20 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 10 h. The crude photolysate was concentrated under reduced pressure, and the residue was chromatographed on a silica gel column with use of hexane as the eluant. The major component isolated from the column was a crystalline solid (mp 106–107 °C) whose structure was assigned as 1-methyl-5,6-diphenyl-4,4,6-trideuterio-2,3-benzobicyclo[3.1.0]hexene: NMR ($CDCl_3$, 100 MHz) τ 8.48 (s, 3 H), 2.48–3.46 (m, 14 H); *m/e* 299 (M$^+$), 284, 222, 207, 206, 205 and 168.

Triplet-Sensitized Irradiation of 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-phenyl)cyclopropene (31). A solution containing 120 mg of **31** and 15 mg of thioxanthone in 200 mL of benzene was irradiated with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 90 min. The solution was concentrated under reduced pressure, and the resulting residue was chromatographed on a thick-layer plate. The first fraction contained 65 mg of unreacted starting material. The second fraction consisted of 40 mg (33%) of a white solid (mp 78–79 °C) whose structure was assigned as 1,5-diphenyl-6-methyl-4,4,6-trideuterio-2,3-benzobicyclo[3.1.0]hexene: NMR ($CDCl_3$, 100 MHz) τ 8.83 (s, 3 H), 2.50–3.41 (m, 14 H); *m/e* 299 (M$^+$), 284 (base), 222, 220, 207, 206, 205, 204.

Preparation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (32) and 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (33). A solution containing 1.9 g of *o*-bromo-α,α,α-trideuteriotoluene was converted to the corresponding Grignard reagent. A 4.0-g sample of diethyl carbonate in 25 mL of ether was added to the above Grignard reagent, the mixture was heated at reflux for 10 h. At the end of this time the mixture was quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with a 10% hydrochloric acid solution and a 5% sodium bicarbonate solution, and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 920 mg (51%) of ethyl *o*-methyl-d_3-benzoate: NMR ($CDCl_3$, 100 MHz) τ 8.82 (t, 3 H, $J = 7.0$ Hz), 5.93 (q, 2 H, $J = 7.0$ Hz), 2.16–3.24 (m, 4 H).

To the above material in 50 mL of ether was added 200 mg of lithium aluminum hydride. The mixture was heated at reflux for 3 h followed by quenching with water. The ether layer was dried over magnesium sulfate and concentrated under reduced pressure to give 605 mg (90%) of *o*-methyl-d_3-benzyl alcohol: NMR ($CDCl_3$, 100 MHz) τ 7.83 (br s, 1 H), 5.47 (s, 2 H), 2.72–3.12 (m, 4 H). A sample of the above alcohol was taken up in ether and heated with 10 mL of concentrated hydrochloric acid for 4 h. The mixture was extracted with ether, washed with water, and dried over magnesium sulfate to give 580 mg (85%) of *o*-methyl-d_3-benzyl chloride: NMR ($CDCl_3$, 100 MHz) τ 5.44 (s, 2 H), 2.55–2.87 (m, 4 H).

A sample of *o*-methyl-d_3-benzyl chloride was converted into the corresponding Grignard reagent which, in turn, was allowed to react with 3-methyl-1,2-diphenylcyclopropenyl perchlorate according to the procedure previously described. Chromatography of the crude reaction mixture on silica gel gave a 10% yield of 1,2-diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (**32**) (*m/e* 313 (M$^+$)) and a 31% yield of 1,3-diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (**33**) (*m/e* 313 (M$^+$)).

Triplet-Sensitized Irradiation of 1,2-Diphenyl-3-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (32) and 1,3-Diphenyl-2-methyl-3-(*o*-methyl-d_3-benzyl)cyclopropene (33). The irradiation of cyclopropenes **32** and **33** were carried out as previously described. The crude reaction mixtures were subjected to thick-layer chromatography in order to isolate pure samples of the photoproducts. The thioxanthone sensitized irradiation of **32** gave 1,7-diphenyl-6-methyl-2,2,7-trideuterio-3,4-benzobicyclo[4.1.0]heptene as the exclusive photoproduct: NMR ($CDCl_3$, 100 MHz) τ 8.72 (s, 3 H), 6.85 (s, 2 H), 2.31–3.26 (m, 14 H); *m/e* 313 (M$^+$), 298, 207 (base), 206, 77. The sensitized irradiation of cyclopropene **33** gave 1,6-diphenyl-7-methyl-2,2,7-trideuterio-3,4-benzobicyclo[4.1.0]heptene as the sole photoproduct: NMR ($CDCl_3$, 100 MHz) τ 8.89 (s, 3 H), 6.94 (d, 1 H, $J = 16.0$ Hz), 6.57 (d, 1 H, $J = 16.0$ Hz), 2.51–3.23 (m, 14 H); *m/e* 313 (M$^+$).

Quantum Yield Determinations. Quantum yields were determined by using a "merry-go-round" apparatus[94] equipped with a 450-W Hanovia lamp housed in a quartz well at the center of the carriage. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in five freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[32] For the sensitized runs a filter solution of potassium dichromate in aqueous potassium carbonate was circulated through the well and the entire unit allowed to run for 1 h prior to use.[95] A Uranium glass filter sleeve and Corning 7-54 filters were also used in conjunction with the filter solution. The concentrations were adjusted so that the sensitizer absorbed more than 98% of the light. Analyses were performed on a 6 ft 10% Carbowax 20 M column on chromosorb P at 265 °C. The conversions were run to 25% or less. The mass balance in these runs was generally better than 98%. *trans*-Stilbene was used as the triplet quencher in the Stern–Volmer plots.

Acknowledgment. We are grateful to the National Science Foundation (Grant CHE-7900919) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Supplementary Material Available: Table II, the positional and thermal parameters obtained from the least-squares refinement (3 pages). Ordering information is given on any current masthead page.

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[94] Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

[95] Wagner, P. J.; Nakahira, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 3668.

Chemiluminescence of Secondary Peroxyesters[1]

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Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. Received November 5, 1980

Abstract: The thermolysis of 1-phenylethyl peroxyacetate and a series of substituted 1-phenylethyl peroxybenzoates was investigated. Thermolysis in benzene gives acetophenone and the corresponding carboxylic acid. The study of the reaction kinetics and kinetic isotope effect indicates that the unimolecular thermolysis proceeds by homolysis of the oxygen–oxygen bond. Electronically excited states are formed in the thermolyses of these peroxyesters. These are detected by their characteristic direct chemiluminescence or by indirect chemiluminescence. In the presence of easily oxidized catalysts these peroxyesters give excited states by the chemically initiated electron-exchange luminescence (CIEEL) path. The mechanism of these luminescent reactions was investigated.

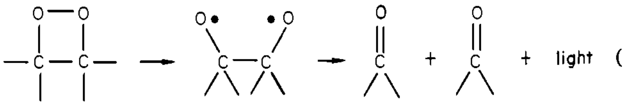
The chemical generation of electronically excited states from the thermolysis of appropriate organic peroxides is an area of active and increasing interest.[2] Most of the peroxides thus far found to generate excited states are cyclic compounds. This fact is the

Table I. Rate Constants at 100 °C and Activation Parameters for Thermolysis of Peroxyesters 1 and 2

	$10^4 k_1$,[b] s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
$PhCH(CH_3)O_3CCH_3$ (1)	1.14 ± 0.07	33.1 ± 0.7	10.8 ± 1.9
$XC_6H_4CO_3CH(CH_3)C_6H_5$			
X = H (2a)	4.03 ± 0.03[c]	29.5 ± 3.3	4.6 ± 8.9
X = *p*-OCH_3 (2b)	3.50 ± 0.02[c]	32.0 ± 3.1	11.4 ± 8.3
X = *p*-$N(CH_3)_2$ (2c)	21.6 ± 0.1	26.6 ± 0.5	0.5 ± 1.4
X = *m*-NO_2 (2e)	5.97 ± 0.05	32.5 ± 1.1	14.1 ± 6.1
X = *p*-NO_2 (2d)	4.10 ± 0.04	34.9 ± 3.6	19.8 ± 10

[a] Benzene solutions were purged with argon before measurements and were ca. 1×10^{-4} M in perester. [b] Perylene (6×10^{-4} M) activated chemiluminescence was monitored to determine the rates. [c] Temperature 99.7 °C.

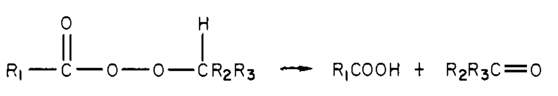
result of two important considerations. First, one of the key prerequisites for efficient excited state generation is that the energy available at the reaction transition state be at least as great as the energy of the lowest excited state of one of the reaction products. Often the strain released in converting a cyclic peroxide to acyclic products provides a significant portion of the energy required to form excited states. A classic example of this is found in the 1,2-dioxetanes where ca. 25 kcal/mol of strain energy is released on fragmentation of the four-membered ring.[3] Second, incorporating the peroxide linkage in an appropriate cycle provides a path whereby cleavage of two or more bonds can result in the formation of closed-shell products. Thus a typical chemiluminescent pathway might involve homolysis of the peroxide linkage to form a biradical followed by cleavage of a second bond to generate the ultimate products. Again, the 1,2-dioxetane ring system provides the most thoroughly studied examples of this behavior. The mechanism for chemiluminescence of these peroxides appears to proceed through the 1,4-dioxybiradical (eq 1).[4]



(1)

One of the difficulties associated with the study of cyclic peroxides is that they are difficult to prepare. This stems in large part from the competition between cyclization and polymerization of their precursors. A second difficulty with strained cyclic systems is that the very strain that contributes to the reaction exothermicity also lowers the reaction activation enthalpy, thereby making isolation and purification of these molecules difficult at best.

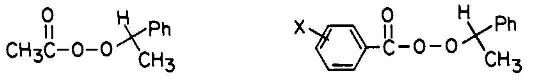
With these restrictions on the properties of cyclic peroxides in mind we were attracted to a report by Hiatt, Glover, and Mosher[5] on the thermal chemistry of acyclic secondary peroxyesters. This report revealed that these compounds undergo unimolecular thermolysis to generate the appropriate carboxylic acid and carbonyl compound (eq 2). We estimated by using Benson's



$$R_1-\overset{O}{\overset{\|}{C}}-O-O-\overset{H}{\overset{|}{C}}R_2R_3 \longrightarrow R_1COOH + R_2R_3C{=}O \qquad (2)$$

group equivalent method[6] that the prototypical reaction, shown in eq 2, is exothermic by ca. 60 kcal/mol. When the exothermicity is combined with the reaction activation energy, reported to be ca. 25 kcal/mol,[5] it is clear that there is sufficient energy available at the transition state of the secondary peroxyester reaction for the formation of the excited state of the carbonyl compound.[7] Unknown at the outset of this work was whether a mechanism exists to channel this energy to the formation of electronically excited states.

We report herein the results of our investigation of both the thermal- and electron-donor-induced reactions of 1-phenylethyl peroxyacetate (1) and a series of substituted 1-phenylethyl peroxybenzoates (2a–e). These results provide new insight into the direct generation of electronically excited states from unimolecular thermolyses and into the details of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.[8]

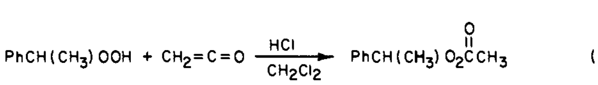


1

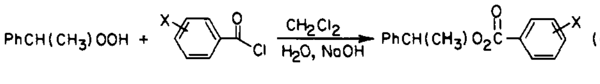
2a X = H
2b X = p-OMe
2c X = p-N(Me)$_2$
2d X = p-NO$_2$
2e X = m-NO$_2$

Results and Discussion

Synthesis of Secondary Peroxyesters. All of the peroxyesters investigated can be conveniently prepared by reaction of 1-phenylethyl hydroperoxide with the appropriate activated acid precursor. We prepared the hydroperoxide by two different routes: oxidation of ethylbenzene[9] and acid-catalyzed substitution of hydrogen peroxide on 1-phenylethanol.[10] The details for preparation of the hydroperoxide by both procedures are given in the Experimental Section. The acid-catalyzed substitution must be carried out with extreme caution. We experienced two violent explosions when we attempted to scale up this preparation. Reaction of the hydroperoxide with ketene in CH_2Cl_2 and HCl followed by vacuum distillation gives analytically pure peroxyacetate 1 (eq 3). The substituted peroxybenzoates are prepared by reaction of the hydroperoxide with the appropriately substituted acid chloride in a two-phase basic mixture (eq 4). Recrystallization, in some cases at low temperature, gives analytically pure peroxyesters. In addition to the normal spectroscopic characterization, all of the peroxyesters except 2c[11] were reduced with triethyl phosphite or triphenylphosphine to the corresponding ester and this product was compared to authentic material. The details of the synthesis, purification, and characterization of the peroxyesters are given in the Experimental Section.



$$PhCH(CH_3)OOH + CH_2{=}C{=}O \xrightarrow[CH_2Cl_2]{HCl} PhCH(CH_3)O_2\overset{O}{\overset{\|}{C}}CH_3 \qquad (3)$$



(4)

Thermolysis of Peroxyesters in Benzene. In all cases examined the only products formed from the thermolysis of dilute solutions of the peroxyesters in benzene are the appropriate acid and acetophenone, both in essentially quantitative yield (eq 5). This observation is particularly pertinent for the case of peroxyacetate

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(1) Some of these results appeared in a preliminary report: B. G. Dixon and G. B. Schuster, *J. Am. Chem. Soc.*, **101**, 3116 (1979).

(2) For recent reviews see: R. C. Hart and M. J. Cormier, *Photochem. Photobiol.*, **29**, 209 (1979). L. R. Faulkner in "Methods of Enzymology", Vol. LVII, M. A. DeLuca, Ed., Academic Press, New York, 1978. M. M. Rauhut in "Kirk-Othmer: Encyclopedia of Chemical Technology", Vol. 5, M. Grayson, Ed., Wiley, New York, 1979. P. D. Bartlett and M. E. Landis in "Singlet Oxygen", Academic Press, New York, 1979.

(3) G. Höhne, A. H. Schmidt, and P. Lechtken, *Tetrahedron Lett.*, 3587 (1976).

(4) (a) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, H. E. O'Neal, *J. Am. Chem. Soc.*, **96**, 7525 (1974); (b) J.-Y. Koo and G. B. Schuster, *ibid.*, **100**, 5403 (1978); (c) K. A. Horn, J.-Y. Koo, S. P. Schmidt, and G. B. Schuster, *Mol. Photochem.*, 9, 1 (1978–1979) and references cited therein.

(5) R. R. Hiatt, L. C. Glover, and H. S. Mosher, *J. Am. Chem. Soc.*, **97**, 1556 (1975).

(6) S. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

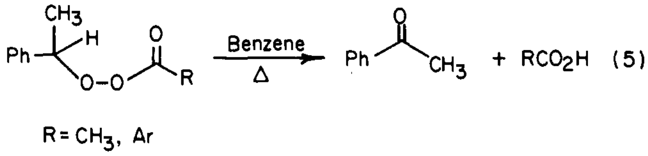
(7) E. B. Wilson, *J. Am. Chem. Soc.*, **98**, 3387 (1976). E. Lissi, *ibid.*, **98**, 3386 (1976).

(8) J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977); G. B. Schuster, *Acct. Chem. Res.*, **12**, 366 (1979).

(9) K. Tanaka and J. Imamura, *Chem. Lett.*, 1347 (1974).

(10) M. Bassey, C. A. Bunton, A. G. Davies, T. A. Lewis, and D. R. Llewellyn, *J. Chem. Soc.*, 2471 (1955).

(11) Reaction of 2c with triphenylphosphine is very slow and does not give the reduction product. This may indicate a relationship between the reaction of the peroxide with the phosphite and its CIEEL behavior (vide infra).

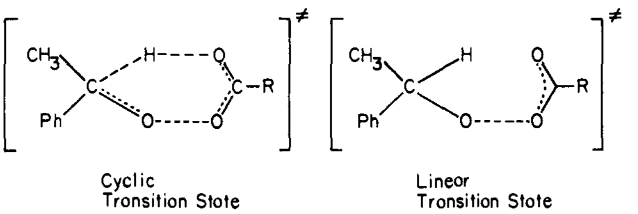


(5)

1 where formation of the acetyloxy radical is expected to lead to rapid loss of CO_2[12] and thus to a concomitant decrease in the yield of acetic acid.

The rates of thermolysis of the peroxyesters in argon-purged benzene can be followed conveniently by their direct, indirect, or activated chemiluminescence. The details of these procedures are described completely below. For the present discussion it is critical to point out only that the chemiluminescent intensity obtained in these kinetic studies is directly proportional to the concentration of the peroxyester and that the derived rate constants are identical with those obtained by using more conventional spectroscopic techniques to monitor the peroxyester concentration. In all of the cases examined, carefully purified benzene and peroxyester solutions show clean first-order consumption of the peroxide. Typical kinetic runs are shown in Figure 1, Eyring plots are shown in Figure 2, and the first order rate constants with their derived activation parameters are listed in Table I. It should be noted that for peroxyacetate **1** at initial concentrations above 10^{-2} M, the first-order rate constants obtained, and the activation parameters derived therefrom, are dependent on the initial peroxyester concentration. However, at low initial peroxyester concentration (10^{-5}–10^{-3} M) the rate constants are independent of the initial peroxide concentration. Apparently, at the higher concentrations a second reaction path, perhaps radical-induced homolysis,[13] becomes significant. All of the kinetic and chemiluminescent experiments on peroxyester **1** are carried out in the low concentration region.

The activation parameters for the peroxyester thermolyses reveal some important details of the reaction mechanism. The activation enthalpy obtained for peroxyester **1** is quite similar to that reported by Hiatt and co-workers[5] for related secondary peroxyesters in the vapor phase but is considerably higher than the values obtained by these workers for solution-phase reactions. Similarly, the activation entropies we obtain are more closely aligned with the vapor-phase values of Hiatt.[5] This observation is of significance since the rather small activation enthalpy and negative activation entropy reported earlier were used to support the notion of a cyclic transition state for these reactions. In contrast, the activation parameters we obtain for peroxyacetate **1** resemble closely the values measured for tertiary peroxyesters where the cyclic transition state is not possible and simple oxygen–oxygen bond homolysis is the accepted mechanism.[14]



To analyze further the degree of carbon–hydrogen bond involvement in the rate-determining step of the unimolecular thermolysis of **1**, we measured the kinetic isotope effect that results from replacement of the methine hydrogen of **1**[15] with deuterium (peroxyester **1d**). In benzene at 100 °C k_H/k_D is 1.11 ± 0.10. We consider this value to be too small to be indicative of significant cleavage on the carbon–hydrogen bond at the reaction transition state.[16] Thus, in contrast to the modified Russell mechanism[17] proposed by Hiatt and co-workers,[5] we favor the linear representation for the reaction transition state.

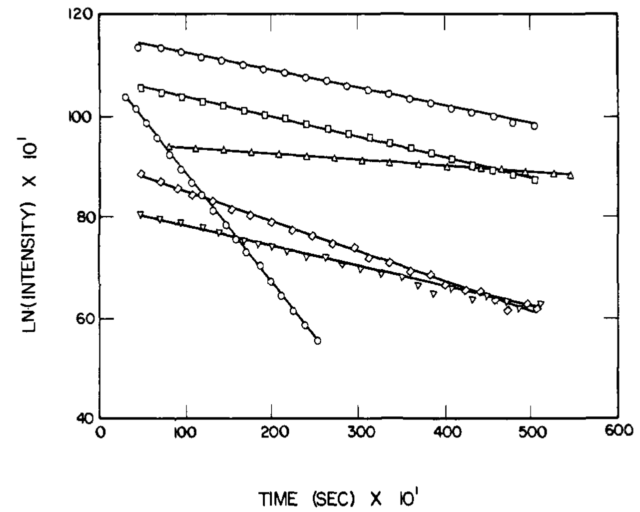


Figure 1. First-order decay of indirect or direct chemiluminescence intensity from peroxyesters at 100 °C in benzene solution. Starting concentrations range from 1 × 10^{-4} to 3 × 10^{-4} M. From the top down the lines represent the following: circles, **2b**; squares, **2a**; circles, **2c**; triangles, **1**; diamonds, **2e**; triangles, **2d**.

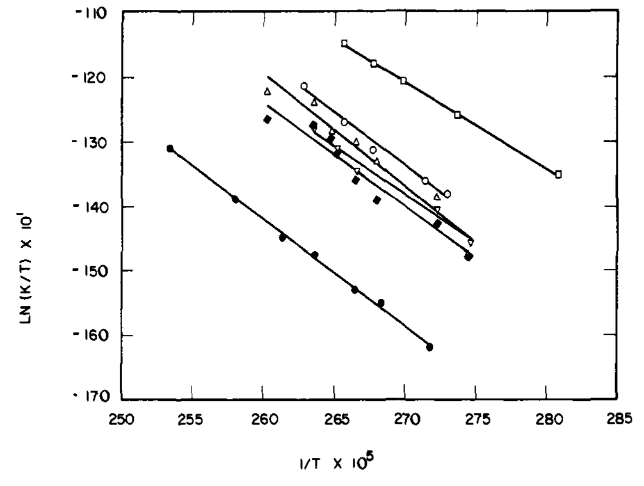


Figure 2. Eyring activation plots from the first-order chemiluminescence decay of peroxyesters in benzene solution. From the top down the lines represent the following: squares, **2c**; circles, **2e**; triangles, **2d**; triangles, **2a**; diamonds, **2b**; circles, **1**.

The activation parameters obtained for the substituted peroxybenzoates show a slight dependence on the nature of the substituent which has statistical significance only for the dimethylamino-substituted peroxybenzoate **2c**. In this case both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considerably smaller than for the other structures examined. For this reason and because this compound also exhibits unusual chemiluminescent properties (see below), we measured the kinetic deuterium isotope effect when the methine hydrogen of this compound is replaced by deuterium. In this case the value of k_H/k_D obtained is 1.18 ± 0.04 which again fails to indicate significant involvement of the carbon–hydrogen bond at the transition state.

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[12] J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Am. Chem. Soc.*, **98**, 129 (1967), and references cited therein.

[13] R. A. Wolf, M. J. Migliore, P. H. Fuery, P. R. Gagnier, I. C. Sabeta, and R. J. Trocino, *J. Am. Chem. Soc.*, **100**, 7967 (1978); P. D. Bartlett and K. Nozaki, *ibid.*, **68**, 1686 (1946).

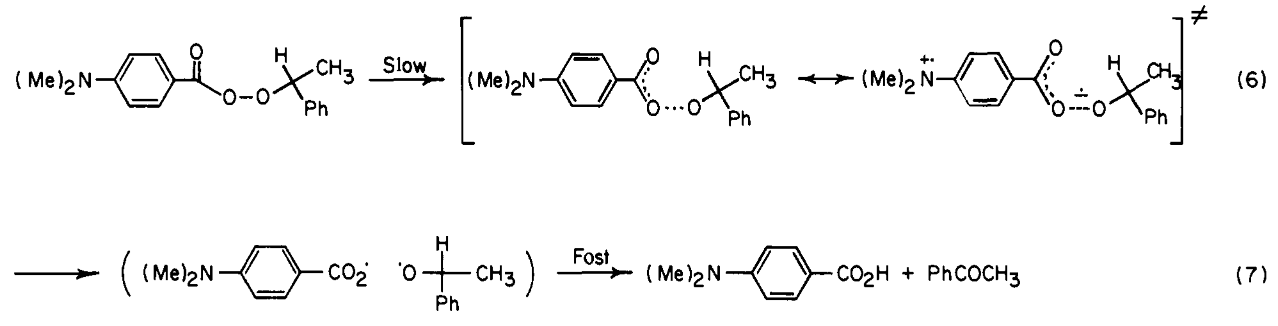
[14] W. A. Pryor and K. Smith, *Int. J. Chem. Kinet.*, **3**, 387 (1971).

[15] The deuterated peroxyester was prepared from the benzyl alcohol[34] obtained by $LiAlD_4$ reduction of acetophenone. NMR analysis indicated greater than 97% deuterium incorporation.

[16] Professor Cheves Walling, in a private communication with the author, has pointed out that for a very exothermic reaction with an early transition state the isotope effect observed might be quite small. However, Mosher has shown that the isotope effect for thermolysis of disecondary peroxides to hydrogen and ketone is 3-4. L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **84**, 2811 (1962); **82**, 4537 (1960).

[17] G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

Scheme I



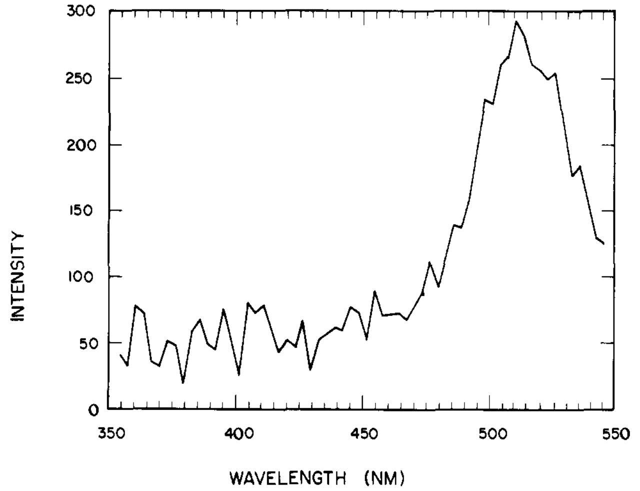
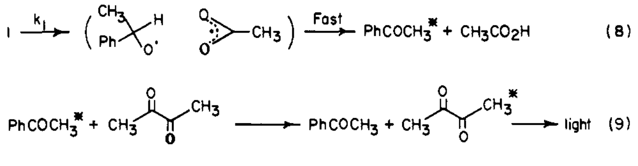


Figure 3. Emission spectrum of indirect chemiluminescence from peroxyacetate **1** (2.2×10^{-3} M) and biacetyl (2.0×10^{-3} M) in benzene solution at 100 °C.

In sum, the thermal and isotopic data indicate that the mechanism for thermolysis of these peroxyesters has as the rate-determining step the cleavage of the oxygen–oxygen bond without much, if any, carbon–hydrogen bond cleavage. The dimethylamino substituent on the peroxybenzoate **2c** may influence the relative position of the transition state along the reaction coordinate by donating electron density to the antibonding σ oxygen–oxygen orbital as this bond cleaves.[18] Our findings, particularly the nearly quantitative yield of acetic acid from **1**, indicate that transfer of the hydrogen atom to generate the final products competes successfully with escape from the solvent cage and with decarboxylation. This mechanism is shown for **2c** in Scheme I.

Direct and Indirect Chemiluminescence. Direct chemiluminescence is observed when one of the products of a unimolecular thermal reaction is formed in an electronically excited state and subsequently emits a photon of light. Thus the emission, fluorescence or phosphorescence, from excited acetone that results from thermolysis of tetramethyldioxetane (**3**) is an example of direct chemiluminescence.[19] Indirect chemiluminescence occurs when energy transfer from the initially formed excited state to an added emitter precedes the generation of light. Thus thermolysis of **3** in the presence of 9,10-diphenylanthracene (DPA) produces indirect chemiluminescence emission from excited DPA formed by energy transfer from the first generated excited singlet acetone.[20]

Scheme II



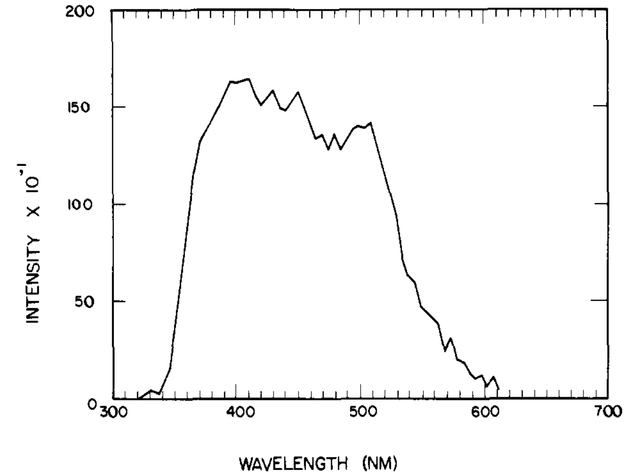


Figure 4. Emission spectrum of direct chemiluminescence from *p*-dimethylamino-substituted peroxybenzoate (**2c**), 1.8×10^{-2} M in benzene solution at 92.2 °C.

We examined the thermal reactions of peroxyacetate **1** and substituted peroxybenzoates **2** for both direct and indirect chemiluminescence. Thermolysis of peroxyacetate **1** in benzene solution at 100 °C gives very weak direct chemiluminescence. The emission is so weak that we are unable to obtain its spectrum. However, we can place the emission maximum between 420 and 480 nm, which is consistent with phosphorescence from triplet acetophenone.[21] The indirect chemiluminescence experiment gives a more satisfying result. When biacetyl, which has a considerably higher phosphorescence quantum efficiency than acetophenone,[22] is used as the energy acceptor a reasonably strong chemiluminescent emission is observed. The spectrum of the emission, shown in Figure 3, is identical with that of biacetyl phosphorescence. Within our limit to detect it, there is no fluorescence component to the indirect chemiluminescence of **1** and biacetyl. This observation indicates either that the excited state formed in the thermal reaction is a triplet or that intersystem crossing of the first formed state is more rapid than singlet–singlet energy transfer to biacetyl. In either case, we assign the structure of the first formed excited state to acetophenone. The yield of excited acetophenone is very low. We estimate, by comparison with tetramethyldioxetane indirect chemiluminescence with biacetyl,[23] that

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(18) It appears to be general that increasing the oxygen–oxygen bond length of a peroxide results in a marked lowering of the energy of this orbital: S. P. Schmidt, M. A. Vincent, C. E. Dykstra, and G. B. Schuster, *J. Am. Chem. Soc.*, **102**, 1292 (1981).

(19) N. J. Turro, P. Lechtken, N. E. Schore, G. B. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).

(20) T. Wilson, *Int. Rev. Sci.: Phys. Chem., Ser. Two*, **9**, 265 (1976), and references cited therein.

(21) R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley, New York, 1969.

(22) H. L. J. Häckström and K. Sandros, *Acta Chem. Scand.*, **12**, 823 (1958).

excited acetophenone is formed under these conditions with a yield of about 0.02% (Scheme II). Finally, we should point out that, as expected for indirect chemiluminescence, the addition of biacetyl has no effect on the rate of the reaction for low peroxyacetate concentrations.

The direct and indirect chemiluminescence observed for the substituted peroxybenzoates is dependent upon the nature of the substituent. The parent peroxybenzoate **2a**, and the *p*-OMe (**2b**), *p*-NO_2 (**2d**), and *m*-NO_2 (**2e**) substituted peroxybenzoates show very little direct chemiluminescence, a result similar to that obtained for the peroxyacetate. Also, the indirect chemiluminescence with 9,10-dibromoanthracene (DBA) as an energy acceptor is very weak with these peroxides. In contrast to these results, the dimethylamino-substituted peroxybenzoate (**2c**) gives reasonably intense direct and indirect chemiluminescence.

Thermolysis of peroxide **2c** in benzene solution gives an emission whose spectrum (Figure 4) is identical with the fluorescence spectrum of photoexcited *p*-(dimethylamino)benzoic acid under similar conditions. We therefore attribute this observed direct chemiluminescence to the formation of the singlet excited acid. The yield of directly generated excited acid was determined, by comparison with the indirect chemiluminescence of dioxetane **3** and DBA, to be 0.24%.[24] Since none of the other peroxybenzoates generate detectable direct chemiluminescence it is not possible to compare this yield directly to these other peroxides. However, when the limit to detectability set by the signal to noise ratio of our chemiluminometer is considered the dimethylamino-substituted peroxide **2c** generates excited singlet products at least 1000 times more efficiently than do any of the ohter peroxybenzoates examined.[25]

Indirect chemiluminescence with DBA as the energy acceptor is unusual in that the DBA is able to accept energy from sufficiently energetic triplets and form its emissive excited singlet state (triplet to singlet energy transfer).[26] Thus it is possible to use the indirect chemiluminescence of DBA as an indicator of excited triplet state formation. Figure 5 shows a double-reciprocal plot of indirect chemiluminescence intensity against DBA concentration for peroxybenzoates **2a** and **2c**. By comparison with a similar experiment using dioxetane **3**, the yields of directly formed triplet (dimethylamino)benzoic acid and benzoic acid obtained from thermolysis of the peroxyesters are 3.8 and 0.002%, respectively. The yields of triplet acid generated from peroxybenzoates **2b**, **2d**, and **2e** as indicted by the DBA indirect chemiluminescence intensity are similar to that obtained from the unsubstituted peroxide **2a**.

Evidently, the *p*-dimethylamino substituent greatly alters the ability of these secondary peroxybenzoates to generate electronically excited-state products directly. There are two likely rationalizations for this effect. The first is that the powerfully electron-donating amino substituent somehow alters the reaction transition state to facilitate excited-state formation. Or, second, that the lower energy of the excited singlet state of (dimethylamino)benzoic acid (the singlet energy of benzoic acid and *p*-(dimethylamino)benzoic acid are 98.3 and 83.5 kcal/mol, respectively) directs the reaction to excited products. As indicated above, the activation enthalpy obtained for **2c** is lower than that of the other peroxyesters examined. This indicates some special stabilization of the transition state. However, the kinetic isotope effect indicates that the linear oxygen–oxygen homolysis model remains an acceptable representation of the structure of the transition state. It should be noted also that there is not a significant primary isotope effect on the direct or indirect (with DBA) chemiluminescence of **2c**. The lowered excited-state energy explanation, however, does not appear to hold for the formation of the triplet acids. We have determined the triplet energy of *p*-(dimethylamino)benzoic acid to be 73.3 kcal/mol, which is only 3.8 kcal/mol below the triplet of benzoic acid. Yet the yield of triplet excited states differ by a factor of ca. 2000. We, at this time, cannot offer an unambiguous explanation for the increased excited state yield from peroxybenzoate **2c**. However, we do note that a similar effect of amino substitution has been reported in the luminol series.[27] We are continuing to investigate the direct chemiluminescence of secondary peroxyesters in the hope of both increasing the efficiency of excited-state formation and gaining insight into the detailed structural requirements and the mechanism of this system.

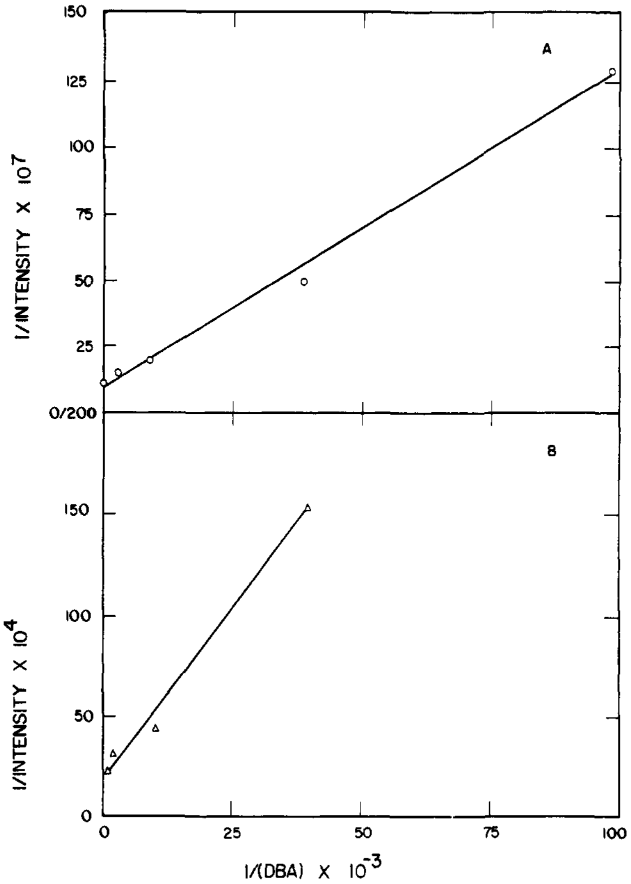

Figure 5. Double-reciprocal plot of total indirect chemiluminescence intensity against DBA concentration for (A) peroxybenzoate **2a** and (B) *p*-dimethylamino-substituted peroxybenzoate **2c** in benzene solution at 100 °C.

Chemically Initiated Electron-Exchange Luminescence. Activated chemiluminescence is observed when an electronically excited state is formed as a direct consequence of the bimolecular reaction of a catalytic activator and an energy-rich compound. Usually the excited state formed is that of the activator. For example, we have shown that dimethyldioxetanone reacts with easily oxidized aromatic hydrocarbons (rubrene, for example) to give the excited state of the hydrocarbon.[28] Activated chemiluminescence differs conceptually and mechanistically from both direct and indirect chemiluminescence. The two most critical observable differences are that for activated chemiluminescence by the CIEEL path the effeciveness of an activator is determined in large part by its oxidation potential and, second, that the addition of the activator may increase the rate of consumption of the peroxide.[29]

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(23) The yield of triplet acetone from **3** was taken to be 30%: T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976).

(24) The efficiency of triplet to singlet energy transfer from acetone and from *p*-(dimethylamino)benzoic acid triplet to DBA is assumed to be the same.

(25) This estimate is based on the observed signal to background ratio for **2c** of 3000:1 and then defining as detectable a signal to background ratio of 3:1. This is a conservative estimate.

(26) T. Wilson and A. P. Schaap, *J. Am. Chem. Soc.*, **93**, 4126 (1971). N. J. Turro, P. Lechtken, G. B. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *ibid.*, **96**, 1627 (1974).

(27) K.-D. Gundermann, *Chimia*, **25**, 261 (1971); H. D. K. Drew and F. H. Pearman, *J. Chem. Soc.*, 586 (1937); H. D. K. Drew and R. F. Garwood, *ibid.*, 386 (1939); R. B. Brundrett and E. H. White, *J. Am. Chem. Soc.*, **96**, 7497 (1974).

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

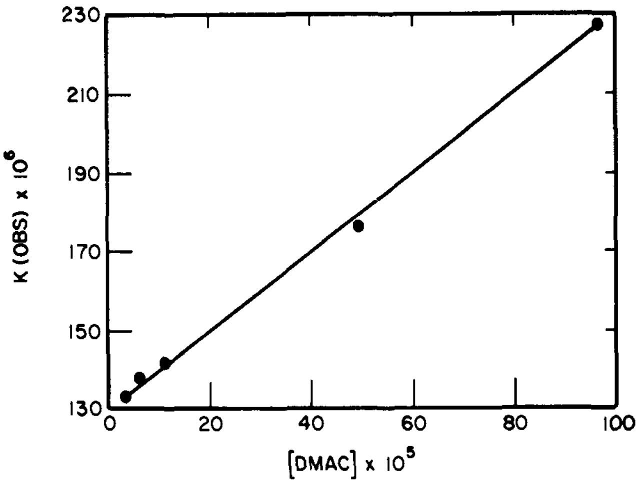


Figure 6. Effect of DMAC concentration on the observed rate of reaction for peroxyacetate 1, 3 × 10^{-4} M in benzene at 100 °C.

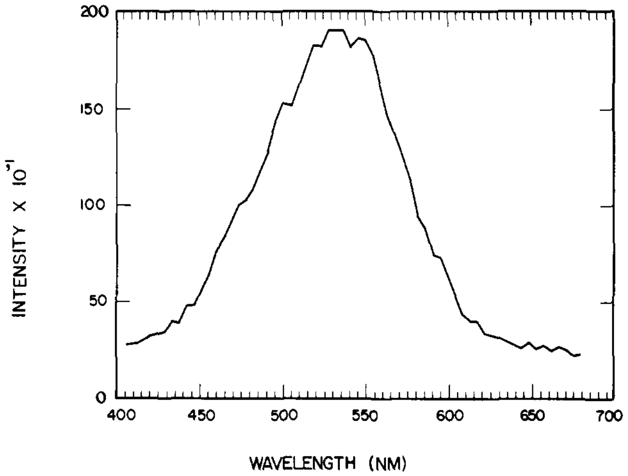


Figure 7. Emission spectrum of activated chemiluminescence from peroxyacetate 1 (3 × 10^{-4} M) and DMAC (6 × 10^{-4} M) in benzene solution at 100 °C.

We examined the possibility that activated chemiluminescence by the CIEEL path occurs for peroxyacetate 1 and for peroxybenzoates 2.

When the thermolysis of peroxyacetate 1 in benzene solution is carried out in the presence of a small amount of an easily oxidized substance, the course of the reaction is changed. For example, addition of *N,N*-dimethyldihydrodibenzo[*a,c*]phenazine (DMAC) to peroxyester 1 in benzene results in an accelerated rate of reaction of 1 (Figure 6) and the generation of a modest yield of singlet excited DMAC. This is evidenced by the chemiluminescence emission spectrum (Figure 7), which is identical with the fluorescence spectrum of DMAC obtained under similar conditions. Spectroscopic measurements indicate that the DMAC is not consumed in its reaction with peroxyester 1 even when the peroxyester is present in 30-fold excess. The products of the reaction in the presence of DMAC remain acetophenone and acetic acid. These observations indicate that DMAC is a true catalyst for the reaction of peroxyacetate 1. The catalytic rate constant, k_{cat}, can be extracted from the kinetic results shown in Figure 6 according to eq 10, where k_{obsd} is the observed first-order rate

$$k_{obsd} = k_1 + k_{cat}[DMAC] \qquad (10)$$

constant for reaction 1 in the presence of ACT and k_1 is the rate constant for the unimolecular reaction of the peroxyacetate. The results of this experiment with DMAC, plotted according to eq 10, gives $k_{cat} = 9.73 \times 10^{-2} \pm 1.87 \times 10^{-3}$ M^{-1} s^{-1}.

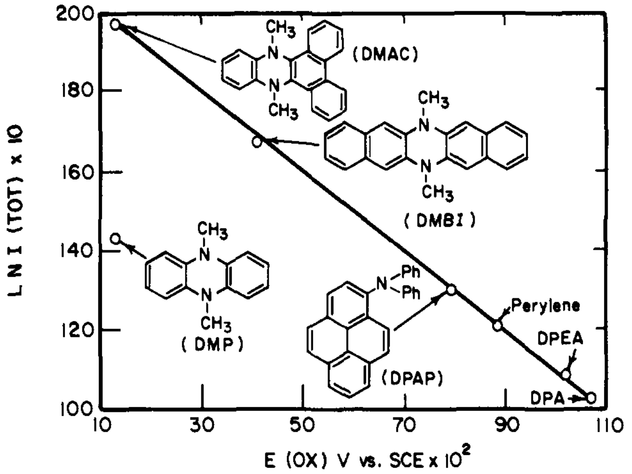


Figure 8. Correlation of total chemiluminescence intensity with activator oxidation potential (E_{ox}) for peroxyacetate 1. Measured in argon-purged benzene with activator at 1 × 10^{-4} M and perester at 1 × 10^{-3} M at 99.5 °C.

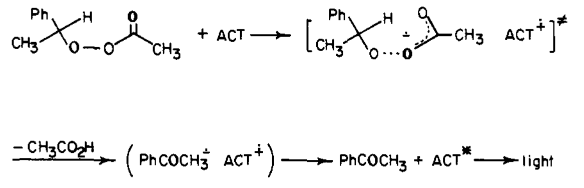
DMAC is not unique in its ability to catalyze the reaction of peroxyacetate 1 and provoke the formation of excited singlet states. The chemiluminescent intensity (corrected for changes in fluorescence efficiency and photomultiplier and monochromator spectral response) is a sensitive function of the nature of the activator. Under conditions of low, but constant, activator concentration the magnitude of this corrected chemiluminescent intensity is related to the one-electron oxidation potential of the activator (Figure 8). Under these experimental conditions $k_1 >> k_{cat}[ACT]$ which ensures that the corrected chemiluminescence intensity is proportional to the magnitude of the catalytic rate constant (eq 11), where ϕ_{Fl} is the fluorescence quantum

$$i_{corr} = F\left(\frac{k_{cat}[ACT]}{k_{cat}[ACT] + k_1}\right)\phi_{Fl}\phi^* \qquad (11)$$

efficiency of the activator, ϕ^* is the efficiency of forming excited singlet states by the activated chemiluminescence path, and F is a constant factor that contains the photomultiplier tube spectral response, light-gathering efficiency of the chemiluminometer, and counting efficiency of the apparatus.

The inverse linear relationship between the log of the corrected chemiluminescent intensity and the oxidation potential of the activator is primafacie evidence for the operation of the CIEEL mechanism (Scheme III). In this mechanism the initiating step for light generation is the thermally activated transfer of an electron from the activator to the peroxide. The electron transfer is followed by the very rapid cleavage of the oxygen–oxygen bond of the reduced peroxide[18] and then by transfer of hydrogen to form acetic acid. This affords acetophenone radical anion and activator radical cation within a solvent cage. Annihilation of these oppositely charged radical ions leads to the formation of the excited state we detect by its luminescence. A recent criticism of this interpretation by Walling[30] has been shown to be unfounded.[31]

Scheme III



(12)

(13)

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[29] Of course it may prove to be experimentally impossible to detect the rate increase if $k_{cat}[ACT] << k_1$. Yet it is still possible that the activated chemiluminescence accounts for all of the observed light.

[30] C. Walling, *J. Am. Chem. Soc.*, **102**, 6854 (1980).

[31] F. Scandola, V. Balzani, and G. B. Schuster, *J. Am. Chem. Soc.*, in press.

Table II. Comparison of the Singlet Energies and Energies Available upon Ion Annihilation of the Various Activators

activator	E_S,[a] kcal/mol	available energy ($E_{+/-}$),[b] kcal/mol	k_{cat},[c] M^{-1} s^{-1}
DMAC	58	59	9.73×10^{-2}
DMP	72	59	1.59×10^{-1} [e]
DMBI	68	67	7.07×10^{-3}
rubrene	54	75	1.40×10^{-4} [d]
DPAP	68	76	2.35×10^{-4}
perylene	65	79	1.19×10^{-4}
DPEA	62	82	3.58×10^{-5}
DPA	72	84	2.22×10^{-5}

[a] Assigned from the O–O band of the fluorescence spectrum. [b] Calculated by taking the difference between the oxidation potential of the activator and the reduction potential of acetophenone. [c] Calculated by comparing the total intensity to that of DMAC and assuming that the light intensity is proportional to the fraction of the reaction that proceeds through the CIEEL path. [d] Unavoidable self absorption by rubrene leads to the observed low calculated value for k_{cat}. [e] Measured by determining the apparent first-order rate constant for reaction of 1 at varying DMP concentration.

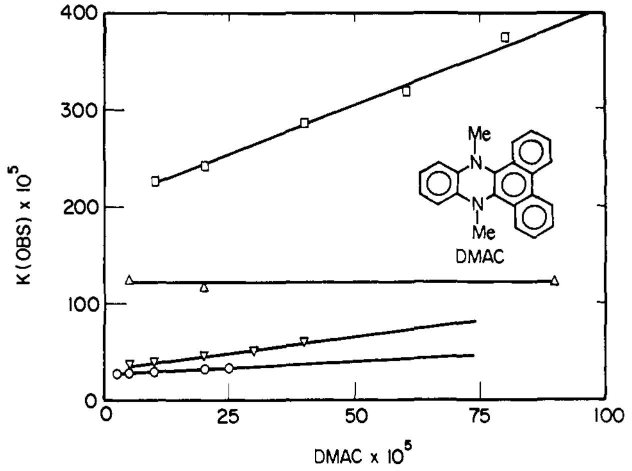

Figure 9. Effect of DMAC concentration on the observed rate of reaction of the substituted peroxybenzoates. The lines correspond to the following: squares, **2d** at 100 °C; triangles, **2c** at 92.2 °C; inverse triangles, **2b** at 100 °C; circles, **2a** at 100 °C. The data for **2d** do not extrapolate to the proper k_1. This may be a result of a chain reaction of the nitro-substituted acid radical anion at low DMAC concentration.

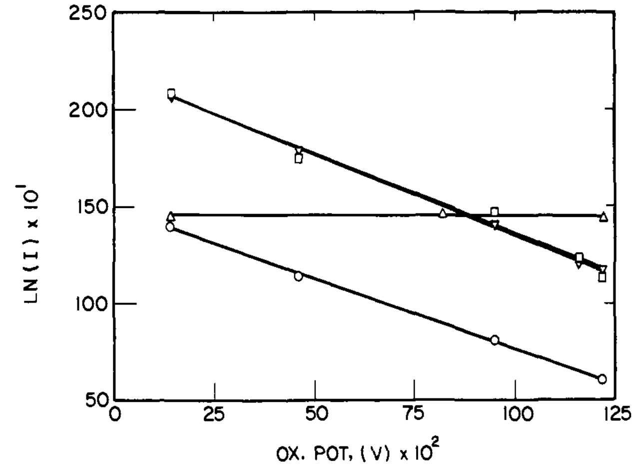

Figure 10. Correlation of activated chemiluminescence intensity with oxidation potential of the catalytic activators. In order of increasing oxidation potential the activators are the following: DMAC, DMBI, rubrene, perylene, DPEA, DPA. The activator concentration is 1×10^{-4} M and in all cases the lines correspond to the following: squares, **2b**; inverse triangles, **2a**; triangles, **2c**; circles, **2e**.

The one exception to the correlation of corrected chemiluminescence intensity and oxidation potential shown in Figure 8 is for dimethyldihydrophenazine (DMP), and this is readily understood with the CIEEL mechanism shown in Scheme III. For an electronically excited state to be formed by an ion annihilation, the energy released by the annihilation must be at least as great as the energy of the excited state. The energy released on annihilation ($\Delta E_{+/-}$) can be estimated by using the available redox potentials[32] and is summarized for the systems of interest in Table II. The energy of the target excited state, in this case the singlet, (ΔE^*_S) can be estimated from optical absorption and emission data and is also shown in Table II for the compounds of interest. It is clear from the data of Table II that for all of the activators used *except DMP* there is sufficient energy released to form the excited singlet. DMP still catalyzes the reaction of peroxyacetate **1**, see k_{cat} in Table II, but it cannot be promoted to its excited singlet state on annihilation because insufficient energy is released. These observations offer convincing evidence for the intermediacy of radical ions in the activated chemiluminescence of peroxyacetate **1**.

The response of the peroxybenzoates to the CIEEL activators depends remarkably on the nature of the substituent. In principle, the substituent on the peroxybenzoate might influence one or several of the steps in proposed CIEEL mechanism. In fact, an entire spectrum of reactivity, depending upon the substituent, is observed.

The unsubstituted peroxybenzoate **2a** behaves in a fashion nearly identical with that observed for the peroxyacetate **1**. The reaction of **2a** is catalyzed by DMAC to give singlet excited DMAC with $k_{cat} = 2.6 \times 10^{-1} \pm 0.01$ M^{-1} s^{-1} (Figure 9). Similarly, other activators catalyze the chemiluminescent reaction of **2a**. The dependence of the corrected chemiluminescence intensity on activator oxidation potential is shown in Figure 10.

The *p*-methoxy-substituted peroxybenzoate **2b** behaves quite like the parent, but the nitro-substituted compounds **2d** and **2e** and the *p*-dimethylamino-substituted peroxybenzoate **2c** behave quite differently. The behavior of these compounds, however, can be understood within the CIEEL mechanism. For example, the nitro-substituted peroxybenzoates **2d** and **2e** exhibit k_{cat} with DMAC approximately ten times greater than for the unsubstituted peroxide **2a**. Yet the yield of excited singlet DMAC generated by **2d** and **2e** is 700 times less than from **2a** (Figure 10). This seeming inconsistency can be easily understood. In the postulated CIEEL path, the reduction of the peroxide results in its fragmentation to acetophenone and an acid. One of these species must be a radical anion. For the peroxyacetate and all of the substituted peroxybenzoates examined with the exception of the nitro-substituted examples the more easily reduced species of this pair is acetophenone. Thus, in these cases the annihilation takes place between acetophenone radical anion ($E_{red} = -2.00$–2.50 V vs. SCE)[33] and activator radical cation. The reduction potentials of the nitro-substituted acids are below the reduction potential of acetophenone.[34] Thus when these reduced peroxides fragment the radical anion species is probably the acid. Annihilation between the nitro-substituted acid radical anions and the activator radical cations used in this work is not sufficiently energetic to form the excited singlet state of the activator. Thus, just as was observed for the peroxyacetate and DMP, an activator can retain its catalytic function but because of the energetics of the reaction

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(32) $\Delta E_{+/-} = E_{ox} - E_{red} + E_{coul}$ where E_{ox} is the one-electron oxidation potential, E_{red} is the one-electron reduction potential, and E_{coul} is the Coulombic work term. It should be noted that the values of E_{ox} and E_{red} are often solvent dependent. The electrochemical values used to estimate $\Delta E_{+/-}$ were obtained in CH_3CN with tetra-*n*-butylammonium perchlorate supporting electrolyte. There is undoubtedly some change in these values in the benzene solvent used in the chemiluminescence experiments. However, the relative magnitudes and the general trends observed are probably reliable.

(33) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-Aqueous Systems", Marcel Dekker, New York, 1970. S. M. Park and A. J. Bard, *J. Am. Chem. Soc.*, **97**, 2978 (1975); R. O. Loutfy and R. O. Loufty, *Can. J. Chem.*, **50**, 4052 (1972).

(34) T. Arai, *Nippon Kaguku Zasshi*, **89** 188 (1968).

of the postulated intermediates lose its chemiluminescent ability.

The final experiments to be discussed are the reactions of dimethylamino-substituted peroxyester **2c** with these activators. For these cases a third type of behavior is observed. The corrected chemiluminescence intensity obtained is independent of the structure of the activator (Figure 10). This is just what is expected for simple indirect chemiluminescence where the activator is excited by energy transfer from some first-formed singlet state. As indicated above, the initial excited state in this system is *p*-(dimethylamino)benzoic acid. Evidently, the electron-donating *p*-dimethylamino substituent renders the peroxybenzoate **2c** sufficiently difficult to reduce[34] that the value of k_{cat} is so small that the bimolecular path never is able to compete successfully with unimolecular decomposition.

In sum, three types of behavior are observed with these peroxyesters and easily oxidized fluorescers. Each of these can be understood within the CIEEL mechanism simply on the basis of expected reactivity of the postulated intermediates.

Conclusions. The primary question posed at the outset of this work was whether the energy released on thermal conversion of a secondary peroxyester to a ketone and a carboxylic acid could be directed to the formation of excited-state products. The answer to that question is a resounding yes. We have discovered also that, depending on the specific structure of the secondary peroxyester, modest yields of direct, indirect, or activated chemiluminescence can be obtained.

Experimental Section

General Data. Gas chromatographic separations were done by using a Varian-Aerograph Model 2700 chromatograph equipped with dual-flame ionization detectors. NMR spectra were recorded on a Varian Associates EM-390 or an HR 220 instrument with use of tetramethylsilane, hexamethylbenzene, or dioxane as the internal standard. UV adsorption spectra were measured on a Cary 14 spectrometer or on a Perkin-Elmer Model 552 UV-vis spectrophotometer. All chemiluminescence data were obtained by using standard photon-counting techniques. Light emission was detected by an EMI 9813B or 9816B photomultiplier tube. Spectral resolution was accomplished by using a Jarrel Ash 0.25 M monochromator. The band-pass under high-resolution conditions is calculated from manufacturers data to be 5 nm. For the low-resolution condition, the band-pass is calculated to be 26 nm. Chemiluminescence cell temperature was regulated within ± 0.1 °C by either a constant temperature recirculating water bath or an electrically heated jacket. All elemental analyses were carried out by the Analyses Laboratory, Department of Chemistry, University of Illinois, Urbana, IL. Fluorescence spectra were obtained on a Farrand optical mark I spectrofluorometer.

All oxidation potentials were run in acetonitrile under an argon atmosphere. The cyclic voltammograms were run on a polarographic analyzer and recorded on a Tectronix 915 X-Y recorder. The electrolyte used was tetrabutylammonium perchlorate (TBAP) at a concentration of 0.1 M. The cell consisted of a saturated calomel electrode as reference, a platinum working electrode, and a platinum wire counterelectrode. The platinum working electrode was polished prior to each set of runs. All voltammograms were reversible.

Materials. Acetonitrile (Aldrich spectrophotometric grade) was dried over calcium hydride with stirring and then slowly distilled from calcium hydride through a 30-cm Vigreux column. The first and last 10% of the distillate were discarded. Benzene (Burdick and Jackson distilled in glass) was washed successively with concentrated sulfuric acid, water (twice), and a saturated water solution of sodium carbonate. It was then thoroughly dried over calcium chloride, run through a basic alumina column, and then slowly distilled. The first and last 10% of the distillate were discarded. Carbon tetrachloride (Mallinckrodt spectrophotometric grade) was washed successively with a concentrated potassium hydroxide–methanol solution and then water (three times). It was then dried thoroughly over calcium chloride and distilled from phosphorous pentoxide, discarding the first 10%. Methylene chloride was washed successively with concentrated sulfuric acid, water, a saturated aqueous sodium carbonate solution, and water. It was then dried over calcium chloride and distilled from phosphorous pentoxide, discarding the first and last 10% of the distillate.

9,10-Diphenylanthracene (DPA) (Aldrich Gold Label) was used without further purification. 9,10-Dibromoanthracene (DBA) was recrystallized from acetonitrile. Rubrene (Aldrich) and 9,10-diphenylethynylanthracene (DPEA) were first chromatographed on neutral alumina, with use of benzene as eluant, and then recrystallized from benzene. Perylene (Aldrich) was chromatographed on basic alumina with use of methylene chloride as eluant and then recrystallized from benzene. The three phenazines, *N,N*-dimethyldihydrodibenzo[*a,c*]phenazine (DMAC), *N,N*-dimethyldihydrophenazine (DMP), and *N,N*-dimethyldihydrodibenzo[*b,i*]phenazene (DMbi) as well as *N,N*-diphenyl-1-aminopyrene (DPAP) (see below) were synthesized and purified by Dr. S. P. Schmidt.[28] DMAC and DMP were recrystallized from hexane and acetonitrile, respectively, just prior to use. Biacetyl (Aldrich) was distilled prior to use.

***N,N*-Diphenyl-1-aminopyrene.** 1-Aminopyrene (488 mg, 2.25 mmol, Aldrich) was stirred in 15 mL of dry THF and 10 mL of HMPT, under a nitrogen atmosphere. Bromobenzene (230 μL, 2.25 mmol) was added to the solution. Lithium tetramethylpiperidide (prepared from the addition of *n*-butyllithium, 5.0 mmol, to 760 μL of tetramethylpiperidine (4.5 mmol) in 5 mL of THF) was added dropwise over 20 min, affording a deep blue and then deep red solution, which was stirred at room temperature for 2 h and then at reflux for 5 h. After the mixture was cooled, bromobenzene (230 μL, 2.25 mmol) and then 7.4 mmol of lithium tetramethylpiperidide were added. The mixture was heated at reflux for 14 h. Bromobenzene (6.75 mmol) and then 10 mmol of lithium tetramethylpiperidide were added, and the mixture was heated at reflux an additional 8 h. After being cooled, the mixture was poured onto 40 mL of ice and extracted with ether. Evaporation gave 950 mg of a black oil, which was chromatographed on a 40 × 4 cm silica gel (Brinkmann 0.05–0.2) column, packed in a 25% methylene chloride–hexane slurry. Elution with 1:1 methylene chloride in hexane yielded *N,N*-diphenyl-1-aminopyrene as yellow crystals (35 mg, 5%) after recrystallization from benzene–hexane.

Anal. Calcd for $C_{28}H_{19}N$: C, 91.02; H, 5.18; N, 3.79. Found: C, 90.77; H, 4.99; N, 3.78.

1-Phenylethyl Hydroperoxide. Method I. *Caution! Syntheses of the hydroperoxide by this method resulted in two violent explosions during preparation carried out as described in the literature.*[10] *The following smaller scale procedure has proved innocuous, but caution is still strongly advised.* One milliliter (8 mmol) of 1-phenylethanol (Aldrich) was stirred in a round-bottom flask with 0.02 mL of concentrated H_2SO_4 and cooled to 0 °C. Behind an explosion shield, 2.7 mL (0.11 mole) of 90% H_2O_2 was dropped in very slowly with stirring and the mixture stirred at 0 °C for 2 h. The mixture was then warmed to 22–28 °C and stirred another 4 h. Water (10 mL) was added followed by 10 mL of ether. The ether layer was washed twice with a 10% aqueous $NaHCO_3$ solution and then water and dried with Na_2SO_4. After the ether was stripped off in vacuo, the residue, a clear to slightly yellow liquid, was distilled at 0.1 mm on a hanging cup distillation apparatus to give a 66% yield of the hydroperoxide: ^1H NMR (CCl_4) δ 1.35 (d, 3 H, methyl), 4.90 (q, 1 H, methine), 8.0 (br s, 1 H, hydroperoxy), 6.85 (s, 5 H, aromatic). Distillation of larger quantities of the hydroperoxide gave a boiling range of 48–52 °C (0.1 mm).

Method II.[9] Ethylbenzene (150 mL, Aldrich) and 0.15 g (1.6 mmol) of AIBN was bubbled with oxygen and heated for 24 h at 110 °C under an oxygen atmosphere. The hydroperoxide was precipitated from solution with 50% aqueous NaOH. Ether was added to the mixture and the peroxide freed by acidification with a 6 M HCl solution. This process is repeated, the ether stripped off, and the hydroperoxide distilled as above. The NMR (CCl_4) spectrum of this material was identical with that of the peroxide prepared by method I.

1-Phenylethyl Peroxyacetate (1). Ketene was generated by cracking acetone according to the literature procedure.[35] The ketene was passed through successive dry ice–acetone traps to remove less volatile contaminants and then into the reaction solution. 1-Phenylethyl hydroperoxide (0.5 mL, 4.7 mmol) was added to 15 mL of CH_2Cl_2 containing 1.6 g of Na_2SO_4 and saturated with gaseous HCl. Ketene was bubbled through the solution for 4 h. Completion of the reaction was determined by NMR spectroscopy. The reaction mixture was washed successively with water, saturated aqueous K_2CO_3, and twice with a 1×10^{-3} M aqueous solution of Na_4EDTA and dried with Na_2SO_4. The CH_2Cl_2 was removed in vacuo leaving a light yellow liquid. This liquid was placed under a vacuum of 0.05–0.1 mm for 2 h at 20–28 C to remove acetophenone. Distillation on a hanging cup apparatus at 0.05–0.07 mm and a surrounding oil bath temperature of 85–95 °C gave a clear, colorless liquid (31%) identified as peroxyacetate **1**: ^1H NMR (CCl_4) δ 1.50 (d, 3 H, methyl, J = 7 Hz), 1.90 (s, 3 H, methyl), 5.17 (q, 1 H, methine, J = 7 Hz), 7.3 (s, 5 H, aromatic); IR (CCl_4) 3000, 1785, 1500, 1285 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_3$: C, 66.64; H, 6.73. Found: C, 66.98; H, 6.66.

Deuterated peroxyacetate (**1d**) was prepared from deuterated hydroperoxide:[36] ^1H NMR (CCl_4) δ 1.48 (broadened singlet, 3 H, methyl),

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(35) C. D. Hurd and J. W. Williams, *J. Org. Chem.*, **5**, 122 (1940).

1.85 (s, 3 H, methyl), 7.20 (s, 5 H, aromatic).

Reduction of 1 to 1-Phenylethyl Acetate. Triethyl phosphite (0.25 mL, 2 mmol) in 4 mL of CCl_4 was added under nitrogen to 2 mmol of **1** in 4 mL of CCl_4 with stirring.[37] The reaction was run for 5 h and followed by NMR spectroscopy which showed the consumption of the phosphite protons and appearance of the phosphate product. Also, absorptions due to **1** were replaced by the following spectrum: ^1H NMR (CCl_4) δ 1.5 (d, 3 H, methyl, J = 6 Hz), 2.00 (s, 3 H, methyl), 5.75 (q, 1 H, methine, J = 6 Hz), 7.25 (s, 5 H, aromatic). This product was shown to be identical with 1-phenylethyl acetate.[38]

1-Phenylethyl Peroxybenzoate (2a). A solution of 1-phenylethyl hydroperoxide (0.1 mL, 0.75 mmol) and benzoyl chloride (0.09 mL, 0.75 mmol) in 5 mL of CCl_4 was cooled to 0 °C. A solution of 10% NaOH, saturated with NaCl (5 mL), was added and the mixture stirred vigorously for 5 min. The CCl_4 layer was washed successively with 10% H_2SO_4 and water, dried (Na_2SO_4), and concentrated to give a clear colorless liquid. Low-temperature (−20 °C) recrystallization from pentane gave 0.01 mL of **2a**: ^1H NMR (CCl_4) δ 1.60 (d, 3 H, methyl, J = 6 Hz), 5.30 (q, 1 H, methine, J = 6 Hz), 7.30 (m, 7 H, aromatic), 7.82 (d, 2 H, aromatic); IR (CCl_4) 1757 cm^{-1}.

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.35; H, 5.84. Found: C, 74.25; H, 5.96.

1-Phenylethyl 4-Methoxyperoxybenzoate (2b). A solution of 1-phenylethyl hydroperoxide (0.1 mL, 0.75 mmol) and anisoyl chloride (0.1 mL, 0.75 mmol) was warmed to 40 °C in 5 mL of CCl_4. A solution of 10% NaOH, saturated with NaCl (5 mL), was added and the mixture stirred vigorously for 10 min. Workup of the reaction mixture was as described for **2a**. Low-temperature (−20 °C) recrystallization gave 0.01 mL of **2b**: ^1H NMR (CCl_4) δ 1.60 (d, 3 H, methyl, J = 6 Hz), 3.7 (s, 3 H, methyl), 5.30 (q, 1 H, methine, J = 6 Hz), 6.81 (d, 2 H, aromatic), 7.3 (m, 5 H, aromatic), 7.60 (d, 2 H, aromatic); IR (CCl_4) 1751 cm^{-1}.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.56; H, 5.93. Found: C, 70.27; H, 6.00.

1-Phenylethyl 4-(Dimethylamino)peroxybenzoate (2c). A solution of 1-phenylethyl hydroperoxide (0.3 mL, 2.25 mmol) and 4-(dimethylamino)benzoyl chloride (0.42 g, 2.29 mmol) was prepared in 15 mL of CCl_4 at 25 °C. A solution of 18% NaOH, saturated with NaCl (15 mL), was added and stirred vigorously for 12 min. The CCl_4 solution was washed successively with 10% H_2SO_4, H_2O, 10% Na_2CO_3, and H_2O and then dried (Na_2SO_4). Crystallization from a minimum of CCl_4, followed by recrystallization from ether–pentane, gives 0.03 g of **2c** as white crystals: ^1H NMR (CCl_4) δ 1.60 (d, 3 H, methyl, J = 6 Hz), 3.05 (s, 6 H, methyl), 5.45 (q, 1 H, methine, J = 6 Hz), 6.62 (d, 2 H, aromatic), 7.55 (m, 5 H, aromatic), 7.82 (d, 2 H, aromatic); IR (CCl_4) 1744 cm^{-1}.

Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.55; H, 6.72; N, 4.91. Found: C, 71.18; H, 6.53; N, 4.61.

1-Phenylethyl 3-Nitroperoxybenzoate (2e). A solution of 1-phenylethyl hydroperoxide (0.2 mL, 1.5 mmol) and 3-nitrobenzoyl chloride (0.28 g, 1.5 mmol) was cooled in 10 mL of CH_2Cl_2 to 0 °C. A solution of 10% NaOH saturated with NaCl was added (10 mL) and the mixture stirred vigorously for 1.5 min. Workup of the CCl_4 layer was as described for **2a** and the CH_2Cl_2 removed in vacuo leaving a white oily residue that was washed twice with pentane. Repeated crystallization from ether–pentane resulted in 0.02 g of **2e** as white crystals: ^1H NMR (CCl_4) δ 1.60 (d, 3 H, methyl, J = 6 Hz), 5.52 (q, 1 H, methine, J = 6 Hz), 7.55 (m, 5 H, aromatic), 8.55 (m, 3 H, aromatic), 8.80 (m, 1 H, aromatic); IR (CCl_4) 1770 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.57; N, 4.88. Found: C, 62.35; H, 4.30; N, 5.09.

1-Phenylethyl 4-Nitroperoxybenzoate (2d). A solution of 1-phenylethyl hydroperoxide (0.1 mL, 0.75 mmol) and 4-nitrobenzoyl chloride (0.14 g, 0.75 mmol) was cooled in 5 mL of CCl_4 to 0 °C. A solution of 10% NaOH (10 mL) was added and the mixture stirred vigorously for 3 min. The CCl_4 layer was washed, dried, and concentrated as described for **2a**, leaving a heavy oil. The oil was washed with pentane and repeatedly crystallized from ether–pentane to give 0.015 g of **2d** as a white solid: ^1H NMR (CCl_4) δ 1.60 (d, 3 H, methyl, J = 6 Hz), 5.33 (q, 1 H, methine, J = 6 Hz), 7.30 (m, 5 H, aromatic), 7.80 (d, 2 H, aromatic), 8.10 (d, 2 H, aromatic); IR (CCl_4) 1767 cm^{-1}.

Anal. Calcd for $C_{15}H_{13}NO_5$: C, 62.71; H, 4.57; N, 4.88. Found: C, 62.74; H, 4.44; N, 4.59.

Thermolyses Product Analyses. 1-Phenylethyl Peroxyacetate (1). Product analyses were done by gas chromatography (6 ft × $^1/_4$ in. Poropak Q, 245 °C) for acetic acid and (6 ft × $^1/_4$ in. SE-30 (3%) on Chromasorb Q, 100 °C) for acetophenone. Samples of **1** were thermolyzed in benzene at 100 °C until reaction was complete under the following conditions: with DPA, concentration of **1**, 3 × 10^{-4} M, and DPA 6 × 10^{-4} M; with DMAC as activator, concentration of DMAC, 1.61 × 10^{-3} M, and **1**, 5 × 10^{-4} M. As a standard, a stock solution of acetic acid (3 × 10^{-4} M) and acetophenone (3 × 10^{-4} M) in benzene with DMAC (1.2 × 10^{-3} M) or DPA (6 × 10^{-4} M) was prepared. Comparison between the samples and the stock solution showed that acetophenone and acetic acid were formed quantitatively from **1**.

Peroxybenzoates (2a–e). The acetophenone yield was determined by gas chromatography under the same conditions and column type as described for **1**. The substituted benzoic acid yields were determined by ^1H NMR (acetone-d_6, 220 MHz) with use of hexamethylbenzene as an internal standard.

Rate of Reaction of 1 Determined by NMR Spectroscopy. The rate of thermolysis of **1** was determined by ^1H NMR spectroscopy as follows. *p*-Dioxane (Mallinckrodt) was used as an internal standard at a concentration of 5 × 10^{-3} M and **1** was 5 × 10^{-2} M in CCl_4. Duplicate runs were made by sealing evacuated NMR tubes containing the samples and following the change in methyl resonances of **1** (disappearance) and acetophenone (appearance) with time. A chemiluminescence decay run was made concurrently under the same conditions with an equivalent sample. These runs both at 72 °C gave the same rate for consumption of **1**.

General Chemiluminescence Conditions. For reproducible results to be obtained, it is important that the glassware used be carefully cleaned. We suspect that trace metal ions adsorbed on the glass may catalyze the decomposition of these peroxyesters. All glassware was cleaned according to the following procedure. The item was heated (steam bath) for 3 h in a 1 × 10^{-3} M aqueous solution of tetrasodium ethylenediaminetetraacetic acid (Na_4EDTA), rinsed thoroughly with distilled water and acetone, and then purified benzene. The item was dried at room temperature under a stream of argon.

The chemiluminescent thermolyses were carried out in 10-mm quartz cuvettes equipped with Teflon stopcocks. The solutions were purged with argon for 3–4 min immediately before heating. Typical experimental procedures are given.

(a) **Direct Chemiluminescence of 2c.** A solution of **2c** (1 × 10^{-4} M, 2 mL) in benzene was purged for 3 min with argon and then placed in a cell holder preheated to 100 °C. The chemiluminescence intensity was recorded at the emission maximum, following a 5 min equilibration period, for 128 equal time intervals covering 4 half-lives. The first-order rate constant was obtained by a linear least-squares analysis. Total chemiluminescent intensities were obtained by integration of the area under the decay curve extrapolated to infinite time.

(b) **Indirect Chemiluminescence of Peroxyacetate 1.** A solution of **1** (2.3 × 10^{-5} M) and biacetyl (Aldrich, distilled immediately before use, 4.5 × 10^{-2} M) in 2 mL of benzene was prepared and purged with argon. The solution was heated at 100 °C and the emission intensities at 128 wavelengths equally spaced between 350 and 550 nm were recorded. The average of four of these spectra gave the emission spectrum shown in Figure 3.

(c) **Activated Chemiluminescence of Peroxybenzoate 2a.** Solutions of **2a** (3 × 10^{-4} M) and DMAC (1 × 10^{-4} M) were prepared in 2 mL of benzene, purged with argon, and the rate of reaction of **2a** was determined by the decay of the DMAC emission intensity as described above. The derived first-order rate constants at increasing DMAC concentration are shown in Figure 6.

Determination of the Fluorescence Quantum Yields (ϕ_{Fl}). The fluorescence yields of the various activators of Table II at high temperature were determined by comparison of the fluorescence intensity at 95–100 °C with that obtained at 25–28 °C on the same sample in argon-purged benzene solution. With the exception of DPAP the room-temperature fluorescence yields were obtained from the literature[39] (rubrene, perylene, DPA, and DPEA) or determined by comparison with an appropriate standard (DMP, DMAC, and DMBI). Experimental details of the latter determinations have been recently published.[40] The fluorescence yield of DPAP was determined relative to perylene (ϕ_{Fl} = 1.0 in benzene at 25 °C) to be 1.0 at 25 °C and was unchanged at 95 °C. The fluorescence yield of 4-(dimethylamino)benzoic acid at 25 °C was determined by using the DPA as a standard (ϕ_{Fl} = 0.85 at 25 °C) to be 0.026. At 94.0 °C this fluorescence yield decreases to 0.0064. Table III contains the fluorescence yields at 25–28 °C and 94–100 °C and oxidation potential of all of the activators used in this work.

Estimation of Yield of Singlet and Triplet Excited States from the

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Table III. Oxidation Potentials and Fluorescence Quantum Yields of the Activators of Figure 8

activator	fluorescence yield[a] 24-28 °C	fluorescence yield[a] 94-100 °C	oxidation potential, V vs. SCE
DMAC	0.04	0.04	0.14
DMP	0.40	0.18	0.14
DMBI	0.88	0.88	0.46
rubrene	1.00	0.56	0.82
DPAP	1.00	1.00	0.90
perylene	0.84	0.84	1.00
DPEA	0.96	0.96	1.16
DPA	0.85	0.85	1.22
DBA	0.10	0.017	1.45

[a] Determined in argon-purged benzene solution. The previously unknown fluorescence quantum yields were determined relative to DPA (DMP, DMBI), perylene (DPAP), or DPEA (DMAC).

Thermolysis of 1 at 100 °C. The direct chemiluminescence from **1** was too weak to permit determination of the yield of excited states. In the presence of perylene, a double-reciprocal plot of perylene concentration against the integrated intensity was done for dioxetane **3** and **1**, both at 1×10^{-3} M in benzene. Comparison of the total intensities at infinite perylene concentration gives a singlet yield from **1** and perylene by activated chemiluminescence of 0.02%. This assumes a singlet yield from **3** of 0.02%.[41,42] A similar comparison, with use of biacetyl indirect chemiluminescence, to obtain the yield of triplet, was not possible due to the very low indirect chemiluminescence intensities observed for **1** and biacetyl. However, an upper limit of 0.02% was established by comparison of the total intensities of TMD and **1** (2.3×10^{-5} M) in the presence of biacetyl (4.5×10^{-2} M) in benzene by assuming a triplet yield of 30% for TMD.

Determination of the Yield of Singlet and Triplet *p*-(Dimethylamino)benzoic Acid from the Thermolysis of 2c at 92.2 °C. The yield of singlet acid from **2c** was determined by comparing the total intensity of **2c** (1×10^{-4} M) with the extrapolated intensity obtained from a double-reciprocal plot of DBA concentration against intensity with TMD (1×10^{-4} M). The intensities are corrected for photomultiplier tube response, DBA fluorescence yield at 95 °C (0.017), TMD yield of triplet acetone (30%), efficiency of energy transfer from acetone to DBA (0.2), and the fluorescence yield of 4-(dimethylamino)benzoic acid at 94 °C (see above).

The yield of triplet acid from **2c** was determined by comparing the extrapolated intensity values of double-reciprocal plots of DBA concentration vs. total intensity for **2c** and TMD. The appropriate corrections, as described above, were made. The assumption is made that the energy-transfer efficiencies of acetone and *p*-(dimethylamino)benzoic acid to DBA are the same.

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Reactions of Phenols with Photoexcited Benzophenones. A CIDNP Study

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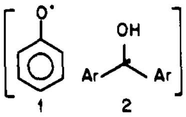
Abstract: The photoreactions of benzophenones with phenols have been studied by using CIDNP techniques. The results suggest that in most solvents triplet benzophenone abstracts a hydrogen atom from phenol to generate phenoxyl radicals. In benzene-d_6, a complex is formed between the reactants resulting in a predominantly singlet-state reaction. During the reaction of tetrafluorophenol, multiplet effects are superimposed on dominant net effects due to the interaction of the strongly coupled fluorine nuclei with the more weakly coupled proton. One system provides evidence for a cross-polarization mechanism.

Introduction

Aroxyl radicals have been identified as intermediates in several important processes such as polymer stabilization.[1] These radicals are often stable and can be studied by spectroscopic techniques.[2] In addition, aroxyl radicals have been postulated as intermediates in many photoreactions including the photo-Fries[3] and the photo-Claisen rearrangements.[4] Phenoxyl radicals have also been suggested as intermeidates in the quenching of photoexcited ketones by phenols.[5] All products formed in this reaction, including fuchsones (**4**) and oxetanes (**5**) appear to be derived from a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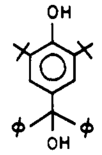
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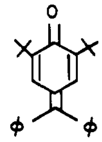
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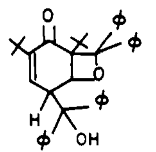
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common intermediate, the photoadduct (**3**). The formation of this adduct can be explained by the coupling of phenoxyl (**1**) and hydroxymethyl radicals (**2**) which, in turn, are generated by abstraction of a phenolic hydrogen atom by triplet-state benzophenone.

We have studied the photoreaction between benzophenones and phenols using chemically induced dynamic nuclear polarization

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