changes may be large enough (~1 kcal/mol) to require consideration. However, the series of compounds within the figures which would seem most likely to exhibit this effect, the hydrocarbons with their numerous rotational degrees of freedom in the gas state, are one of the two series showing the greatest regularity. Thus additional explanation of the irregularities in Figures 2 and 3 must be sought.
(21) G. L. Amidon, S. H. Yalkowsky, S. T. Anik, and S. C. Valvani, *J. Phys. Chem.*, **79**, 2239 (1975); P. Mookerjee, *Adv. Colloid Interface Sci.*, **1**, 241 (1967); J. A. V. Butler, C. M. Ramachandani, and D. W. Thomson, *J. Chem. Soc.*, 952 (1935).
(22) Reference 4e, p 3.
(23) The *absolute* values of ΔG in solute transfer processes will depend on the standard state convention, since the relative number of molecules in the two phases varies during the transfer process. In keeping with most workers in this field (ref 4e, 28, 32), mole fractions are used here, but conventional concentrations are equally satisfactory (ref 12, 35) if ideal mixing entropy is then explicitly considered. In any case, the choice of standard state does not significantly influence the *relative* values of ΔG, on which most of these arguments are based; furthermore, none of the usual standard state conventions produce nonzero $\Delta G_{(MV=0)}$. (See also ref 27.)
(24) This surprising observation was independently noted and also found inexplicable by hermann (ref 25). The marked increase in hydrophilicity when a hydrocarbon chain is cyclized persists as unsaturations are successively introduced into the hydrocarbons (C. McAuliffe, *J. Phys. Chem.*, **70**, 1267 (1966)).
(25) The "scaled particle" theory is reviewed by R. A. Pierotti, *Chem. Rev.*, **76**, 717 (1976). A somewhat different cavity model is due to R. O. Neff and D. A. McQuarrie, *J. Phys. Chem.*, **77**, 413 (1973). Cavity models may also be regarded as a first-order truncation of the highly successful Barker–Henderson perturbational treatment of solutions (R. B. Hermann, *J. Phys. Chem.*, **79**, 163 (1975)).
(26) See, for example, S. Glasstone, "Textbook of Physical Chemistry", Van Nostrand, Princeton, N.J., 1946, Chapter 5.
(27) Most of the intercept is accounted for by $RT \ln (RT/\bar{V}$ solvent), the chemical potential of the solvent required with this standard state convention, which is −4.27 kcal/mol for pure water and −2.99 kcal/mol for pure octanol.
(28) R. A. Pierotti, *J. Phys. Chem.*, **69**, 281 (1965); H. D. Nelson and C. L. deLigny, *Recl. Trav. Chim. Pays-Bas*, **87**, 623 (1968). With regard to the free energy of cavity formation, water is by no means a unique solvent, iodobenzene and nitrobenzene being comparable and hydrazine even greater (E. Wilhelm and R. Battino, *J. Chem. Phys.*, **56**, 563 (1972)).
(29) M. Lucas, *J. Phys. Chem.*, **80**, 359 (1976).
(30) Derived in a straightforward manner from empirical linear equations relating log (partition coefficients) between water and various lipid phases (A. Leo, C. Hansch, and D. Elkins, *Chem. Rev.*, **71**, 525 (1971), and ref 34), assuming the ΔG of −0.72 kcal/mol for partitioning of $-CH_2-$ from water to octanol.
(31) E. Wilhelm, R. Battino, and R. J. Wilcox, *Chem. Rev.*, **77**, 219 (1977).
(32) E. Wilhelm and R. Battino, *Chem. Rev.*, **73**, 1 (1973).
(33) However, the scaled particle theory seems to share this deficiency of predicting an unusually negative dependence of water solvation entropy on solute bulk, which is not observed experimentally (ref 29). Could there be a "colligative" ordering of the configuration of water molecules accompanying the solution process, an ordering which might be present but obscured by other processes during the dissolution of *polar* substances? Other explanations of the anomalous ΔS have been given (D. D. Eley, *Trans. Faraday Soc.*, **35**, 1281, 1421 (1939); R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 139 (1951); D. H. Everett, *Discuss. Faraday Soc.*, **24**, 216 (1957)).
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Chemiluminescence from the Base-Catalyzed Decomposition of α-Hydroperoxy Ketones. Competitive Cyclic and Acyclic Reactions

Yasuhiko Sawaki and Yoshiro Ogata*

Contribution No. 234 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan.

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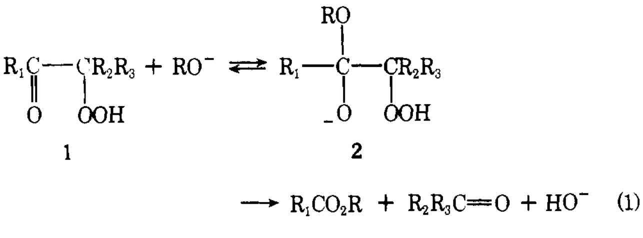
Abstract: Chemiluminescence (CL) is observed from the base-catalyzed decomposition of α-hydroperoxy ketones (**1**) in the presence of a fluorescer. The efficiency of fluorescers is in the order dibromoanthracene (DBA) ≫ diphenylanthracene (DPA) and eosin > fluorescein, suggesting a predominant formation of triplet ketone. Most peroxides exhibit the CL in the presence of DBA, although the quantum yields are low, i.e., in the range of 10^{-5}–10^{-6}. These results suggest that the chemiluminescent dioxetane mechanism is actually operating to produce triplet ketone. However, the nonchemiluminescent acyclic pathway is generally predominant in view of the ester formation, the low quantum yield of the CL, and solvent effects on the CL and the decomposition rate. The kinetics for decomposition and CL suggest competitive cyclic and acyclic pathways. Thus, the acyclic decomposition of α-hydroperoxy-α,α-diphenylacetophenone (**1j**) is too fast to compete with the dioxetane path.

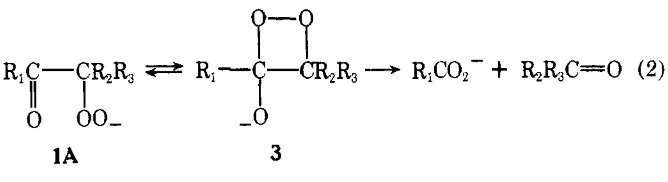
Chemiluminescence (CL) from the thermolysis of dioxetanes is efficient and an important key step for bioluminescence.[1,2] Although the observation of the CL from base-catalyzed decomposition of α-hydroperoxy ketones (**1**) suggested an operation of a dioxetane mechanism,[3] our previous report[4] has shown that the decomposition proceeds predominantly via an acyclic C=O addition mechanism (eq 1) rather than via cyclic dioxetane (eq 2).

Acyclic mechanism:[4]



$$\underset{\mathbf{1}}{R_1\underset{\underset{O}{\|}}{C}-\underset{\underset{OOH}{|}}{C}R_2R_3} + RO^- \rightleftharpoons \underset{\mathbf{2}}{R_1-\overset{\overset{RO}{|}}{\underset{\underset{{}^-O}{|}}{C}}-\underset{\underset{OOH}{|}}{C}R_2R_3} \longrightarrow R_1CO_2R + R_2R_3C{=}O + HO^- \quad (1)$$

Cyclic or dioxetane mechanism:[3]



$$\underset{\mathbf{1A}}{R_1\underset{\underset{O}{\|}}{C}-\underset{\underset{OO^-}{|}}{C}R_2R_3} \rightleftharpoons \underset{\mathbf{3}}{R_1-\overset{O-O}{\underset{\underset{{}^-O}{|}}{C}-CR_2R_3}} \longrightarrow R_1CO_2^- + R_2R_3C{=}O \quad (2)$$

The choice of mechanism, however, was ambiguous for the case of R_1 = *i*-Pr and a question remains open about the extent of operation of the cyclic pathway for various peroxy ketones. The present paper will describe the predominance of the acyclic path (eq 1) for all substrates and the minor cyclic path (eq 2) with CL (~10^{-3}% at most) producing triplet ketone.

Results and Discussion

Decomposition Kinetics. The rate of MeONa-catalyzed decomposition of α-hydroperoxy ketones (**1**, R′OOH) was

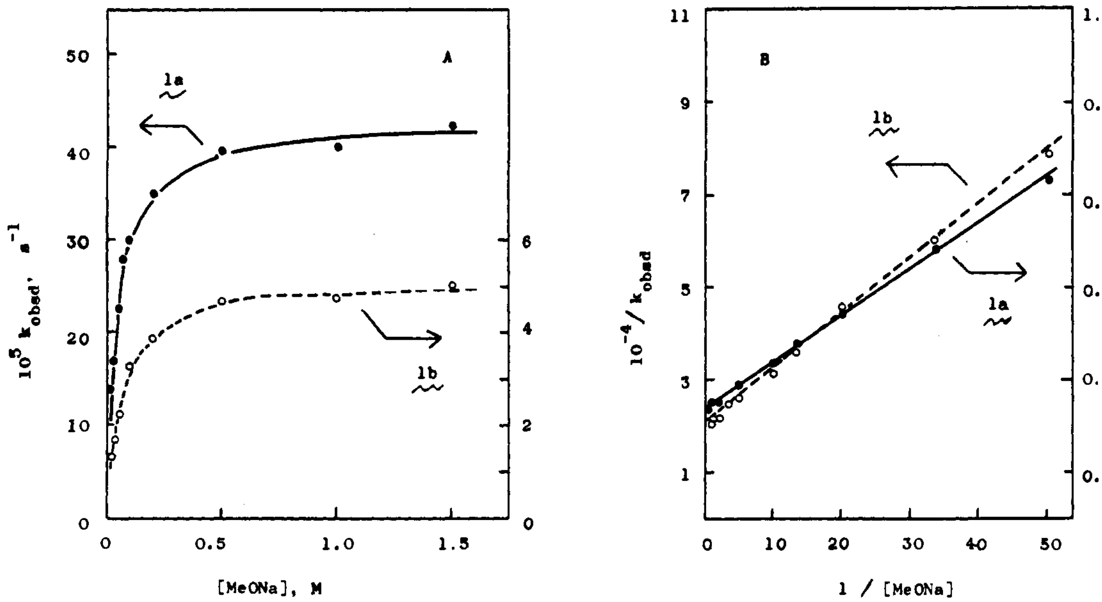


Figure 1. Effect of [MeONa] on k_{obsd} for alkaline decomposition of **1** (0.01 M) in 50% aqueous MeOH (see Table IA for conditions).

determined iodometrically and expressed as

$$v = k_{obsd}[R'OOH]_s \qquad (3)$$

Here, subscript s denotes stoichiometric concentration.

Our previous report[4] revealed that the base-catalyzed decomposition of **1a** ($R_1 = R_2 = R_3 = Me$) proceeds predominantly via the acyclic path, while the behavior of **1b** ($R_1 = i\text{-}Pr$; $R_2 = R_3 = Me$) was ambiguous from product analysis. Hence, the rates of decomposition of **1a** and **1b** were studied in order to compare kinetics of the two peroxides. The decomposition rates of **1a** and **1b** increase with increasing [MeONa] and then approach a constant value[5] (Table IA). A plot of $1/k_{obsd}$ vs. 1/[MeONa] gives a straight line (see Figure 1). However, this reciprocal linearity is consistent with both of the two mechanisms, eq 1 and 2, as stated below.

The acyclic and cyclic pathways can be simply written as

$$R'OOH + RO^- \overset{K_4}{\rightleftarrows} R'OO^- + ROH \qquad (4)$$

$$R'OOH + RO^- \xrightarrow{k_5} \text{products} \qquad \text{(acyclic path)} \qquad (5)$$

and/or

$$R'OO^- \xrightarrow{k_6} \text{products} \qquad \text{(cyclic path)} \qquad (6)$$

The product formation by the acyclic path (eq 5) alone affords the equation $k_{obsd}[R'OOH]_s = k_5[R'OOH][RO^-]$, which leads to

$$\frac{1}{k_{obsd}} = \frac{K_4}{k_5} + \frac{1}{k_5[RO^-]} \qquad (7)$$

whereas the cyclic path (eq 6) gives $k_{obsd}[R'OOH]_s = k_6[R'OO^-]$ and hence

$$\frac{1}{k_{obsd}} = \frac{1}{k_6} + \frac{1}{k_6K_4[RO^-]} \qquad (8)$$

Thus, both pathways satisfy the linear relationship for the plot of $1/k_{obsd}$ vs. 1/[MeONa]. The observed slopes and intercepts (Figure 1B) give the K_4 and k_5 or k_6 values. That is, the acyclic mechanism (eq 4 and 5) affords $k_5 = 9.6 \times 10^{-3}$ and 8.4×10^{-4} M^{-1} s^{-1} and $K_4 = 22$ and 17 M^{-1} for **1a** and **1b**, respectively. Or, if the cyclic mechanism is predominant, eq 8 affords $k_6 = 4.2 \times 10^{-4}$ and 5.1×10^{-5} M^{-1} s^{-1}, and $K_4 = 23$ and 17 M^{-1} for **1a** and **1b**, respectively. The K_4 values from these treatments are adequately close to the values from UV spectra ($K_4 = 26$ and 22 M^{-1} for **1a** and **1b**, respectively).[6] Hence, the choice of a predominant pathway is impossible only by these treatments as reported previously.[3,4]

Table I. Rates for Base-Catalyzed Decomposition of $R_1COC(OOH)Me_2$ at 25 °C[a]

[RONa], M	Solvent[b]	$10^5 k_{obsd}$,[c] s^{-1} 1a (R_1 = Me)	1b (R_1 = *i*-Pr)
	A. Effect of [RONa]		
0.02	50% MeOH	13.7	1.27
0.03	50% MeOH	17.0	1.65
0.05	50% MeOH	22.6	2.20
0.10	50% MeOH	30.0	3.23
0.20	50% MeOH	34.8	3.84
0.50	50% MeOH	39.7	4.64
1.0	50% MeOH	40.0	4.77
1.5	50% MeOH	42.2	5.01
	B. Effect of Solvent		
0.20	100% H_2O	100	10.4
0.20	50% MeOH	34.8 (104)[d]	3.84 (11.5)[d]
0.20	50% EtOH	39.9 (48)[d]	5.93 (7.1)[d]
0.20	50% *t*-BuOH	49.0	5.88
0.20	50% MeCN	53.8	20.2
0.20	50% dioxane	78.7	11.5
0.20	100% MeOH[e]	7.94	0.57

[a] Reaction with [**1**] = 0.01 M and [EDTA] = 4×10^{-3} M. Aqueous NaOH or methanolic MeONa was added as a base. The rates without EDTA were the same. [b] Volume % in water. [c] Determined iodometrically. [d] The value in parentheses is the k_{HO} value assuming $v = k_{HO}[\mathbf{1}][HO^-]$, $[HO^-]$ being estimated from the competitive dissociation of ROH and H_2O (see ref 7b). [e] [EDTA] = 0.

Our previous report[4] has revealed that peroxy ketone **1a** decomposes via a predominantly acyclic pathway; i.e., the yield of methyl ester was 90%. To compare the decomposition of **1a** and **1b**, solvent effect was examined with 0.20 M alkali, where over 77% of **1** is dissociated into $R'OO^-$; i.e., the change in $[R'OO^-]$ is rather small (within a factor of 1.3). Peroxy ketones **1a** and **1b** exhibited a significant solvent effect similarly (Table IB). That is, the decomposition is very slow in 100% MeOH and the reaction in aqueous alcohols is considerably slower than that in pure water or aqueous dioxane or acetonitrile. This order is independent of the solvent polarity. The

Table II. Chemiluminescence from Base-Catalyzed Decomposition of **1** at 40 °C[a]

	$R_1C(=O)$-$C(OOH)R_2R_3$				10^5k_{obsd},[c]	0.0025 M DBA			0.01 M fluorescein	
	R_1	R_2	R_3	Solvent[b]	s^{-1}	rel I	$10^8\Phi_{obsd}$	$10^6\Phi$[d]	rel I	$10^8\Phi_{obsd}$[e]
1a	Me	Me	Me	MeOH	40.7	1.4	4	1.5	0.23	0.67
1b	*i*-Pr	Me	Me	MeOH	8.9	0.3	4	1.5	~0.1	~1.4
1a	Me	Me	Me	50% H_2O	380				0.45	0.14
1b	*i*-Pr	Me	Me	50% H_2O	41				0.24	0.70
1c	Ph	Ph	CH(Et)Ph	25% PhH	155	43	33	13.2	4.5	3.44
1d	Ph	Ph	CH_2Ph	MeOH	198	20	12	4.8	6.1	3.67
1e	Ph	Ph	*i*-Pr	MeOH	200	7.1	4.2	1.7	0.7	0.42
1f	Ph	Ph	Et	MeOH	600	8.9	1.8	0.72		
1g	Me	Ph	CH_2Ph	MeOH	74	12	19	7.6	1.9	3.0
1h	*i*-Pr	Ph	CH_2Ph	MeOH	17	2.9	21	8.3	0.8	5.7
1i	Mes	Ph	Ph	MeOH	<0.1[f]	0.0	0	0	0	0
1j	Ph	Ph	Ph	MeOH	>1000[g]	0.0	0	0	0	0

[a] With [**1**] = 0.01 M and [MeONa] = 0.25 M. Ph = C_6H_5 and Mes = mesityl. [b] Volume % in MeOH. [c] Determined by iodometry. [d] Quantum yield of the CL was calculated according to the relation $\Phi = \Phi_{obsd}/(\Phi_{ET}{}^{TS}\,\Phi_F{}^A) = \Phi_{obsd}/(0.25 \times 0.1) = 40\Phi_{obsd}$, as the case of energy transfer from triplet acetone to DBA.[9a] Here, $\Phi_{ET}{}^{TS}$ and $\Phi_F{}^A$ are the quantum yields of triplet–singlet energy transfer and fluorescence of the accepter. [e] Since $\Phi = \Phi_{obsd}/\Phi_F{}^A$ and $\Phi_F{}^A < 0.01$ with 0.01 M fluorescein, Φ is higher than Φ_{obsd} by a factor of over 100. [f] Peroxide **1i** was not decomposed. [g] Too fast to determine the rate of decomposition.

Table III. Effect of [MeONa] on the Chemiluminescence[a]

1g (40 °C)		**1c** (30 °C)	
[MeONa], M	Rel I	[MeONa], M	Rel I
0.0057	0.8	0.032	3.6
0.014	2.8	0.063	6.3
0.028	4.4	0.118	9.8
0.054	7.5	0.167	13
0.125	11.0	0.25	17
0.25	11.0	0.50	18
0.50	10.0		

[a] Reaction with [**1**] = 0.01 M and [DBA] = 0.0025 M in MeOH-PhH (3:1) at 30 or 40 °C.

cyclic mechanism cannot explain the slower rate in MeOH, in spite of over 77% dissociation into $R'OO^-$, compared to that in water. On the other hand, the acyclic mechanism seems to explain reasonably the observed solvent effect, since the reactivities are in the order of $HO^- \gg MeO^- \simeq EtO^-$ as reported previously.[4] Thus, the corrected rate constant for the reaction of R′OOH with HO^- in 50% aqueous MeOH[7a] is very close to the constant in pure water (see note *d* in Table IB). The similar effect of solvents for **1a** and **1b** seems to suggest the same mechanism, i.e., the acyclic one, as a major pathway.

Chemiluminescence. Chemiluminescence (CL) was observed from the base-catalyzed decomposition of **1** in the presence of a suitable fluorescer, e.g., dibromoanthracene (DBA) or fluorescein (Table II). The exceptional case is **1i** and **1j**; i.e., peroxide **1i** (R_1 = Mes) does not decompose at 40 °C, while the decomposition of **1j** (R_1 = Ph) proceeds very fast via the nonluminescent acyclic path. Bubbling of N_2 has no effect on the CL intensity from **1** and DBA, suggesting that energy transfer to DBA (2.5 mM) is much faster than that to dissolved O_2 (~2 mM).

The quantum yield (Φ) of the CL was calculated from the CL intensity (rel I) and the decomposition rate (k_{obsd}) as described previously.[8] The resulting Φ values are 10^{-5}–10^{-6} with 2.5 mM DBA (see Table II). There is no marked relationship between k_{obsd} and rel I, but the Φ values for aromatic peroxides tend to be inversely proportional to the decomposition rate constant, k_{obsd}. This implies competition between cyclic and acyclic decompositions. An extreme case is **1j** without the cyclic pathway and **1i** with steric inhibition for carbonyl addition, intramolecularly (eq 2) or intermolecularly (eq 1).

The decomposition (k_{obsd}) and rel I of **1a** (R_1 = Me) are five- to tenfold faster than those of **1b** (R_1 = *i*-Pr) in MeOH. The decomposition rates of **1a** and **1b** rise up to five- to tenfold by addition of 50% water to MeOH, while the increase in CL intensity is below twofold, resulting in a large reduction in Φ. These facts suggest that the acyclic decomposition with HO^- in 50% aqueous MeOH is much faster than that with MeO^- in MeOH, while the cyclic decomposition (i.e., rel I) is not so affected by changing the media from MeOH to aqueous MeOH. A similar solvent effect on k_{obsd} and CL intensity has also been observed for the base-catalyzed decomposition of α-hydroperoxy esters.[8]

Effect of Concentration of MeONa. The CL intensity from DBA and **1c** or **1g** changes with [MeONa] (Table III) in a manner similar to the decomposition rate of **1**, e.g., Figure 1A. This dependence of rel I on [MeONa] suggests that rel I is proportional to [$R'OO^-$] and hence to [**3**] (see eq 2 and 6). The similar dependence on [MeONa] for rel I and k_{obsd} is understandable, since the rates of the cyclic and/or the acyclic paths are likewise dependent on [MeONa] as shown in eq 7 and 8.

Effect of Fluorescers. The CL intensity from **1c** changes with fluorescers, and the resulting Φ values are in the order DBA ≫ diphenylanthracene (DPA) > anthracene and eosin > fluorescein (Table IV). Similar results are obtained for the case of **1a** (Table IV) and **1g**. This orders in Φs clearly show a significant heavy atom effect on the energy transfer in these CL systems. According to the reported analysis,[9a] the I values with DBA and DPA in Table IV show that a ratio of [triplet ketone]/[singlet ketone] is over 300; i.e., the excited ketone produced from dioxetane intermediate **3** is overwhelmingly triplet. A similar formation of triplet ketone has been reported starting from stable dioxetanes.[9]

Luminescence Kinetics. Formation of excited triplet ketone ($^TC{=}O$) is described above. Now, a simplified mechanism for the CL in the presence of fluorescers (A) may be written as

$$R'OOH \text{ or } R'OO^- \xrightarrow{k_9} C{=}O \tag{9}$$

$$R'OOH \text{ or } R'OO^- \xrightarrow{k_{10}} {}^TC{=}O \tag{10}$$

$${}^TC{=}O \xrightarrow{k_{11}} C{=}O \tag{11}$$

$${}^TC{=}O + A \xrightarrow{k_{12}} C{=}O + {}^SA \tag{12}$$

Table IV. Effect of Fluorescers on the Chemiluminescence from Base-Catalyzed Decomposition of **1** at 40 °C[a]

Peroxide	Solvent[b]	Fluorescer ($\Phi_F{}^A$)[c]	Rel I	$10^8\ \Phi_{obsd}$	$10^8\ \Phi$[d]
1c	50% PhH	DBA (0.11)	43.0[e]	33.0	330
	25% PhH	DPA (0.85)	5.0[e]	3.8	4.5
	25% PhH	Fl (0.015)	4.0	3.1	21
	25% PhH	Eosin (0.0039)	4.0	3.1	80
	50% PhH	An (0.21)	0.0	0	0
1a	MeOH	Fl (0.015)	~0.25	~0.7	~50
	25% PhH	DBA (0.11)	1.4[f]	4.0	36
	25% PhH	DPA (0.85)	<0.2[f]	<0.6	<0.7

[a] Reaction with [**1**] = 0.01 M, [MeONa] = 0.25 M, and [fluorescer] = 0.0025 M. [b] Volume % in MeOH. [c] $\Phi_F{}^A$ was determined at 0.0025 M fluorescer, which is lower than $\Phi_F{}^A$ at diluted solution because of self-quenching. DBA = dibromoanthracene, DPA = diphenylanthracene, Fl = fluorescein, and An = anthracene. [d] $\Phi = \Phi_{obsd}/\Phi_F{}^A$. [e] According to the reported analysis,[9a] triplet/singlet ketone = 340. [f] The same analysis as footnote *e*, triplet/singlet > 300.

Table V. Effect of [DBA] on the Chemiluminescence of **1c** at 30 °C[a]

1[DBA], mM	Rel I	$10^6\Phi_{obsd}$[b]	$10^6\Phi$[c]
4.0	15.6	0.476	19.0
2.5	10.6	0.324	13.0
1.67	7.37	0.225	9.0
1.18	5.50	0.168	6.7
0.625	3.20	0.098	3.92
0.322	1.80	0.055	2.20
0.244	1.60	0.049	1.96
0.164	1.20	0.034	1.36
0.083	0.57	0.017	0.68

[a] Reaction with [1] = 0.01 M and [MeONa] = 0.25 M in PhH-MeOH (1:3) at 30 °C. [b] Φ_{obsd} was calculated from the initial rel I and $k_{obsd} = 39 \times 10^{-5}\ s^{-1}$. [c] See footnote *d* in Table II.

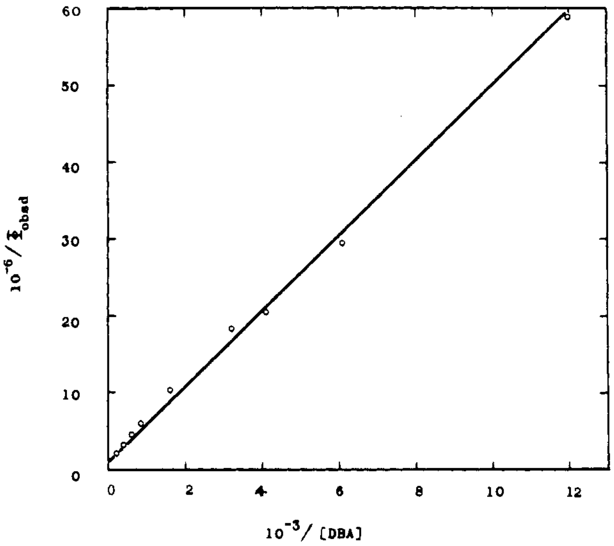


Figure 2. Plot of $1/\Phi_{obsd}$ vs. $1/[DBA]$ for the CL from **1c** and DBA (see Table V).

$$^SA \xrightarrow{k_{13}} A + h\nu \qquad (13)$$

Here, C=O is a ketone produced and ^SA is an excited singlet fluorescer. Assuming a steady-state concentration of $^TC{=}O$,

$$k_{10}[R'OOH]_s = k_{11}[^TC{=}O] + k_{12}[^TC{=}O][A] \qquad (14)$$

Since the yield of $^TC{=}O$ is very low, i.e., $k_{10} \ll k_9$,

$$k_{obsd} = k_9 + k_{10} \simeq k_9 \qquad (15)$$

The CL yield may be written as

$$\Phi_{obsd} = \frac{k_{12}[^TC{=}O][A]\Phi_{12}\Phi_F{}^A}{k_{obsd}[R'OOH]_s} \qquad (16)$$

Here, Φ_{12} is the quantum yield of ^SA formation (a competitive reaction: $^TC{=}O + A \rightarrow C{=}O + {}^TA$) and $\Phi_F{}^A$ is the fluorescence yield of A (eq 13) under the reaction condition. Equations 14-16 lead to

$$\frac{1}{\Phi_{obsd}} = \frac{1}{(k_{10}/k_{obsd})\Phi_F{}^A} + \frac{k_{11}}{(k_{10}/k_{obsd})k_{12}\Phi_{12}\Phi_F{}^A}\frac{1}{[A]} \qquad (17)$$

The CL data from **1c** with A = DBA in Table V satisfy a linear relationship between $1/\Phi_{obsd}$ vs. $1/[A]$ (Figure 2). This supports the above mechanism (eq 9-13) and the derivations (eq 14-17). The intercept in Figure 2 afford $\Phi_{obsd} = 0.80 \times 10^{-6}$ and then Φ is 3.2×10^{-5} from the equation $\Phi = \Phi_{obsd}/(\Phi_{12}\Phi_F{}^A)$ where $\Phi_{12} = 0.25$ and $\Phi_F{}^A = 0.1$ for DBA.[9a] That is, the limiting Φ value of $^TC{=}O$ formation at infinite [DBA] is 3.2×10^{-5}.

From the slope of 4.9×10^3 M in Figure 2, $4.9 \times 10^3\ k_{11} = (k_{10}/k_{obsd})k_{12}\Phi_{12}\Phi_F{}^A$. Since $\Phi_{12} = 0.25$, $\Phi_F{}^A = 0.1$, $k_{12} = 5 \times 10^{10}\ M^{-1}\ s^{-1}$,[9a] and $(k_{10}/k_{obsd}) = 3.2 \times 10^{-5}$, k_{11} is calculated to be $2 \times 10^8\ s^{-1}$;[10] i.e., lifetime of $^TC{=}O$ is 5×10^{-7} s, which is consistent with the reported triplet lifetimes of 10^{-6}-10^{-8} s for deoxybenzoins.[12] This coincidence supports the validity of the CL mechanism of eq 9-13.

The decomposition rates determined from the CL decay were the same with those from iodometry for the reported case of **1b**;[3] i.e., rel I is proportional to [**1b**]. On the other hand, rel I is not proportional to [**1c**] for the present case of **1c**; e.g., rel I is 880 and 1180 and then Φ is 0.53×10^{-6} and 0.39×10^{-6} with 0.005 and 0.010 M **1c** in the presence of 0.0025 M DBA in benzene-MeOH (1:3) at 30 °C. The smaller Φ with higher concentration of peroxide suggests an energy transfer from $^TC{=}O$ to peroxide **1c**. Thus, the rate constant for energy transfer (k_{et}) is calculated to be $4 \times 10^9\ M^{-1}\ s^{-1}$ from observed half-quenching concentration of ~0.01 M peroxide.[13] The reported k_{et} values to other peroxides are ca. 10^9-$10^{10}\ M^{-1}\ s^{-1}$ for singlet sensitization[14] and ca. 10^5-$10^6\ M^{-1}\ s^{-1}$ for triplet sensitization.[15] For the present case of **1c**, the k_{et} value from triplet α-phenylbutyrophenone (E_T = 74 kcal/mol) to peroxide **1c** is probably comparable to the diffusion-controlled rate constant ($2 \times 10^{10}\ M^{-1}\ s^{-1}$),[16] since α-oxy substitution does not alter its E_T values from the parent ketone[17] and hence E_T of **1c** is probably close to 74 kcal/mol. In other words, excited energy of $^TC{=}O$ is transferred to peroxide **1c** as a ketone (with ΔE_T ~0) rather than as a hydroperoxide. This conclusion may be reinforced by the fact that the CL intensity is proportional to the peroxide concentration for the case of aliphatic α-hydroperoxy ketone **1b**.

Cyclic and Acyclic Mechanism. Products from MeONa-catalyzed decomposition of several peroxides are shown in

Table VI. Products from Base-Catalyzed Decomposition of α-Hydroperoxy Ketones in MeOH at 25 °C[a]

Peroxide	Reaction time, h	Conversion, %	Products,[b] %		
			R_1CO_2Me	R_1CO_2H	$R_2R_3C{=}O$
1c	4	78	79	12	94
	19	100	46	33	84
1e	4	76	82	~15	64
1g	4	100	34	*d*	57[e]
	19[c]	100	4.6	*d*	52[f]
1h	19	52	23	*d*	38[g]

[a] Reaction with [**1**] = 0.02–0.03 M and [MeONa] = 0.1 M. [b] Determined by GLC analysis; % yield based on decomposed peroxide. [c] Reaction in PhH–MeOH (1:1). [d] R_1CO_2H was not determined. [e,f,g] Basic autoxidation of deoxybenzoin produces benzil and methyl benzoate, yields being 13 and 6, 7 and 8, 32 and 12%, respectively.

Table VI. It is apparent that produced ester is significantly hydrolyzed under the reaction conditions, since the yield of ester is largely reduced by a prolonged reaction time. Ester formation via the acyclic mechanism (eq 1) is a major path even for the case of **1c** with the most efficient CL, and the ester selectivity of 79% is a lower limit in view of accompanying hydrolysis.

Our conclusion of a predominantly acyclic pathway is different from the earlier one by Richardson et al.[3] They reported ca. 30% yield of the ester from **1b** but did not describe the formation of ester from **1c.** The data in Table VI show that the hydrolysis of aliphatic ester is considerably faster than that of methyl benzoate. The 30% selectivity of ester reported by Richardson et al.[3] seems to be considerably high in view of the faster hydrolysis of aliphatic esters. The solvent effect was examined with 0.25 M MeONa, where over 80% of **1** is dissociated into anion **1A.** That is, the decomposition of **1a** and **1b** in 50% aqueous MeOH is 5–10 times as fast as that in MeOH, while the increase in CL intensity is rather small (Table II). This contrast in solvent effect between k_{obsd} and rel I can only be explained by the predominance of acyclic decomposition via the reaction of R′OOH with HO^-.

It may thus be concluded from product selectivities, CL yields, and solvent effect on the decomposition rate and the CL that the acyclic pathway is generally predominant. The low yield of the CL ($\Phi \leq 10^{-5}$) suggests that the dioxetane pathway (eq 2) is quite a minor reaction.[18] Formation of triplet ketone can be shown for aromatic and aliphatic peroxides.

Experimental Section[20]

Materials. α-Hydroperoxy ketones **1** were synthesized via the *t*-BuOK-catalyzed autoxidation of ketones according to the method I in our previous paper.[4] Peroxides **1a,b,d–f,j** were described previously,[4] and peroxides **1g,h,i** of over 98% purity were crystallized from benzene-petroleum ether, mp 104-107, 125.5-126.0, and 18-20 °C, respectively. Peroxide **1c** was obtained according to the literature,[21] mp 147-148 °C (lit.[21] mp 152-153 °C).

Chemiluminescence. The CL was monitored by a Hitachi MPF-2A fluorescence spectrophotometer using a 4-mL quartz cell. Mostly, the decomposition rate of **1** was moderate at 40 °C and then the CL intensity was practically constant for the initial several minutes. When the decomposition was fast, the initial I at time zero was determined from the plot of I vs. time. The CL spectra were the same as the fluorescence spectra of fluorescer under the same conditions; e.g., $E_{\max}$ is at 540 nm for fluorescein, 430 nm for DBA, and 425 nm for DPA.

The quantum yields were determined according to the reported method[8,22] using $\Phi_{\text{obsd}} = I/(k_{\text{obsd}}[\mathbf{1}]_s \times 6 \times 10^{23})$ where I is the number of photons produced per second. The incident light (310-330 nm) from a Xe arc was determined by ferrioxalate actinometry.[23]

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(6) Determined from UV absorbance at 300 nm in 50% aqueous MeOH at 25 °C.

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