# Thermal Chemistry of Cyclopropyl-Substituted Malonyl Peroxides. A New Chemiluminescent Reaction

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The thermal properties and chemiluminescent behavior of 4-cyclopropyl-4-methyl-1,2-dioxolane-3,5-dione (**2**) and 4-spiro[(2'-spirocyclopropyl)cyclohexyl]-1,2-dioxolane-3,5-dione were investigated. The gross chemical properties of these malonyl peroxides are analogous to other alkyl-substituted examples. Thermolysis leads to rate-limiting homolytic rupture of the oxygen–oxygen bond, loss of $CO_2$, and then cyclization to an $\alpha$-lactone. This sequence of reactions can be catalyzed by aromatic hydrocarbons through an apparent electron-transfer process. Chemiluminescence from these peroxides can be observed in the presence of the aromatic hydrocarbons. The mechanism for light generation is postulated to be chemically initiated electron-exchange luminescence (CIEEL) proceeding through a cyclopropylcarbinyl to allylcarbinyl rearrangement.

The reactions of organic peroxides that can produce visible light generally fall into two broad classes. The first is a unimolecular, concerted or stepwise, rearrangement of a high energy content molecule directly to an electronically excited state of a product. The second is the process we have recently described as chemically initiated electron-exchange luminescence (CIEEL).[1]

The key elements of the CIEEL mechanism are electron transfer from some donor to the peroxide resulting in bond rupture and a rearrangement of the peroxide that, in essence, increases the reducing potential of the transferred electron. Next, an electron is given back to the donor generating its excited state, which finally emits a photon of visible light.[2] In this sequence of reactions the peroxide plays several roles; therefore, there are important constraints on the structure of peroxides that will generate light efficiently by this path.

First, the peroxide must be easily reduced. It has been observed that peroxides containing adjacent carbonyl groups are reduced at low potential.[3] Thus, diacyl peroxides are more easily reduced than peroxy esters, which in turn are more easily reduced than dialkyl peroxides. Also, it has been our observation that cyclic peroxides are reduced more easily than their acyclic isomers. These considerations direct the search for new chemiluminescent molecules to cyclic diacyl peroxides.

Next, in order to produce light by the CIEEL process the reduced peroxide must undergo a rearrangement that generates a radical anion capable of a sufficiently energetic annihilation with the oxidized electron donor. For most of the examples of CIEEL so far reported this rearrangement involves splitting off a stable small molecules such as $CO_2$. Also, it is widely held that the rearrangement must be very rapid so that it can compete successfully with back electron transfer from the peroxide to the donor.

To facilitate the investigation of the mechanism of light generation, it is desirable that the peroxide be isolable so that its purity and concentration can be easily assessed. Several efficient chemiluminescent systems proceed through presumed unisolated peroxides. Among these are some of the most efficient light generators known, such as the oxalate esters[4] and luminol.[5] However, because of uncertainties associated with the unisolated key peroxide,

the mechanism of light generation for these systems remains poorly defined.

Finally, if the chemiluminescent reaction is to have any practical significance, the peroxide should be relatively easy to prepare. The considerations led us to consider the possible generation of light by the CIEEL path from malonyl peroxides.

The preparation of a malonyl peroxide was reported first by Adam and Rucktäschel in 1971.[6] Their synthesis is accomplished by treating the appropriate malonic acid with hydrogen peroxide in concentrated sulfuric acid. They observed that thermolysis or photolysis of di-*n*-butylmalonyl peroxide in an inert solvent results primarily in the formation of polymeric ester.[7] They reasoned, and later confirmed by matrix isolation infrared spectrometry,[8] that the polymer arises from an intermediate $\alpha$-lactone (eq 1). The bis(trifluoromethyl)-substituted $\alpha$-lactone pre-

$$\tag{1}$$

pared from the appropriate peroxide was shown to be stable in dilute solution at low temperature.[9]

These observations led us to suspect that the first steps in the thermolysis of malonyl peroxides in inert solvent are the homolytic cleavage of the oxygen–oxygen bond, followed by rapid decarboxylation to form a 1,3-biradical, which closes to generate the observed $\alpha$-lactone (eq 2).

$$\tag{2}$$
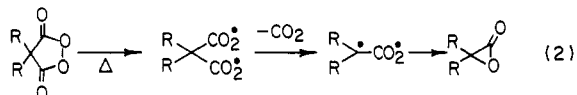
There is ample precedent for each of these steps.[10] Whether two or more of these steps happen in concert is not known, and the examination of that question provides some of the motivation for the research reported herein.

A critical question surrounding the use of malonyl peroxides in chemiluminescent systems is the amount of energy released in their reaction. The heat of reaction for the transformation shown in eq 2 is difficult to measure experimentally because of the instability of the $\alpha$-lactone product. However, application of Benson's group eqivalent

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(2) Schuster, G. B. *Acc. Chem. Res.* **1979,** *12,* 366.
(3) Silbert, S. S. In "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. II, p 755.
(4) Rauhut, M. M. *Acc. Chem. Res.* **1969,** *2,* 80.
(5) White, E. H.; Roswell, D. F., *Acc. Chem. Res.* **1970,** *3,* 541.

(6) Adam, W.; Rucktäschel, R. *J. Am. Chem. Soc.* **1971,** *93,* 557.
(7) Adam, W.; Rucktäschel, R. *J. Org. Chem.* **1978,** *43,* 3886.
(8) Chapman, O. L.; Wojtkowski, P. W.; Adam, W.; Rodriguez, O.; Rucktäshel, R. *J. Am. Chem. Soc.* **1972,** *94,* 1365.
(9) Adam, W.; Liu, J.-C.; Rodriguez, O. *J. Org. Chem.* **1973,** *38,* 2269.
(10) Hiatt, R. In ref 3; p 812.

method to the prototypical parent peroxide reveals a $\Delta H_r$ of ca. $-30$ kcal/mol.[11] Thus, this reaction is probably not sufficiently exergonic to generate visible light, and no chemiluminescence from the thermolysis of a malonyl peroxide has been reported to date.

In typical chemiluminescent reactions of organic peroxides, the bulk of the energy needed to produce a visible photon comes from conversion of the weak oxygen–oxygen bond of the peroxide to strong carbonyl bonds in the product. This feature is present in the thermal reactions of malonyl peroxide. However, in this case the formation of the strained α-lactone ring system greatly reduces the overall exothermicity of the transformation. It was our intention to construct malonyl peroxides substituted so that one of the suspected intermediates in eq 2 could be diverted away from α-lactone toward a more exergonic path.

The cyclopropylcarbinyl–allylcarbinyl rearrangement (eq 3) has been studied extensively.[12] This process, examined

$$\text{(3)}$$
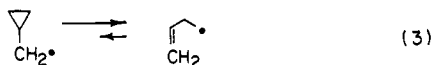
spectroscopically by Kochi,[13] has been investigated by Ingold, Griller, and co-workers,[14] who have measured the rate of reaction and Arrhenius activation parameters for several examples. This reaction has been used as a "free-radical clock" and is one of the most rapid unimolecular rearrangements of an organic free radical yet discovered. Thus, it appeared reasonable to us that substitution of a cyclopropyl group on the position between the carbonyl groups of malonyl peroxide would provide a second reaction pathway for the presumed biradical precursor to α-lactone (eq 4).

$$\text{(4)}$$
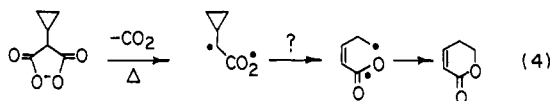
Benson group equivalent calculations indicate that the transformation shown in eq 4 is exothermic by ca. $-70$ kcal/mol.[11] This reaction is therefore expected to be sufficiently exergonic to generate a photon of visible light. We set out to prepare appropriate cyclopropyl-substituted malonyl peroxides and to examine their thermal and chemiluminescent properties. The results of that investigation are reported herein.

## Results

**Synthesis.** We prepared malonyl peroxides 1–3 to test
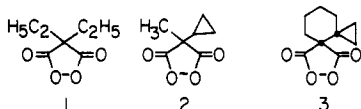
the effect of cyclopropyl substitution on the thermal and chemiluminescent properties of this ring system.

Preparation of peroxide 1 proceeds smoothly from diethylmalonic acid by the acid-catalyzed cyclization procedure first introduced by Adam.[7] The synthesis of cyclopropyl methyl substituted peroxide 2 can be accom-

plished by methylation of cyclopropylmalonic acid[15] and then dicyclohexylcarbodiimide (DCC) mediated cyclization (eq 5).[16] The preparation of bisspirocyclic peroxide 3

$$\text{(5)}$$
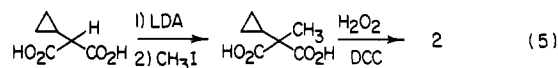
proceeds from spiro[5.2]octan-4-one[17] through the malonic acid and then cyclization with DCC (eq 6). The details

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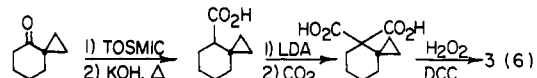
of these reactions are presented under Experimental Section.

**Thermal Reactions of Cyclopropyl-Substituted Malonyl Peroxides.** Thermolysis of peroxide **2** in nitrogen-saturated benzene solution proceeds smoothly at reflux and gives a nearly quantitative yield of polymeric ester (eq 7). The polyester was characterized by reduction

$$\text{(7)}$$
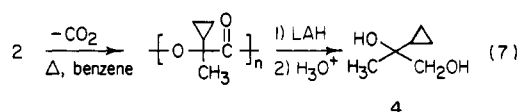
with lithium aluminum hydride to diol **4**. By analogy with previous studies, we conclude that the polymer arises from the intermediate α-lactone.

If the hoped for cyclopropylcarbinyl–allylcarbinyl rearrangement takes place, we expect the formation of lactone **5** (eq 8). To examine this possibility, we prepared

$$\text{(8)}$$
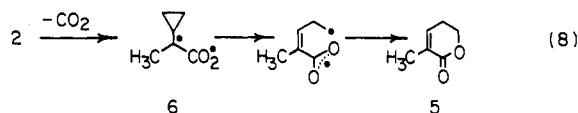
**5** independently (see Experimental Section) and showed that it is stable to the reaction conditions. Analysis of the reaction mixture from **2** under a variety of conditions by gas chromatography showed that less than 1% of **5** is present. Evidently, the closure of the suspected biradical intermediate **6** (eq 8) to α-lactone occurs much more rapidly than the desired ring-opening rearrangement.

When the thermolysis of peroxide **2** is carried out in dilute acetonitrile solution, a different result is obtained. Polymeric ester is still formed, but the major product is a crystalline white solid that we have identified as the amide-substituted carboxylic acid **7** (eq 9). Also, a small

$$\text{(9)}$$
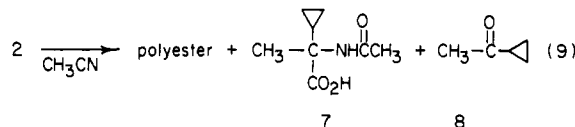
amount of methyl cyclopropyl ketone **8** is formed under these conditions. Acid **7** evidently results from the attack of acetonitrile solvent on the intermediate α-lactone, and ketone **8** from the decarbonylation of this species.

The reactions of malonyl peroxides can be catalyzed with electron donors, such as polynuclear aromatic hydrocarbons (vide infra). Under these conditions, we expect that the intermediate of eq 8 will be a radical anion rather than a biradical. Thermolysis of **2** with perylene as catalyst in acetonitrile solution at 112 °C proceeds rapidly. The product of this reaction is predominantly the polymeric ester. Under these conditions, acid **7** is not formed, pre-

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(12) Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York; Vol. I, chapter 8.

(13) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877. Kocki, J. K.; Krusic, P. J.; Eaton, D. R. *Ibid.* **1969**, *91*, 1879.

(14) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(15) Krapcho, A. P.; Kashdan, D. S. *Tetrahedron Lett.* **1975**, 707.

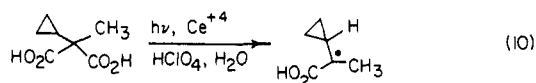(16) Greene, F. D. *J. Am. Chem. Soc.* **1956**, *78*, 2246.

(17) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611.

sumably because the higher steady-state concentration of α-lactone formed in the presence of catalyst polymerizes more rapidly than it adds solvent. No lactone 5 could be detected from this reaction. It appears that the presumed radical anion intermediate also favors a path leading to α-lactone rather than opening of the cyclopropane ring. Thermolysis of spirocyclic peroxide 3 leads to qualitatively similar results.

**Electron Paramagnetic Resonance Spectroscopy.** Kochi and co-workers have reported the EPR spectra of several substituted cyclopropycarbinyl radical systems at low temperature.[13] They conclude, based on the magnitude of the coupling constants, that the plane of the carbinyl carbon bisects the cyclopropane ring. They also report that warming these radicals to ca. -100 °C results in rearrangement to the corresponding allylcarbinyl radical.

We measured the EPR spectrum of the carboxylic acid substituted cyclopropylcarbinyl radical 9 The radical was generated by photochemical oxidation of the malonic acid with $Ce(NH_4)_2(NO_3)_6$ in $HClO_4$ according to the procedure of Greatorex and Kemp[18] (eq 10). The EPR spectrum of

$$\text{HO}_2\text{C}\overset{\text{CH}_3}{\underset{\text{CO}_2\text{H}}{\bigtriangleup}} \xrightarrow[\text{HClO}_4, \text{H}_2\text{O}]{h\nu, \text{Ce}^{+4}} \text{HO}_2\text{C}\overset{\text{H}}{\underset{\text{CH}_3}{\bigtriangleup}}\cdot \qquad (10)$$

9 at -140 °C showed a broadened four-line pattern centered at 2.0026 G. By computer simulation, the coupling constants for the methyl hydrogens (20.5 G) and for the tertiary cyclopropyl hydrogen (2.85 G) are obtained. These coupling constants are essentially identical with those reported for the simple alkyl-substituted cyclopropyl carbinyl radicals.[13,14] This observation indicates that the geometry of 9 is the same as that of the substituted analogues.

Unlike the simple alkyl-substituted radicals, warming the frozen solution of 9 did not result in rearrangement to the allylcarbinyl radical. The maximum temperature we could obtain was -80 °C, however, since above that temperature the EPR signal disappeared, presumably due to softening of the matrix and bimolecular reactions of the radical.

**Kinetics of Thermal Decomposition.** The rate of the thermal reaction of the malonyl peroxides can be determined by any procedure that provides a reliable measure of the peroxide concentration. We employed two methods to determine the rate of reaction. The first used infrared spectroscopy, which followed the intensity of the peroxide carbonyl absorption. The second relied on the activated chemiluminscence from the peroxide, which was shown to be directly proportional to the peroxide concentration. Both methods give the same results. This observation supports our conclusion that the malonyl peroxide is the source of the observed chemiluminescence (vide infra).

Since bisspirocyclic peroxide 3 was the most efficient light generator of the malonyl peroxides that we examined, we concentrated most of our effort on this compound. However, to the extent we examined peroxide 2, its behavior was found to be exactly analogous to that of 3.

Thermolysis of a dilute solution of peroxide 3 in benzonitrile containing 9,10-diphenylethynylanthracene (DPEA) as chemiluminescent activator gives light emission that decays in an approximately first-order fashion. When $1 \times 10^{-2}$ M acetic acid is included in the reaction mixture, the chemiluminescence intensity is decreased dramatically, and the decay kinetics become cleanly first order. Evidently, the acetic acid is reacting with an intermediate that
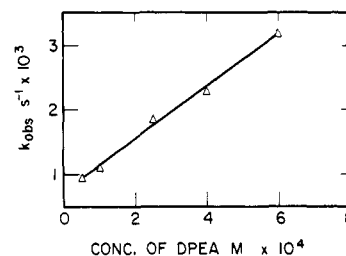


**Figure 1.** The effect of DPEA concentration on the observed first-order rate constant for reaction of peroxide 3 in benzonitrile containing $1 \times 10^{-2}$ M acetic acid at 130 °C.

**Table I. Rate of Reaction of Peroxide 3 in Benzonitrile Containing $10^{-2}$ M Acetic Acid**

| activator | temp, °C | $k_1$,[a] s$^{-1}$ | $k_{cat}$,[a] M$^{-1}$ s$^{-1}$ |
|-----------|----------|--------------------|---------------------------------|
| DPEA | 149 | 4.7 × 10$^{-3}$ | 9.7 |
| DPEA | 144 | 2.8 × 10$^{-3}$ | 8.8 |
| DPEA | 140 | 1.8 × 10$^{-3}$ | 7.6 |
| DPEA | 135 | 1.4 × 10$^{-3}$ | 5.2 |
| DPEA | 130 | 7.8 × 10$^{-4}$ | 4.1 |
| DPEA | 120 | 7 × 10$^{-5}$ | 2.5 |
| perylene | 130 | 1.1 × 10$^{-3}$ | 60 |
| DPA | 130 | 1.0 × 10$^{-3}$ | 1.7 |

[a] The average deviation of replicate determinations of the first-order rate constants used to determine $k_1$ and $k_{cat}$ is 10% of the measured value.

is capable of going on to generate light and that also can react with the peroxide. This point will be examined further below.

The observed first-order decay of the chemiluminescence intensity yields a rate constant, $k_{obsd}$. The magnitude of $k_{obsd}$ depends upon the concentration of DPEA (Figure 1) according to eq 11, where $k_1$ is the rate constant for uni-

$$k_{obsd} = k_1 + k_{cat}[\text{DPEA}] \qquad (11)$$

molecular reaction of peroxide 3 and $k_{cat}$ is the rate constant for catalysis of DPEA. Extrapolation of the data shown in Figure 1 to [DPEA] = 0 gives $k_1$, while the slope of the line in Figure 1 gives $k_{cat}$. Both $k_1$ and $k_{cat}$ are independent of the starting concentration of peroxide 3 and of the concentration of acetic acid. Also, other hydrocarbons capable of generating light from 3 give the same $k_1$ but yield different values for $k_{cat}$. The rate data are summarized in Table I. By monitoring the temperature dependence of $k_1$ and $k_{cat}$, we are able to extract the activation parameters for these two processes.

The activation enthalpy for the unimolecular thermolysis of peroxide 3 ($\Delta H_1^*$) in benzonitrile is 31.1 ± 2.3 kcal/mol, and the activation entropy for this process ($\Delta S_1^*$) is 3.8 ± 5.6 cal/mol·deg. These values are entirely consistent with unassisted homolysis of the oxygen–oxygen bond of the peroxide.[19] Thus, these activation parameters tend to confirm the assumed mechanism shown in eq 2.

The activation enthalpy for the DPEA-catalyzed reaction of peroxide 3 ($\Delta H^*_{cat}$) is 15.6 ± 1.0 kcal/mol, and the activation entropy for this process ($\Delta S^*_{cat}$) is -17.6 ± 2.6 cal/mol·deg. These values point to efficient catalysis by DPEA through a transition state that is composed of one molecule of peroxide and one molecule of the hydrocarbon. The mechanism of the catalytic process is revealed by using different hydrocarbons as catalysts. The data in Table I show that the effectiveness of the hydrocarbon as a catalyst is strongly dependent on the structure of the hydrocarbon.

(18) Greatorex, D.; Kemp, T. J. *Trans. Faraday Soc.* **1971**, *67*, 1576.

(19) (a) Bartlett, P. D.; Hiatt, *J. Am. Chem. Soc.* **1958**, *80*, 1398. (b) Pryor, W. A.; Smith, K. *Int. J. Chem. Kinet.* **1971**, *3*, 387.
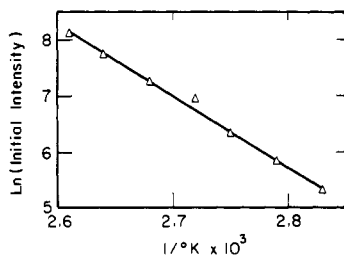
**Figure 2.** The effect of temperature on the initial chemiluminescence intensity from peroxide **3** and DPEA in benzonitrile solution.

A semilogarithmic plot of $k_{cat}$ against the one-electron oxidation potential of the hydrocarbon ($E_{ox}$) gives an excellent linear correlation indicative of rate-limiting electron transfer from the hydrocarbon to the peroxide.[20] The slope of this line is $-18 \pm 2$ V$^{-1}$, which yields a transfer coefficient ($\alpha$) of 0.64. This observation substantiates the notion stated earlier that cyclic diacyl peroxides, such as malonyl peroxide, are easily reduced by ground-state organic electron donors.

The total activation enthalpy of the reactions leading to the eventual generation of light in a chemiluminescent reaction ($\Delta H^{\ddagger}_{chl}$) can be obtained by measuring the effect of temperature on the light output.[21] Application of this technique to peroxide **3** and DPEA in benzonitrile (Figure 2) gives an apparent $\Delta H^{\ddagger}_{chl}$ of $23.5 \pm 1.0$ kcal/mol. This value is approximately 8 kcal/mol greater than the activation enthalpy for the rate-limiting step in the catalytic reaction of **3**. This observation indicates that there is at least one additional step in the chemiluminescent reaction sequence with a significant activation energy. It is crucial to understand that only the peroxide molecules destined to give a photon of light need suffer the additional 8 kcal/mol activation enthalpy. The major part of the reaction is free to follow a lower energy path if one exists.

**Chemiluminescence of Malonyl Peroxides.** The thermal decomposition of cyclopropyl-substituted malonyl peroxides **2** and **3** in the presence of fluorescent aromatic hydrocarbons results in weak but easily detected chemiluminescence. The presence of the cyclopropyl group is an absolute requirement for light generation. Diethylmalonyl peroxide **1** does not give detectable light under any conditions we have explored. Also, spirocyclic peroxide **3** is ca. 30 times more effective at generating light than its bicyclic counterpart **2**. For this reason we concentrated our investigation on the properties of peroxide **3**.

Thermolysis of **3** in benzene or benzonitrile solution in the absence of a fluorescent hydrocarbon does not give any detectable light. This observation indicates that generation of an emisive electronically excited state from the unimolecular reactions of **3** is quite improbable. However, chemical light generation is easily detected when an aromatic hydrocarbon, such as DPEA, 9,10-diphenylanthracene (DPA), or perylene, is included with the peroxide. In all cases, the chemiluminescence emission spectrum corresponds perfectly to the fluorescence spectrum of the added hydrocarbon. Significantly, when 9,10-dibromoanthracene (DBA) is included in peroxide **3** solutions the amount of light observed is more than 200 times lower than when DPA is used. This finding indicates that the chemiluminescence in the presence of the fluorescer is not due to the direct formation of a nonemissive triplet excited state, followed by a triplet to singlet energy
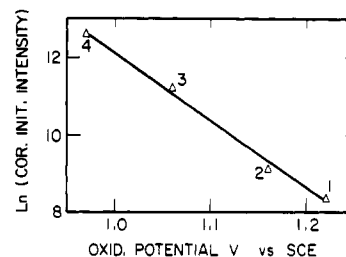
**Figure 3.** Correlation of the initial chemiluminescence intensity from peroxide **3** and various activators, corrected for fluorescence quantum yield, photomultiplier tube, and monochromator spectral response, with the 1 electron oxidation potential of the activator. Activator 1 is DPA, 2 is DPEA, 3 is perylene, and 4 is 5,10-diphenylethynyltetracene.
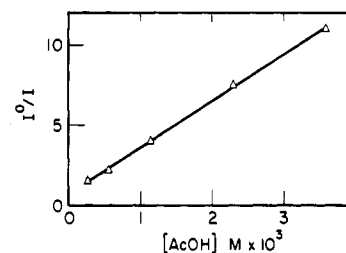


**Figure 4.** Stern–Volmer plot for the quenching of the DPEA-activated chemiluminescence of peroxide **3** in benzonitrile with acetic acid.

transfer. If that were the case, then DBA, after correction for different emission quantum yields, should generate light more efficiently than does DPA.[22]

The process responsible for chemical light generation is revealed by examining the light-producing effectiveness of various aromatic hydrocarbons. The chemiluminescent intensity can be measured under conditions where the concentration of peroxide is essentially constant. Comparison of the emission intensity at constant hydrocarbon concentration, corrected for different fluorescence quantum yields, gives the results shown in Figure 3. The slope of this line is $-17 \pm 2$ V$^{-1}$, which is the same, within experimental error, as that obtained for the catalytic decomposition of the peroxide by these hydrocarbons. This finding indicates that the same process that is responsible for the catalysis of the peroxide decomposition is also responsible for light generation. That is, the efficiency of excited state generation is directly related to the ability of the aromatic hydrocarbon to act as a one-electron donor. This observation is strong evidence in support of the operation of the CIEEL mechanism.

In all of the previously reported examples of CIEEL chemiluminescence, the light-generating path is remarkably insensitive to the presence of low concentrations of $O_2$ or protic solvents. This is not the case with peroxide **3**. In particular, we find that $O_2$, or low concentrations of acetic acid or methanol, are quite effective quenchers of the chemiluminescence. However, these substances do not change the rate at which the peroxide reacts. This observation indicates that these quenchers are intercepting an intermediate on the path to light generation that is formed after the rate-limiting step of the reaction. The quenching by acetic acid and methanol was investigated quantitatively (Figure 4). The effectiveness of the quencher appears to be related to acid strength. Acetic acid gives a $k_q\tau$ of 2900 M$^{-1}$, while methanol gives a slope of only 10 M$^{-1}$. Thus, it seems that some species capable of being protonated plays a crucial role in the chemilu-

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

(21) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.

(22) Vassil'ev, R. F. *Prog. React. Kinet.* **1967**, *4*, 305.

Scheme I
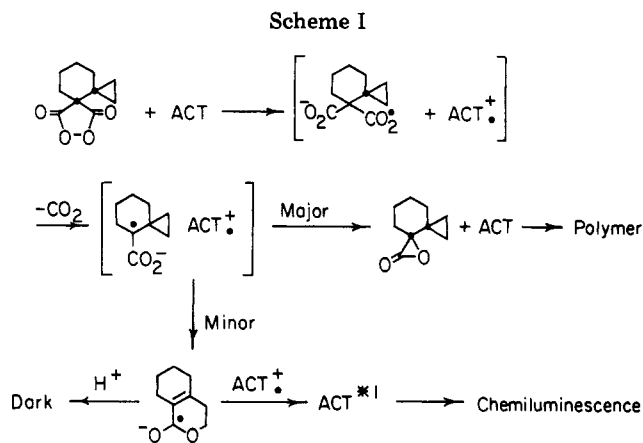


minescence of these malonyl peroxides. Moreover, it is apparent that protonation of this species removes it from the path leading to the generation of light.

## Discussion

The results reported herein reveal information about the mechanism of thermal decomposition of malonyl peroxides, the rate of ring closure of 1,3-biradicals relative to the cyclopropylcarbinyl–allylcarbinyl rearrangement, and the mechanism for generation of light from the thermal reactions of organic peroxides.

Cleavage of the oxygen–oxygen bond of a peroxide is typically the initiating step in its thermal reaction. For diacyl peroxides, this bond dissociation is sometimes coupled to rupture of the adjacent carbon–carbon bond to give $CO_2$ in one step. The activation parameters for reactions of these peroxides have been used as a guide to the degree of simultaneous two, or more, bond cleavage.[19] Our results are entirely consistent with unassisted oxygen–oxygen bond homolysis as the rate-limiting step in the reaction of malonyl peroxides.

The major products observed from the thermolysis of cyclopropyl-substituted malonyl peroxides 2 and 3 apparently result from decarboxylation of the initially generated biradical to form the appropriate cyclopropylcarbinyl biradical. This biradical in principle can partition between ring closure to the $\alpha$-lactone and opening of the cyclopropyl ring, the process we hoped to detect by ring expansion to the $\delta$-lactone. Our inability to detect any of the ring-expanded lactone shows that the rate of closure to the $\alpha$-lactone is much greater than the cyclopropylcarbinyl–allylcarbinyl rearrangement for these molecules.

Chemiluminescence can be a more sensitive indicator of the reaction pathways than is the product study. Scheme I shows a path leading to light generation that is consistent with all the information that we have gathered about the reactions of these substituted malonyl peroxides.

The first step in the sequence is activated electron transfer from the aromatic hydrocarbon (activator, ACT) to the peroxide resulting in cleavage of the oxygen–oxygen bond, giving the malonate radical anion and the activator radical cation. The next step is the rapid loss of $CO_2$ to generate the carboxylate-substituted cyclopropylcarbinyl radical. This radical is presumably formed in the solvent cage with the activator radical cation. Back electron transfer within the solvent cage to generate eventually the $\alpha$-lactone is apparently the predominant reaction path.

The light generation path must involve the cyclopropyl substituent, since analogous alkyl-substituted malonyl peroxides do not generate light. Scheme I shows our postulate that the ring opening of the cyclopropane leads to a $\delta$-lactone radical anion that eventually is responsible

for the chemiluminescence. If the difference in activation energy between the catalytic path and the light generating path of 8 kcal/mol corresponds to the partitioning between the ring opening and back electron transfer, then we estimate that the minor chemiluminescent path accounts for only ca. 0.002% of the reaction. This is well below our limit of detectability for products but can easily account for all of the chemiluminescence that we detect. The difference between the chemiluminescence yield of peroxides 2 and 3 is accomodated by this mechanism as well. The rigidity of the spirocyclic system ensures the proper stereoelectronic arrangement for ring opening and formation of the $\delta$-lactone.

The postulated mechanism also accounts easily for the effect of protic substances on the chemiluminescence of these malonyl peroxides. Protonation of the ring-expanded lactone, as shown in Scheme I, removes the radical anion from the light-generating path. The lactone radical anion should also easily reduce the starting malonyl peroxide in a chain reaction contributing to the non-first-order kinetic behavior observed in the absence of proton donors.

The penultimate step in the CIEEL light-generating sequence is the annihilation of the oppositely charged radical ions. This process leads to generation of the excited activator, which we detect by its luminescence.

In conclusion, the question asked at the outset of this research is answered in part. It is possible to harness the energy released in the decomposition of a malonyl peroxide substituted with a proximate cyclopropyl group and convert it to a photon of light. However, the efficiency of this process is very low. This eppears to result from slow conversion of the cyclopropylcarbinyl radical to the allylcarbinyl radical compared to the rate of back electron transfer. We are continuing to investigate ways to decrease the activation barrier for the chemiluminescent path and thereby increase the yield of light from these reactions.

## Experimental Section

**Chemiluminescence Measurements and Techniques.** The photon-counting technique was used for all chemiluminescence measurements. An EMI 9813B photomultiplier tube was employed for detection of chemiluminescence. Spectral resolution was accomplished with a Jarrel-Ash 0.25-m monochromator, equipped with a grating with 1180 grooves/mm. The band-pass under high-resolution conditions is calculated to be 5 nm, and under low-resolution conditions it is calculated to be 26 nm. The data were collected in a 128-channel digital input buffer with a variable time per channel of 1 to 800 s. The buffer was interfaced with a Digital Equipment Corp. VAX 11/780, which was used for all data analysis. The chemiluminescence sample temperature

was regulated to within ± 0.1 °C by means of an electrically heated cell holder.

A 1-cm Pyrex cuvette equipped with a Teflon stopcock was used for all measurements. To obtain reproducible results, we scrupulouly cleaned all glassware used in the preparation of samples or used in the actual measurement of chemiluminescence. The following procedure was used to clean all glassware used for these purposes. The glassware was soaked in a solution of concentrated Nochromix (Godax Laboratories) in reagent-grade sulfuric acid and then rinsed with deionized water, distilled in glass acetone (Burdick & Jackson), and purified benzene. It was then allowed to dry at room temperature. Once the glassware was cleaned by this method and shown to be free of contaminants by reproducible chemiluminescent results, it was cleaned between individual experiments by rinsing well with purified benzene. The solvent used for all chemiluminescence experiments was freshly distilled benzonitrile unless specifically stated otherwise.

**4,4-Diethyl-1,2-dioxalane-3,5-dione (1).** Peroxide 1 was prepared by the general method reported by Adam and Rucktäschel.[6,7] Diethylmalonic acid (1.30 g, 8 mmol) in methanesulfonic acid (5 mL) was stirred at 25 °C behind a safety shield, while 90% $H_2O_2$ (1.0 mL) was added in portions over an hour. The reaction mixture was stirred at 25 °C for an additional 24 h, and the solution was poured onto crushed ice. Saturated ammonium sulfate was added, and the cold aqueous mixture was extracted with pentane. The combined pentane extracts were washed with aqueous $(NH_4)_2SO_4$ (sat.), aqueous $NaHCO_3$ (10%), and aqueous NaCl (sat.). The pentane solution was dried with $MgSO_4$, and the solvent was removed in vacuo. Distillation of the crude material at reduced pressure gave a colorless liquid (0.84 g, 65%): bp 45 °C (3 mm); ^{1}H NMR $(CCl_4)$ δ 1.03 (t, 6 H, $CH_3$), 1.97 (q, 4 H, $CH_2$); IR $(CCl_4)$ ν 1795 (C=O) cm^{-1}.

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37; active oxygen, 10.12; molecular weight, 158. Found: C, 53.41; H, 6.52; active oxygen, 10.23; molecular weight (osmometry), 160.

**2-Methyl-2-cyclopropylmalonic Acid.** Under a dry nitrogen atmosphere, 45 mL of *n*-BuLi (2.2 M in hexane) was slowly added to a stirred solution of cyclopropylmalonic acid (4.86 g, 30.8 mmol) in 150 mL of dry, freshly distilled THF at −78 °C. The reaction mixture was allowed to warm to 25 °C, stirred for an additional hour, and then cooled to −78 °C. Methyl iodide (9.2 g, 64 mmol) was added, and the contents of the flask were allowed to warm to 25 °C. After stirring for an additional 2 h, the solution was diluted with an equal volume of water and washed with $Et_2O$. The aqueous extract was acidified at 0 °C with 10% HCl to pH 5–6 and extracted with $Et_2O$. The ether layer was washed with saturated NaCl and dried $(MgSO_4)$, and the solvent was removed in vacuo. The solid residue was recrystallized from nitromethane to yield 3.99 g (75%) of white crystals: mp 143–144 °C (gas evolution); ^{1}H NMR (acetone-$d_6$) δ 0.030–0.55 (m, 4 H, cyclopropyl), 1.20 (s, 3 H, $CH_3$), 1.30–1.70 (m, 1 H); IR (Nujol) ν 1700 (C=O) cm^{-1}.

Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.95; 6.32.

**4-Cyclopropyl-4-methyl-1,2-dioxolane-3,5-dione (2).** Cyclopropylmethyl malonic acid (1.83 g, 11.6 mmol) was dissolved in 8.75 mL of $Et_2O$ and 3.75 mL of methanesulfonic acid and stirred at 25 °C behind a safety shield. Hydrogen peroxide (2 mL, 90%) was slowly added in order to avoid heating of the reaction mixture. Six hours later an equal amount of hydrogen peroxide was added following the same precautions. The solution was stirred at 25 °C for an additional 24 h and was worked up in the same way as described for peroxide 1. Distillation of the crude material at reduced pressure gave a colorless liquid (0.92 g, 51%): bp 43 °C (0.5 mm); ^{1}H NMR $(CCl_4)$ δ 0.56–0.76 (m, 4 H, cyclopropyl), 1.13–1.50 (m, 1 H), 1.60 (s, 3 H, $CH_3$); IR (Film) ν 1800 (C=O) cm^{-1}.

Anal. Calcd for $C_7H_8O_4$: C, 53.84; H, 5.16; active oxygen, 10.25; molecular weight 156. Found: C, 54.10; H, 5.12; active oxygen, 10.18; molecular weight (osmometry), 163.

Peroxide 2 can be prepared by the alternate method of DCC and $H_2O_2$, which is described in full detail for peroxide 3. The crude peroxide 2 that is prepared by this method is purified by reduced pressure distillation, and all of its physical properties are identical with the material prepared by the acid-catalyzed procedure.

**4-Cyanospiro[5.2]octane.** Under a nitrogen atmosphere and with rapid stirring with a mechanical stirrer, a solution of *t*-BuOK (12.3 g, 110 mmol) in 40 mL of dry $Me_2SO$ was cooled to just above the freezing point of the solution. Solid tosylmethyl isocyanide (Tosmic; 6.8 g, 35 mmol) was added all at once to the cold solution and allowed to stir for 5 min. Dry methanol (1.0 mL) and spiro[5.2]octan-4-one[17] (3.0 g, 24 mmol) were added and stirred for 24 h at 25 °C. The reaction mixture was diluted with $H_2O$, acidified at 0 °C with 10% HCl to pH ~6, and extracted with petroleum ether. The combined organic extracts were washed with saturated NaCl solution, dried $(Na_2SO_4)$, and passed through a short column of neutral alumina, and the solvent was removed in vacuo. Vacuum distillation gave a colorless liquid (2.3 g, 70%): bp 70–72 °C (5 mm); ^{1}H NMR $(CCl_4)$ δ 0.30–0.70 (m, 4 H, cyclopropyl), 1.00–2.00 (m, 8 H, cyclohexyl), 2.30 (t, 1 H, CHC≡N); IR (liquid) ν 2260 (C≡N) cm^{-1}.

Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: 79.68, H, 9.48; N, 10.13.

**Spiro[5.2]octane-4-carboxylic Acid.** A solution of 4-cyanospiro[5.2]octane (22.1 mmol), ethylene glycol (25 mL), and KOH (10.3 g) was heated at reflux until the evolution of ammonia ceased (approximately 48 h). The reaction mixture was allowed to cool, diluted with $H_2O$, and continuously extracted with $Et_2O$ until all the ethylene glycol was removed. The aqueous portion was acidified to pH 5 with HCl and extracted with $Et_2O$. The organic layer was washed with saturated NaCl and dried $(MgSO_4)$, and the solvent was removed in vacuo. Vacuum distillation yielded a colorless liquid (2.59 g, 76%): bp 75 °C (0.5 mm); ^{1}H NMR $(CCl_4)$ δ 0.20–0.70 (m, 4 H, cyclopropyl), 0.80–1.10 (m, 1 H, cyclohexyl), 1.30–2.20 (m, 8 H, cyclohexyl); IR (liquid) ν 1700 (C=O) cm^{-1}.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.29; H, 9.31.

**Spiro[5.2]octane-4,4-dicarboxylic Acid.** Under a dry nitrogen atmosphere, lithium diisopropylamide (LDA; 11.4 mmol) in 5 mL of dry THF was slowly added to a stirred solution of spiro[5.2]octane-4-carboxylic acid (0.552 g, 3.6 mmol) in 10 mL of dry, freshly distilled THF at −78 °C. The contents of the flask were allowed to warm to 25 °C, stirred for an additional 2 h, and cooled again to −78 °C. A rapid stream of dry $CO_2$ was bubbled through the solution while the temperature of the solution was allowed to rise slowly to 25 °C. The reaction mixture was diluted with $Et_2O$ (100 mL) and extracted with $H_2O$ (2 × 50 mL). The aqueous layer was acidified to pH 5 with HCl at 0 °C and extracted with $Et_2O$ (3 × 50 mL). The organic extract was washed with saturated NaCl and dried $(MgSO_4)$, and the solvent was removed in vacuo. The solid residue was recrystallized from nitromethane to yield 0.440 g (62%) of white crystals: mp 203–204 °C (gas evolution); ^{1}H NMR $(Me_2SO-d_6)$ δ 0.20 (m, 2 H, cyclopropyl), 0.50 (m, 2 H, cyclopropyl), 1.40 (s, 6 H, cyclohexyl), 1.90 (br s, 2 H, cyclohexyl); IR (Nujol) ν 1700 (C=O) cm^{-1}.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.55; H, 7.17.

**4-Spiro[(2′-spirocyclopropyl)cyclohexyl]-1,2-dioxolane-3,5-dione (3).** Spiro[5.2]octane-4,4-dicarboxylic acid (0.20 g, 1.0 mmol) dissolved in 8 mL of $Et_2O$–$CH_2Cl_2$ (1:1) was added dropwise over 6 h to a mechanically stirred solution of dicyclohexylcarbodiimide (DCC; 0.60 g, 2.9 mmol), $CH_2Cl_2$ (2 mL), and $H_2O_2$ (2 mL, 3.5 M in $Et_2O$) maintained at 4 °C. Oxalic acid (50 mg) was added to the cold reaction mixture 24 h after the final addition of $H_2O_2$–DCC and stirred for an additional 15 min. The suspended urea and undissolved oxalic acid were removed by filtration through a sintered glass funnel and washed with pentane. The combined filtrate and pentane washings were washed with cold saturated $(NH_4)_2SO_4$, $Na_2CO_3$ (10%), and saturated NaCl. The organic layer was dried with $MgSO_4$, and the solvent was removed in vacuo. The crude product was chromatographed on silica with 1% $Et_2O$ in pentane at −20 °C and then sublimed at $10^{-4}$ torr onto a dry ice–acetone cooled trap. Analytically pure material was obtained by repeating the cold-column procedure and the sublimation. This resulted in 35 mg (17%) of a white solid: mp 40–41 °C; ^{1}H NMR $(CCCl_4)$ δ 0.33–0.83 (m, 4 H, cyclopropyl), 1.53–2.15 (m, 8 H, cyclohexyl); IR $(CCl_4)$ ν 1792 (C=O) cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.17; active oxygen, 8.15; molecular weight, 196. Found: C, 61.35; H, 6.05; active oxygen, 8.00; molecular weight (osmometry), 204.

**1-Oxa-3-methylcyclohex-3-en-2-one.** Under a dry nitrogen atmosphere, 5.0 mL of *n*-BuLi (2.4 M in hexane) was added to a stirred solution of diisopropylamine (1.96 g, 19.3 mM) in 60 mL of dry THF at –78 °C. The reaction mixture was allowed to warm to 25 °C, stirred for an additional 0.5 h, and then cooled to –78 °C. *δ*-Valerolactone (2.00 g, 20 mM) in 50 mL of dry THF was added over an hour to the cold solution and stirred for another 0.5 h. Phenylselenyl bromide (PhSeBr) in 7 mL of dry THF was added rapidly to the cold stirred enolate solution (immediate discoloration), and the cold reaction mixture was diluted with Et₂O. The ether solution was washed with 10% HCl, saturated NaHCO₃, and saturated NaCl. The organic layer was dried (MgSO₄) and concentrated in vacuo. The crude material (1.7 g) was dissolved in 20 mL of THF and 0.5 mL of AcOH at 0 °C. Hydrogen peroxide (30 mL, 30%) was added to the cold solution over 0.5 h and then stirred for an additional 0.5 h. The reaction mixture was poured into cold saturated NaHCO₃ and extracted with Et₂O. The organic layer was washed with H₂O and saturated NaCl and dried (MgSO₄), and the solvent was removed in vacuo. Vacuum distillation afforded a colorless liquid (0.56 g, 25%): bp 54–66 °C (0.4 mm); ¹H NMR (CCl₄) δ 1.85 (s, 3 H, CH₃), 2.25–2.50 (m, 2 H), 4.30 (t, 2 H), 6.53 (m, 1 H); IR (film) ν 1703 (C=O) cm⁻¹; MS (70 eV), *m/e* (relative abundance) 112 (67), 94 (11), 82 (62), 67 (41), 66 (11), 55 (18), 54 (100), 53 (37), 43 (16), 41 (24), 39 (94).

Anal. Calcd for C₆H₈O₂: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.38.

**3-Oxabicyclo[4.4.0¹,⁶]decen-2-one.** Peroxide 3 (10 mg, 0.05 mM) was added to a solution of *p*-toluenesulfonic acid (8 mg) in 10 mL of benzene and heated at reflux for 27 h. The reaction mixture was diluted with Et₂O, washed with 10% NaHCO₃ and saturated NaCl and dried (MgSO₄). The solvent was removed in vacuo, and the crude lactone was purified by column chromatography (silica gel, Et₂O) to yield 4 mg (52%) of lactone: ¹H NMR (CCl₄) δ 1.65 (m, 4 H), 2.20 (m, 6 H), 4.25 (t, 2 H); IR (CCl₄) ν 1720 (C=O) cm⁻¹; MS, *m/e* (relative abundance) 152 (67), 134 (19), 122 (10), 107 (62), 106 (23), 93 (22), 91 (42), 80 (12), 79 (100), 78 (10), 77 (28), 67 (13), 65 (13).

Anal. Calcd for C₉H₁₂O₂: 152.0837. Found: 152.0828.

# Mechanism of the Water-Catalyzed Photoisomerization of *p*-Nitrobenzaldehyde

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*p*-Nitrobenzaldehyde is observed to photoisomerize cleanly to *p*-nitrosobenzoic acid in aqueous solutions but to be photostable in pure acetonitrile or acetic acid. The dimethyl acetal of *p*-nitrobenzaldehyde is photostable in water. The quantum yield (0.034 at 254 nm in 99% H₂O/1% CH₃CN) depends upon the water concentration in mixtures of acetonitrile and water but is unaffected by pH in the range of 0–10, by the concentration of starting material, and by free radical trapping agents such as dioxane, methanol, or oxygen in aqueous solution. The reaction is sensitized efficiently by sodium anthraquinone-2-sulfonate ($E_T$ = 62 kcal/mol) and quenched by the triplet quencher 3,3,4,4-tetramethyl-1,2-diazetine 1,2-dioxide. Deuterium isotope effects were determined for the solvent ($\Phi_{H_2O}/\Phi_{D_2O}$ = 1.37 ± 0.05) and for the formyl hydrogen ($\Phi_{\alpha\text{-}H}/\Phi_{\alpha\text{-}D}$ = 1.05 ± 0.10). Photoisomerization in water containing 0.01–0.10 M ammonia causes *p*-nitrosobenzamide to appear as a photoproduct. This result implicates a quinoid ketene intermediate. The new evidence reported allows elimination of a number of plausible mechanisms for the photoisomerizaton, including two mechanisms proposed previously. A mechanism is proposed for which the primary process is exciplex formation involving electron transfer from water to the nitrophenyl triplet n,π* state, this interaction being followed by a rapid proton transfer from H₂O⁺· to its geminate radical, *p*-O₂NC₆H₄CHO⁻·.

*ortho*-Nitrobenzaldehyde has long been known to undergo clean and efficient photoisomerization to *o*-nitrosobenzoic acid[2,3] in a variety of media including the solid state.[4] The meta and para isomers have been reported to be stable to the analogous photoisomerization, though other products are formed on irradiation in alcohol.[2] The finding that *p*-nitrobenzaldehyde in water is cleanly photoisomerized to *p*-nitrosobenzoic acid[5] was
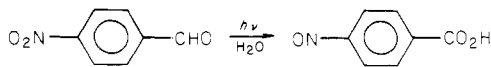


therefore unexpected. The reaction was an exception to a rule formulated by Sachs and Hilpert[6] that photosensitivity of aromatic nitro compounds is associated with an ortho arrangement of nitro and aliphatic C–H groups.

When the nitro and formyl groups are situated ortho, the lowest energy triplet state is of n,π* configuration and is that associated with the nitrophenyl chromophore.[7,8] The primary process leading to photoisomerization is hydrogen abstraction from formyl by a nitro oxygen atom.

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