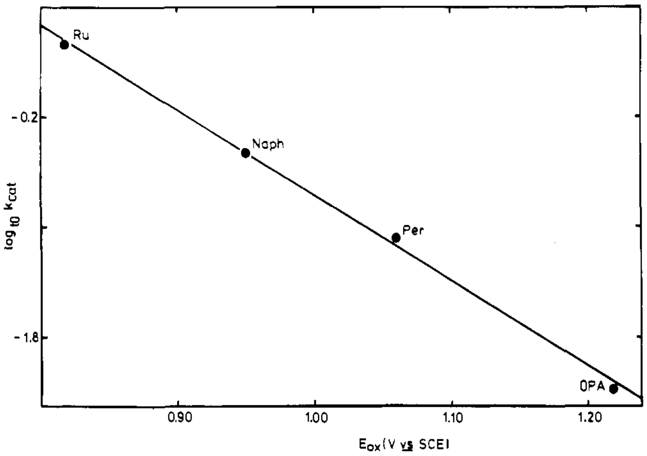


Figure 3. Catalytic rate constants (log k_{cat}) as a function of the oxidation potentials of fluorescers (E_{ox}) at 293 K for dimethyl α-peroxylactone in CH_2Cl_2.

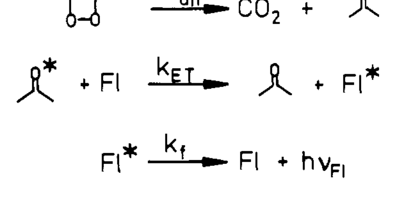
The molecular property which parallels the catalytic ordering Ru > Naph > Per > DPA of the fluorescers is their oxidation potential (E_{ox}). For example, in Figure 3 a plot of log k_{cat} vs. E_{ox} is linear for the α-peroxylactone. Furthermore, in Figure 4 the activation energies (E_a) for the catalytic process depend linearly on the oxidation potentials (E_{ox}) of the fluorescers. Thus, the CIEEL mechanism[9] operates in the fluorescer-enhanced chemiluminescent decomposition of α-peroxylactones.

Discussion

The present results confirm that the fluorescers, especially rubrene, become chemienergized by the α-peroxylactone via two distinct but concurrent mechanisms. These are the classical energy transfer and the novel electron exchange processes.

In the classical energy transfer mechanism (eq 3), decar-

(eq 3)



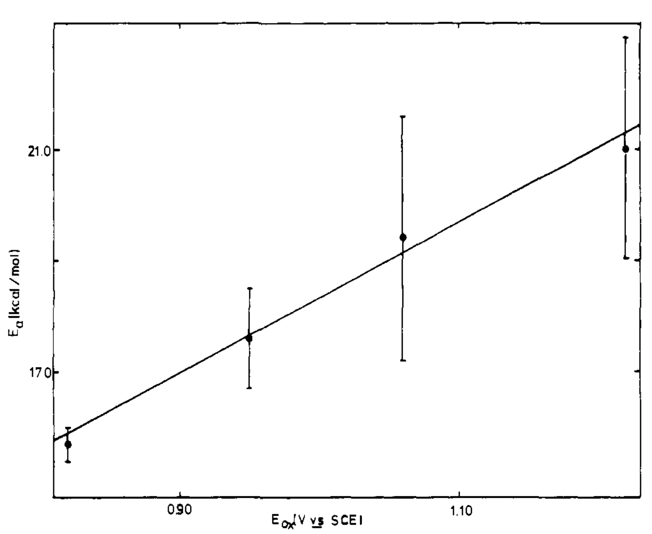


Figure 4. Activation energy (E_a) as a function of the oxidation potentials of fluorescers (E_{ox}) for the dimethyl α-peroxylactone in CH_2Cl_2.

boxylation affords directly electronically excited carbonyl product (k_{dir}), e.g., acetone from the dimethyl α-peroxylactone, via a unimolecular process. Subsequently, the electronically excited product may transfer (k_{ET}) its excitation energy to the fluorescer, which then photodeactivates (k_f) via fluorescence. The rate-determining step is the chemienergizing step, i.e., the first step k_{dir}. The chemiluminescence efficiency (ϕ_{CL}) depends on the efficiency of chemienergization (ϕ_{dir}), the energy-transfer efficiency (ϕ_{ET}), and the fluorescence yield (ϕ_f) of the fluorescer (eq 4). Since the fluorescers used in this

$$\phi_{CL} = \phi_{dir}\phi_{ET}\phi_f \qquad (4)$$

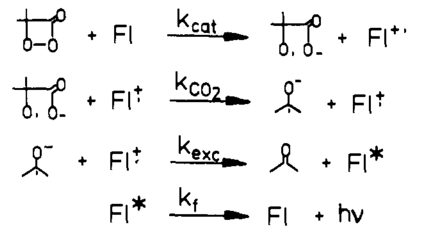
$$\text{where } \phi_{dir} = \phi_S$$

study can only be efficiently energized by singlet-singlet energy transfer, the chemienergization efficiency (ϕ_{dir}) is equal to the efficiency of singlet excited state production (ϕ_S). From direct chemiluminescence measurements[7] we determined previously that $\phi_S \sim 5 \times 10^{-4}$. With the help of the published fluorescence quantum yield values[20] and under conditions of complete energy transfer, i.e., at infinite [Fl], the maximum possible chemiluminescence yield should be $\phi_{CL} \sim 5 \times 10^{-4}$ or 0.05%. More important, the higher the [Fl], the higher the light yield, but the rate of α-peroxylactone decomposition is not altered since the rate-determining chemienergizing step (k_{dir}) is a unimolecular process, not engaging the fluorescer at this point.

We observed previously,[7] however, that the total maximum light yield with rubrene as enhancer was ca. 2.6% for the dimethyl α-peroxylactone. Clearly this is ca. 50-fold greater than expected from a singlet-singlet energy transfer process. Originally we suggested that this light amplification by rubrene was derived from triplet-triplet energy transfer between chemienergized carbonyl product and rubrene, followed by rubrene triplet-triplet annihilation. Our present findings speak against this interpretation. First of all, in the presence of molecular oxygen such a process should be efficiently quenched.[7] Second, 9,10-dibromoanthracene (DBA), an established counter of triplet states,[21] gave a lower light intensity than DPA. Finally, Schuster[22] and we[23] showed that the triplet yield of acetone from the α-peroxylactone was ca. 1%, using direct phosphorescence and triplet titration.

In view of these results and the facts that the fluorescer is involved in the rate-determining step (Figure 1) and the chemienergization process depends on the ease of oxidation of the fluorescers (Figure 3), the electron exchange mechanism shown in eq 5 was offered instead to account for these unusual findings.[14] In this novel mechanism the rate-determining step (k_{cat}) involves electron transfer from the fluorescer to the α-peroxylactone, generating a radical cage of fluorescer radical cation and α-peroxylactone radical anion. Subsequent in-cage decarboxylation (k_{CO_2}) affords a ketyl radical, which on electron back exchange (k_{exc}) leads to electronically excited fluorescer. The latter photodeactivates by fluorescence (k_f).

(eq. 5)



The rate of this type of electron exchange process is controlled by the rate law given in eq 6.[24] It is, therefore, imme-

$$I_t = k_{cat}[\text{Fl}][\alpha\text{-peroxylactone}] \qquad (6)$$

$$\text{where } k_{cat} = (k_B T/Nh)e^{-\Delta S^{\ddagger}/R}e^{-(E_{ox}-E_{red}-e^2/\epsilon R_0)/RT}$$

diately apparent that the rate of α-peroxylactone decomposition is catalyzed by the fluorescer (Figure 1) and that in this catalysis log k_{cat} (Figure 3) and $\Delta H^{\ddagger}$ (Figure 4) follow a linear dependence on the oxidation potential (E_{ox}) for a particular α-peroxylactone.

The Weller rate law for electron exchange (eq 6) demands a slope of $-1/RT$ for full electron transfer, i.e., -1.67 at 300 K. From Figure 3 or the data in Table II we calculate a slope of -0.6 ± 0.1, i.e., ca. one-third of the expected theoretical value. Consequently, the charge transfer is extensive (ca. 36%) between the α-peroxylactone and fluorescer in the activated complex of the catalyzed process, but it is not complete. Apparently only a fraction of the available reaction free energy is available in the activated complex for the electron-transfer process.[25]

The light yield of this electron exchange process is given by

$$\phi_{CL} = \phi_{CIEEL}\phi_f \qquad (7)$$

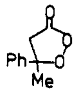
$$\text{where } \phi_{CIEEL} = \phi_{cat}\phi_{CO_2}\phi_{exc}$$

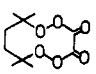
in which the chemienergization efficiency ϕ_{CIEEL} depends on how effective the catalytic step (ϕ_{cat}) is in generating the initial radical cage, how much of the α-peroxylactone radical anion in the initial radical cage decarboxylates (ϕ_{CO_2}) into the ketyl radical prior to diffusion, and how efficient the electron back exchange (ϕ_{exc}) is. No experimental or even theoretical data are available on these individual efficiencies; but, since the overall light yields are of the order of a few percent, it is clear that chemienergization via electron exchange can be an effective luminescent process. For example, for the simple α-peroxylactone examined in this study, the electron exchange process is several magnitudes more effective in enhancing the fluorescer chemiluminescence than the energy transfer process.

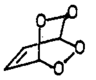
On the basis of thermokinetic estimates ca. 100 kcal/mol or 4.5 eV of chemical energy is bound in the α-peroxylactones. This guarantees that sufficient energy is available in the α-peroxylactone-fluorescer system to produce the ketyl radical anion-fluorescer radical cation pair after electron transfer (k_{cat}) and decarboxylation (k_{CO_2}). For example, in the case of the dimethyl α-peroxylactone and DPA (the least effective fluorescer), ca. 3.38 eV is required minimally to generate the acetone radical anion-DPA radical cation pair since the reduction potential of acetone is 2.16 eV[26] and the oxidation potential of DPA is 1.22 eV. For the dimethyl α-peroxylactone–rubrene (the most effective fluorescer) combination ca. 2.98 eV is required to produce the acetone radical anion–rubrene cation pair since the rubrene oxidation potential is only 0.82 eV. In the electron back transfer step (k_{exc}) of eq 5, i.e., charge annihilation between the radical cations and anions, these energies, i.e., at least 3.38 eV for DPA and 2.98 for Ru, are released for the generation of fluorescer excited states. Since the singlet excited states[27] of DPA and Ru are 3.16 and 2.51 eV, respectively, charge annihilation is energy sufficient and chemienergization probable.

DBA (9,10-dibromoanthracene) could not be chemienergized by the α-peroxylactone via electron exchange, although its singlet excited state lies at 3.04 eV[28] and it does fluoresce appreciably ($\phi_f \sim 0.10$).[27] Since its oxidation potential is 1.42 eV,[29] during electron back transfer (charge annihilation) between the acetone radical anion and DBA radical cation minimally ca. 3.58 eV should be released. This is more than enough to chemienergize DBA fluorescence. Apparently the oxidation potential of DBA is too high and the α-peroxylactone is not a powerful enough oxidant to generate the acetone radical anion–DBA radical cation pair. Without this initial electron transfer (k_{cal}) there can be no enhanced chemiluminescence via the CIEEL mechanism.

It is of interest to mention that β-peroxylactones are ineffective in generating rubrene fluorescence by electron exchange. Even upon heating solutions of the β-peroxylactone in the presence of rubrene to the point of appreciable unimolecular decomposition (100–120 °C), the light yields are at least four magnitudes below that of the α-peroxylactone. On the other hand, the cyclic peroxalate[30] and the α-pyrone endoperoxide[31] both exhibit enhanced chemiluminescence on thermal decomposition with significant rate enhancement in the presence of readily oxidized rubrene. Therefore, also for these substrates the CIEEL mechanism operates.







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(19) We have observed that k_{obsd} is also dependent on α-peroxylactone concentration, i.e., at higher concentration the k_{obsd} is larger.[7] For example, for naphthacene k_{obsd} values are 5.41×10^{-3} and 1.71×10^{-3} s^{-1}, respectively, at 1.95×10^{-4} and 1.00×10^{-4} M α-peroxylactone concentrations and 1×10^{-3} M naphthacene concentration at 300 K in CH_2Cl_2. This effect is perfectly reproducible and appears not to be due to impurities since α-peroxylactone samples with completely different synthetic histories behaved identically. We have no explanation as yet for this concentration effect; however, our original k_{obsd} values in ref 14b and the present values are not directly comparable because they are at different α-peroxylactone concentrations.
(20) The fluorescence yields of the fluorescers used are unity [cf. Wilson, T.; Schaap, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 4126] except for naphthacene, for which ϕ_f is 0.16 [cf. Stevens, B.; Algar, B. E. *Chem. Phys. Lett.* **1967**, *1*, 58].
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