

Chemiluminescence of Diphenoyl Peroxide. Chemically Initiated Electron Exchange Luminescence. A New General Mechanism for Chemical Production of Electronically Excited States¹

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Abstract: The thermal reactions of diphenoyl peroxide (**1**) were probed. It was found that when **1** was heated at 24 °C for 24 h in CH₂Cl₂, benzocoumarin (**2**) and a small amount of polymeric peroxide were formed. Under these conditions the reaction was essentially nonchemiluminescent. However, addition of any one of several easily oxidized fluorescent molecules resulted in readily detected chemiluminescence. The mechanism for chemical light formation was probed by investigating the (1) effect of the additives' structure, (2) reaction kinetics, (3) effect of solvent polarity and viscosity, (4) effect of reaction conditions on the products, (5) chemiluminescence emission, and (6) independent generation of proposed intermediates. These studies show that the chemiluminescence of **1** does not proceed by one of the classical mechanisms. We propose a new general chemical light producing scheme identified as chemically initiated electron exchange luminescence.

Chemical reactions that result in light emission have been intensively investigated for the past half century.³ Two general schemes have evolved to explain most observations on these intriguing reactions. In the first sequence, shown schematically in Figure 1, a high-energy reactant molecule undergoes an exergonic reaction to generate an electronically excited state of a product molecule. Subsequent fluorescence or phosphorescence from this excited state species, or one derived from it, results in chemiluminescence.⁴ Examples of chemiluminescent reagents currently thought to proceed along this path are simply substituted 1,2-dioxetanes,⁵ Dewar benzene and its derivatives,⁶ luminol,⁷ and several other less well characterized systems.⁸

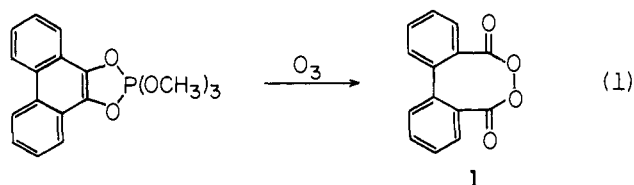
The second approach to chemical light generation is known as electrogenerated chemiluminescence (ecl), shown schematically in Figure 2.⁹ In this procedure, a radical anion, usually formed by the reduction of a suitable species at a cathode, and a radical cation, typically the result of a one-electron oxidation, form a diffusive encounter pair and mutually annihilate. The result of the charge annihilation is an electronically excited state species which may then go on to emit a photon of light. Light yields of typical ecl reactions are low because of the required diffusive encounter of two rather reactive species.

In this report we would like to fully describe the findings from our investigation of the chemiluminescence of diphenoyl peroxide (**1**).¹ These results have led to delineation of a new general mechanism for chemiluminescence described as chemically initiated electron exchange luminescence (CIEEL). This mechanism appears to explain chemical light generation in many important systems and provides for the ready rationalization of many of the most perplexing observations of chemi- and bioluminescent systems.

Results

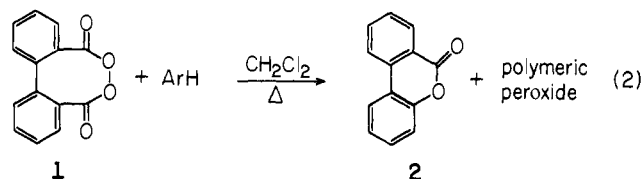
Preparation and Thermal Reactions of Diphenoyl Peroxide.

The preparation of diphenoyl peroxide (**1**) has been reported by Ramirez and co-workers¹⁰ and is shown in eq 1. Details of



the purification and characterization of peroxide **1** are given in the Experimental Section.

The thermolysis of diphenoyl peroxide was carried out in several different solvents. The results in CH₂Cl₂ are typical. In this case, heating a 1 × 10⁻⁴ M solution under a nitrogen atmosphere, in the dark, for 24 h at ca. 24 °C gave benzocoumarin (**2**) in 75% yield and a polymeric peroxide. No di-



phenic acid (**3**) or diphenic anhydride (**4**) could be detected as reaction products under these conditions.

Chemiluminescence from the Reaction of Diphenoyl Peroxide. The reaction of diphenoyl peroxide to form benzocoumarin (**2**) and CO₂ is exothermic by ca. 70 kcal/mol. The activation energy (see below) for this reaction is ca. 24 kcal/mol. Thus, at the transition state, there is about 94 kcal/mol available for the formation of electronically excited state products.¹¹ The singlet energy of benzocoumarin (**2**) is estimated to be 88 kcal/mol. Therefore, formation of excited singlet benzocoumarin is thermodynamically permitted. However, it is observed that photoexcited benzocoumarin is essentially nonfluorescent. Thus, no chemiluminescence is expected or detected during thermolysis of solutions of diphenoyl peroxide (**1**). If electronically excited benzocoumarin is formed during thermolysis of **1**, its presence should be confirmed with an energy transfer (trapping) reaction to a suitable emitting acceptor. Biacetyl, which has accessible emissive singlet and triplet states, and 9,10-dibromoanthracene (DBA), which can undergo both singlet-singlet and triplet-singlet energy transfer, do not produce sensitized chemiluminescence when added to solutions of **1** in CH₂Cl₂.¹² These observations make the possibility remote that high yields of electronically excited benzocoumarin are formed during thermolysis of peroxide **1**.

Bright, readily seen chemiluminescence from thermolysis of diphenoyl peroxide is observed, however, when any one of several relatively easily oxidized emitting molecules is added to solutions of **1**. For example, addition of 9,10-diphenylanthracene (DPA) to **1** in CH₂Cl₂ results in DPA fluorescence. This observation further supports the proposal that no de-

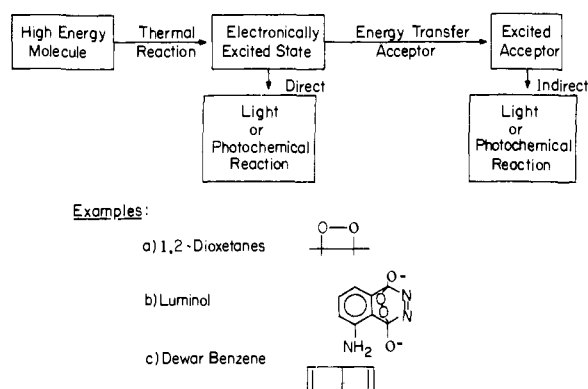


Figure 1. Conventional chemiluminescence of organic molecules.

tectable amount of excited benzocoumarin is formed during thermolysis of **1**. Instead DPA must be excited by some mechanism other than conventional energy transfer since singlet-singlet energy transfer to DPA and DBA should occur with the same rate. Moreover, we observe that the rate of reaction of peroxide **1** is accelerated by the added molecule when chemiluminescence results. Thus, we refer to these additives as the catalytic chemiluminescence activators.

We find that the activator concentration is essentially constant (see below) during the reaction with peroxide **1** and that the rate acceleration is directly proportional to the concentration of the activator. These results are consistent with the simple kinetic law shown in eq 3, where k_{obsd} is the rate con-

$$K_{\text{obsd}} = k_1 + k_2[\text{activator}] \quad (3)$$

stant for the observed first-order decrease in the concentration of peroxide **1**, and k_1 and k_2 are the rate constants for the unimolecular and activator induced reactions, respectively. Also consistent with this rate law, the reaction of **1** follows strictly first-order kinetics and the chemiluminescence intensity is directly proportional to the concentration of peroxide **1**. The kinetic analyses for the thermolysis of **1** with a variety of activators are shown in Figure 3 and the kinetic data are summarized in Table I.

The products of thermolysis of peroxide **1** depend upon the reaction path. In the presence of a quantity of rubrene (the catalytic chemiluminescence activator) sufficient to ensure that essentially all of **1** reacts by the bimolecular path, the reaction products are benzocoumarin and polymer (as in the uncatalyzed reaction), singlet excited rubrene, and diphenic acid.¹³ The excited rubrene singlet is, of course, responsible for the observed chemiluminescence. Since the diphenic acid is only produced in the presence of the activator it must arise by the induced bimolecular path.

To further demonstrate that the chemiluminescence is the result of the bimolecular reaction, the effect of catalytic activator concentration on the chemiluminescence intensity was probed. As shown in Figure 4, the reciprocal of the relative light yield is a linearly increasing function of the reciprocal of activator concentration, in this case DPA. This observation is consistent with excited state production resulting from the bimolecular reaction of peroxide **1** with the activator.

The magnitude of the bimolecular rate constant, k_2 , is strongly dependent upon the structure of the catalytic chemiluminescence activator. From the data in Table I it is clear that the rate constant k_1 (the intercept in Figure 3) does not depend upon the structure of the activator. Most significantly, it is observed that the magnitude of the bimolecular rate constant k_2 (the slope in Figure 3) is inversely correlated with the one-electron oxidation potential of the chemiluminescence activator. As shown in Figure 5, an increase in the oxidation potential of the activator causes a decrease in the magnitude of

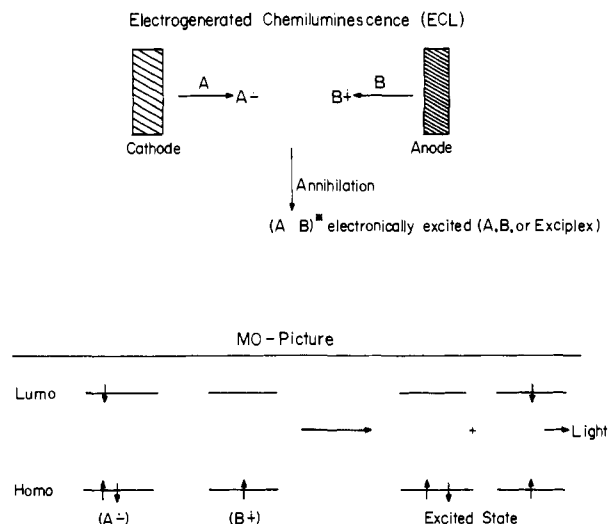


Figure 2. General pathway for electrogenerated chemiluminescence.

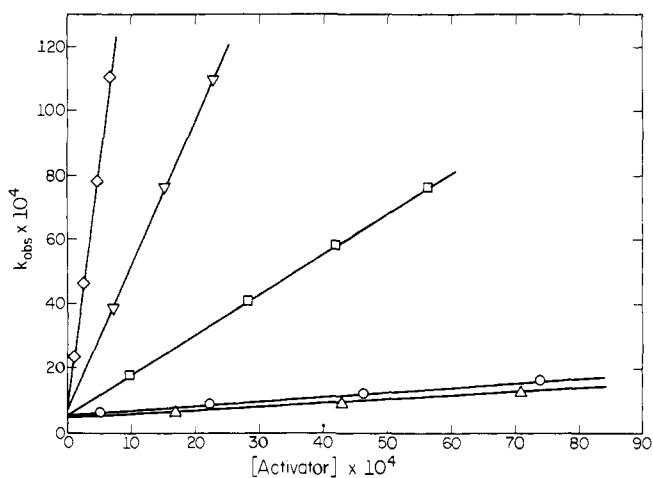


Figure 3. The effect of activator structure and activator concentration on the observed first-order decay of diphenoyl peroxide: \diamond , rubrene; ∇ , naphthalene; \square , perylene; \circ , DPA; \triangle , coronene.

k_2 . This observation is consistent with electron transfer from the activator to diphenoyl peroxide in the rate-determining step of the chemiluminescent process.¹⁴ This finding also explains why the relatively difficultly oxidized biacetyl and DBA molecules do not cause light generation or accelerate the rate of reaction of diphenoyl peroxide.

The effect of activator structure on the reaction rate is reflected in the free energy of activation for the catalytic light path. As shown in Table II, the activation energy for the bimolecular reaction varies with activator structure. These activation energies were determined by two independent techniques. The first technique involves measurement of the effect of temperature on the magnitude of the bimolecular rate constants (kinetics). This procedure yields thermal data on the entire bimolecular path. The second technique used probes the effect of temperature on the chemiluminescence light yield (intensity). This approach generates activation parameters for only that portion of the reaction that leads to light emission.¹⁵ A significant result, shown in Table II, is that for cases studied, the activation energies determined by these two independent techniques are identical. This result implies that the induced decomposition and the light-forming reaction path have the same rate-determining step. This finding is consistent with light formation as a result of the bimolecular electron transfer interaction.

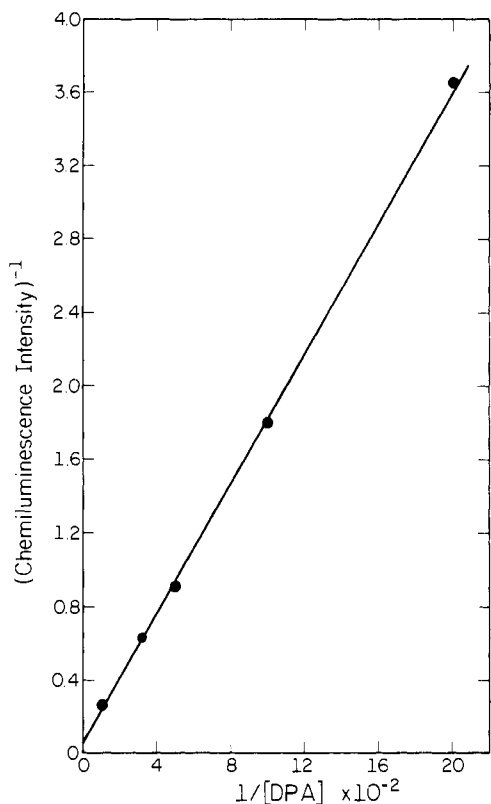


Figure 4. Reciprocal plot of chemiluminescent intensity against concentration of DPA in CH_2Cl_2 at 32°C .

Table I. Effect of Activator Structure and Oxidation Potential on Uni- and Bimolecular Reaction of Diphenyl Peroxide in CH_2Cl_2 at 32.5°C

activator	$E_{\text{ox}}, \text{eV}^a$	$k_1 \times 10^4, \text{s}^{-1}$	$k_2, \text{M}^{-1} \text{s}^{-1}$
rubrene	0.82 ^b	4.57 ± 0.04^c	14.7 ± 0.6
tetracene	0.95 ^d	5.4 ± 0.2	4.52 ± 0.04
triphenylamine	0.92 ^e	4.2 ± 0.2	2.60 ± 0.03
perylene	1.06 ^d	4.45 ± 0.07	1.45 ± 0.01
DPA	1.22 ^b	4.3 ± 0.1	0.103 ± 0.004
coronene	1.23 ^b	4.74 ± 0.1	0.100 ± 0.001
anthracene	1.35 ^d	4.94 ± 0.05	0.056 ± 0.001
pyrene	1.36 ^d	4.0 ± 0.5	0.034 ± 0.005

^a vs. SCE. ^b In CH_2Cl_2 ; C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Non-Aqueous Systems", Marcel Dekker, New York, N. Y., 1970. ^c All errors are standard deviations calculated by the least-squares technique. ^d V. D. Parker, *J. Am. Chem. Soc.*, **98**, 98 (1976). ^e E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, O. W. Leedy, and R. N. Adams, *ibid.*, **88**, 3498 (1966).

Effect of Solvent on the Chemiluminescence. To further examine the light-forming path, the influence of solvent dielectric constant (Table III) and viscosity (Table IV) on both the magnitude of the bimolecular rate constant and the efficiency of light production was investigated. The data in Table III show that, in general, as the dielectric constant of the solvent increases, the bimolecular reaction of diphenyl peroxide with the activator (perylene in this case) proceeds with a larger rate constant. Benzene is the exception and this may be due to the high polarizability of the π electron cloud for this solvent.¹⁶ Also, the data in Table III show that the efficiency of excited state production along the bimolecular path generally decreases as the solvent dielectric constant increases, again benzene being the exception. Thus, although the rate constant for catalytic activator increases, the fraction of the reaction that proceeds by the bimolecular route that ultimately leads to an electronically excited product goes down as the dielectric

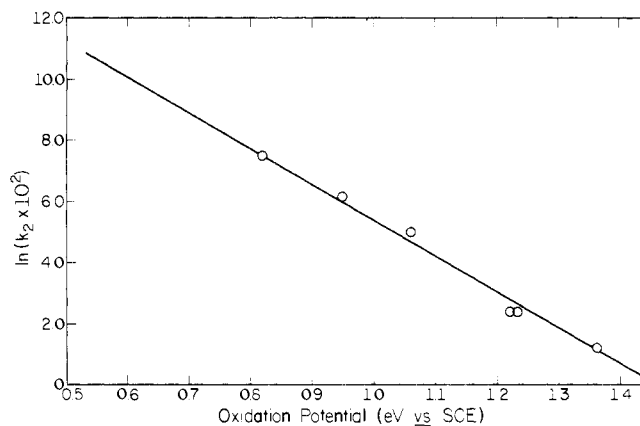


Figure 5. Correlation of the magnitude of k_2 with the oxidation potential of the activators. In order of increasing E_{ox} the points are rubrene, naphthalene, perylene, DPA, coronene, pyrene.

constant for the solvent goes up. These observations are consistent with a reaction path that creates charge in the rate-determining step and in which a subsequent step on the light-forming path is in competition with a charged species diffusing away from and never returning to the light path.

The effect of solvent viscosity is shown in Table IV. These data show that as the solvent viscosity is increased, the efficiency of excited state generation by the bimolecular path also increases. This observation is again consistent with the notion that diffusion of an intermediate from the initial solvent cage is in competition with excited state formation.

Spectral Examination of Diphenyl Peroxide Chemiluminescence. The spectrum of the chemiluminescence emission from diphenyl peroxide and various activators reveals some important information about the mechanism for the generation of the electronically excited state. In the case when the catalytic activator is an aromatic hydrocarbon, the chemiluminescence emission spectrum is identical with the photoexcited fluorescence of the hydrocarbon. When triphenylamine or *N*-phenylcarbazole is employed as the catalytic activator, chemiluminescence is still observed, the decay rate still depends on activator concentration, and the magnitude of the bimolecular rate constant is predictable from the activator oxidation potential. However, the chemiluminescence spectra no longer correspond to the activator fluorescence spectra. In these cases, the chemiluminescence emission spectra are broad, structureless, and shifted toward lower energy from the normal fluorescence. Also, with the amine activators the chemiluminescence is rapidly quenched by the addition of polar solvents such as acetonitrile. This behavior is consistent with formation of and emission from an exciplex resulting from reaction of **1** with the amine.¹⁷ This conclusion is confirmed by the behavior of photoexcited solutions of benzocoumarin and triphenylamine. At high concentrations of benzocoumarin, the normal fluorescence of triphenylamine is quenched and a new emission appears with a maximum at 455 nm; see Figure 6. This photoexcited exciplex emission is identical in all respects with the chemiluminescence from diphenyl peroxide and triphenylamine. Significantly, there is no detectable triphenylamine fluorescence component in the chemiluminescence emission. Thus, the exciplex must be the initially formed electronically excited species in this reaction. That is, the exciplex is not formed by a diffusive encounter of an excited triphenylamine with a ground state benzocoumarin.

Yield of Electronically Excited States. The yield of electronically excited states by the induced path for diphenyl peroxide and perylene was determined by comparison with the yield of excited acetone from tetramethyldioxetane. In this experiment the total integrated chemiluminescent intensity

Table II. Activation Parameters for Uni- and Bimolecular Reaction of Diphenoyl Peroxide in CH_2Cl_2

activator	rubrene		perylene		DPA	
	k_1	k_2	k_1	k_2	k_1	k_2
ΔG^\ddagger ^a (kinetics)	23.2 ± 0.8	16.3 ± 1.1	24.0 ± 0.1	17.6 ± 0.1	23.7 ± 0.3	19.3 ± 0.8
E_A ^a (intensity)		15.5 ± 1.0		17.6 ± 0.7		19.3 ± 0.4

^a kcal/mol; all errors are standard deviations.

Table III. Effect of Solvent Dielectric Constant on the Reaction of Diphenoyl Peroxide with Perylene at 32.5 °C^a

solvent	acetonitrile	CH_2Cl_2	ethyl acetate	diethyl ether	benzene
dielectric constant	36.2	8.9	6.02	4.34	2.28
viscosity	3.45	3.9	4.41	2.22	6.03
$k_1 \times 10^4, \text{s}^{-1}$	5.87 ± 0.11	4.45 ± 0.07	5.10 ± 0.01	5.58 ± 0.01	5.50 ± 0.01
$k_2, \text{M}^{-1} \text{s}^{-1}$	2.76 ± 0.20	1.45 ± 0.01	0.210 ± 0.007	0.0572 ± 0.0003	0.47 ± 0.01
excited state generating efficiency	1.1	1	4.9	15.4	3.3

^a Perylene concentration, 1.0×10^{-5} to 1.4×10^{-4} M, $[\text{I}] = 5 \times 10^{-5}$ M.

Table IV. Effect of Solvent Viscosity on the Reaction of Diphenoyl Peroxide with Perylene at 32.5 °C^a

solvent	viscosity (mp)	dielectric constant	$k_1 \times 10^4, \text{s}^{-1}$	$k_2, \text{M}^{-1} \text{s}^{-1}$	relative excited state yield
CH_2Cl_2	3.9 (30 °C)	8.9	4.45 ± 0.07	1.45 ± 0.01	1
dimethyl phthalate	172 (25 °C)	8.5	5.54 ± 0.04	2.09 ± 0.15	3.5
di- <i>n</i> -butyl phthalate	97.2 (37.8 °C)	6.44	5.32 ± 0.01	1.12 ± 0.02	3

^a Perylene concentration = 8×10^{-6} to 5×10^{-5} M, $[\text{I}] = 5 \times 10^{-5}$ M.

at extrapolated infinite activator concentration for CH_2Cl_2 solutions of diphenoyl peroxide containing perylene and CCl_4 solutions of tetramethyldioxetane containing DBA were compared. Since the chemiluminescence efficiency of tetramethyldioxetane under these conditions has been well defined,⁵ it serves as our standard. After correction for the spectral response of the monochromator and the photomultiplier tube, the measured total intensity ratio showed excited state generation from tetramethyldioxetane to be ca. three times greater than that from diphenoyl peroxide. Thus this analysis shows that in CH_2Cl_2 at 32 °C, $10 \pm 5\%$ of the diphenoyl peroxide molecules that react by the bimolecular path lead to the formation of a perylene singlet excited state. Detection of the triplet excited state of the aromatic hydrocarbon is very difficult because these states are essentially nonemissive in fluid solution.¹⁸ Moreover, the low energy of typical aromatic triplet states mitigates against efficient energy transfer to an emitter. An exception to this last generalization is chrysene.¹⁹ The lowest excited triplet of this molecule has been located at 57 kcal/mol above the ground state. Thus, this triplet is sufficiently energetic to permit efficient energy transfer to the emissive triplet of biacetyl. When diphenoyl peroxide is reacted with chrysene in the presence of biacetyl, no biacetyl phosphorescence is detected. Therefore, at least under these conditions, the formation of the triplet excited state of the aromatic hydrocarbon appears to be considerably less efficient than excited singlet formation.

The relative light yield for the series of aromatic hydrocarbons studied is shown in Table V. At fixed diphenoyl peroxide and activator concentration, the light yield reflects the competition between unimolecular and induced reaction of peroxide **1**. Thus, comparison of the chemiluminescence intensity of rubrene and DPA activated systems at identical

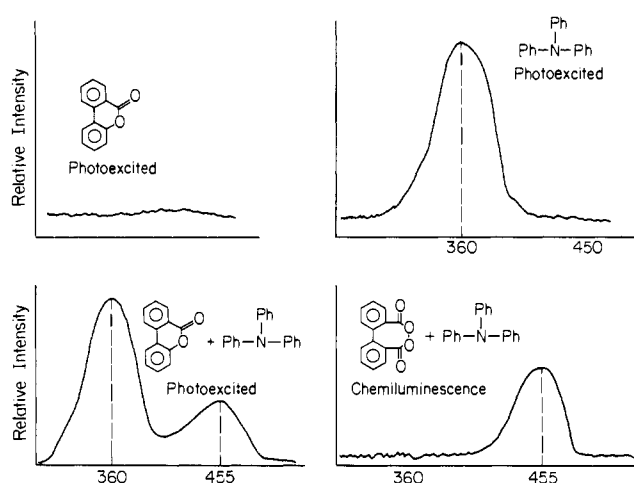


Figure 6. Fluorescence, chemiluminescence, and exciplex emission from the triphenylamine system. The fluorescence spectra were recorded at room temperature in benzene solution, the chemiluminescence at 32 °C.

concentrations shows that about 200 times more light is generated by the rubrene than DPA. Normalization of the observed relative light yields for the measured value of the bimolecular rate constants (k_2) and fluorescence yields of the hydrocarbons shows that the light-forming efficiency is essentially independent of the nature of the activator (see Table V). This observation suggests that after the initial catalytic event, the factors that control partitioning between excited and ground state products are approximately independent of the nature of the activator.

Table V. Effect of Activator Structure on Light Yield and Light Efficiency for Diphenoyl Peroxide in CH₂Cl₂ at 32.5 °C

activator	normalized light yield ^a	normalized light efficiency ^b
DPA	1	1.0
coronene	1	1.0
perylene	19	1.3
tetracene	56	1.2
rubrene	220	1.5

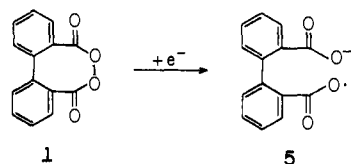
^a Observed total photon yield corrected for photomultiplier tube response, monochromator efficiency, and fluorescence efficiency normalized so that DPA = 1.0. ^b Efficiency of excited state generation for those diphenoyl peroxide molecules that react by the CIEEL path.

Attempts to Detect an Intermediate Ground State Complex.

Several attempts were made to detect a stable ground state complex between diphenoyl peroxide and the catalytic chemiluminescence activators. Two approaches were employed. The first measures the effect of added peroxide on the UV-visible absorption spectrum of the activator.²⁰ In particular, it is found that peroxide **1** has no effect on the absorption spectrum of rubrene. The absorption spectrum of the mixture is quantitatively the sum of the spectrum of the components. The second technique measures the oxidation potential of the activator in the presence of varying amounts of peroxide **1**.²¹ Again for the case of rubrene in CH₂Cl₂, no effect of added diphenoyl peroxide on the oxidation potential was observed. These findings indicate that a high steady-state concentration of a relatively stable complex between rubrene and peroxide **1** is not formed in these cases.

Independent Chemical Generation of Proposed Intermediates.

Electron transfer from the chemiluminescence activator to diphenoyl peroxide followed by cleavage of the oxygen-oxygen bond in **1** is expected to generate the 2,2'-dicarboxybiphenyl radical anion **5** (Scheme I). This species is a postulated key intermediate in the formation of benzocoumarin during chemiluminescence of **1** (see discussion below). As a test of this

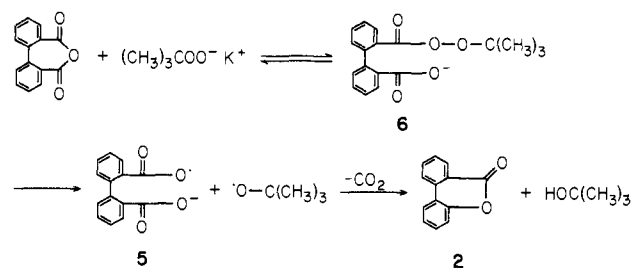


proposal, radical anion **5** was generated by an independent route.

The reaction of diphenic anhydride with potassium *tert*-butyl hydroperoxide in refluxing THF results in the formation of benzocoumarin **2**. We suggest that this reaction involves thermal cleavage of the oxygen-oxygen bond in peroxide **6**²² to generate the desired radical anion **5** (Scheme I). While other pathways can be written, the formation of benzocoumarin under conditions which we consider to generate **5**, a precursor to benzocoumarin in the chemiluminescent reaction of **1** with the activators, clearly can be taken to support the postulates of Schemes I and II (see below).

Discussion

Chemical light generation from the reaction of diphenoyl peroxide with the chemiluminescence activators does not occur by the commonly considered reaction path shown in Figure 1. Many of our observations are inconsistent with this mechanism. Most significantly, the specific involvement of the activator in the chemical step responsible for initial excited state production rules out the "classical" explanation. In Scheme II a mechanism consistent with the experimental findings is

Scheme I

shown. We designate this pathway chemically initiated electron exchange luminescence (CIEEL).

In this scheme, the initiating step in the light-generating sequence is an electron transfer from the activator to peroxide **1**. Following this transfer, the reduced peroxide cleaves and loses CO₂. Cyclization of the decarboxylated intermediate generates benzocoumarin radical anion. Annihilation of the benzocoumarin radical anion and the activator radical cation results in excited state generation.

The initiating, and rate-determining, reaction in the proposed CIEEL mechanism is an electron transfer from the chemiluminescence activator to the diphenoyl peroxide. The experimental evidence for this step is quite conclusive. The rate constant for this process is the bimolecular parameter k_2 . Critically, the activation energy, and hence the magnitude of k_2 , for the electron transfer must depend upon the oxidation potential of the activator (E_{ox}), the reduction potential of peroxide **1** (E_{red}), and the Coulombic attractive force between the developing oppositely charged radical ions according to the equation

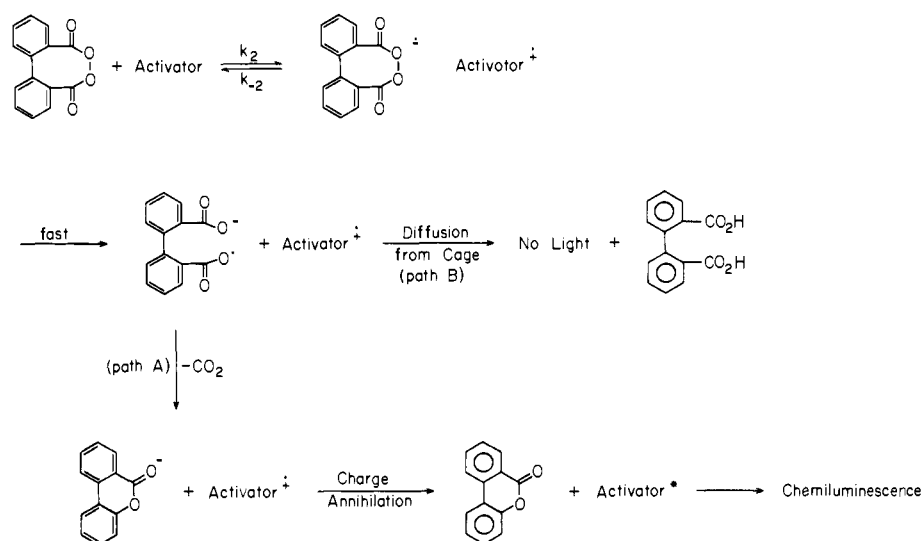
$$k_2 = A \exp \left(- \left(E_{ox} - E_{red} - \frac{e^2}{\epsilon R_0} \right) / RT \right) \quad (4)$$

where e is the electronic charge, ϵ the dielectric constant, and R_0 the distance between the ions at the transition state. Significantly, eq 4 predicts that for a given solvent the magnitude of the rate constant for electron transfer from the activator to peroxide **1** should be determined by E_{ox} . This prediction is exactly the observed result. The correlation of $\log k_2$ with E_{ox} , shown in Figure 5, is general for activators of diverse structure and composition. It is important to note that no other parameter, such as singlet energy, absorption spectrum, fluorescence efficiency, or lifetime of the activator, correlates with the measured value of k_2 .

Polarographic and cyclic voltammetric studies of diacyl peroxide reductions show an irreversible wave.²³ This finding is interpreted to indicate that a rapid chemical reaction follows injection of the electron into the LUMO of **1**. We surmise that the LUMO of diphenoyl peroxide strongly resembles the antibonding σ_{00}^* orbital localized on the oxygen-oxygen bond. Thus, we associate the chemical reaction following one-electron reduction of **1** with cleavage of the oxygen-oxygen bond to generate the ring-opened radical anion **5**.

The exothermic back electron transfer from reduced **1** to regenerate starting materials is in competition with cleavage of the oxygen-oxygen bond. Partitioning between ring opening and reverse electron transfer may be responsible for the effect of solvent dielectric constant we observe on the magnitude of k_2 . According to this interpretation, for high dielectric constant solvents the radical ions formed by the electron transfer are stabilized relative to low dielectric constant solvents. This stabilization results in a decrease in the exothermicity, and thereby the rate of the back electron transfer. Since the cleavage of the oxygen-oxygen bond does not result in creation or destruction of charge, its rate should be more or less independent of solvent polarity. Thus, the increase in k_2 in high dielectric constant solvents can be a result of retarding the

Scheme II



reaction rate for regeneration of starting materials and is consistent with electron transfer from the activator to diphenoyl peroxide as the rate-determining step in the light-generating sequence.

A second possible explanation for the observed solvent polarity effect is based upon the influence of the dielectric constant on E_{ox} and E_{red} . It is generally observed that the magnitude of the oxidation and reduction potential for a substrate is solvent dependent.²⁴ Thus, in the more polar solvent, the magnitude of k_2 may be larger due to a decrease in the barrier for oxidation of the activator and reduction of peroxide **1**. Importantly, this interpretation also implicates electron transfer as the rate-limiting step in the chemiluminescent sequence.

Cleavage of the oxygen-oxygen bond in the reduced peroxide generates radical anion **5**. To form benzocoumarin, the observed product, this species must lose the elements of CO_2 and cyclize. The exact mechanism for CO_2 loss is not known at the present time and is under study. However, the independent generation of this suspected intermediate from the reaction of diphenic anhydride with potassium *tert*-butyl hydroperoxide indicates that this route for benzocoumarin formation is available.

Decarboxylation of the benzoyloxy radical is known to be competitive with diffusion from the solvent cage.²⁵ We suggest that decarboxylation of **5** (path A, Scheme II) is also in competition with diffusion from the initial solvent cage (path B, Scheme II). Evidence for this proposal comes from three sources. First, the reduced yield for excited state generation in high dielectric constant solvents is consistent with this suggestion. The rate of diffusion of radical anion **5** from the reaction cage will depend on solvent dielectric constant because of the presence of the radical cation of the activator within the cage. Thus, a polar solvent would be expected to permit more rapid cage escape. Once the ions have escaped the solvent cage, the probability for generation of a photon then becomes very low. Evidence for this conclusion derives from the observation of the almost negligible effect that additives such as O_2 and tetramethylethylene, which are expected to react rapidly with the radical ions, have on the efficiency of light production by the CIEEL path.

The second line of evidence that shows that decarboxylation is competitive with cage escape comes from the effect of solvent viscosity on the light yield. The data in Table III indicate that for the cases studied the fraction of the diphenoyl peroxide molecules that participate in the electron transfer reaction that ultimately generate a photon goes up as the solvent viscosity

increases. Of particular relevance is the comparison of CH_2Cl_2 and dimethyl phthalate. These solvents have very similar dielectric constants but quite different viscosities. The relative light yield in the more viscous dimethyl phthalate is 3.5 times that in CH_2Cl_2 . We interpret this finding to show that the reaction sequence leading to light generation is at some point in competition with diffusion. We surmise that this competition is between the decarboxylation of **5** and the separation of the radical ions.

Finally, the detection of diphenic acid as a product of the reaction of diphenoyl peroxide with the activator indicates that an undecarboxylated species is available for reaction under these conditions. Significantly, we detect no diphenic acid when the thermal decomposition of **1** is carried out in the absence of the activator. We conclude that the most probable precursor to the acid is the cage-escaped radical anion **5**. Interaction of this species with solvent, CH_2Cl_2 in this case, resulting in a hydrogen atom abstraction is anticipated to generate the observed diphenic acid. Also, we find that under the conditions that result in the formation of diphenic acid a small amount (ca. 5%) of the catalytic activator is consumed during the reaction. This finding is consistent with our suggestion that separation of the radical ions is in competition with excited state generation. That is, the activator radical cation, once it has escaped the initial solvent cage, may be consumed during the reaction.

Based upon these findings, we suggest that the major factor determining the efficiency of excited state generation from peroxide **1** by the CIEEL mechanism is the rate of decarboxylation of radical anion **5**. If decarboxylation occurs within the initial solvent cage containing the activator radical cation, then an electronically excited state will ultimately result; see below. In competition with decarboxylation is diffusion of **5** from the solvent cage and, possibly, endothermic²⁶ electron transfer from **5** to the activator radical cation. This electron transfer generates neutral activator and the 2,2'-dicarboxydiphenyl diradical. Free radical anion **5** may, among other possibilities, lead to the observed diphenic acid. The biradical can generate the observed polymeric peroxide.

Thermochemical calculations indicate that decarboxylation of **5** followed by ring closure is exothermic by ca. 10–20 kcal/mol.²⁷ Thus we suggest that if the decarboxylation-ring closure sequence is stepwise, the decarboxylation of **5** is slow and closure to form the radical anion of benzocoumarin is rapid. Alternatively, the ring closure and decarboxylation can occur simultaneously. In either event, the result is the same. Benzocoumarin radical anion is formed in the same solvent

cage as the activator radical cation.

The penultimate step in the light-generating CIEEL sequence is charge annihilation of the cage radical ions resulting in generation of an electronically excited state species. Electrochemical studies of benzocoumarin indicate that the radical anion is 1.92 eV vs. SCE higher in energy than the neutral form. This energy plus the energy of the radical cation of the activator is available for excited state generation. For the hydrocarbon activators investigated there is sufficient energy released during the charge annihilation to generate directly the excited singlet state of the hydrocarbon.

Conclusive evidence that the benzocoumarin and the catalytic chemiluminescence activator are together within the same solvent cage at the instant of excited state generation comes from the study of the exciplex formed with triphenylamine. In this case, only emission from the exciplex is seen during the chemiluminescence experiment. If the exciplex was a result of a diffusive encounter of an excited triphenylamine singlet with ground state benzocoumarin we should have detected fluorescence from the triphenylamine as well. Furthermore, exciplex formation as a result of the diffusive encounter of the excited singlet of benzocoumarin with ground state triphenylamine is eliminated for several reasons. First, it has not been possible to detect excited benzocoumarin in solution by energy transfer to any one of several expected acceptors. In particular, 9,10-dibromoanthracene, which cannot undergo CIEEL owing to its high oxidation potential,²⁸ generates no detectable chemiluminescence when used as activator. Second, based upon the estimated radiative lifetime of benzocoumarin, and the lack of detectable fluorescence from this molecule, we calculate the lifetime of the singlet state to be no greater than 1 ns.²⁹ Under the conditions of the chemiluminescence experiment, a diffusive encounter of such a short-lived species with triphenylamine is quite improbable and cannot account for the observed efficient chemiluminescence. In light of this, the only way that exciplex emission can result from this reaction is that the required partners be together before the excited state is created. Thus, the activator and peroxide are together for the rate-determining electron transfer and are together for excited state generation. Consistent with the observed solvent effects and product studies, we suggest that the entire light-generating sequence occurs within the initial solvent cage.

The yield of electronically excited states from the CIEEL process can be quite high. We have determined that ca. 10% of the diphenoyl peroxide molecules that participate in the CIEEL process with perylene in CH₂Cl₂ at 32 °C generate an excited perylene singlet state. This represents one of the highest singlet yields observed for a chemiluminescent reaction. If spin equilibration occurs at some time during the reaction sequence leading to chemiluminescence then we would anticipate that the majority of the excited states produced would be of triplet multiplicity. Several unsuccessful attempts were made to detect the triplet excited state of the chemiluminescence activators. There are numerous experimental problems associated with the detection of the nonemissive relatively low energy triplet state of the hydrocarbon activators. Nevertheless, if the yield of excited triplets is at least comparable to the singlet yield, we should detect them by our procedure. Thus, we can tentatively conclude that chemiluminescence by CIEEL appears to favor the formation of singlet excited states, at least for diphenoyl peroxide.

The reaction sequence described as chemically initiated electron exchange luminescence appears to accommodate the experimental observations on light generation from diphenoyl peroxide and various catalytic chemiluminescence activators. In particular, the kinetic dependency on E_{ox} , the observed solvent dielectric constant and viscosity dependence, and the nature of the isolated products as well as the direct generation of exciplex emission are all consistent with the reaction path

shown in Scheme II. The yield of excited states by the CIEEL path from diphenoyl peroxide appears to be limited mainly by the rate of decarboxylation of radical anion **5** and the efficiency of the ion annihilation step. We are continuing to probe the details of these and of the other steps in this sequence.

Conclusion

The reaction sequence for chemical light generation by electron exchange that we have described in this paper in terms of the reactions of diphenoyl peroxide provides a new general mechanism for chemiluminescence. The CIEEL process is capable of generating remarkably high yields of electronically excited state molecules. It is potentially applicable to many chemi- and bioluminescent phenomena which have previously been rationalized in other ways.³⁰

We would also like to note some recently recognized examples of the CIEEL process.³¹ Thermal cleavage of a dioxetanone has been shown to be a key step in the chemiluminescence and bioluminescence of many efficient light-producing systems.³² Our investigation of dimethyldioxetanone has shown the CIEEL process to be operative for these molecules.³³ Another case is that of our recently discovered chemiluminescent reaction of diphenyl-*o*-xylylene peroxide.³⁴ In this example, the initial electron transfer generates the final ion pair directly and circumvents the intermediate chemical reactions. McCapra has recently reported generation of high yields of excited singlet *N*-methylacridone during thermal reaction of a 1,2-dioxetane by an intramolecular CIEEL path.³⁵ Schaap has noted a remarkable increase in the yield of excited singlet state anthroate ester during thermolysis of an anthracene-substituted dioxetane on silica gel.³⁶ This observation may be interpreted as intramolecular CIEEL to a protonated form (which should be much more easily reduced) of the dioxetane. Finally, we would like to suggest that electron exchange may also be responsible for many reactions of peroxides in solution. For example, Dervan's³⁷ recent observations on the chemistry of succinoyl peroxides can be viewed as a result of an electron transfer from a diradical intermediate to the starting peroxide. Pathways of this sort may underlie many poorly understood reactions of organic peroxides.

In summary, the findings reported herein generate many new possible approaches to preparing and understanding chemiluminescence in particular and the behavior of high energy content molecules in general. We are continuing to expand our probe into the chemistry of this new reaction path.

Experimental Section

General. All melting points are uncorrected. The solvents used for measurement of chemiluminescence emission spectra, kinetics, and fluorescence spectra were spectrograde and used as received unless otherwise indicated. Perylene, diphenylanthracene (DPA), and anthracene (99.9% pure) were used as purchased from Aldrich. Naphthalene and coronene were recrystallized in spectrograde benzene (Fisher). Rubrene was purified by chromatography on Al₂O₃ and recrystallized in spectrograde benzene. The triphenylamine (Aldrich) was purified by recrystallization three times in *n*-hexane-benzene (10:1) and finally sublimation. The photon counting technique with an EMI 9813 photomultiplier was used for measurements of chemiluminescence emission spectra and kinetics. A Farrand Mark I spectrofluorometer was employed for obtaining fluorescence spectra of the aromatic hydrocarbons. A Varian Aerograph Series 2700 was used for analytical gas chromatography.

Diphenoyl Peroxide (1). **1** was prepared by the ozonolysis procedure of Ramirez.¹⁰ Purification was accomplished by repeated recrystallization from MeOH-CH₂Cl₂ at -20 °C and gave pale yellow needles that decomposed at ca. 73 °C. Molecular weight determination by vapor pressure osmometry indicated that the compound was monomeric and peroxide titration showed that it was at least 95% pure.

Exciplex Emission from 1 and Triphenylamine. The chemilumi-

nescence emission from **1** (1.2×10^{-4} M) and Ph_3N (3.8×10^{-4} to 1.4×10^{-3} M) in benzene (Fisher, spectrograde) at 32.6 °C showed a structureless, broad peak with maximum intensity at 455 nm. This spectrum was identical with the spectrum which emerges when a nitrogen-purged solution of benzocoumarin (1.0×10^{-2} M) and Ph_3N (2.7×10^{-3} M) in benzene was irradiated at 339 nm at room temperature. When benzocoumarin and Ph_3N were photoexcited in benzene separately, there was no emission at 455 nm.

The chemiluminescence intensity of **1** and Ph_3N reached a maximum with benzene: $\text{CH}_3\text{CN} = 43:7$ and thereafter decreased rapidly upon further addition of CH_3CN .

Chemical Yields from the Reaction of 1 with Various Aromatic Hydrocarbons. A. Yields of Benzocoumarin from DPP Alone. A solution of **1** (3.30 mg, 0.0138 mmol) in 130 mL of CH_2Cl_2 was purged with nitrogen for 4 min, wrapped with aluminum foil, and stirred for 24 h under nitrogen at room temperature. The volume of the solution was reduced to ca. 3 mL and the resulting solution was transferred to a 5-mL volumetric flask. Benzocoumarin was the only product detected by gas chromatography (SE-30 3% on Chromosorb G, 4-ft glass column at 200 °C). The yield of benzocoumarin was determined to be 75% by using an authentic sample.³⁸

B. Yields of Benzocoumarin and Diphenic Acid from the Reaction of DPP with Rubrene. A solution of **1** (2.50 mg, 0.0104 mmol) and rubrene (28 mg, 0.053 mmol) in 50 mL of CH_2Cl_2 was purged with nitrogen for 4 min, wrapped with aluminum foil, and stirred for 3 h under nitrogen at room temperature. Following the same procedure as above, the yield of benzocoumarin was determined to be 74% by gas chromatographic analysis.

A solution of **1** (8.10 mg, 0.0337 mmol) and rubrene (24.6 mg, 0.0462 mmol) in 70 mL of CH_2Cl_2 was treated as above. After the volume of the reaction mixture was reduced to about 5 mL, the resulting solution was treated with an excess of diazomethane (generated via Diazald obtained from Aldrich) for 1 h at room temperature. The volume of the resulting mixture was further reduced in vacuo and transferred to a 5-mL volumetric flask. Benzocoumarin (60% yield) and dimethyl diphenate (4% yield) were detected by gas chromatography (SE-30 3% on Chromosorb G, 4-ft glass column at 190 °C) by comparison with authentic samples.³⁹

Note that no diphenic acid from reaction of **1** alone was detected as its dimethyl ester by gas chromatography under conditions similar to those above but without the activator, and that benzocoumarin (62% yield) was the only detectable decomposition product of DPP after treatment with diazomethane.

Benzocoumarin from the Reaction of Diphenic Anhydride with Potassium *tert*-Butyl Hydroperoxide in Tetrahydrofuran. A solution of diphenic anhydride (1.5 g, 0.0070 mol) and potassium *tert*-butyl hydroperoxide (0.050 g, 0.0039 mol) in 50 mL of dry THF was refluxed under nitrogen for 1 day. After the volume of the reaction mixture was reduced to ca. 10 mL, the resulting suspension was poured onto 100 mL of 1 N H_2SO_4 . The mixture was extracted with CH_2Cl_2 (3×30 mL) and the combined extracts were washed with 5% Na_2CO_3 (2×50 mL), then brine, and dried over anhydrous Na_2SO_4 . After evaporation of the solvent, the residue was chromatographed on silica gel using CH_2Cl_2 -hexane (1:1). The first fraction gave a white solid (60 mg) that was identical with that of an authentic sample of benzocoumarin. The yield of benzocoumarin was determined to be 30% based upon the consumed hydroperoxide.

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