

# Chemiluminescence of Organic Peroxides. Conversion of Ground-State Reactants to Excited-State Products by the Chemically Initiated Electron-Exchange Luminescence Mechanism

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The generation of visible light by a living organism or by a chemical reaction is an event of sufficient peculiarity to attract the interest of biologists, biochemists, chemists, and, much to the detriment of slowly flying creatures, small children. Witnesses of these bioluminescent or chemiluminescent displays are almost always moved to the question: how does that work? This query has been under increasingly intense investigation in our laboratory. Our studies have led to the postulation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism as an apparently general path leading from certain high-energy content reagents to electronically excited states.

## Chemical Light Generation in Solution

Generation of light by a chemical process in solution may be divided into three steps. The first is the synthesis of a reagent, or an intermediate, that can react to liberate sufficient energy to produce a photon of visible light. The visible spectrum extends from 400 to 700 nm. Thus our reagent must release between 41 and 72 kcal/mol on its way to product if such a photon is to result directly. This energy requirement restricts the number of potential chemiluminescent reactions and sometimes makes the study of their mechanism quite difficult. Indeed, the availability of a reaction path of such high exothermicity makes most such reagents sufficiently unstable that their physical characterization is prohibited. Fortunately, this situation was relieved with the successful synthesis, isolation, and characterization of 1,2-dioxetanes<sup>1</sup> and by our discovery of efficient chemiluminescence from diphenoyl peroxide.<sup>2</sup> The study of these compounds has contributed greatly to our understanding of chemi- and bioluminescence.

The second step of the chemiluminescence process is the conversion of the reagent formed in the first step, or of some other molecule present in the system, to an electronically excited state. It is this excitation step that distinguishes reactions that generate visible light from all other chemical transformations. The excitation step provides the mechanism whereby the energy released during the conversion of reactant to product is diverted from heat to light. There has been considerable diversity of opinion regarding the details of this transformation. Our principal objective has been to

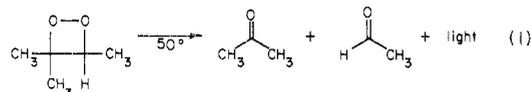
gain a better understanding of this step.

The final step in all chemi- and bioluminescent reactions is the emission of light from an electronically excited state. The ultimate emitter may be the excited state formed as a direct consequence of the excitation step or it may be a state formed indirectly by energy transfer from the first formed excited state. The first circumstance is referred to as direct chemiluminescence and the second as indirect chemiluminescence.

The yield of light from a chemiluminescent process is the product of the yields of each of the above steps. If our aim is to maximize the yield of light, then we must maximize the yield in each individual step. Fortunately, the factors that influence the success of the first and last steps are more or less well understood. It is in the middle step, the excitation step, that most of the mystery lies.

## Mechanism of the Excitation Step

Well before they were actually prepared and isolated, 1,2-dioxetanes were proposed as key reactants in numerous chemi- and bioluminescent reactions.<sup>3</sup> The preparation and characterization of this elusive ring system were reported first by Kopecky and Mumford in 1969.<sup>1a</sup> Subsequent investigations in numerous



laboratories uncovered many revealing details of the reactions of dioxetanes. Much of this chemistry has been reviewed recently.<sup>4</sup> We confine our discussion to those findings that bear most directly on the mechanism of the excitation step for these peroxides.

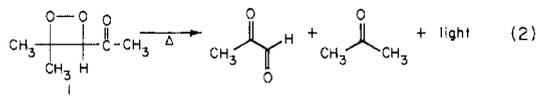
Many experiments have shown that the thermal unimolecular fragmentation of a dioxetane leads to two carbonyl compounds (aldehyde, ketone, ester, or amide), some fraction of which is electronically excited. To accomplish this chemical transformation two bonds of the dioxetane must be broken. McCapra<sup>5</sup> and Kearns<sup>6</sup> suggested that these bonds cleave in concert by what amounts to a symmetry-forbidden pericyclic rearrangement. Turro<sup>7</sup> elaborated the concerted mecha-

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- (3) F. McCapra, *Q. Rev. Chem. Soc.*, 485 (1966).
- (4) K. A. Horn, J.-y. Koo, S. P. Schmidt, and G. B. Schuster, *Mol. Photochem.*, **9**, 1 (1978-79); W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977); T. Wilson, *Int. Rev. Sci.: Phys. Chem., Ser. Two*, **9**, 265 (1976).
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Gary B. Schuster was born in Brooklyn, NY, in 1946. He completed his B.S. degree at Clarkson College and his Ph.D. at the University of Rochester with Louis Friedrich. Following 2 years with the U.S. Army, he did postdoctoral work at Columbia University with Nicholas Turro. In 1975 he joined the faculty at the University of Illinois where he is Associate Professor of Chemistry. He is an Alfred P. Sloan Fellow (1977-1979).

nism to account for the observation, among others, that thermolysis of simple alky substituted dioxetanes yields more than 50 triplets for every singlet excited state produced. He proposed a special spin-orbit coupling interaction as the transition state is approached. On the other hand, Richardson<sup>8</sup> advocated an excitation mechanism that proceeds by rate-determining oxygen-oxygen bond cleavage to generate initially a 1,4-biradical.

Many experiments have been done to attempt to distinguish between the two mechanistic extremes.<sup>4</sup> Richardson<sup>9</sup> found the effect of various substituents on the kinetics of the dioxetane fragmentation to be consistent with the biradical mechanism. We determined the effect of deuterium substitution on the thermal decomposition of *trans*-3,4-diphenyldioxetane and found it to be indicative of the biradical path.<sup>10</sup> We found also that thermolysis of 3-acetyl-4,4-dimethyldioxetane (1) yields a ratio of triplet to singlet



excited methylglyoxal closer to the statistical limit of 3:1 than do simply substituted dioxetanes.<sup>11</sup> The lowest singlet and triplet excited states of the  $\alpha$ -dicarbonyl compound methylglyoxal are, in contrast to the corresponding states in simple carbonyl compounds, both well below the energy of the expected intermediate biradical. Thus, the small difference in energy between the singlet and triplet excited states should influence less the partitioning of the biradical, and lead to a more nearly statistical ratio of excited-state products. Finally, Goddard and Harding have carried out an ab initio GVB-CI calculation of the reaction coordinate for dioxetane cleavage.<sup>12</sup> This calculation indicates that cleavage of the oxygen-oxygen bond is the first step.

In light of the results described above, it seems prudent to conclude that the biradical mechanism is a satisfactory description of the excitation step for simply substituted 1,2-dioxetanes. For the sake of classification, we refer to this excitation mechanism as unimolecular biradical cleavage.

The observation that the annihilation of oppositely charged radical ions can generate electronically excited states was made independently in several laboratories, more or less simultaneously.<sup>13,14</sup> The radical ion reactants for this process are typically prepared at an electrode. Oxidation of some compound D to the radical cation ( $D^{\cdot+}$ ) occurs at an anode while reduction of another molecule (A) to the radical anion ( $A^{\cdot-}$ ) occurs at a cathode. The potential energy stored in the ions can be estimated simply from the electrochemical oxidation and reduction potentials of D and A, re-

spectively. If this quantity is at least as great as the energy of the lowest excited state of D, A, or an exciplex of these two, then formation of an excited state can occur when the oppositely charged radicals meet and annihilate.

Electronic excitation by the electron-transfer process is not restricted to the annihilation of radical ions. The reduction of molecular chlorine by sodium 9,10-diphenylanthracene, for example, gives the excited singlet state of the neutral anthracene.<sup>14</sup> Disproportionation of ruthenium(III) and ruthenium(I) complexes generates an electronically excited state of the ruthenium(II) product.<sup>15</sup> Reaction of solvated electrons, generated by pulse radiolysis, with suitable radical cations also produces electronically excited states.<sup>16</sup> Electron transfer from potassium naphthalide to a suspected enol radical has been implicated in the chemiluminescence of the resulting enolate.<sup>17</sup> In short, generation of excited states by sufficiently energetic simple redox processes appears to be a general phenomenon.

A third, apparently general, reaction that results in excited-state products is the concerted elimination of singlet oxygen ( $^1\text{O}_2$ ) from certain peroxides. The relatively low energy of  $^1\text{O}_2$  (23 kcal/mol) renders the emission of a visible photon from this state impossible. However, Kasha has discovered that the simultaneous transition of two  $^1\text{O}_2$  is capable of generating a photon of red light.<sup>18a</sup> Indirect chemiluminescence by energy transfer from the  $^1\text{O}_2$  dimer to suitable energy acceptors has also been postulated.<sup>18b</sup> This excitation mechanism may be responsible for the chemiluminescence observed on thermolysis of some aromatic hydrocarbon endoperoxides and for that observed during decomposition of some diperoxides.

The three excitation mechanisms described are capable of providing a basis for understanding a wide variety of chemiluminescent reactions. One notable exception to this is the reaction of oxalic acid esters with hydrogen peroxide in the presence of certain fluorescers. The mechanism of this reaction is quite complex, and the key high-energy content intermediate has not yet been identified unambiguously.<sup>19</sup> Most speculation on the structure of this substance, however, centers around dioxetanedione. One of the intriguing observations made during the study of this reaction by Rauhut and his co-workers is that the fluorescer is apparently able to catalyze the release of the energy stored in the intermediate and to direct it toward the formation of excited states. Rauhut speculated that the catalysis is due to the initial formation of a charge-transfer complex between the intermediate and the fluorescer.<sup>20</sup> Subsequent to an early suggestion by Linschitz,<sup>21</sup> McCapra has considered, as an interesting possibility, electron

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(17) E. Rapaport, M. N. Cass, and E. H. White, *J. Am. Chem. Soc.*, **94**, 3160 (1972).

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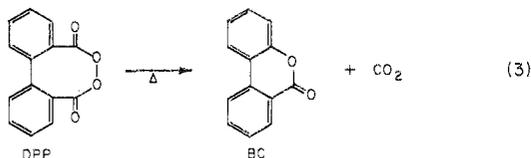
(20) M. M. Rauhut, L. J. Bollyky, B. G. Roberts, M. Loy, R. H. Whitman, A. U. Iannotta, A. M. Semsel, and R. A. Clarke, *J. Am. Chem. Soc.*, **89**, 6515 (1967).

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transfer from the fluorescer to the presumed dioxetanedione, followed by annihilation of oppositely charged radicals, to be responsible for the excitation.<sup>22</sup> These suggestions foreshadow our work which has shown that a specific, predictable, electron-exchange reaction between suitable donor molecules and many organic peroxides indeed does underlie the chemiluminescence of many systems and may, in fact, be the single most prevalent excitation mechanism.

### Chemically Initiated Electron-Exchange Luminescence

**Diphenoyl Peroxide.** Thermolysis of diphenoyl peroxide (DPP) in solution leads to the loss of CO<sub>2</sub> and the formation of benzocoumarin (BC) (eq 3). We were

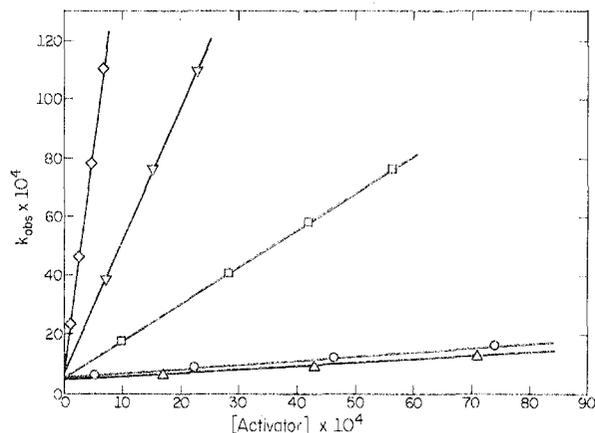


attracted to this reaction because it is sufficiently exothermic to permit generation of electronically excited BC. Also, we speculated that the unimolecular biradical cleavage mechanism might provide a path for the formation of excited products. Our supposition was incorrect. We could not detect any significant direct chemiluminescence as a result of the thermolysis of DPP. Moreover, we failed to detect a meaningful amount of indirect chemiluminescence when biacetyl (which phosphoresces efficiently) or 9,10-dibromoanthracene (DBA can be excited to its luminescent singlet state by both singlet and triplet donors) was included in the reaction mixture as energy acceptors. We were therefore very much surprised when we discovered that 9,10-diphenylanthracene (DPA) and DPP react to form efficiently the excited singlet state of DPA. The study of this reaction has provided direct evidence for the operation of a general path for the conversion of chemical bond energy to electronic excitation energy.<sup>2</sup>

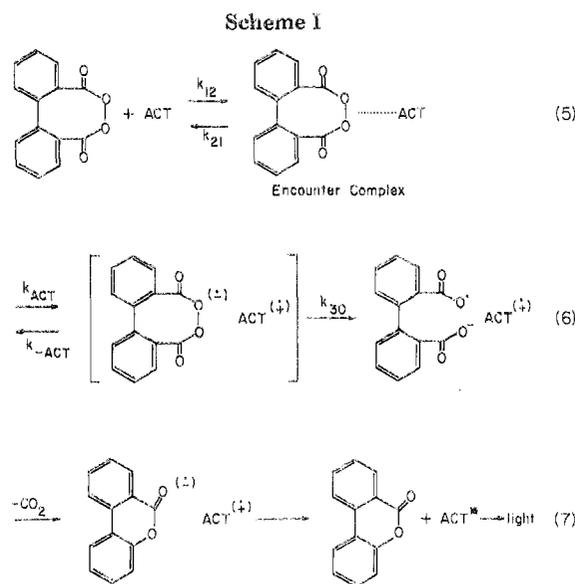
The kinetics of the chemiluminescent reaction of DPP and DPA are first order in both the peroxide and the aromatic hydrocarbon. Moreover, the hydrocarbon is not consumed in this reaction; it functions as a catalyst for the decarboxylation of the peroxide, and we refer to it as the catalytic chemiluminescence activator (ACT). The kinetic behavior we observe is described by eq 4 where  $k_{\text{obsd}}$  is the observed first-order rate constant for consumption of peroxide. Analysis of the reaction kinetics for a series of activators, plotted according to eq 4, is shown in Figure 1. The rate constant

$$k_{\text{obsd}} = k_1 + k_{\text{CAT}}[\text{ACT}] \quad (4)$$

$k_1$  (intercept in Figure 1) is, as expected, independent of the nature of the activator. We attribute this rate constant to the unassisted unimolecular cleavage of the oxygen-oxygen bond of the peroxide. The bimolecular rate constants  $k_{\text{CAT}}$  (the slopes in Figure 1) obviously depend strongly on the nature of the activator; structurally similar rubrene and DPA have slopes that differ by a factor of about 150. Further investigation showed that the electronically excited activator is formed as a direct consequence of the bimolecular



**Figure 1.** Dependence of the observed first-order rate constant for reaction of DPP on the concentration and structure of the aromatic hydrocarbon activators. In order of increasing slope the activators are: corone, DPA, perylene, naphthalene, and rubrene.

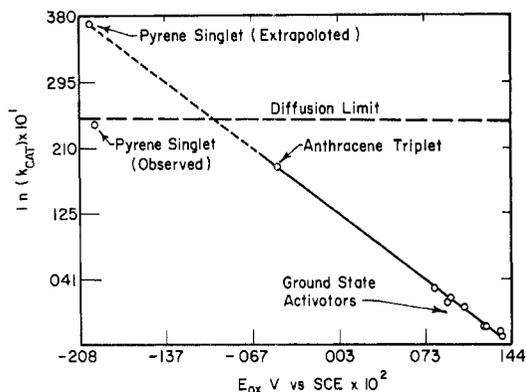


reaction. Thus the amount of light generated is directly proportional to the fraction of the reaction that proceeds by the bimolecular path.

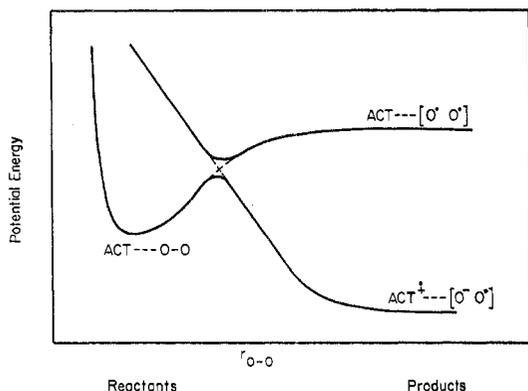
It is apparent that the magnitude of  $k_{\text{CAT}}$  must be related somehow to an important feature of the excitation step for the chemiluminescent reaction of DPP. The key to our understanding of this relationship is shown in Figure 2. The magnitude of  $k_{\text{CAT}}$  is predicted uniquely by the one-electron oxidation potential ( $E_{\text{ox}}$ ) of the activator. The lower is  $E_{\text{ox}}$ , the more easily oxidized is the activator, and the larger is the value of  $k_{\text{CAT}}$ . This finding indicates that the one-electron transfer from the activator to the peroxide determines, at least in part, the magnitude of  $k_{\text{CAT}}$ . The mechanism we propose for the reaction of DPP with the various activators is presented in Scheme I.

The first process that must occur in any bimolecular reaction is the diffusion together of the reactants to form an encounter complex (rate constant  $k_{12}$ ). In the Weller model for electron transfer,<sup>23</sup> which we adopt here, the reverse reaction ( $k_{21}$ ) is diffusion limited also. Thus the encounter complex is predicted to have only

(23) D. Rehm and A. Weller, *Isr. J. Chem.*, 8, 259 (1970), and references cited therein.



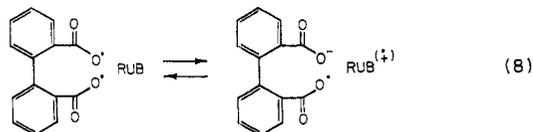
**Figure 2.** Correlation of the magnitude of  $k_{\text{CAT}}$  with the one-electron oxidation potential of ground- and excited-state activators. In order of increasing  $E_{\text{ox}}$  the ground-state activators are: rubrene, tetracene, triphenylamine, perylene, DPA, coronene, anthracene, and pyrene.



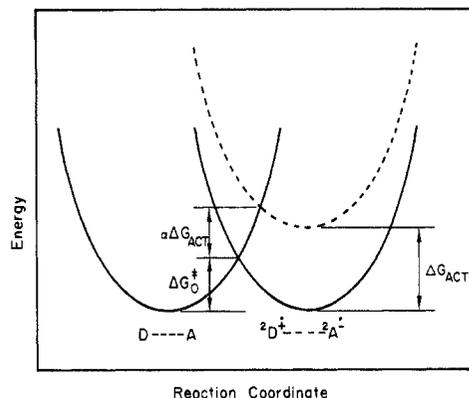
**Figure 3.** State correlation diagram for the activated electron transfer with simultaneous cleavage of the oxygen-oxygen bond.

a fleeting existence. Indeed, we have not been able to detect the complex in the absorption spectrum of mixtures of the peroxide and activator, or by measuring  $E_{\text{ox}}$  of the activator in the presence of peroxide.

The electron-transfer ( $k_{\text{ACT}}$ ) and bond-cleavage ( $k_{30}$ ) steps constitute the central feature of our proposed path, and, in fact, these steps are probably linked. The electron transfer from activator to peroxide is endergonic and will not occur spontaneously. Consider, however, what may happen as the oxygen-oxygen bond of the encounter complex stretches. One possibility is that this bond cleaves homolytically, as in the uncatalyzed case, to give a new complex of activator and biradical. This path is shown in Figure 3 as the correlation of encounter complex (ACT--O-O), through the dotted avoided crossing, with the state ACT--[O $^{\cdot-}$ O $^{\cdot-}$ ]. Importantly, there is another electronic state available to this complex, one in which an electron is transferred from ACT to an oxygen radical. This state is represented on Figure 3 as ACT $^+$ --[O $^{\cdot-}$ O $^{\cdot-}$ ]. In terms of DPP and some activator, say rubrene (RUB), we can associate these two states with the species shown in equilibrium in eq 8.



It is of great relevance to decide which of these states is of lower energy. Fortunately, this is not difficult to



**Figure 4.** Origin of the factor  $\alpha$  in the semilog plot of  $k_{\text{CAT}}$  against  $E_{\text{ox}}$ .

do, and the needed electrochemical measurements are available. Comparison of the oxidation potential of rubrene with the calculated oxidation potential of benzoate ion<sup>24</sup> (a model for the diphenate ion) shows that the zwitterionic state ACT $^+$ --[O $^{\cdot-}$ O $^{\cdot-}$ ] is some 18 kcal/mol lower in energy than the diradical state. Therefore, as the oxygen-oxygen bond of the complex stretches, these states avoid a crossing (dotted region in Figure 3), and this simple motion thus provides the activation for the electron transfer. This analysis predicts that the electron transfer gives directly a vibrationally excited radical ion pair which we show in brackets in eq 6. This species may be an intermediate or, more likely, a transition state. In either case, we suspect that the oxygen-oxygen bond of this state cleaves rapidly ( $k_{30} \gg k_{\text{ACT}}$ ) and irreversibly to give the diphenate radical anion and activator radical cation.

The correlation of reaction rate constant with the oxidation potential of the activator follows directly from the above considerations.<sup>25</sup> The usual steady-state approximations yield eq 9, where  $K_{12} = k_{12}/k_{21}$ . Shown

$$k_{\text{CAT}} = K_{12}k_{\text{ACT}} \quad (9)$$

in Figure 4 is an analysis of the Horiuchi-Polanyi<sup>26</sup> relationship between  $k_{\text{ACT}}$  and the free energy of the electron-transfer reaction,  $\Delta G_{\text{ACT}}$ . When  $\Delta G_{\text{ACT}} = 0$  the activation barrier is  $\Delta G_0^{\ddagger}$  (intersection of the two solid curves) and has been often associated with solvent reorganization.<sup>27</sup> If we increase the activation energy for the electron transfer by increasing the oxidation potential of ACT by an amount  $\Delta G_{\text{ACT}}$ , for example, the activation barrier for reaction increases also (intersection of the solid and dotted curves), but not by the full amount,  $\Delta G_{\text{ACT}}$ . As a consequence of geometry, only a fraction ( $\alpha$ ) of the total free energy change is realized as an increase in the activation barrier. The factor  $\alpha$  is analogous to the well-known transfer coefficient, which generally takes a value between 0.3 and 0.7 for electrode reactions.<sup>28</sup> We can express  $k_{\text{CAT}}$  in terms of  $E_{\text{ox}}$ , the reduction potential of the peroxide ( $E_{\text{red}}$ ), and the Coulombic attractive stabilization of the

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charged ions ( $E_{\text{coul}}$ ), as in eq 10, where  $k_i$  is the rate

$$\ln k_{\text{CAT}} = \ln k_i K_{12} + \frac{\alpha(E_{\text{red}} + E_{\text{coul}})}{RT} - \frac{\alpha E_{\text{ox}}}{RT} \quad (10)$$

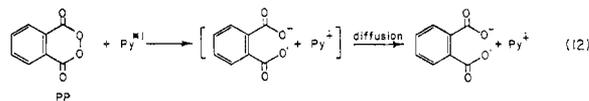
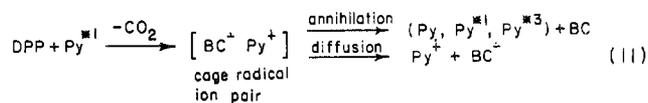
constant for the reaction when  $\Delta G_{\text{ACT}} = 0$ . It is important to realize that changing the activator affects only  $E_{\text{ox}}$ . Thus the semilog plot of  $k_{\text{CAT}}$  against  $E_{\text{ox}}$  for the reaction of DPP with various activators is expected to give a line with slope of  $-\alpha/RT$ . This is exactly the correlation we observe in Figure 2 with  $\alpha = 0.3$ .

The electron transfer–bond cleavage sequence we have just described yields, eventually, benzocoumarin radical anion and activator radical cation within a solvent cage. We have developed a direct experimental verification for the existence of these species and for their intermediacy in the chemiluminescent process.<sup>29</sup>

The fluorescence of excited singlet pyrene ( $\text{Py}^*1$ ) is quenched by DPP. When  $\text{Py}^*1$  is generated by irradiation with a nitrogen laser it is possible to record the absorption spectrum of the transient products that result from its reaction with the peroxide. The spectrum we observe 200 ns after the excitation of the pyrene is identical with that which has been attributed previously to pyrene radical cation ( $\text{Py}^{\bullet+}$ ).<sup>30</sup> The yield of cage escaped  $\text{Py}^{\bullet+}$  can be determined simply by measuring the optical density of its characteristic absorption after all of the  $\text{Py}^*1$  has reacted. Comparison of the yield of  $\text{Py}^{\bullet+}$  from the several systems we investigated is particularly revealing.

Weller has shown that the quenching of  $\text{Py}^*1$  by *p*-dicyanobenzene (DCB) in acetonitrile occurs by electron transfer from  $\text{Py}^*1$  to generate  $\text{Py}^{\bullet+}$ .<sup>31</sup> We have measured the yield of cage escaped  $\text{Py}^{\bullet+}$  in this system to be 67% of the  $\text{Py}^*1$  that reacts with DCB. The remaining 33% of the  $\text{Py}^*1$  must be converted to ground- or triplet-state pyrene, apparently, by in-cage ion annihilation. Similarly, when phthaloyl peroxide (PP) reacts with  $\text{Py}^*1$ , the yield of cage escaped  $\text{Py}^{\bullet+}$  is 48%. However, when DPP is the electron acceptor the yield of escaped  $\text{Py}^{\bullet+}$  is only 5%. It should be noted also that, in comparison to DPP, phthaloyl peroxide is not chemiluminescent.<sup>32</sup> The CIEEL mechanism provides a convincing explanation for the different behavior of phthaloyl and diphenoyl peroxides.

As is shown in Scheme I, one-electron reduction of DPP initiates a series of facile reactions that produce the powerful reducing agent  $\text{BC}^{\bullet-}$  in the same solvent cage as  $\text{ACT}^{\bullet+}$ . For the radical ion pair  $\text{Py}^{\bullet+}\text{BC}^{\bullet-}$ , formed in the laser experiment, there are several energetically possible reaction channels (eq 11). Annihilation within the cage can generate singlet or triplet excited pyrene or pyrene ground state. In competition with annihilation, diffusion into bulk solution generates the observed low yield of escaped  $\text{Py}^{\bullet+}$ . On the other hand, one-electron reduction of PP generates phthalate



radical anion. The structure of this species precludes its efficient rearrangement to a reducing agent. The cage annihilation reactions that consume the  $\text{BC}^{\bullet-}\text{Py}^{\bullet+}$  pair from DPP do not occur with PP because electron transfer from phthalate radical anion to  $\text{Py}^{\bullet+}$  is endergonic. As a result, diffusion competes more effectively within cage reactions, and we observe a relatively high yield of escaped  $\text{Py}^{\bullet+}$ . These reactions are summarized in eq 11 and 12.

Confirmation of the notion that reaction of  $\text{Py}^*1$  with DPP can eventually regenerate  $\text{Py}^*1$  comes from analysis of the reaction kinetics and from measurement of the reaction quantum efficiency. Pyrene singlet reacts with PP with a diffusion-limited rate constant of  $(1.67 \pm 0.01) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and consumes peroxide with a quantum efficiency of  $0.81 \pm 0.05$ . In contrast, DPP reacts with  $\text{Py}^*1$  with an apparent rate constant of only  $(1.02 \pm 0.007) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  but with a quantum efficiency of  $1.56 \pm 0.15$ . These observations can be reconciled if, as we suggest in eq 11,  $\text{Py}^*1$  is, to some extent, regenerated from the cage-radical ion pair resulting from its reaction with DPP but not from its reaction with PP.

Finally, we have established a kinetic link between the chemiluminescence of DPP and its reactions with electronically excited states. The CIEEL mechanism demands that the rate constant for reaction between a peroxide and an activator be predicted by the  $E_{\text{ox}}$  of the activator for excited states as well as ground-state activators. The oxidation potential of  $\text{Py}^*1$  is  $-2.00 \text{ V}$  (vs. SCE). Extrapolation of the ground-state chemiluminescence data to the oxidation potential of  $\text{Py}^*1$  (Figure 2) predicts a bimolecular rate constant of  $1.2 \times 10^{16} \text{ M}^{-1} \text{ s}^{-1}$ . Of course, this is much greater than the diffusion limit, and the rate we observe indicates, essentially, a diffusion-controlled reaction. The oxidation potential of triplet anthracene is calculated to be  $-0.47 \text{ V}$ . We have measured the rate of reaction of triplet anthracene with DPP by monitoring the triplet–triplet absorption spectrum following laser excitation. The rate constant for this reaction was found to be  $(1.44 \pm 0.03) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . The excellent correlation of this rate constant with the previously determined ground-state activator rate data is shown also in Figure 2. This correlation demands that the rate-determining step for the ground- and excited-state reactions of DPP with the various activators be the same, namely, electron transfer from the activator to the peroxide.

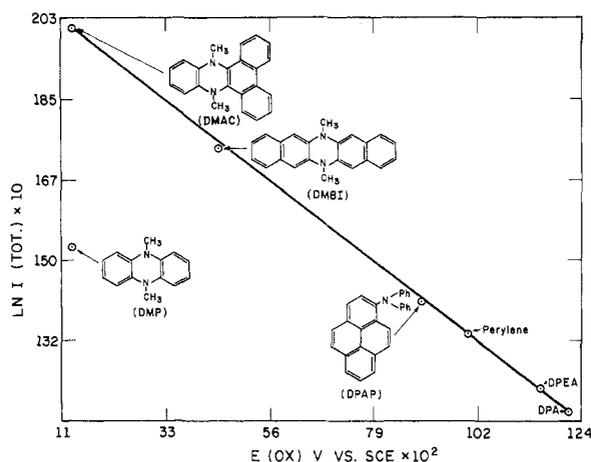
The last steps in our reaction mechanism (eq 7) are the familiar ion annihilation and the emission of light by excited activator. For the hydrocarbon activators we have examined, this emission is identical with the photoexcited fluorescence. With the amines *N*-phenylcarbazole and triphenylamine, however, a new emission, which we ascribe to an exciplex of the amine and benzocoumarin, is observed. This finding indicates that the reaction sequence, from initial electron transfer to annihilation, occurs within the solvent cage. This

(29) K. A. Horn and G. B. Schuster, *J. Am. Chem. Soc.*, submitted for publication.

(30) P. Balk, S. de Bruijn, and G. J. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, **76**, 907 (1957); Z. H. Khan and B. N. Khanna, *J. Chem. Phys.*, **59**, 3015 (1973).

(31) K. H. Gellman, A. R. Watkins, and A. Weller, *J. Phys. Chem.*, **76**, 469 (1972).

(32) K.-D. Gundermann, M. Seinfatt, and H. Fiege, *Angew. Chem.*, **83**, 43 (1971). The report that phthaloyl peroxide generates singlet oxygen on thermolysis (K.-D. Gundermann and M. Seinfatt, *Angew. Chem., Int. Ed. Engl.*, **14**, 560 (1975)) is in error: J. J. Zupancic, G. B. Schuster, to be submitted for publication.

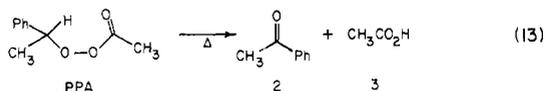


**Figure 5.** Correlation of the total chemiluminescent intensity of PPA with the oxidation potential of various activators in benzene solution at 99 °C.

conclusion is substantiated by the observation that the yield of excited activator increases with increasing solvent viscosity and that low concentrations of reagents such as water, oxygen, and tetramethylethylene, which are expected to react rapidly with diffused radical ions, have essentially no effect on the yield of excited activator.

The excitation mechanism we attribute to DPP provides a powerful paradigm for the chemiluminescence of other systems. We set out next to show the generality of this mechanism and to probe further each of the steps postulated.

**1-Phenylethyl Peroxyacetate.** Thermolysis of 1-phenylethyl peroxyacetate (PPA) in benzene solution at 95 °C gives quantitatively acetic acid and acetophenone (eq 13). Group-equivalent calculations<sup>33</sup>



predict this transformation to be exothermic by 58 kcal/mol. The activation enthalpy for this unimolecular reaction is 33.2 kcal/mol.<sup>34</sup> Thus, the transition state is 91 kcal/mol above ground-state product and is sufficiently energetic to form either singlet or triplet excited acetophenone. Indeed, we detect weak indirect chemiluminescence from this reaction when biacetyl is used as the energy acceptor. Our observations indicate that it is the unimolecular conversion of PPA to acetophenone that produces this luminescence. This mechanism is shown as path A in Scheme II.

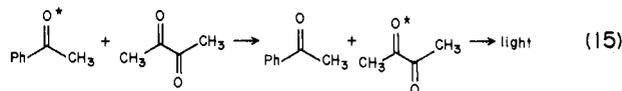
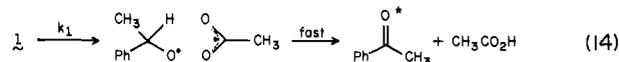
When a small amount of an easily oxidized substance is added to a benzene solution of PPA the thermolysis takes a different course. For example, *N,N*-dimethyldihydrodibenzo[*a,c*]phenazine (DMAC) accelerates the reaction of PPA without itself being consumed. The products of this reaction, acetic acid and acetophenone, are formed quantitatively as in the uncatalyzed case. Electronically excited states formed by the catalytic reaction are, in contrast to the unimolecular transformation, detected as fluorescence from the excited singlet activator. DMAC is not unique in its catalytic ability. Similar observations were made for

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

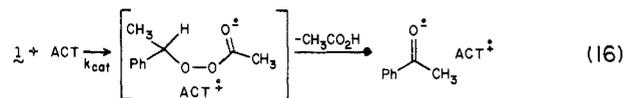
(34) B. G. Dixon and G. B. Schuster, *J. Am. Chem. Soc.*, 101, 3116 (1979).

### Scheme II

#### Path A - Indirect Chemiluminescence



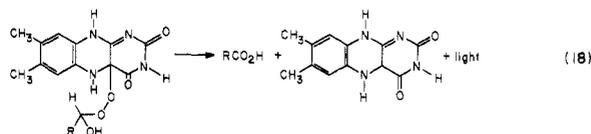
#### Path B - Activated Chemiluminescence



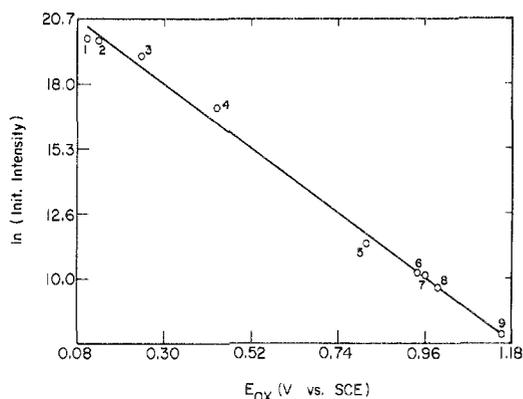
other phenazines, *N,N*-diphenyl-2-aminopyrene (DPAP), rubrene, perylene, 9,10-diphenylethynyl-anthracene (DPEA), DPA, and others.

The efficiency of light generation from the reaction of various activators with PPA was determined by measuring the total chemiluminescence intensity under conditions where essentially all the PPA reacts by the unimolecular path (i.e., low activator concentration so that  $k_1 \gg k_{\text{CAT}}[\text{ACT}]$ ). After correcting for differences in fluorescence quantum yield, photomultiplier tube, and monochromator spectral efficiency it is apparent that the only predictor of chemiluminescence efficiency is  $E_{\text{ox}}$  of the activator, except for *N,N*-dimethyldihydrophenazine (DMP); see Figure 5. The failure of the DMP oxidation potential to predict its chemiluminescence intensity is, in fact, a remarkable triumph of the CIEEL mechanism.

The CIEEL mechanism applied to the reaction of PPA is shown as path B in Scheme II. Conceptually, the sequence of reactions for PPA is identical with that described for DPP. Endergonic one-electron transfer from activator to peroxide followed by oxygen-oxygen bond cleavage gives acetate ion, 1-phenylethylalkoxyl radical, and activator radical cation. Rapid proton transfer from the radical to acetate forms acetic acid and acetophenone radical anion. When PPA deu-



terated at the methine hydrogen is employed, there is no measurable primary isotope effect on the unimolecular reaction ( $k_1$ ), on the catalyzed reaction ( $k_{\text{CAT}}$ ), or on the yield of electronically excited activator. These findings indicate that cleavage of the carbon-hydrogen bond does not occur at, or prior to, the rate-limiting step for either path A or B of Scheme II or in the distribution of the product between ground and excited state.<sup>34</sup> Finally, charge annihilation of the cage radical ions generates the excited activator which we detect by its characteristic luminescence. In the general case, the magnitude of  $k_{\text{CAT}}$  is directly proportional to the efficiency of excited-state generation. The exception is DMP.

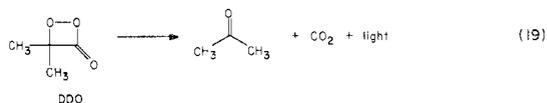


**Figure 6.** Semilog plot of initial chemiluminescent intensity of DDO with the oxidation potential of various activators. The points are: (1) DMP, (2) DMAC, (3) dimethylphenanthrylphenazine, (4) DMBI, (5) RUB, (6) tetracene, (7) diphenylethynyltetracene, (8) perylene, and (9) DPEA.

To generate light directly the energy release by the ion annihilation reaction must be at least as great as the energy of the lowest singlet state of the emitter. This requirement is apparently fulfilled by all of the activators of Figure 5 except DMP. For this activator the ion annihilation is expected to release ca. 59 kcal/mol. The singlet energy of DMP is 72 kcal/mol. As is predicted by its  $E_{ox}$ , DMP is a powerful catalyst for the reaction of PPA, but DMP generates less than 1% of the expected chemiluminescence because of the energy deficit in the annihilation reaction. This observation provides further convincing evidence for the radical ion intermediates proposed in the CIEEL mechanism.

Interestingly, the activated PPA reaction bears some structural resemblance to the postulated energizing transformation for the bacterioluminescence system shown in eq 18.<sup>35</sup> In this case the dihydroflavin nucleus may serve as an intramolecular activator. We have more to say about intramolecular systems below.

**Dimethyldioxetanone.** Thermolysis of dimethyldioxetanone (DDO) in  $\text{CH}_2\text{Cl}_2$  or in benzene gives acetone in quantitative yield, (presumably)  $\text{CO}_2$ , and light<sup>36</sup> (eq 19). The chemiluminescence observed under



these conditions is due to emission from singlet and triplet excited acetone which are formed at 30 °C with efficiencies of 0.1 and 1.5%, respectively.<sup>37</sup> We suspect that this uncatalyzed excitation is similar to the reaction of simple dioxetanes and proceeds through a biradical formed by simple homolytic cleavage of the oxygen-oxygen bond.

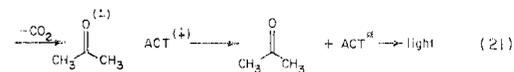
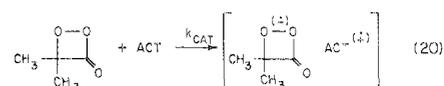
In the presence of easily oxidized activators the reaction of DDO takes a new course. With no activator, at 25 °C in a benzene solution, DDO has a half-life of about 1000 s. With  $1 \times 10^{-3}$  M DMAC present the half-life decreases to less than 5 s. This rate acceleration is directly proportional to the DMAC concentration. Moreover, the bimolecular rate constant for

(35) J. W. Hastings and K. H. Neelson, *Annu. Rev. Microbiol.*, **31**, 549 (1977).

(36) W. Adam and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2894 (1972).

(37) S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, **100**, 5559 (1978).

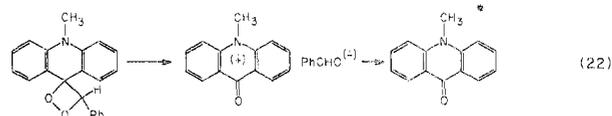
## Scheme III



reaction of DDO with DMAC predicts the intensity of the observed chemiluminescence. Other activators behave similarly; the magnitude of the bimolecular rate constant,  $k_{\text{CAT}}$ , and the initial chemiluminescence intensity are predicted by  $E_{ox}$  for activators of diverse chemical structure. This is displayed in Figure 6 which shows the dependence of initial chemiluminescence intensity on activator structure for over a 200 000-fold range. Note particularly that DMP is not an exception in this case. The difference in reduction potential between acetophenone and acetone is apparently great enough to permit the direct formation of DMP singlet excited state.

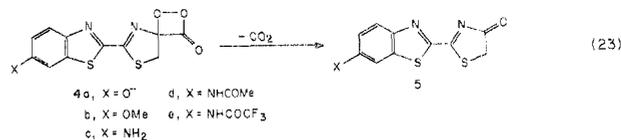
The reaction mechanism for DDO is entirely analogous to that for DPP and PPA. The sequence we propose for the activated excitation step is shown in Scheme III. As in the previous examples, the rate-limiting step is the transfer of an electron from activator to peroxide. Cleavage of the oxygen-oxygen bond followed by loss of  $\text{CO}_2$  leaves acetone radical anion.<sup>38</sup> Finally, charge annihilation generates the electronically excited activator which we detect by its characteristic emission.

McCapra and co-workers have reported recently on their observation of a dioxetane that reacts to form singlet excited product with unusually high efficiency (eq 22).<sup>39</sup> They speculate that a mechanism concep-



tually similar to the CIEEL process is operating. The major difference is that the electron donor and the acceptor are within the same molecule. Similarly, Schaap and co-workers have observed that certain *p*-(dimethylamino)phenyl substituted dioxetanes give high singlet yields and have invoked intramolecular electron transfer to explain this.<sup>40</sup>

After considerable debate it is now widely accepted that the key transformation in the firefly bioluminescence process is the conversion of dioxetanone 4a to amide 5a<sup>41</sup> (eq 23). The discovery of activated



chemiluminescence of simple dioxetanones and finding

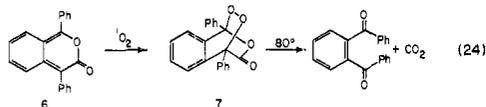
(38) S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, **100**, 1966 (1978). In fact, we cannot rule out the possible cleavage sequence for which neutral acetone leaves and  $\text{CO}_2^{\cdot-}$  annihilates to form excited states.

(39) F. McCapra, I. Beheshti, A. Burford, R. A. Hann, and K. A. Zaklika, *Chem. Commun.*, 944 (1977).

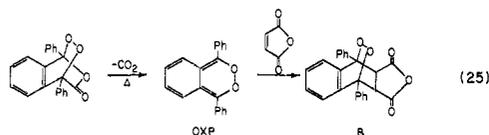
(40) K. A. Zaklika, A. L. Thayer, and A. P. Schaap, *J. Am. Chem. Soc.*, **100**, 4916 (1978).

that intramolecular electron transfer generates singlets efficiently have led us to speculate that an intramolecular version of the CIEEL mechanism is operating in the bioluminescence of the firefly.<sup>42</sup> This proposal neatly rationalizes some early observations of White and co-workers.<sup>43</sup> Their work indicates that the dioxetones **4a** and **4c** generate light whereas **4b**, **4d**, and **4e** do not. Of course, we now recognize quickly that **4a,c** are good intramolecular electron donors while **4b,d,e** are not.

**1,4-Diphenyl-2,3-benzodioxin (o-Xylylene Peroxide)**. Photooxidation of 1,4-diphenyl-2-benzopyran-3-one (**6**) gives endoperoxide **7** as a white crystalline solid in 60% yield<sup>44</sup> (eq 24). Thermolysis of **7**



in benzene at 80 °C gives *o*-dibenzoylbenzene and (presumably) CO<sub>2</sub>. With an appropriate energy acceptor, or activator, this reaction generates light. Interestingly, if the thermolysis of **7** is carried out in the presence of maleic anhydride, then *o*-dibenzoylbenzene is no longer the major product. Instead, the Diels-Alder adduct **8** is isolated in 70% yield (eq 25). This finding,



among others, led us to postulate *o*-xylylene peroxide (OXP) as an intermediate in the thermolysis of **7**.

Our data show that it is OXP which gives rise to excited-state products. Unimolecular cleavage of the oxygen-oxygen bond apparently generates triplet *o*-dibenzoylbenzene, as is shown as path A of Scheme IV. The CIEEL mechanism, shown as path B in Scheme IV, accounts for our observation of activated chemiluminescence.

The OXP results may be applicable to the chemiluminescence of luminol. The key reaction intermediate in the luminol system has not been identified unambiguously. However, most informed speculation centers on the endoperoxy azo compound **9**.<sup>45</sup> The resemblance of this structure to endoperoxide **7** is apparent im-

(41) O. Shimomura, T. Goto, and F. H. Johnson, *Proc. Natl. Acad. Sci. U.S.A.*, **74**, 2799 (1977).

(42) J.-y. Koo, S. P. Schmidt, and G. B. Schuster, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 30 (1978).

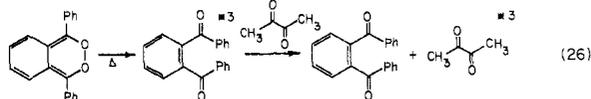
(43) E. H. White, H. Worthen, H. H. Seliger, and W. D. McElroy, *J. Am. Chem. Soc.*, **88**, 2015 (1966).

(44) J. P. Smith and G. B. Schuster, *J. Am. Chem. Soc.*, **100**, 2564 (1978).

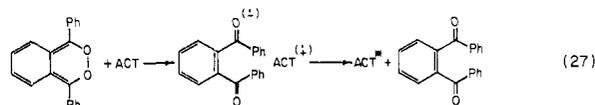
(45) E. H. White, E. G. Nash, D. R. Roberts, and O. C. Zafirou, *J. Am. Chem. Soc.*, **90**, 5932 (1968); K.-D. Gundermann, *Angew. Chem., Int. Ed. Engl.*, **7**, 480 (1968).

#### Scheme IV

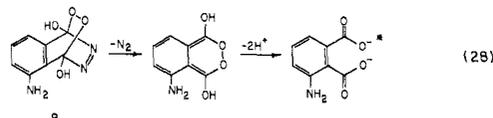
Path A - Indirect Chemiluminescence:



Path B - Activated Chemiluminescence:



mediately and suggests that a similar mechanism may be operating in the luminol system (eq 28).<sup>46</sup> Of course,



application of the intramolecular CIEEL mechanism to luminol nicely explains the well-known importance of the amino group to the chemiluminescence of luminol and suggests several trapping experiments.

#### Concluding Remarks

The chemically initiated electron-exchange luminescence (CIEEL) mechanism we have described provides a fabric for understanding the excitation step for peroxides of diverse structure and properties. Moreover, recognition of the several reactions involved in this excitation process permits us to contemplate the rational design of new, and perhaps efficient, chemiluminescent reagents. This new capability, we think, will lead to the discovery of novel light-yielding reactions. The key concept of the CIEEL mechanism, activated electron transfer to generate radical ion intermediates, may find further applicability in the understanding of the reactions of numerous electrophiles with easily oxidized electron donors. We are continuing to investigate these and other aspects of chemical reactivity.

*The work described in this Account could not have been done without the efforts and contributions of my colleagues, Brian Dixon, Keith Horn, Ja-Young Koo, Steve Schmidt, and Jimmie Smith. We also thank Professor Larry Faulkner for many helpful discussions and Mr. James Wehmer for his assistance with the laser experiments. Finally, we express our gratitude to the Office of Naval Research, to the National Science Foundation, to the Research Corporation, and to the Petroleum Research Fund, administered by the American Chemical Society, for their support of our work.*

(46) A similar suggestion has been made on theoretical grounds: J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).