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α-Pyrone Endoperoxides. Synthesis, Thermal Decomposition, and Chemiluminescence[1]

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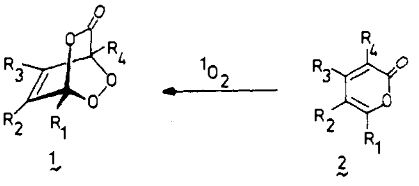
Abstract: Singlet oxygenation of α-pyrones **2** affords the corresponding endoperoxides **1** in high yield. On heating, these peroxides quantitatively decarboxylate into the respective 1,2-diacylethylenes **4**. The suspected intermediary *o*-dioxins **3** could not be trapped with maleic anhydride, tetracyanoethylene, and *N*-phenyl-1,2,4-triazoline-3,5-dione, suggesting that the decarboxylation of the endoperoxides **1** takes place with concomitant peroxide bond fission. Easily oxidized polycyclic aromatic hydrocarbons, e.g., rubrene, perylene, and 9,10-diphenylanthracene, induce the decarboxylation of the endoperoxides **1** with light emission by an electron exchange mechanism.

α-Pyrone endoperoxides **1**, conveniently accessible through singlet oxygenation of α-pyrones **2** (eq 1),[3] are potential sources for the thermal generation of electronic excitation.[4] Indeed, even a very rudimentary estimate[5] of the enthalpy change associated with the thermal decarboxylation of **1** into the diacylethylene **4**, as shown in eq 2, reveals that enough energy is set free in the **1** → **4** process to render **4** electronically excited. Our preliminary observations[3] confirmed that the α-pyrone endoperoxides **1** are hyperenergetic in that chemiluminescence accompanied their thermal decarboxylation.



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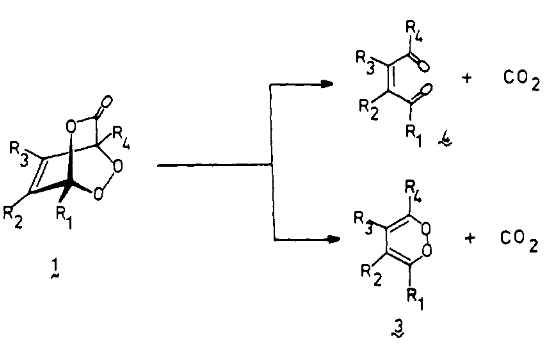

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In the course of our more detailed investigation of these functionalized endoperoxides, a preliminary report by Smith and Schuster[6] focused on a still more fascinating aspect of this problem. Thus, thermal decomposition of 1,4-diphenyl-2-benzopyran-3-one endoperoxide led to the novel *o*-xylylene peroxide **5a** (eq 3), which subsequently rearranged into electronically excited *o*-dibenzoylbenzene. The unusual feature of this chemielectronic process is that decarboxylation preserves the peroxide linkage in the form of the 1,2-dioxin moiety in the xylylene peroxide **5a**. An analogous process was first suggested by Michl[7] to rationalize the chemiluminescence of luminol, in which the postulated endoperoxide **6** loses molecular nitrogen with preservation of the peroxide linkage to afford the xylylene peroxide **5b** (eq 4). The latter affords electroni-

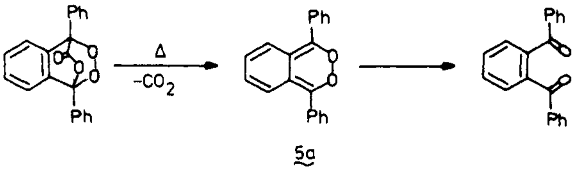

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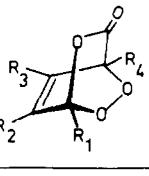
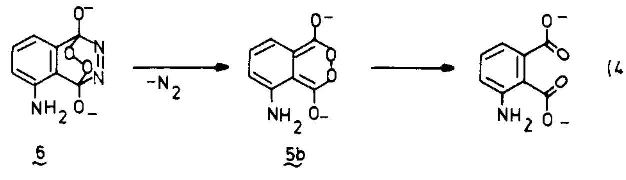
Table I. Yields, Physical Constants, and Spectral Data of α-Pyrone Endoperoxides **1**



	R_1	R_2	R_3	R_4	yield, %	mp, °C[a]	^{1}H NMR ($CDCl_3$) type	no. H	δ, ppm	*J*, Hz	IR, cm^{-1}
1a	H	H	H	H	85	liquid	H_1	1	5.25	m	CCl_4: 3040, 2960, 1810, 1635, 1030, 960
							$H_{2,3}$	2	6.80	m	
							H_4	1	5.02	m	
1b	Ph	Ph	Ph	Ph	98	68-70 (MeOH)	Ph	8	6.62 6.82	m	CCl_4: 3070, 1795, 1590, 1440
							Ph	12	7.12	m	
1c	H	CO_2H	H	H	90	70-71 (MeOH)	H_1	1	6.49	m	KBr: 3400-2600, 1800, 1710, 1400
							CO_2H	1	8.88	br s	
							H_3	1	7.27	dd (2.5, 6.0)	
							H_4	1	5.09	d (6.0)	
1d	H	CO_2CH_3	H	H	84	72 (MeOH)	H_1	1	6.86	m	$CHCl_3$: 3010, 1800, 1720, 1625, 1430
							CO_2CH_3	3	3.86	s	
							H_3	1	7.41	dd (2.5, 6.0)	
							H_4	1	5.11	d (6.0)	

[a] Melts with CO_2 evolution; too unstable for elemental analysis; at least 97% peroxide titer by iodometry.



(4)

cally excited 3-aminophthalate presumably via an intramolecular electron exchange process.[6]

The possibility that our α-pyrone endoperoxide **1** decarboxylated thermally by retaining the peroxide linkage and thus provided a facile entry into the intriguing 1,2-dioxins **3** (eq 2) gave us additional incentive for exploring the chemistry of α-pyrone endoperoxides. Herein we report the details of our investigation.

Experimental Section

All melting points and boiling points are uncorrected. Solvents and starting materials were purified according to standard literature procedures to match reported physical constants. The starting materials were either purchased from common suppliers or prepared according to literature procedures, except α-pyrone, which was generously supplied by Professor A. de Meijere, University of Hamburg. The fluorescers 9,10-diphenylanthracene (Eastman), perylene (Aldrich), and rubrene (Eastman) were used without further purifications. The infrared spectra were measured on a Perkin-Elmer Model 237B or 283 infrared spectrophotometer, the ^{1}H NMR spectra on an Hitachi Perkin-Elmer R-24B or a Varian T-60 spectrometer, and the mass spectra on a Hitachi Perkin-Elmer Model RMS-4 spectrometer. Elemental analysis were performed by Atlantic Analytical Laboratories, Atlanta, Ga.

General Procedure for the Preparation of α-Pyrone Endoperoxides 1. A 0.25 M solution (25 mL) of the respective α-pyrone **2** in dry CH_2Cl_2, which contained tetraphenylporphyrin (4 mg in 25 mL of solution) as sensitizer, was irradiated with a 150-W General Electric sodium street lamp at 0 °C while bubbling dry oxygen through the solution. The progress of the singlet oxygenation was monitored by subambient ^{1}H NMR spectroscopy. Once all the α-pyrone **2** was consumed, the CH_2Cl_2 was rotoevaporated (0 °C at 10-15 mmHg) and the crude endoperoxide **1** purified by either silica gel column chromatography at ca. −40 °C, eluting with CH_2Cl_2, or recrystallization from MeOH at −20 °C. Iodometric titration confirmed a peroxide content of better than 97% for each endoperoxide. The yields, physical constants, and spectral data are given in Table I.

General Procedure for the Thermal Decomposition of the α-Pyrone Endoperoxides 1. A 0.8 M $CDCl_3$ solution (5 mL) of the respective endoperoxide **1** was syringed into a constricted Pyrex test tube, sealed under vacuum, and heated at 80 °C for 45 min. After cooling to room temperature the product mixture was analyzed by means of ^{1}H NMR and IR spectroscopy. The only products that could be detected were the respective 1,2-diacylethylenes **4**, i.e., malealdehyde from **1a** and dibenzoylstilbene from **1b**, as confirmed by comparison with authentic samples.

Attempts at Trapping the Cyclic Peroxide Intermediate 3 with Dienophiles. Into a constricted Pyrex test tube was syringed 5 mL of a 0.8 M $CDCl_3$ solution of the α-pyrone endoperoxide **1** containing a fivefold molar excess of the dienophile (maleic anhydride, tetracyanoethylene, or *N*-phenyl-1,2,4-triazoline-3,5-dione). The solution was thoroughly deaerated with argon gas by applying five freeze-pump-thaw cycles and finally sealed under vacuum. These ampules were then heated in a water bath at 80 °C until complete disappearance of the 1800-cm^{-1} lactone band in the IR. On ^{1}H NMR and IR spectral analysis of the decarboxylated reaction mixture, only the 1,2-diacylethylene **4** product could be observed in each case. Neither did careful TLC analysis of the reaction mixture reveal any trapping product.

Preparation of Trapping Product 7b. A solution of 3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride (0.20 g, 0.44 mmol) in 5 mL of $CHCl_3$, containing tetraphenylporphyrin (2 mg) as sensitizer, was irradiated with a 150-W General Electric sodium street lamp at 0 °C while dry oxygen gas was bubbled through the solution. The progress of singlet oxygenation was monitored by ^{1}H NMR. After consumption of the diene, the solvent was rotoevaporated (0 °C at 5 Torr) and the residue recrystallized from MeOH, affording the endoperoxide **7b** in 90% yield, mp 190 °C. Its structure assignment rests on the following spectral data: ^{1}H NMR ($CDCl_3$, Me_4Si) shows resonances at δ 4.38 (singlet, 2 H), 6.67 and 6.84 (multiplets, 8 H), and 7.19 ppm (multiplet, 12 H); IR ($CHCl_3$) shows bands at 3050 (aromatic C-H), 2980 (aliphatic C-H), 1865 and 1780 (anhydride C=O), and 1600 cm^{-1} (phenyl C=C); satisfactory elemental analysis based on the $C_{32}H_{22}O_5$ formula. Additional chemical structure proof consists of palladium on carbon catalyzed hydrogenation in EtOAc at 10 °C in 97% yield to the corresponding diol: mp 110 °C dec (from 1:2 benzene-hexane); ^{1}H NMR ($CDCl_3$, Me_4Si) shows peaks at δ 3.48 (broad singlet, 2 H, exchanged by D_2O), 4.08 (singlet, 2 H), and 6.79-7.70 ppm (multiplet, 20 H); IR ($CHCl_3$) shows bands at 3500-3200 (OH), 3040 (aromatic C-H), and 1875 and 1795 cm^{-1} (anhydride C=O); satisfactory elemental analysis based on the $C_{32}H_{24}O_5$ formula.

Chemiluminescence Measurements. The total chemiluminescence intensities were determined with a Mitchell-Hastings photometer,[8] equipped with an RCA PF-1006 or a Hamamatsu Type RP28HA photomultiplier tube and a Hewlett-Packard Model 17501A recorder.

Table II. Chemiluminescence Data of α-Pyrone Endoperoxides **1**[a]

entry[b]	endoperoxide	temp, °C	fluorescer (Fl)[c]	10^3[Fl], M	$10^4 k_{obsd}$, s^{-1}	ln I_0,[e] einstein/s·L
1	**1a**	80	none		2.71	−33.55
2	**1a**	80	Ru	(0.0)[d]	3.55	−27.98
3	**1a**	80	Ru	0.10	3.34	−30.37
4	**1a**	80	Ru	1.0	4.05	−27.95
5	**1a**	80	Ru	10.0	4.77	−26.57
6	**1a**	80	Ru	20.0	6.52	−25.65
7	**1a**	80	Ru	10.0		−22.22
8	**1a**	80	Per	10.0		−26.94
9	**1a**	80	DPA	10.0		−30.39
10	**1b**	40	none		6.20	−36.36
11	**1b**	40	Ru	(0.0)[d]	6.56	−32.47
12	**1b**	40	Ru	1.0	6.86	−32.65
13	**1b**	40	Ru	4.0	7.08	−31.91
14	**1b**	40	Ru	10.0	8.16	−31.79
15	**1b**	40	Ru	20.0	9.90	−31.20
16	**1b**	40	Ru	10.0		−28.09
17	**1b**	40	Per	10.0		−30.62
18	**1b**	40	DPA	10.0		−32.24

[a] In benzene as solvent. [b] Entries 1-6 are at [**1a**] = 0.04 M; entries 10-15 are at [**1b**] = 0.013 M. [c] Ru = rubrene; Per = perylene; DPA = 9,10-diphenylanthracene. [d] Extrapolated to [Ru] = 0.00 from Figure 1. [e] Total emission intensities extrapolated to t_0.

Constant temperature in the photometer cell compartment was maintained within 0.5 °C of the desired temperature by means of a Haake thermostated variable temperature circulating bath.

The emission intensities were measured by charging a Packard scintillation glass vial with 3.0 mL of a 0.04 (**2a**) or 0.013 M (**2b**) solution of the respective α-pyrone endoperoxide **1** in benzene in the absence of fluorescer (direct chemiluminescence) or in the presence of the fluorescer (enhanced chemiluminescence), sealed with a serum cap, placed into the cell compartment of the Mitchell-Hastings photometer, and allowed to equilibrate thermally for 1 min, and the voltage signal was continuously recorded vs. time usually beyond 3 half-lives. The voltage output was converted to luminescence units (einstein/s·L) using the experimentally established conversion factor $15.86 \pm 0.02 \times 10^{-12}$ einstein/s·L·V. The latter was determined with the help of a calibrated POPOP-PPO scintillation cocktail, kindly supplied by Professor J. W. Hastings, Harvard University. The initial total intensity emissions of the enhanced chemiluminescence were corrected for relative spectral response of the phototube.[9] At the concentrations of fluorescers used, reabsorption was negligible.

From the intensity vs. time plots, the initial total chemiluminescence intensities (I_0) were extrapolated to zero time (t_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 II.

Results

Synthesis of α-Pyrone Endoperoxides. The dienic reactivity of α-pyrones **2** is well established[10] and it was expected[3] that singlet oxygenation of **2** should afford the desired endoperoxides **1**. In view of the ease of thermal decarboxylation the photosensitized oxygenations had to be carried out under subambient conditions. ^{1}H NMR and IR monitoring clearly indicated the formation of the bicyclic peroxide **1** in that the dienic protons at δ 5.9-6.3 and 7.0-7.5 ppm of **2** were replaced by the bridgehead protons at δ 5.02 and 6.25 ppm and by the olefinic protons at δ 6.80 ppm in **1** and the α-pyrone carbonyl at 1752 cm^{-1} was replaced by the bicyclic lactone carbonyl at 1810 cm^{-1}.

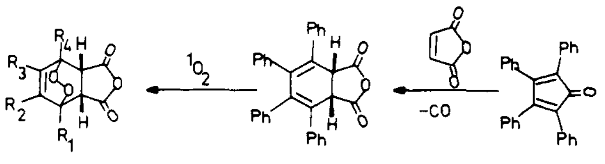
Isolation and purification[11] presented a problem since on warmup the endoperoxide **1** readily decomposed as evidenced by CO_2 liberation and formation of the 1,2-diacylethylene **4**. However, subambient solvent removal and low-temperature silica gel chromatography or recrystallization afforded the pure materials in high yield. In fact, for most mechanistic experiments the crude product is pure enough (>95%) for direct use without further purification.

The bicyclic peroxide structure for **1** was assigned on the fact that each derivative displayed a peroxide titer greater than 97% by iodometry, a characteristic lactone carbonyl band at 1795-1810 cm^{-1}, and a characteristic bridgehead proton resonance at δ 5.02-5.11 ppm for R_4. In addition, the structure of endoperoxide **1a** was confirmed by diimide reduction to its stable saturated endoperoxide.[3] While this saturated peroxide exhibited a satisfactory elemental analysis, the α-pyrone endoperoxides **1** were too unstable to be send out for analysis. For example, the solid derivatives **1b,c** melted with decarboxylation.

Attempts at Trapping the *o*-Dioxin Intermediate. On thermal decomposition the α-pyrone endoperoxides **1** lost CO_2 to afford the respective 1,2-diacylethylenes **4** essentially quantitatively. Whether **1** underwent direct decarboxylation or decomposed via the intriguing *o*-dioxin **3** to afford **4** (eq 2) was of obvious mechanistic interest. Thus, in view of the success in trapping the xylylene peroxide **5a** with maleic anhydride,[6] analogous experiments were carried out to ascertain whether the *o*-dioxin **3** intervened in the thermal decarboxylation of the endoperoxides **1**.

A solution of **1a** and a fivefold molar excess of maleic anhydride in $CDCl_3$ was heated at 80 °C under rigorous exclusion of molecular oxygen[6] until consumption of the endoperoxide was complete. Neither IR nor ^{1}H NMR analysis was definitive in assessing whether the [4 + 2] cycloadduct **7a** (R = H) had been formed. Careful TLC work did not reveal the presence of *o*-dioxin trapping product.

In view of these disappointing results, we turned to the tetraphenyl endoperoxide **1b** since the *o*-dioxin derivative **3b** (R = Ph) more closely resembles **5a,** which could be trapped with maleic anhydride. Furthermore, we expected that the endoperoxide **1b** should decarboxylate at considerably lower temperature than **1a,** thus enhancing the chances of trapping the corresponding *o*-dioxin **3b** (R = Ph). Since ^{1}H NMR was of



(5)

7a (R=H)
7b (R=Ph)

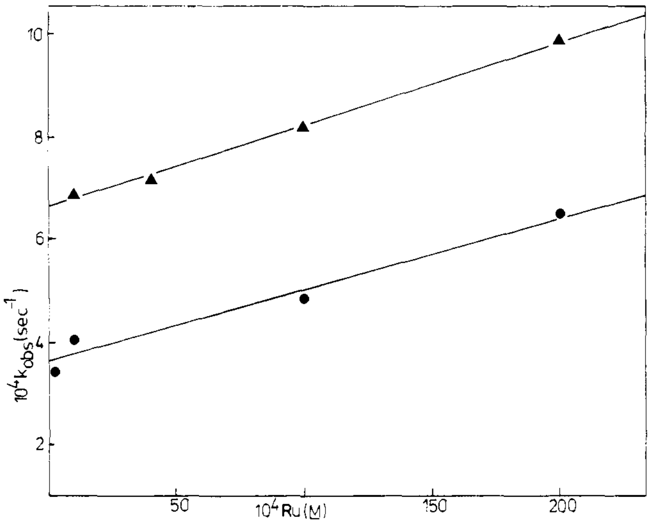


Figure 1. Observed rate constants (k_{obsd}) vs. rubrene concentration in the enhanced chemiluminescence of α-pyrone endoperoxides: -●-●-, **1a**; -▲-▲-, **1b** (cf. Table II for conditions).

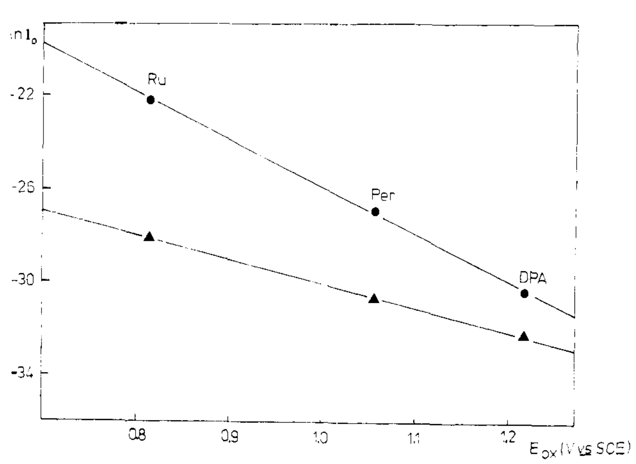


Figure 2. Natural logarithm of initial intensities (ln I_0) vs. fluorescer oxidation potentials (E_{ox}) in the enhanced chemiluminescence of α-pyrone endoperoxides: -●-●-, **1a**; -▲-▲-, **1b**.

limited value for detecting the tetraphenyl [4 + 2] cycloadduct **7b** (R = Ph), we decided to prepare an authentic sample by the synthetic sequence shown in eq 5. Thermal decarboxylation of **1b** in the presence of maleic anhydride did not afford the *o*-dioxin [4+ 2] cycloadduct **7b** (R = Ph), as confirmed by careful ^{1}H NMR analysis of the reaction mixture and comparison with the authentic sample. Even heating a solid mixture of **1b** and maleic anhydride failed to produce **7b**. The endoperoxide **7b** was stable to the thermolysis conditions of the trapping experiment. Furthermore, the considerably more reactive dienophiles tetracyanoethylene and *N*-phenyl-1,2,4-triazoline-3,5-dione did not result in *o*-dioxin trapping products analogous to **7b**. Unfortunately the authentic trapping product of *N*-phenyl-1,2,4-triazoline-3,5-dione could not be prepared because heating of a mixture of tetraphenylcyclopentadienone and the 1,2,4-triazoline-3,5-dione did not generate the dienic urazole necessary for singlet oxygenation.[12]

Direct and Fluorescer-Enhanced Chemiluminescence. Thermal decarboxylation of endoperoxides **1** is accompanied by light emission, but it is so feeble that it could only be detected with a sensitive photomultiplier tube by decomposing **1** directly in the Mitchell-Hastings photometer. The decay of the direct emission intensity is exponential, following the first-order rate law. From the total initial intensity (I_0), the first-order rate constant (k_{obsd}), and the initial endoperoxide concentration, we calculate[9] a direct chemiluminescence efficiency (ϕ^{DC}) of ca. 2.50 × 10^{-10} einstein/mol (cf. entry 1, Table II). Indeed, this is not very impressive! Similarly, the endoperoxide **1b** displayed a direct chemiluminescence efficiency of ca. 2.0 × 10^{-11} einstein/mol (cf. entry 10, Table II). However, as expected endoperoxide **1b** decarboxylated considerably easier than **1a**. For example, the direct k_{obsd} for **1b** at 40 °C is about twice that of **1a** at 80 °C. The singlet excitation yield (ϕ^S) could not be calculated since no fluorescence quantum yield (ϕ^{fl}) data is reported on malealdehyde or dibenzoylstilbene, the respective 1,2-diacylethylene products from the endoperoxides **1a** and **1b**.

Thermal decomposition of endoperoxides **1** in the presence of efficient fluorescers such as rubrene (Ru) exhibits intense rubrene fluorescence. The decay of the enhanced emission intensity is also exponential, affording the k_{obsd} values shown in Table II. The interesting feature of this rate data is that k_{obsd} increases linearly with increasing [Ru], as shown in Figure 1 for both endoperoxides **1a** and **1b**. Thus, the fluorescer catalyzes the decomposition of **1** with enhancement of the light intensity. In fact, from Figure 1 the linear relationship

$$k_{obsd} = k_1 + k_2[\mathrm{Ru}] \tag{6}$$

obtains, where the intercept k_1 represents the direct and the slope k_2 the rubrene-catalyzed decarboxylation rate constants. The extrapolated k_1 values from Figure 1 are 3.55 × 10^{-4} s^{-1} for **1a** (entry 2, Table II) and 6.56 × 10^{-4} s^{-1} for **1b** (entry 11, Table II), which check reasonably well with the k_{obsd} values obtained from the direct chemiluminescence data, i.e., 2.71 × 10^{-4} s^{-1} for **1a** (entry 1, Table II) and 6.20 × 10^{-4} s^{-1} for **1b** (entry 10, Table II); the error in this data is ca. 10%.

The respective k_2 values for the rubrene-catalyzed decarboxylation are 6.52 × 10^{-4} and 9.90 × 10^{-4} s^{-1} M^{-1} for **1a** and **1b**. Taking these rate constants and the intensity and endoperoxide and rubrene concentration data of Table II (entries 6 and 15), we estimate that the enhanced chemiluminescence efficiencies (Φ^{EC}) for the catalytic process are 1.13 × 10^{-8} and 2.85 × 10^{-10} einstein/mol, respectively, for **1a** and **1b**.

The fact that rubrene enhanced the light intensity by catalyzing the decomposition of the endoperoxide **1** immediately brought to mind the recently recognized CIEEL mechanism[13] to rationalize our results. As a crucial test for the CIEEL mechanism, the catalysis rate must be an exponential function of the oxidation potential (E_{ox}) of the fluorescer. Consequently, we examined the enhanced chemiluminescence of **1** also with perylene (Per) and 9,10-diphenylanthracene (DPA). Although these fluorescers enhanced the chemiluminescence intensities (cf. entries 8 and 9 vs. 1 for **1a** and entries 17 and 18 vs. 10 for **1b**, Table II), their effect on k_{obsd} was too small to acquire sufficiently accurate rate data for the correlation with the E_{ox} of the fluorescers. However, as shown in the equation

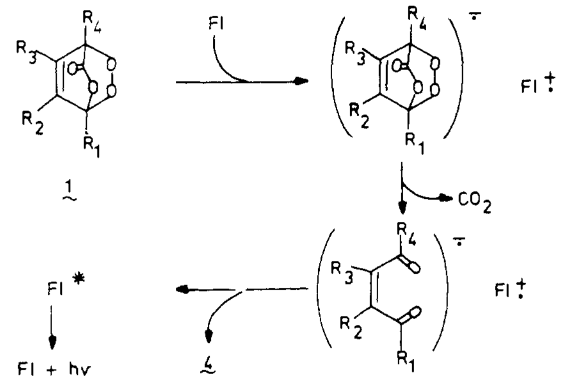
$$I_t = k_2[\mathrm{Fl}][\mathbf{1}] \tag{7}$$

where

$$k_2 = \left(\frac{k_B T}{Nh}\right) \exp(\Delta S^{\ddagger}/R) \exp\left[-\left(E_{ox} - E_{red} - \frac{e^2}{\epsilon R_0}\right)\Big/ RT\right]$$

the enhanced emission intensity (I_t) depends exponentially on the fluorescer oxidation potential (E_{ox}).[14] As anticipated, the logarithm of the total initial intensities (ln I_0) in the presence of the fluorescers Ru, Per, and DPA (entries 7–9 for **1a** and entries 16–18 for **1b**, Table II) correlate linearly with the E_{ox} of these fluorescers (cf. Figure 2), both for **1a** and **1b**. Clearly the catalytic component of the fluorescer-enhanced chemiluminescence of α-pyrone endoperoxides **1** follows the electron exchange mechanism.

Scheme I



1

4

Discussion

Our results clearly indicate an electron-exchange mechanism for the fluorescer-enhanced chemiluminescence. On the one hand, a fluorescer like rubrene catalyzes the decarboxylation of the α-pyrone endoperoxide **1** with concurrent light amplification; on the other hand, the enhanced emission intensity is an exponential function of the oxidation potential of the fluorescers. Both criteria together are taken as evidence for the CIEEL mechanism.[13]

It was not possible to trap the *o*-dioxin **3** in the thermal decarboxylation of **1** even with such reactive dienophiles as 4-phenyl-1,2,4-triazoline-3,5-dione. Either **3** is not formed or it suffers valence isomerization to the diacylethylene **4** before bimolecular trapping with the dienophile occurs. If the latter situation should apply, it would also be unlikely that bimolecular electron exchange between the *o*-dioxin **3** and the fluorescer would compete with valence isomerization into **4**. This expectation is especially reasonable since the concentration of the triazolinedione trapping agent is fivefold that of the fluorescer electron donor. Furthermore, the fluorescer catalyzes the decarboxylation of the endoperoxide **1**, i.e., **1** disappears faster in the presence of rubrene. This is contrary to the observation made for the benzo-annulated endoperoxide (eq 3), for which the fluorescer does not directly catalyze the decarboxylation of the endoperoxide.

On the basis of our results we suggest the electron exchange mechanism shown in Scheme I to rationalize the enhanced chemiluminescence of α-pyrone endoperoxides **1** with easily oxidized fluorescers. Apparently the electron transfer between **1** and the fluorescer in the first step is quite inefficient since the catalyzed decomposition of **1** by Fl is slow and thus the enhanced light yield low.

Presently we are exploring the possibility of altering the structure of the endoperoxide **1** to increase the enhanced light efficiency by affording the intriguing *o*-dioxins **3**. For example, benzoannulation (eq 3) is very effective in enhancing the light yield by promoting the formation of the xylylene peroxide **5a**,[6] and the latter enters into an efficient electron-exchange mechanism. In the case of our α-pyrone endoperoxides **1** it seems that decarboxylation takes place concurrently with peroxide bond cleavage to afford **4** directly without the intervention of the *o*-dioxin **3**.

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Multiphase Fluorescence Quenching by a Surfactant Nitroxyl Radical

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Abstract: The self-association of 4-[*N*,*N*-dimethyl-*N*-(*n*-hexadecyl)ammonium]-2,2,6,6-tetramethylpiperidinyl-*N*′-oxyl bromide (**1**), a surfactant nitroxyl radical, into micelles was studied by ESR spectroscopy giving an estimate of its critical micelle concentration (cmc) as $(4.6 \pm 0.5) \times 10^{-4}$ M, in the absence of added salt. The fluorescence quenching of a series of cationic fluorophors of the structure $[(1\text{-pyrenyl})(CH_2)_nN(CH_3)_3]^+ X^-$ (**2**-*n*) by **1** was investigated over a concentration range below and above the cmc. A comparison of fluorescence lifetime and yield measurements indicates that **2**-1 and **2**-5 are quenched by a simple diffusional mechanism while **2**-11 is quenched by a static mechanism below the cmc. Discontinuities occur in the Stern-Volmer plots at the cmc owing to the onset of static quenching of fluorophors solubilized in the micelle phase. Analysis of a kinetic scheme incorporating the several quenching mechanisms operating below and above the cmc leads to estimates of K_b/N for the **2**-*n* fluorophors: (**2**-1), 27; (**2**-5), 336; (**2**-11), 38 000 M^{-1}, where K_b is the association constant with the micelle and N is the aggregation number of the host micelle.

The study of bilayer and micellar assemblies with fluorescence probes is well established.[1] Recently, we[2] showed the usefulness of using nitroxyl radicals as fluorescence quenchers[3] in ionic micellar environments. Further, we have presented a

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