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Electron Transfer and Chemiluminescence. Two Inefficient Systems: 1,4-Dimethoxy-9,10-diphenylanthracene Peroxide and Diphenoyl Peroxide

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Abstract: The 1,4-endoperoxide of 1,4-dimethoxy-9,10-diphenylanthracene (**1**) rearranges under mild acidic conditions to the 1,2-dioxetane **3**, which has now been characterized by NMR. The decomposition of **3** is catalyzed by fluorescers (such as **1**) in a bimolecular process which populates their singlet excited state and generates the well-known chemiluminescence. There are significant similarities between this indirect chemiluminescence and that of other peroxides which have been interpreted as examples of the CIEEL mechanism:[1] the pseudo-first-order rate of decomposition of **3** is a linear function of the activator (fluorescer) concentration, $k_{obsd} = k_1 + k_2[ACT]$, where k_2 increases as the oxidation potential of the activator decreases. A linear plot of log k_2 vs activator's E_{ox} is scattered but reasonably convincing. The quantum yield associated with the activated decomposition of **3** is only ca. 2×10^{-5} einstein per mol of **3** reacting with activator. Since this value is 4 orders of magnitude lower than that reported for the very similar reaction of diphenoyl peroxide, the latter system was reinvestigated and found, under our conditions, to be equally inefficient. The implications of these results are discussed.

The suggestion that *intermolecular* electron transfer plays a key role in some solution chemiluminescence has received a great deal of attention in recent years.[1] Fluorescers, it is proposed, can act as catalysts of the decomposition of some peroxides by a process of "chemically induced electron exchange luminescence" (CIEEL),[1a,2] which is regarded as an efficient pathway of generation of excited singlet states. We have tested the CIEEL hypothesis on one of the classic examples of chemiluminescence, that of polyacenes endoperoxides. Strong analogies between this system and the chemiluminescence of diphenoyl peroxide,[2] the prototypical example of intermolecular CIEEL, led us to reinvestigate this reaction. We found both chemiluminescences to be disappointingly inefficient.

Sixty years ago, Dufraisse and co-workers[3] reported that decomposition of polyacenes peroxides generates molecular oxygen and the polyacene. The most chemiluminescent of these compounds, the 1,4-endoperoxide **2** of 1,4-dimethoxy-9,10-diphenylanthracene (**1**), is also the most thermally labile; the formation of the peroxide is fully reversible.[3-5] This is truly a unique photochemical reaction: formation of the peroxide is a singlet oxygen reaction, while its decomposition regenerates molecular oxygen quantitatively, a large fraction, if not all of it, in the singlet excited state.[4] The sharp peak at 1.28 μm associated with the (0,0) transition of $O_2\ {}^1\Delta_g \rightarrow {}^3\Sigma_g$ was recently recorded.[6] Moreover, the activation energy of the decomposition of **2**, ca. 19-25 kcal/mol, is roughly equal to the excitation energy of ${}^1O_2({}^1\Delta_g)$, i.e., 22.5 kcal. Thus this process could be regarded as a spin-controlled, infrared chemiluminescent reaction with a quantum yield of ~1.

But the visible chemiluminescence has a different origin. The endoperoxide **2** is highly sensitive to traces of acids, which catalyze a rearrangement to aldehyde ester **4** and other minor products.[7] We previously showed[5] that it is this rearrangement, presumably via dioxetane **3**, which leads to visible chemiluminescence, not the process which regenerates **1** and ${}^1O_2$. In pyridine the thermolysis of **2** reforms **1** quantitatively with no visible chemiluminescence; in toluene, due to adventitious traces of acid, little **1** is reformed, while a blue-green chemiluminescence develops with a spectrum matching the fluorescence of **1** (peak at ca. 480 nm). We proposed[5] at the time that the chemiluminescence results from a compromise between the uncatalyzed path producing **1** (the emitter) and the acid-catalyzed rearrangement of **2** giving the dioxetane and a hypothetical "energy-rich precursor". This excited intermediate was thought to excite **1** via energy transfer, an assumption shown here to be incorrect.

The goals of the present study were to confirm the intermediacy of dioxetane **3** and to identify the excitation mechanism which, as that of diphenoyl peroxide, remains a topic for discussion, due to the low quantum yields of these two reactions.

Results

1. Intermediacy of a Dioxetane. Organic acids (acetic or benzoic acid) and mineral acids (HCl to H_2SO_4) as well as silica gel act as catalysts of the rearrangement of peroxide **2** to **3**; but these acids also quickly decompose the dioxetane through a nonchemiluminescent pathway, making it impossible to isolate the already thermally unstable dioxetane. Its presence was neverthless established by low-temperature NMR spectroscopy[8] (Figure 1). The assignment of protons in position 2, 3, 5, and 6 was based on decoupling experiments and similarity with known structures.[9] The carbons at positions 1-6 were assigned on the

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(1) Reviews: (a) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187. (b) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. (c) Wilson, T. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC: Boca Raton, FL, 1985; Vol. II, pp 37-57.

(2) Koo, J.-Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *18*, 187.

(3) (a) Moureu, C.; Dufraisse, C.; Dean, P. M. *Compt. Rend. Acad. Sci.* **1926**, *182*, 1584. (b) Dufraisse, C.; Velluz, L. *Bull. Soc. Chim. Fr.* **1942**, *9*, 171. (c) Dufraisse, C.; Rigaudy, J.; Basselier, J. J.; Cuong, N. K. *Compt. Rend. Acad. Sci.* **1965**, *260*, 5031.

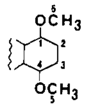
(4) Turro, N.; Chow, M.-F.; Rigaudy, J. *J. Am. Chem. Soc.* **1981**, *103*, 7218.

(5) (a) Wilson, T. *Photochem. Photobiol.* **1969**, *10*, 441. (b) Other authors reached the same conclusion independently: Lundeen, G. W.; Adelman, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 3414.

(6) Wilson, T.; Khan, A. U.; Mehrotra, M. M. *Photochem. Photobiol.* **1986**, *43*, 661.

(7) (a) Rigaudy, J.; Deletang, C.; Sparfel, D.; Cuong, N. K. *Compt. Rend. Acad. Sci.* **1968**, *267*, 1714. (b) Baldwin, J. E.; Basson, H. H.; Krauss, H. *Chem. Commun.* **1968**, 984.

(8) NMR assignments (d in ppm) for protons (500 MHz, $CDCl_3$) and for carbons (125 MHz, $CDCl_3$): (**1**) ${}^1H$ NMR 6.61 (s, 2 H), 3.38 (s, 6 H); ${}^{13}C$ NMR (bb) 150.8, 104.2, 56.2; (**2**) ${}^1H$ NMR 7.09 (s, 2 H), 3.29 (s, 6 H); ${}^{13}C$ NMR (bb) 105.6, 104.1, 53.1; (**3**) ${}^1H$ NMR 6.31 (d, 1 H, ${}^2J = 6.4$ Hz), 4.92 (d, 1 H, ${}^2J = 6.4$ Hz), 3.33 (s, 3 H), 3.24 (s, 3 H); ${}^{13}C$ NMR (bb, DEPT) 160.0, 105.0, 91.5, 79.5, 55.0, 49.5; (**4**) ${}^1H$ NMR 9.26 (d, 1 H, ${}^2J = 8.1$ Hz), 5.42 (d, 1 H, ${}^2J = 8.1$ Hz), 3.61 (s, 3 H), 3.51 (s, 3 H); ${}^{13}C$ NMR (bb, DEPT) 192.5, 178.3, 168.9, 107.2, 56.8, 52.4.



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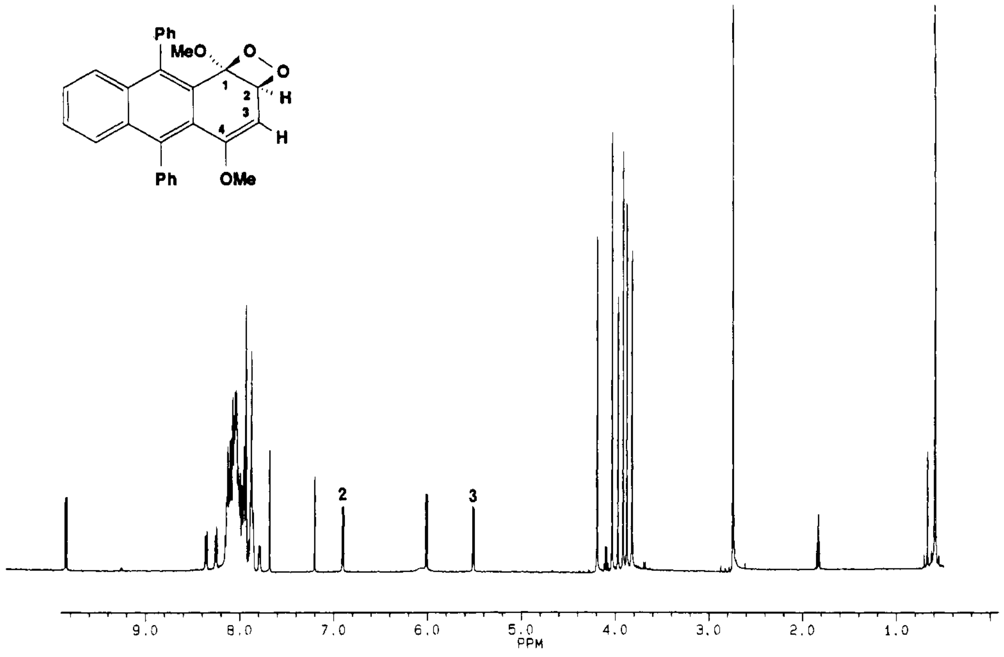
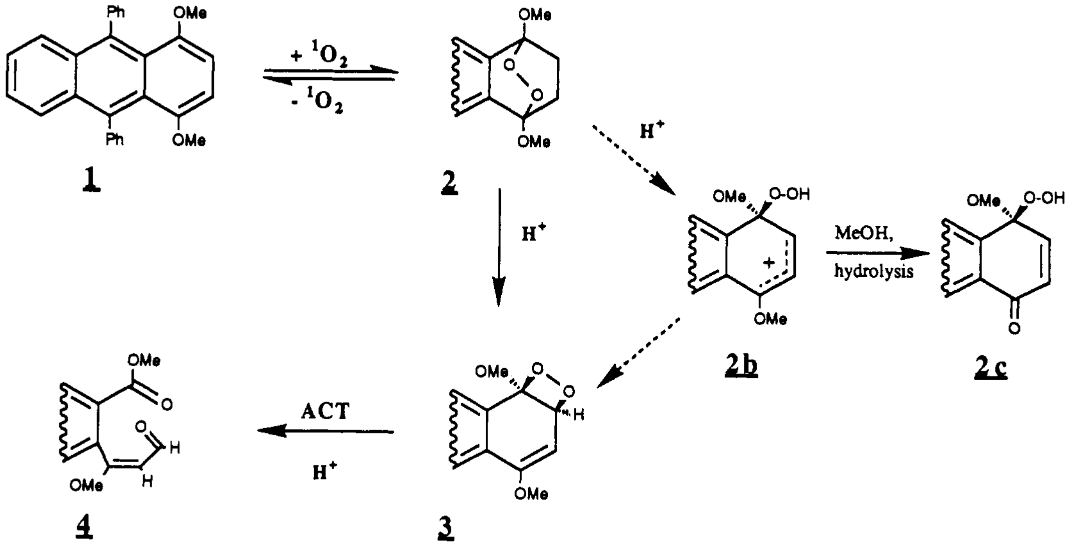


Figure 1. ^1H NMR spectrum of dioxetane **3** in a $CDCl_3$ solution of endoperoxide **2** and acetic acid at −35 °C.

Scheme I



basis of broad-band, DEPT, and specific-decoupling experiments against authentic material of **1**, **2**, and **4**. Upon heating in the NMR probe, the dioxetane signals decrease with concomitant increase of the peaks assigned to aldehyde ester **4**, the sole product.

The ^1H NMR of a solution of **2** in toluene-d_8 (no added acid) shows that **3** and **4** grow at the expense of **2**, along a time course of days at −20 °C. The relative rates of rearrangement of **2** to **3** and decomposition of **3** to **4** determine the maximum dioxetane concentration (5–10% of the initial concentration of **2** in these conditions). The addition of 1 equiv of acetic acid directly to a $CDCl_3$ solution of **2** at −35 °C resulted in up to 43% conversion of **2** to **3** but with faster decomposition of **3** to **4** (half-life of **3**, 1 h). In contrast, in pyridine-d_5 the decomposition of endoperoxide **2** led to exclusive formation of anthracene **1**, as previously reported.

The intramolecular rearrangement of endoperoxide to dioxetane is probably a double bond shift, via a hydroperoxide-like intermediate **2b** which subsequently cyclizes to the dioxetane **3**. An indication of the involvement of structure **2b** was obtained when a trapping product **2c** was detected in the reaction of **2** with acetic acid, at 20 °C in MeOH as solvent.[10]

2. Conditions for Light Emission. The time course of the chemiluminescence form a toluene solution of **2** at 50 °C is as follows. After an initial peak, attributed to the thermolysis of preaccumulated dioxetane, the light intensity increases to a maximum in ca. 1 h and then slowly decays (not first order). This behavior can be explained by the rearrangement of **2** to **3**, catalyzed by traces of acid present as impurity, and the subsequent thermolysis of **3**. If **1** is added to a solution of **2**, the intensity reaches a maximum earlier but decays faster. Addition of acetic

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(9) For comparison with similar structures, see: (a) Clennan, E. L.; L'-Esperance, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 5178. (b) Clennan, E. L.; Lewis, K. K. *J. Am. Chem. Soc.* **1987**, *109*, 2475.

(10) Endoperoxide **2** (100 mg) was suspended in 50 mL of MeOH at 0 °C, and 50 μL of HAc was added. After 12 h 50 mL of CH_2Cl_2 was added, and the solution was washed with $NaHCO_3$ (aqueous) and brine, dried over $MgSO_4$, and rotaevaporated. The residue was purified by thin-layer chromatography (SiO_2 eluted with CH_2Cl_2/Ethylacetate, 95:5). The spot at R_f 0.35 was removed, washed, and reapplied to TLC plate (SiO_2 eluted with CH_2Cl_2/ethylacetate, 88:12). The peroxidic spot at R_f 0.47 was removed and analyzed by ^1H NMR. The analyses showed signals corresponding to aldehyde ester **4** and hydroperoxide **2c** in a mixture of 2:1 ratio: ^1H NMR for **2c** (300 MHz, $CDCl_3$) d in ppm 9.09 (b, 1 H), 7.13 (d, 1 H, ^2J = 10.5 Hz), 6.48 (d, 1 H, ^2J = 10.5 Hz), 3.12 (s, 3 H).

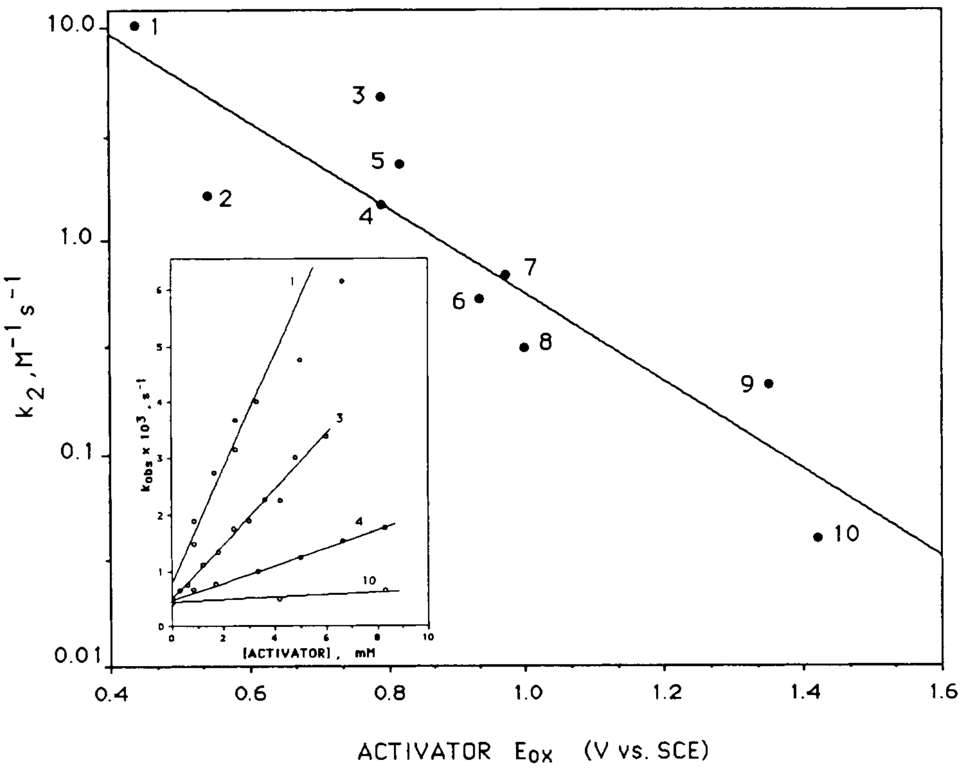


Figure 2. Dependence of catalytic rate constant k_2 on oxidation potential of activator. Inset: effect of activator concentration on rate of decay of chemiluminescence intensity (slope is k_2). All in *p*-dioxane–toluene (11/1, v/v) at 50 °C. Activators numbered as in Table I.

acid increases the peak intensity and also shortens the time needed to reach it. Pyridine or triethylamine rapidly quench the light-emitting reaction, an effect which can be reversed by addition of acid.

The effects of solvents on the course of chemiluminescence from **2** seems to be mainly a function of their ability to provide the right amount of acid as impurities. In $CHCl_3$, CH_2Cl_2, and other solvents where formation of traces of acid is difficult to prevent or control, **2** decomposes fast to **4** but with very low chemiluminescence. **2** is stable in toluene freshly filtered over basic alumina, but the concentration of **3** slowly builds up in untreated toluene (see above), where the concentration of acid-catalyzing impurities seems optimum for dioxetane accumulation.

In freshly distilled *p*-dioxane, endoperoxide **2** is fairly stable against rearrangement, and no dioxetane formation is observed. The addition of an aliquot of an "aged" solution of **2** in toluene, used as a dioxetane "stock" solution, to a solution of a fluorescer in *p*-dioxane gives a luminescence which now decays according to first-order kinetics. Thus chemiluminescence is strictly due to decomposition of dioxetane already present in the toluene solution. Because of the clean kinetics in these conditions, most experiments reported here were performed in *p*-dioxane containing a small volume of a toluene solution of dioxetane (usually *p*-dioxane–toluene 11/1, v/v) at 50 °C. Note that such solutions are unavoidably contaminated by traces of **1**; see below.

3. Evidence for an "Activated" Chemiluminescence. In general, we found that the first-order rate constants, k_{obsd}, of chemiluminescence decay in *p*-dioxane are linearly dependent on the concentration of added fluorescer (eq 1); thus the major pathway

$$k_{obsd} = k_1 + k_2[ACT] \qquad (1)$$

to light emission is a bimolecular process between dioxetane and fluorescer (or "activator", in Schuster's terminology).[1] Figure 2 (inset) shows examples of the dependence of k_{obsd} on the concentration of added activators. (As mentioned above, the intercept k_1 comprises a small contribution from the decomposition of **3** catalyzed by traces of **1** in the toluene stock solution). With some fluorescers, notably perylene, the light intensity decay deviates from first-order: the plots of log *I* vs time show upward curvature, especially at high concentrations of perylene, and the plots according to eq 1 are not strictly linear either. We do not yet understand the cause of these deviations. The chemiluminescence spectrum matches the fluorescence spectrum of the activator present, and the initial chemiluminescence intensity is proportional to its concentration; plots of I_0 vs [ACT] are similar to those of Figure 2.

Table I. Dependence of Catalytic Rate Constant k_2 on Activator Oxidation Potential[a]

	activator	E_{ox}, V (vs SCE)	k_2, $M^{-1}\ s^{-1}$
1.	2-aminoanthracene	0.44[b]	10.1
2	1-aminonaphthalene	0.54[b]	1.64
3.	1,4-dimethoxy-9,10-diphenylanthracene (**1**)	0.79[c]	4.82
4.	1,3-diphenylisobenzofuran	0.79[d]	1.49
5	10-methylphenothiazine	0.82[e]	2.30
6.	perylene	0.93[f]	0.53
7.	rubrene	0.97[g,h]	0.69
8.	triethylamine	1.00[i]	0.31
9.	9,10-diphenylanthracene	1.35[e,j]	0.21
10.	9,10-dibromoanthracene	1.42[k]	0.04

[a] At 50 °C in *p*-dioxane–toluene (11/1, v/v). The E_{ox} values refer to measurements in acetonitrile solutions unless otherwise indicated. [b] Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. [c] This work and Cruanes, M., University of Illinois, personal communication. [d] Zweig, A.; Metzler, G.; Maurer, A. H.; Roberts, B. G. *J. Am. Chem. Soc.* **1967**, *89*, 4091. [e] In dimethyl formamide: Faulkner, L. R.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1971**, *94*, 691. [f] This work. Range in lit: 0.12. [g] Chang, M.-M.; Saji, T.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 5399. [h] 0.82 V in CH_2Cl_2: Phelps, J.; Santhanan, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1967**, *89*, 1752. [i] Calcd from E_{ox} = 0.66 vs Ag/0.1 M $AgNO_3$: Mann, C. K. *Anal. Chem.* **1964**, *36*, 2424. [j] 1.20 V in CH_2Cl_2, ref h. [k] Parker, V. D. *Acta. Chem. Scand.* **1970**, *24*, 2775.

It is clear that k_2 and I_0 depend on the nature of the activator. In the case of the chemiluminescent decomposition of diphenoyl peroxide, Schuster et al.[2] showed that k_2 depends on the oxidation potential of the activator; they presented a linear free energy plot of ln k_2 vs E_{ox} for six activators with oxidation potentials in the rather narrow range 0.8–1.36 V (vs SCE).[2] Table I and Figure 2 demonstrate a similar dependence of k_2 on E_{ox}[11] over a wider

Table II. Solvent Effects on the Chemiluminescence of Diphenoyl Peroxide at 32.5 °C with Perylene as Activator[a]

solvent	$k_1 \times 10^4$, s^{-1}	k_2, $M^{-1}\ s^{-1}$	rel Φ_{CL}	ϵ[b]	η, mp[c]
CH_2Cl_2	4.4 (4.5)	1.6 (1.5)	1 (1)	8.9	3.9
benzene	6.1 (5.5)	0.6 (0.5)	2.3 (3.3)	2.3	6.0
ether	5.2 (5.6)	0.1 (0.06)	8.5 (15.4)	4.3	2.2
p-dioxane	5.4	0.5	2.1	2.2	12.0

[a] Comparison of the results of this work with those of Koo and Schuster[2] (values in parentheses). [b] Dielectric constant. [c] Viscosity.

range. A plot of log I_o vs E_{ox} has the same slope. Although the data points are scattered, in part because of uncertainties on the values of E_{ox}, the *trend* is evident; it indicates the role of either electron transfer or charge transfer.

4. Chemiluminescence Quantum Yield. Equations 2–6 where D is dioxetane **3** describe our observations without presuming the mechanism:

$$D \xrightarrow{k_1} \mathbf{4} \tag{2}$$

$$D + ACT \xrightarrow{\Phi_{CL}k_2} \mathbf{4} + ACT^* \tag{3}$$

$$D + ACT \xrightarrow{(1-\Phi_{CL})k_2} \mathbf{4} + ACT \tag{4}$$

$$ACT^* \xrightarrow{\Phi_F k_F} ACT + h\nu \tag{5}$$

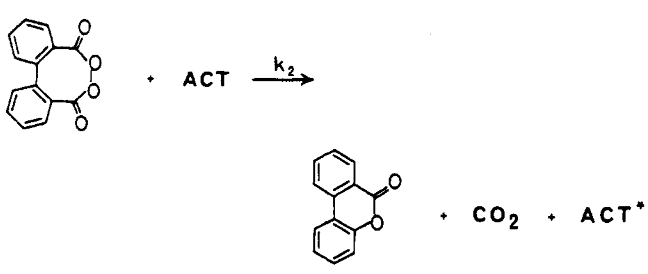
$$ACT^* \xrightarrow{(1-\Phi_F)k_F} ACT \tag{6}$$

Steady-state treatment leads to the following expression for the chemiluminescence quantum yield from the activated reaction path

$$\Phi_{CL} = I_o/\{\Phi_F k_2[ACT][D]_o\} \tag{7}$$

where I_0 and $[D]_0$ are the initial intensity and concentration of dioxetane **3**, [ACT] is the concentration of the activator, and Φ_F its fluorescence efficiency in *p*-dioxane at the temperature of the experiment ($\Phi_F = 0.75$ for **1**; 1.0 for rubrene, at 50 °C). (**Note Added in Proof**: As defined by eq 3, Φ_{CL} is an excitation yield, not an overall photon production yield. These two yields are the same with such activators as rubrene or perylene, which have fluorescence efficiencies of unity.) $[D]_0$ was calculated from the molarity of the toluene stock solution, which was determined by ^1H NMR in toluene-d_8 at −20 °C using acetone as standard 1 h prior to the experiment. The chemiluminescence quantum yield Φ_{CL} of **3** activated by **1** or by rubrene is $(2 \pm 1) \times 10^{-5}$ E/mol.

5. Comparison with Diphenoyl Peroxide. Such a low value of Φ_{CL} led us to reinvestigate the chemiluminescence of diphenoyl peroxide. Table II lists the values of Φ_{CL}, k_1, and k_2 in three different solvents with perylene as activator. All rate constants are in reasonable agreement with the literature, but our values of Φ_{CL} are *4 orders of magnitude* lower than the value (10%) reported by Koo and Schuster.[2] In our hands the perylene-activated decomposition of diphenoyl peroxide in CH_2Cl_2 at 32.5 °C has, like **3**, a quantum efficiency of $(2 \pm 1) \times 10^{-5}$ E/mol.[12]



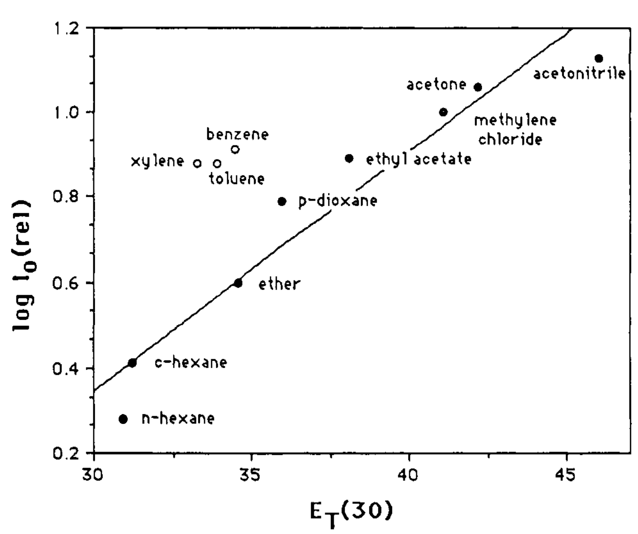


Figure 3. Effect of solvent polarity on initial intensity of chemiluminescence from diphenoyl peroxide: plot of log I_0(rel) vs solvent $E_T(30)$, with log I_0 = 1.0 for methylene chloride. Perylene (7.4×10^{-5}M) as activator. Diphenoyl peroxide concentration: 4.0×10^{-4}M. All solutions contained 3% CH_2Cl_2 per volume.

Table III. Comparison of Reaction Rates in Peroxide Chemiluminescence Reported To Follow CIEEL Mechanisms[f]

peroxide	solvent	temp, °C	k_1, s^{-1}	k_2, $M^{-1}\ s^{-1}$	k_2/k_1, M^{-1}
diphenoyl peroxide[a]	CH_2Cl_2	32.5	4.5×10^{-4}	1.5	3300
dimethyl-dioxetanone[b]	benzene	24.5	7.8×10^{-4}	5.2×10^{-3}	6.6
phenylethyl peroxyacetate[c]	benzene	99.5	1.1×10^{-4}	1.2×10^{-4}	1.1
malonyl peroxide[d]	CH_3CN	80.0	8.0×10^{-4}	1.6	2000
dioxetane **3**[e]	dioxane	50.0	4.4×10^{-3}	0.5	120

[a] Reference 2. [b] Reference 15. [c] Reference 16. [d] 4-Methyl-4-(1-propenyl)malonyl peroxide, ref 14. [e] This work. [f] With perylene as activator.

Table II as well as already available data in a few other solvents shows that Φ_{CL} varies little with solvent. Since with a given activator $I_o = Bk_2\Phi_{CL}$ (where B is a constant determined by temperature and concentrations of activator and peroxide), it is implicit in these results that I_0 is quite independent of the solvent. We have verified this conclusion and extended it to a larger range of solvents. Figure 3 shows a plot of log I_0 versus the polarity parameter $E_T(30)$ based on charge-transfer transitions;[13] the initial chemiluminescence intensity increases with solvent polarity but only by a factor of 7 between nonpolar hexane and strongly polar acetonitrile. (Aromatic solvents do not fit on the line, as previously noted.)[2] The solvent viscosity appears to have very little effect on I_0 judging by an experiment in dibutylphthalate, which gave an I_0 value similar to that in acetonitrile. The $E_T(30)$ value of dibutylphthalate is unfortunately not known, but since it is both aromatic and more polar than benzene, the high viscosity of this solvent (ca. 20× that of benzene) has clearly no major effect on I_0.

Discussion

The role of long-suspected dioxetane **3** was confirmed. We have shown that fluorescers, including anthracene **1**, are active participants in its chemiluminescent thermolysis, not mere acceptors of energy, and that the oxidation potential of these fluorescers influences both reaction rate and chemiluminescence intensity.

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(11) In the case of 1-aminonaphthalene and triethylamine, the reaction rate was followed by monitoring the fluorescence of traces of **1** in the solution. Note that 9,10-dibromoanthracene is a poorer activator than 9,10-diphenylanthracene, indicating that excitation does not result from energy transfer from a high-energy triplet donor. The absorption spectra and the S_1 energies of these two anthracenes are very similar, so that in an energy-transfer process they should have similar efficiencies as acceptors of singlet energy.

(12) At our request, Dr. Schuster kindly sent us copies of J.-Y. Koo's primary data (luminescence intensity vs concentration of perylene in the case of diphenoyl peroxide and intensity vs [DBA] in the case of tetramethyldioxetane which was used for calibration). From these data we calculate $\Phi_{CL} \sim 10^{-4}$ E/mol. We were pleased to learn, after submission of this paper, that Gary Schuster agrees with this re-evaluation and thus with the very low efficiency of the diphenoyl peroxide chemiluminescence.

(13) Reichert, C. *Solvent Effects in Organic Chemistry*; Verlag-Chemie: Weinheim, 1979.

Thus in all major aspects, the reaction of dioxetane **3** follows a course similar to that of diphenoyl peroxide. Apart from the important difference in quantum yield, we reproduced here the key points (eq 1 and 7 and Figure 2) which led Schuster and co-workers to formulate the influential CIEEL mechanism. These authors have described three peroxide reactions as prime examples of intermolecular CIEEL:[14] diphenoyl peroxide,[2] dimethyldioxetanone,[15] and peroxyesters.[16] Table III compares the k_1 and k_2 values in these reactions with the corresponding values in the reaction of **3**; it shows that in the cases of **3**, the ratio k_2/k_1, although not as high as in the case of diphenoyl peroxide, is still quite favorable to the study of the activated pathway of peroxide decomposition.

The CIEEL hypothesis is compatible with our results. It provides a framework for discussion by substituting concrete steps 8–10 for the formal reactions 3 and 4 above, as follows:

$$\mathbf{3} + \mathrm{ACT} \rightleftarrows [\mathbf{3}^{\bullet-}\ \mathrm{ACT}^{\bullet+}] \tag{8}$$

$$[\mathbf{3}^{\bullet-}\ \mathrm{ACT}^{\bullet+}] \rightarrow [\mathbf{4}^{\bullet-}\ \mathrm{ACT}^{\bullet+}] \tag{9}$$

$$[\mathbf{4}^{\bullet-}\ \mathrm{ACT}^{\bullet+}] \rightarrow \mathbf{4} + \mathrm{ACT}^{*} \tag{10}$$

The rate-controlling step, eq 8, is viewed as a dissociative electron transfer. The electron affinity of the peroxide is expected to increase as the O–O bond stretches, in agreement with MO calculations,[17] so that bond cleavage and electron transfer may occur simultaneously. While still in the original solvent cage, $\mathbf{3}^{\bullet-}$ rearranges fast to $\mathbf{4}^{\bullet-}$, a stronger reductant than $\mathbf{3}^{\bullet-}$; the annihilation of $\mathbf{4}^{\bullet-}$ and $\mathrm{ACT}^{\bullet+}$ then results in electronic excitation of the activator, eq 10.

The main argument for a CIEEL mechanism is the LFER plots of log k_2 (or log I_0) vs activator E_{ox} (Figure 2). Here the slope of the plot (which is equal to $\alpha F/2.3RT$)[18] is only 2.0 V^{-1}, which at 50 °C corresponds to $\alpha = 0.13$. This value of α is ca. 2 times smaller than the values reported by Schuster in the cases of diphenoyl peroxide, dimethyldioxetanone, and peroxyesters. It is comparable, however, to the α values obtained in the quenching of triplet ketones by amines[19] or by enol ethers[20] or of naphthalene fluorescence by strained saturated hydrocarbons,[21] for example. Although it has been argued that such small α is not incompatible with "full electron transfer" from the activator, it implies that the dioxetane must already have undergone, thermally, considerable stretching of the O–O bond.[22]

Within the framework of the CIEEL model, a high quantum yield of chemiluminescence requires that several conditions be satisfied, besides the trivial one of a high efficiency of activator fluorescence: (a) the bond rearrangement (eq 9) must be fast to compete with exothermic back electron transfer (note that our expression for Φ_{CL} is independent of back transfer) and with diffusion of the radical ions out of the solvent cage; (b) this rearrangement and the subsequent charge annihilation must also be faster than intersystem crossing in the caged pair of radicals, originally singlet; and (c) the enthalpy $-\Delta H$ released in the critical electron transfer between $\mathbf{3}^{\bullet-}$ and $\mathrm{ACT}^{\bullet+}$ must be sufficient for promotion of the activator to its singlet excited state. We will now examine how these requirements apply to the cases of **3** and of diphenoyl peroxide. If a CIEEL type of mechanism obtains, what are the factor(s) responsible for the very low quantum yields (ca. 10^{-5})? By definition (eq 7), these yields refer to the number of excited activator molecules generated per molecule of peroxide decomposed via electron transfer (second order rate constant k_2) in the bimolecular reaction with activator.

Following Weller and Zachariasse,[23]

$$-\Delta H = E_{\mathrm{ox}} - E_{\mathrm{red}} + \Delta\Delta H - e_0^{2}/\epsilon a \tag{11}$$

where $\Delta\Delta H$ is a correction term necessary when the reaction solvent (here *p*-dioxane) is not the solvent in which the redox potentials were measured (acetonitrile). E_{red} of **4** and E_{ox} of **1** are −1.55 and 0.78 V, respectively, from cyclic voltammetry measurements.[24] In *p*-dioxane, $\Delta\Delta H$ is ca. 2 eV, and the coulombic energy is ca. 1 eV. Thus $-\Delta H \simeq 3.3$ eV, which is sufficient for excitation of **1** ($E_{\mathrm{S}} \simeq 63$ kcal). Singlet excitation of rubrene, 2,5-diphenylisobenzofurane, perylene, naphthacene, and 9,10-diphenylanthracene should also be exothermic. It seems therefore unlikely that the energetics of the charge annihilation are responsible for the low quantum yield with these fluorescers. Excitation of 2-aminoanthracene and of 10-methylphenothiazine may just be energetically possible also, whereas excitation of 1-aminonaphthalene should be endothermic by ca 0.5 eV.[25] No chemiluminescence was observed with this activator, even though it is a strong catalyst of the decomposition of **3**.

Escape of either of the radical anions $\mathbf{3}^{\bullet-}$ or $\mathbf{4}^{\bullet-}$ from the proximity of the counter ion would evidently reduce the chemiluminescence efficiency. But if most radicals escaped and reacted with solvent, one would expect to find major products other than **4**, contrary to data. In the case of diphenoyl peroxide, formation of small amounts (5%) of diphenic acid was interpreted as resulting from the reaction of some radical anions (prior to $\mathrm{CO_2}$ loss) with solvent;[2] but clearly this minor side reaction does not account for the low Φ_{CL}. Schuster has argued that ion escape from the primary solvent cage should be facilitated by solvents of high polarity and low viscosity and has presented some evidence for such solvent effects.[2,26]

Another possible cause of low quantum yield is a competition between two parallel bimolecular processes involving activator: one "dark" process and one leading to excited-state generation, both a function of the oxidation potential of the activator. If this were the case, one would expect two different values of activation energies, one for the catalytic rate constant k_2 based on rates of peroxide decomposition, the other based on chemiluminescence intensities. Koo and Schuster found no differences between these two activation energies with either perylene, rubrene, or DPA. Therefore it is most likely that the efficiency of chemiluminescence is primarily governed by losses *after* a common transition state.[30]

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(14) The case of malonyl peroxides is more complex, see below: Porter, J. E.; Schuster, G. B. *J. Org. Chem.* **1985**, *50*, 4068.

(15) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 306.

(16) Dixon, B. G.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 3068.

(17) (a) Schmidt, S. P.; Vincent, M. A.; Dykstra, C. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 1292. (b) Yamaguchi, K. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. III, p 119.

(18) α is considered as analogous to the transfer coefficient in electrode reactions: the activation energy of reaction 8 is only a fraction of the total free-energy change in this redox process,[1b,19] i.e., $k_2 = Ae(-\alpha E_{\mathrm{redox}}/RT)$. If only E_{ox} varies with activator, then the plot of log k_2 vs E_{ox} should be linear with slope $\alpha F/2.3RT$.

(19) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040.

(20) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482.

(21) Gassman, P. G.; Olson, K. D.; Walter, L.; Yamaguchi, R. *J. Am. Chem. Soc.* **1981**, *103*, 4977.

(22) Scandola, F.; Balzani, V.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 2519.

(23) Weller, A.; Zachariasse, K. In *Molecular Luminescence*; Lim, E. C., Ed.; Benjamin: New York, 1969; p 895.

(24) In acetonitrile vs SCE; we thank Prof. R. Holm for permission to use his equipment. The E_{ox} of **1** was also kindly determined in the same solvent by Maria Cruanes at University of Illinois: the two determinations were in excellent agreement.

(25) The energy requirement for singlet excitation is $\Delta H > E_{\mathrm{S}}$, with $\Delta H = E_{\mathrm{ox}} + 2.55$ eV. For 2-aminoanthracene, $E_{\mathrm{ox}} = 0.44$ V, $\Delta H = 3.0$ eV, $E_{\mathrm{S}} = 2.9$ eV. For 1-aminonaphthalene, $E_{\mathrm{ox}} = 0.54$ V, $\Delta H = 3.1$ eV, $E_{\mathrm{S}} = 3.6$ eV. For 10-methylphenothiazine, $E_{\mathrm{ox}} = 0.82$ V, $\Delta H = 3.4$ eV, $E_{\mathrm{S}} = 3.4$ eV.

(26) However, tempting,[27] it seems premature to try to apply Marcus' theory of electron transfer to these chemiluminescence reactions, where the transition states can only be reached after considerable bond reorganization. The effect of solvent polarity is necessarily very complex, since not one but three electron-transfer steps are involved (eq 8 and the back reaction and eq 10). In spite of having the lowest viscosity, the solvent in which the chemiluminescence yield from diphenoyl peroxide is the highest is diethyl ether, where k_2 is the smallest. In the case of dioxetane **3** we found *p*-dioxane to be the best solvent. Both ether and *p*-dioxane are good n-donors in CT complexes,[29] which may be significant.

(27) Eberson, L. *Chem. Scr.* **1982**, *20*, 29.

(28) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265 and references therein.

(29) See: Foster, R. *Molecular Complexes*; Academic Press: New York, 1975.

(30) In the case of the thermolysis of 4-methyl-4-(1-propenyl)malonyl peroxide, the activation barrier for chemiluminescence is reported to be a few kcal higher than the barrier to ground-state products. This may explain the apparently very low quantum yield of this fluorescer-catalyzed reaction.[14]

Intersystem crossing can occur at different times during the reaction course.[31] Once the spins of two radical ions are randomly oriented, electron transfer between these radicals will produce 75% triplets and 25% singlets. This "interpair" process[31] could thus reduce the yield of singlet excited products by a factor of 4 but not by 4 orders of magnitude. Prior to that point, however, hyperfine interactions can bring about fast "intrapair" intersystem crossing in the original singlet contact ion pair presumably present at the transition state. If intrapair intersystem crossing is important, then the modest solvent polarity effects observed on I_0 (and Φ_{CL}) could be rationalized by increased ion solvation and faster formation of the solvent-separated ion pair. Although Koo and Schuster[2] have been unsuccessful at detecting triplet products, the possibly important role of intersystem crossing in reducing Φ_{CL} deserves to be further addressed. The low triplet energies of the activators, which are not phosphorescent in solution, render this search difficult. The effect of an external magnetic field may be worth exploring; by reducing intrapair intersystem crossing, it may result in modest enhancement of Φ_{CL}.

To summarize the discussion so far, it is difficult to single out one specific step in the CIEEL mechanism (eq 8–10) as the cause of the reaction inefficiency, although it would appear that intersystem crossing could be significant. Turning the question around, one might ask whether an intermolecular CIEEL mechanism is indeed capable of generating high yields of excited products. Our results with **3** and with diphenoyl peroxide reopen this question. Clearly neither diphenoyl peroxide nor **3** (with $\Phi_{CL} \lesssim 10^{-4}$) can be regarded as a realistic model of efficient chemiluminescence. The question therefore is the following: what specific properties of the peroxide would render an intermolecular CIEEL more efficient?

The groups of Schuster[15] and Adam[32] reported high quantum yields also from dimethyldioxetanone in the presence of easily oxidized activators: 10% according to Schuster, coincidentally the same yield as he reported for diphenoyl peroxide. We have not checked this value. Even if it was overestimated by an order of magnitude, a Φ_{CL} of 0.01, i.e., 100 times higher than from **3** or from diphenoyl peroxide, would still be a very significant result, since it may lead to an understanding of why the same mechanism, with the same activators, could be orders of magnitude more efficient in one system than in another. Why, for example, would one pair of radical ions spend less time than another as a contact ion pair, susceptible to intrapair intersystem crossing? CO_2 is a product of the decomposition of diphenoyl peroxide as well as of dioxetanone. The reduction potential of CO_2 is −2.2 V[33] compared to −2.3 V (all vs SCE) for acetone[34] and −1.92 V for benzocoumarin,[2] the other main product from DPP. Therefore dissociative electron transfer is expected to generate the radical anion of CO_2 in the dioxetanone case but the anion of benzocoumarin in the case of diphenoyl peroxide (Table IV). Is $CO_2^{\bullet-}$ likely to be an especially suitable partner in the final electron-transfer step which generates the excited state? The electrochemical work of Bard et al.[33] does not suggest it, partly because the small size of $CO_2^{\bullet-}$ should lead to a large difference in solvation energy between it and uncharged CO_2 and thus to a slower electron-transfer rate. On the other hand, strong solvation could favor the quicker separation of this anion from the proximity of the cation and consequently reduce intersystem crossing in the contact ion pair.

The discussion of $CO^{\bullet-}$ brings to mind the very efficient chemiluminescences from oxalate esters/hydrogen peroxide,[35] where electron transfer from fluorescers has long been proposed to play a determining role.[36] The main reaction products are phenols which do not participate in the photoexcitation step and again CO_2. Conflicting evidence exists for the involvement of dioxetanedione, the hypothetical four-membered ring dimer of CO_2, as one of possibly several energy-rich intermediates,[35,37] which again suggests a possible connection between product CO_2 and high quantum yield. To be sure, the generation of CO_2 from dioxetanone or dioxetanedione are very exothermic processes. Thermochemical estimates of the energy released in the reactions discussed here are listed in Table IV; chemiluminescence yields and reaction enthalpy run suggestively parallel. Whatever the reaction pathway, more energy is definitely available in the oxalate system than in the other examples in Table IV, and the annihilation step would also be more exothermic. Provided enough energy is available for excitation in reaction 10, the CIEEL hypothesis does not offer an immediate rationale for an increase in Φ_{CL} with ΔH. In fact, if the generation of excited activator by reaction 10 was too exothermic, even this electron transfer could fall in Marcus' "inverted region" and be slower. The quantum yield may depend on the size and rigidity of the radical anion involved in the final charge annihilation and/or the degree of charge delocalization. Although too little is known to speculate further on the factors reponsible for the high efficiency of the oxalate–ester reaction, it is important to keep in mind that an intermolecular activated chemiluminescence *can* be a remarkably efficient process.

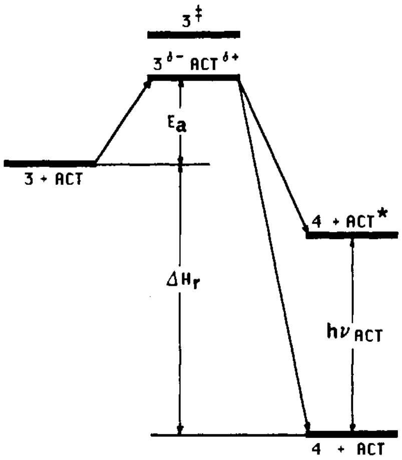

Figure 4. Representation of energy levels in a hypothetical charge-transfer mechanism of activated chemiluminescence.

Conclusions

In our opinion, the mechanism of peroxide chemiluminescence activated by fluorescers of low oxidation potentials, of which the reaction of **3** is unquestionably an example, is still open to question. Although our results are consonant with a CIEEL scheme, is it *necessary* to postulate the successive and distinct steps of a CIEEL mechanism? Or could one account for the observations by a simpler hypothesis? One such mechanism might assume as the rate-determining step the formation of a charge-transfer complex between vibrationally excited dioxetane and fluorescer, resulting in peroxide breakdown with simultaneous generation of some singlet-excited fluorescer, directly from the transition state (Figure 4). The small slope of the LFER plot of k_2 vs E_{ox} is compatible

$$\begin{aligned} \mathbf{3} + \mathrm{ACT} \rightarrow [\mathbf{3}^{\delta-}\mathrm{ACT}^{\delta+}] &\rightarrow \mathbf{4} + \mathrm{ACT}^* \\ &\rightarrow \mathbf{4} + \mathrm{ACT} \qquad (12) \end{aligned}$$

with this interpretation. Similarly, the correlation between I_0 and solvent polarity is more understandable, since I_0 now reflects the rate of a single process. The energy available for excitation would be $-(\Delta H_r + E_a)$, where E_a is the activation energy for peroxide decomposition catalyzed by fluorescer, i.e., the energy required

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Table IV. Chemiluminescence Quantum Yields, Energies Released in Redox Process (with Rubrene Radical Cation)[a] and Heats of Reaction from Peroxides to Products[b]

peroxide	products	E_{red}[c]	E_{redox}[a]	ΔH_r[b]	Φ_{CL}[d]
3	4	-1.55	2.52		$<10^{-4}$[e]
diphenoyl peroxide	benzocoumarin	-1.92*	2.89*	3.04	$<10^{-4}$[e]
	CO_2	-2.2	3.17		
dimethyl dioxetanone	acetone	-2.3	3.27	3.5	0.1[f]
	CO_2	-2.2*	3.17*		
dioxetane dione?	CO_2	-2.2	3.17	4.8	0.3[g]

[a] For comparison between peroxide reactions, calculated as $E_{red} - E_{ox}$ with $E_{ox} = 0.97$ V; in eV. The asterisk indicates the most likely redox couple. [b] Literature values from thermochemical calculations; in eV. Not calculated for **3** because of unavailability of some group values. [c] In V vs SCE; the asterisk indicates the radical anion most likely to be generated. [d] In einstein per mol of peroxide reacting via the activated route. [e] This work. [f] Reference 15. [g] Reference 35.

to elongate the O–O bond and form the charge-transfer complex. The trend toward higher Φ_{CL} as ΔH_r increases, so clear in Table IV, cannot be rationalized without a knowledge of the potential surfaces involved; but there is no longer a need to explain how two identical annihilation processes between two identical ion pairs could have different efficiencies. A mechanism which does not call for the transfer of a "full electron", back and forth between donor and acceptor, may be a more realistic picture of intramolecularly activated chemiluminescence, as in the series of efficient dioxetanes synthesized by Schaap[38] and by McCapra.[39] Alternatively, the nonvertical electron-transfer process of CIEEL and the admittedly more vague charge-transfer mechanism suggested above could represent two extremes in a spectrum of activated reactions, within which each example of Table IV occupies a different position. In any case, one must remember that unless a sharp, mechanistic distinction is drawn between promotion to a singlet or to a triplet excited state, the classic dioxetanes such as tetramethyldioxetane are still remarkably efficient ($\Phi \sim 0.3$) converters of chemical energy to electronic energy,[40] apparently without the development of charge.

Irrespective of the precise mechanism of chemiexcitation, the thermolysis of anthracene endoperoxide **2** is an interesting example of peroxide chemiluminescence. Subtle changes in medium have a profound effect on the course of the reaction, leading to either the near infrared emission of singlet oxygen or, via an unstable dioxetane, to visible light of any color, depending on the fluorescer present. Features of the reaction path, with its many branching points, make it an interesting model for some bioluminescences.

Experimental Section

General Methods. The solvents used in chemiluminescence experiments were of spectral grade and distilled from calcium hydride. Perylene, rubrene, 9,10-diphenylanthracene, 9,10-dibromoanthracene, naphthacene, 2-aminoanthracene, and 1-aminonaphthalene were purchased from Aldrich and vacuum sublimed prior to use. 10-Methylphenothiazine from Eastman was recrystallized twice from benzene, 1,3-diphenylisobenzofuran was purchased from Columbia Org. Chem. and recrystallized twice from ethanol.

1,4-Dimethoxy-9,10-diphenylanthracene (**1**) was synthesized according to Dufraisse and Velluz.[3b] Its photooxygenation to peroxide **2** was performed at −20 °C by irradiation of a 10 mM ethyl ether solution containing a few crystals of tetraphenylporphyrine and a few drops of pyridine, to avoid acid-catalyzed decomposition of the product. After 1 h of irradiation the product **2** (insoluble in ether) was filtered and washed several times with ether. This crude peroxide was then resuspended in ether and washed with ether prior to use in any experiments.

Diphenoyl peroxide was synthesized by the method of Ramirez et al.[41] and freshly recrystallized from $MeOH/CH_2Cl_2$ at −20 °C prior to use.

NMR Spectra of Dioxetane 3. Peroxide **2** (8 mg, 19 μmol) was dissolved in 0.5 mL of $CDCl_3$ and frozen in dry ice. HAc (11 μL, 19 μmol) was placed on top of the frozen solution. This sample was then placed in the spectrometer at −35 °C, and spectra recorded after the solution thawed.

Chemiluminescence Measurements. Chemiluminescence intensity was followed in either photon counting mode (cooled PMT Hamamatsu R943-02) or in analog mode (cooled PMT EMI 9558-B and Keithley electrometer). Quantum yields were determined on the basis of the Hastings–Weber light standard[42] and confirmed by comparison with the tetramethyldioxetane/DBA chemiluminescent system.[40]

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Registry No. 1, 6274-79-9; **2**, 118949-89-6; **3**, 118949-90-9; **4**, 21768-85-4; diphenoyl peroxide, 6109-04-2; 2-aminoanthracene, 613-13-8; 1-aminonaphthalene, 134-32-7; 1,3-diphenylsiobenzofuran, 5471-63-6; 10-methylphenothiazine, 1207-72-3; perylene, 198-55-0; rubrene, 517-51-1; triethylamine, 121-44-8; 9,10-diphenylanthracene, 1499-10-1; 9,10-dibromoanthracene, 523-27-3.

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