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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY
CHEMICAL MECHANISMS OF CHEMI- AND BIOLUMINESCENCE. REACTIONS OF--ETC(U)
JUL 78 G B SCHUSTER, B DIXON, J KOO

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Reactions of High Energy Content Organic Compounds,

by

10 Gary B./Schuster, Brian/Dixon, Ja-young/Koo,
Steven P./Schmidt J. P./Smith

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School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

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Abstract: The chemistry of high energy content molecules was investigated. In particular, the mechanisms by which these compounds rearrange to generate electronically excited states was probed. A new mechanism for chemiexcitation involving chemically initiated electron transfer was discovered. It was shown that this mechanism is applicable to many chemi- and bioluminescent processes.

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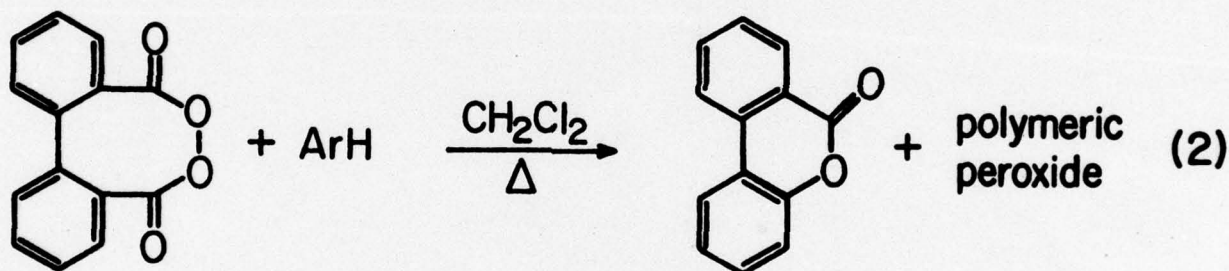
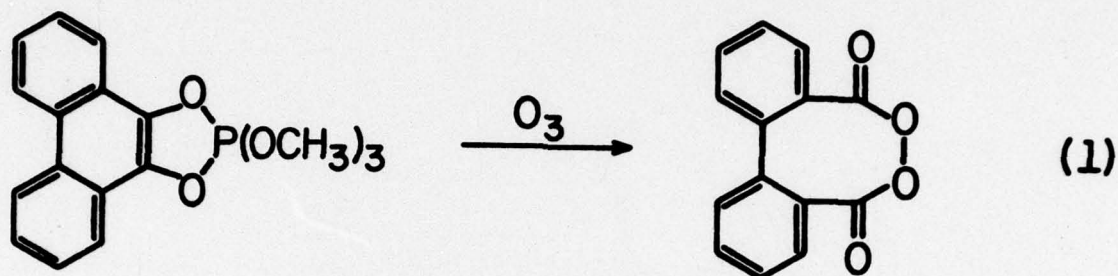
Our interest in the chemiluminescence of organic molecules has centered around the step that converts a ground state molecule to an electronically excited state species. Two classical mechanisms have enjoyed popularity as explanations for this chemiexcitation step. The first, shown in Figure 1, is one in which a high energy molecule is converted through a thermal reaction to an electronically excited state. This electronically excited state may then go on to emit a photon of light either as fluorescence or phosphorescence (direct chemiluminescence) or undergo a chemical reaction. Alternatively, this electronically excited state may transfer energy to a suitable acceptor and the thus formed excited acceptor may then go on to emit a photon of light (indirect chemiluminescence) or undergo a chemical reaction. Molecules thought to generate excited states by this pathway are simply substituted 1,2-dioxetanes (Wilson, 1976), luminol (McCapra, 1976), and Dewar benzene (Lechtken, 1973).

The second general mechanism that has evolved to explain chemical generation of electronically excited state is referred to as electrogenerated chemiluminescence (ECL) (Faulkner, 1976). In this mechanism a molecule is reduced at a cathode to form a radical anion, while in a subsequent or simultaneous step, a second molecule is oxidized at an anode to form a radical cation. The thus formed radical ions diffuse together in solution and annihilate. Simple molecular orbital considerations predict that this annihilation will result in the generation of an electronically excited state. In practice, either a locally excited state or an exciplex is generated. The excited state may go on then to emit a photon of light and chemiluminescence results. This path for excited state generation is shown in Figure 2.

In this report we will describe the results of several of our recent investigations of chemiluminescent processes. These studies have provided evidence for a new and pervasive route for the generation of excited states from high energy organic molecules.

Chemiluminescence of Diphenoyl Peroxide

Diphenoyl peroxide was first prepared by Ramirez and coworkers (1961) through the ozonolysis of the corresponding phosphorane (eq 1). Thermolysis of diphenoyl peroxide (eq 2) results in the generation of benzocoumarin, carbon dioxide, and a small amount of polymeric peroxide. This reaction is exothermic by more than 60 kcal/mol. The activation energy has been measured



to be approximately 25 kcal/mol (Koo, 1977). Thus, a total of 85 kcal/mol is available for the formation of electronically excited states. Attempts to observe direct chemiluminescence from the thermolysis of diphenoyl peroxide were unsuccessful. This result was not unanticipated since benzocoumarin neither fluoresces nor phosphoresces in fluid solution at room temperature. It was observed that the addition of the energy acceptor 9,10-dibromoanthracene (DBA) did not lead to the generation of DBA fluorescence. Also, the addition of biacetyl to a solution of diphenoyl peroxide did not result in the generation

of the fluorescence or phosphorescence of biacetyl, which should have been detectable under the conditions of the reaction. This indicated that electronically excited benzocoumarin was not formed by the thermolysis of diphenoyl peroxide. Addition of the energy acceptor 9,10-diphenylanthracene (DPA) to a solution of diphenoyl peroxide, however, resulted in bright, readily detectable chemiluminescence which was identified as the fluorescence of DPA.

In order to probe the mechanism for the formation of electronically excited DPA, we investigated the kinetics of the chemiluminescent reaction. It was found that the diphenoyl peroxide decayed in a first order way for more than five half-lives. Addition of DPA to the diphenoyl peroxide solution resulted in an increase in the rate of reaction of the diphenoyl peroxide. The kinetic analysis is shown in Figure 3. A simple kinetic law can be derived to explain this behavior. In this analysis the observed rate constant (k_{obs}) depends upon a unimolecular rate constant, k_1 , and a bimolecular rate constant, k_2 , multiplied by the DPA concentration (eq 3). Thus, a plot of k_{obs} against the concentration of DPA gives a straight line for which the intercept corresponds to k_1 , and the slope of the line corresponds to k_2 .

$$k_{obs} = k_1 + k_2 [DPA] \quad (3)$$

Diphenylanthracene was not unique in its ability to cause the chemiluminescence of diphenoyl peroxide, in Figure 4 are shown the kinetic plots for a series of aromatic hydrocarbons. It is seen from these results that the intercept is independent of the nature of the aromatic hydrocarbon; however, the slope of the line is strongly dependent upon the identity of the aromatic hydrocarbon. The magnitude of the bimolecular rate constant, k_2 , did not depend upon the singlet energy, triplet energy, or absorption spectrum of the particular hydrocarbon molecule used. The correlation of the log of the

observed bimolecular rate constant, k_2 , with the oxidation potential of the aromatic hydrocarbons is shown in Figure 5. As can be seen in this Figure, there is a strong inverse correlation between the oxidation potential and the magnitude of k_2 (as the oxidation potential increases the magnitude of k_2 decreases). We interpret this observation to indicate that the initiating step in the chemiluminescence of diphenoyl peroxide with these various aromatic hydrocarbons is an electron transfer from the aromatic hydrocarbon to diphenoyl peroxide. Such an electron transfer is well preceded in the reactions of metal ions and amines with organic peroxides (Reynolds, 1966).

A simple scheme, identified as chemically initiated electron exchange luminescence (CIEEL), for the generation of light from diphenoyl peroxide and these aromatic hydrocarbons is shown in Figure 6. Electron transfer from the aromatic hydrocarbon (the catalytic chemiluminescence activator) generates the radical anion of diphenoyl peroxide and the radical cation of the activator within the same solvent cage. This electron transfer may or may not be reversible. After the electron is transferred to the diphenoyl peroxide, the oxygen-oxygen bond cleaves. Decarboxylation of the cleaved radical anion of diphenoyl peroxide followed by ring closure generates the radical anion of benzocoumarin. Importantly, this radical anion is formed within the same solvent cage as the activator radical cation. Charge annihilation of this ion pair generates the electronically excited state of the activator and benzocoumarin, the observed products. Of course, the electronically excited state generates the observed chemiluminescence. In competition with the light generating path, our results indicate that diffusion of the undecarboxylated cleaved radical anion of diphenoyl peroxide occurs, which results, eventually, in the formation of diphenic acid.

Investigation of the effect of solvent on the chemiluminescence of diphenoyl peroxide with various activators indicated that as the viscosity increased the yield of light also increased. This observation is consistent with diffusion from a solvent cage in competition with light generation. A study of the effect of solvent polarity showed that the magnitude of the bimolecular rate constant (k_2) increased as the dielectric constant of the solvent increased. However, the yield of light decreased as the dielectric constant of the solvent increased. These observations are also consistent with the mechanism outlined in Figure 6.

Further evidence for the reaction sequence shown in Figure 6 was obtained by the reaction of diphenoyl peroxide with various tertiary amines. As expected, the magnitude of the bimolecular rate constant for reaction of diphenoyl peroxide with the tertiary amines was predicted by the oxidation potential of the amine. However, in contrast to the observations made with the aromatic hydrocarbons, the chemiluminescence emission spectrum did not correspond to the amine fluorescence. Instead, as is shown in Figure 7 for triphenylamine, a broad structureless emission centered at 455 nm was observed. This emission was shown independently to correspond to the exciplex formed from benzocoumarin and excited triphenylamine. This result demands that the triphenylamine and benzocoumarin be together within the same solvent cage when the excited state is formed. Thus the dependence upon the activator oxidation potential, the solvent effects, and the direct generation of exciplex emission indicate that the entire light generating sequence occurs within the solvent cage.

Final confirmation of this conclusion was obtained by studying the effect of quenchers such as oxygen and tetramethylethylene on the chemiluminescence

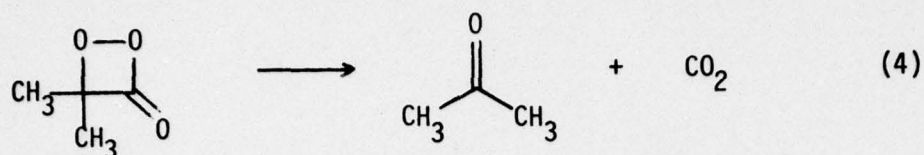
intensity. It was shown that these quenchers had almost no effect on the chemiluminescence light generating efficiency. If diffused radical ions or diffused excited states were responsible for light generation, then these quenchers should have resulted in a marked decrease in the light intensity.

The CIEEL path demonstrated for diphenoyl peroxide is capable of generating very high yields of electronically excited states. For diphenoyl peroxide and perylene as activator in di-*n*-butylphthalate solvent, we have determined (by comparison with tetramethyldioxetane) that the yield of perylene singlet excited states can be as high as 30%. Thus this system represents one of the most efficient chemiluminescent processes yet discovered.

Chemiluminescence of the Dioxetane Ring System

The thermal unimolecular reaction of the 1,2-dioxetane ring system to generate electronically excited state carbonyl group containing compounds is by far the most carefully and extensively studied of all chemiluminescent reactions. We have investigated both the unimolecular thermal decomposition of the dioxetane ring system to generate electronically excited carbonyl compounds and the chemically initiated electron exchange path to excited state activator molecules. In this report we will confine ourselves to the discussion of the chemiluminescent reactions of the dimethyldioxetanone system.

Dimethyldioxetanone was prepared and purified according to the procedure of Adam (1972). Thermolysis of the dioxetanone in any one of a number of solvents leads to the quantitative generation of acetone and to light emission (eq 4). The observed chemiluminescence under these conditions is a result of acetone emission. The activation energy for the unimolecular



thermal decomposition of the dioxetanone was determined by two different techniques in a series of four solvents (Schmidt, 1978 b). First, the total rate of reaction of the dioxetanone was measured at several temperatures by monitoring the kinetics of the chemiluminescence decay. Standard Arrhenius analysis of the decay rate constants gives the activation energies (E_a) shown in Table 1. The second method of analysis of the activation parameters gives the activation energy for that fraction of the total reaction that leads to electronically excited states (E_{Chl}). This was determined by probing the effect of temperature on the instantaneous chemiluminescence intensity. Critically, and in contrast to the activation parameters of simply substituted dioxetanes, E_{Chl} for the dioxetanone is 3-4 kcal/mol greater than E_a . This difference is independent of the solvent.

The yield of excited state acetone from thermolysis of the dioxetanone also demonstrates the unusual effect of temperature. Thermolysis of the dioxetanone in Freon at 30° generates electronically excited singlet and triplet acetone with efficiencies of 0.1% and 1.5%, respectively. The yield of singlet acetone depends significantly upon the reaction temperature. Analysis of the effect of temperature on the yield of excited acetone from the dioxetanone gives a temperature coefficient of 4.2 kcal/mol. This quantity represents the difference in activation energies between a higher energy path leading to light generation and the dark decomposition of the dioxetanone.

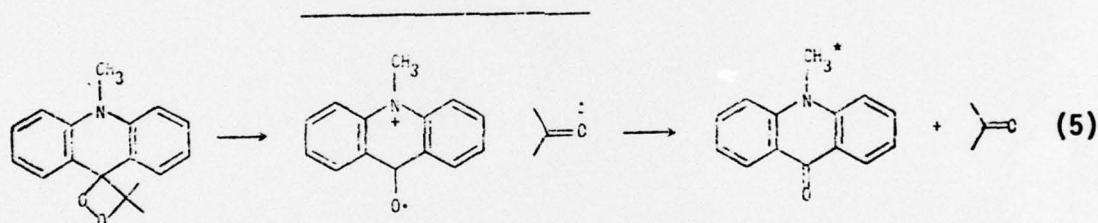
The effect of temperature on the efficiency of chemiluminescence from the dioxetanone is composed of the temperature dependence of the efficiencies of all steps leading to photon generation. The temperature dependence of the fluorescence efficiency of acetone is negligible under these conditions (Steinmetzer, 1974). Our finding that E_{Chl} is 3-4 kcal/mol higher than E_a requires that there be two or more competitive pathways with discrete transition states for dioxetanone decomposition. This situation is analyzed in Figure 8. Figure 8a shows two competitive concerted reactions. In this case, the measured difference in the activation energy between the light generating and dark paths is equated with the difference in energies between the two transition states. In the mechanism shown in 8b, a common rate determining step leads to generation of an intermediate biradical. This biradical proceeds along a lower energy path to generate ground state acetone and a more highly activated route to produce singlet excited acetone. In this case, the difference between E_a and E_{Chl} represents the difference in the barriers leading out of the biradical intermediate. Our results are most consistent with the mechanistic scheme shown in Figure 8b in which the most exothermic reaction has the lowest activation barrier. However, neither this line of reasoning, nor any mechanism yet postulated to explain chemical formation of excited states, is capable of explaining why the total yield of excited acetone from thermolysis of the dimethyldioxetanone is nearly twenty times lower than the excited state yield from the less exothermic thermolysis of tetramethyldioxetane. We are continuing to probe this question by the use of ab initio theoretical methods.

Dimethyldioxetanone in the presence of suitable easily oxidized fluorescent aromatic hydrocarbons generates chemiluminescence much in excess of that

observed for the unimolecular decomposition. We have identified the major excited state generating pathway for dioxetanone in the presence of an aromatic hydrocarbon as chemically initiated electron exchange luminescence (Schmidt, 1978 a; Adam, 1978). It has been previously reported that the addition of certain aromatic hydrocarbons to solutions of the dioxetanone results in the generation of hydrocarbon luminescence and markedly increases the light yield (Adam, 1972). We have also observed this effect and, significantly, have found that the aromatic hydrocarbon also increases the rate of reaction of the dioxetanone. The rate acceleration is directly proportional to the concentration of the hydrocarbon and depends upon the structure of the hydrocarbon. The nature of the interaction between the dioxetanone and the aromatic hydrocarbon was probed by measuring the efficiency of light generation with various activators. We observed that at identical hydrocarbon concentrations there is a hundredfold range in the ability of the different activators to catalyze excited state formation. Critically, the only predictor of activator efficiency is the one-electron oxidation potential of the hydrocarbon. This result is shown in Figure 9. These findings are entirely consistent with excited state production from dioxetanone by the chemically initiated electron exchange luminescence mechanism. This mechanism is shown in Figure 10. The rate of this process depends upon the activation barrier for the reaction which is determined in part by the oxidation potential of the activator and the reduction potential of the dioxetanone. After electron transfer the oxygen-oxygen bond of the dioxetanone is cleaved, carbon dioxide is lost, and the radical anion of acetone is generated within the same solvent cage as the radical cation of the activator. Charge annihilation of these cage radical ions results in electronically excited state generation.

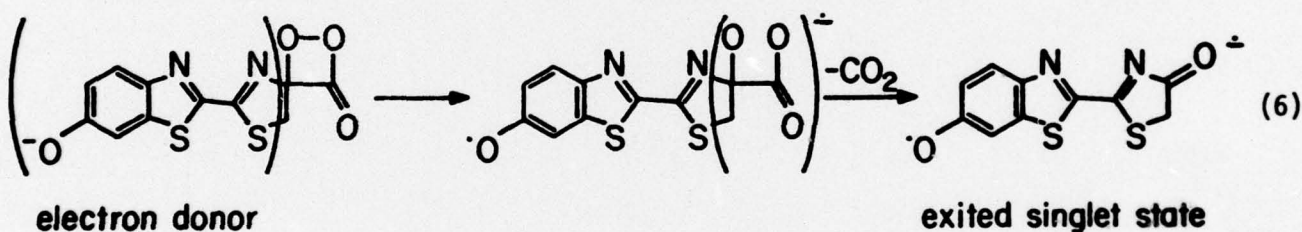
The efficiency of production of excited singlet activator by the induced decomposition of the dioxetanone was investigated by measuring the absolute chemiluminescence yield when rubrene was employed as the activator. It was found that about 10% of the dioxetanone molecules that proceed through the bimolecular path generate an excited rubrene singlet state.

The occurrence of an intramolecular chemically initiated electron exchange path was recently demonstrated by McCapra (1977), whose investigation of the N-methylacridan substituted dioxetane revealed a singlet yield of N-methylacridone approaching 25%. A singlet yield of this magnitude is quite uncharacteristic of simply substituted dioxetanes where the triplet yield is usually several orders of magnitude greater than the singlet yield. McCapra suggests that excited state generation from this dioxetane proceeds through radical ion intermediates as shown in eq 5.



One of the major reasons for the intense interest in the chemistry of dioxetanes and dioxetanones has been the application of these studies to the understanding of the bioluminescence, particularly that of the firefly. The effect of structural variation on the luciferin for firefly bioluminescence has been studied by White (1966). This enzyme-catalyzed reaction has now been unequivocally shown to proceed through a dioxetanone intermediate. As indicated in Figure 11 luciferins substituted with non-electron-donating substituents are not bioluminescent. It was observed that these are similar to the natural substrates in that they still bind strongly to the enzyme, undergo the catalytic loss

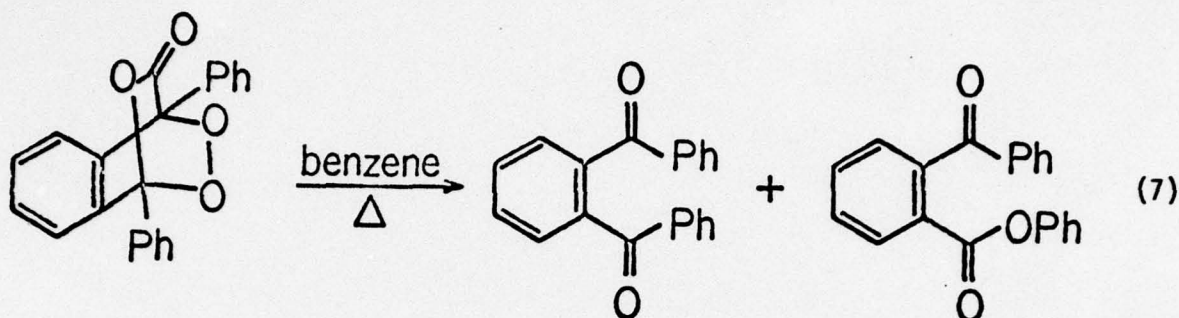
of carbon dioxide, and also generate fluorescent products. No molecular explanation was offered for the lack of bioluminescent activity. We would like to suggest that this effect of substituents can be easily understood in terms of an intramolecular chemically initiated electron exchange path. We propose that electron transfer from the phenoxythiazole portion of the luciferin to the dioxetanone portion generates a radical ion intermediate. Loss of carbon dioxide from this intermediate generates directly the charge transfer resonance structure of the excited singlet state of the amide. This reaction path is shown in eq 6. The effect of the substituents then is to inhibit the electron transfer reaction and thus the formation of electronically excited states. While we have no direct evidence for this pathway, it is consistent with our emerging knowledge of the dioxetanone chemistry and with the results of intramolecular electron exchange in the dioxetane system.



Chemiluminescence of *o*-Xylylene Peroxides

The dioxetane ring system is one of but a few known compounds that rearrange thermally to generate electronically excited states. Recent results of our investigation of the thermolysis of the endoperoxide shown in Figure 12 reveal the intervention of a novel cyclic peroxide that reacts along two separate pathways that lead to light generation (Smith, 1978).

The endoperoxide was prepared by the photooxidation of 1,4-diphenyl-2-benzopyran-3-one in acetone at 0° with methylene blue as sensitizer. Thermolysis of this compound in refluxing benzene leads to the generation of o-dibenzoylbenzene and phenyl(o-benzoyl)benzoate in 85 and 5% yield, respectively (eq 7). When thermolysis is carried out in deoxygenated solvent, a deep yellow color



develops in the solution. Thermolysis of the endoperoxide in the presence of excess maleic anhydride causes the yellow color not to develop and the yield of o-dibenzoylbenzene to be much reduced. The major product of the reaction under these conditions is identified as the Diels-Alder adduct of maleic anhydride with 1,4-diphenyl-2,3-benzodioxin (o-xylylene peroxide). This reaction sequence is outlined in Figure 12.

Thermolysis of the endoperoxide in a photon-counting apparatus at 92° in benzene solution does not produce detectable luminescence. This result is not unanticipated, since only inefficient emission is expected from the excited states of o-dibenzoylbenzene under these conditions. However, addition of biacetyl to the reaction solution resulted in easily detected phosphorescence from triplet excited biacetyl. Moreover, it was observed that addition of rubrene, perylene, or any one of several easily oxidized aromatic hydrocarbons results in readily detected luminescence. In these cases the luminescence corresponds to the fluorescence from the singlet excited state of the added aromatic hydrocarbon.

The energy stored in the o-xylylene peroxide system must ultimately appear as the energy of electronic excitation on the added emitter. We have found that there are two kinetically and spectroscopically distinguishable mechanisms operating to transform the potential energy of o-xylylene peroxide to an excited state emitter. First, unimolecular thermolysis of the o-xylylene peroxide results directly in the formation of an excited state of o-dibenzoyl benzene. The rate of intersystem crossing of o-dibenzoyl benzene singlet is so fast as to preclude observation of this state. In our chemiluminescence experiments, we have indirectly observed only the triplet state of this molecule. It should be noted that stretching of the peroxide bond of a planar o-xylylene peroxide to form o-dibenzoyl benzene is formally a forbidden process which would result in generation of a high energy doubly excited state. Consistent with this mechanistic interpretation, we observe classical consecutive reaction kinetics for the buildup and decay of chemiluminescence emission intensity under these conditions. This mechanism for light generation from o-xylylene peroxide is shown as Path A in Figure 13.

The second route leading to light emission from o-xylylene peroxide occurs in the presence of any one of several easily oxidized aromatic hydrocarbons. The intensity of the chemiluminescence observed under these conditions indicates the intervention of a chemically initiated electron exchange mechanism. In this circumstance, the initial interaction between the o-xylylene peroxide and the activator is an electron transfer from the activator to the peroxide. Subsequent ring opening of the reduced peroxide followed by the annihilation of the resulting radical ions generates the electronically excited state of the hydrocarbon. This mechanism is summarized as Path B in Figure 13. As predicted for this mechanism, increasing concentrations of the activator result in more rapid decay of the chemiluminescence intensity.

These observations may be extrapolated to the much studied isoelectronic luminol system in which intramolecular electron exchange is possible. We are continuing to investigate the interesting and novel chemical and chemiluminescent reactions of this system.

Bacterial Luminescence

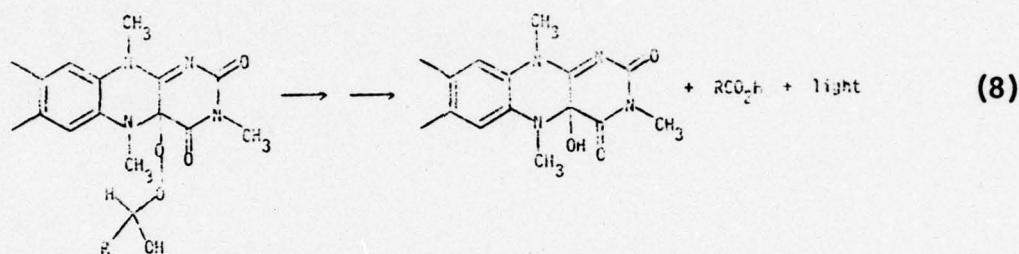
The thermolysis of secondary peresters, studied by Hiatt and coworkers (1975), generate high yields of carbonyl compounds and carboxylic acids. We have investigated the thermal and chemiluminescent reactions of 1-phenylethyl peroxyacetate, Figure 14. Thermolysis of this compound in benzene generates acetophenone and acetic acid in nearly quantitative yields. Calculations indicate that this reaction is exothermic by approximately 56 kcal/mol. We have measured the activation enthalpy of this reaction to be 38 kcal/mol and have found $\Delta S^\ddagger$ to be 25 eu. Thus, there are approximately 94 kcal/mol available for formation of electronically excited states. The singlet and triplet states of acetophenone have been located at 74 and 79 kcal/mol, respectively. Thus, there is sufficient energy released in this reaction for formation of excited acetophenone.

Indeed, upon thermolysis we have detected the triplet excited state of acetophenone from this reaction. The mechanism of excited state generation was probed by following the kinetics of this reaction in dilute benzene solution. It was observed that the decay of the chemiluminescence intensity was first order for at least three half-lives. The chemiluminescence was not affected by the incorporation of free radical traps in the reaction solution.

These observations lead us to suggest a mechanism in which oxygen-oxygen bond cleavage to form a cage radical pair is the rate-determining step.

Subsequent to oxygen-oxygen bond cleavage a hydrogen atom is transferred from the benzyl carbon to the oxygen of the acetoxy radical to form the electronically excited state of acetophenone and acid. This mechanism is outlined in Figure 14.

This transformation is formally analogous to the postulated key transformation (Kemal, 1977) in the light forming steps of bacterial luminescence. In this case, the nitrogen atom of the flavin is the hydrogen atom acceptor. This mechanism is outlined in Equation 8. Further efforts are underway to examine these chemiluminescent processes.



Conclusions

In this report we have described the results of several of our recent studies of the chemistry of high energy content molecular systems. In particular, we have examined the mechanisms by which these compounds rearrange to generate electronically excited products. The major finding to emerge from these experiments is that chemical generation of cage ion intermediates is perhaps the most important mechanism operating to produce electronically excited states. The CIEEL mechanism, and its ramifications on purely ground state chemistry, are under vigorous continuing investigation in our laboratory.

Acknowledgment

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Table 1. Activation Parameters for the Thermolysis of Dimethyldioxetanone^a

Solvent	E_a , kcal/mol ^b	E_{chl} , kcal/mol ^c
$\text{C}_2\text{Cl}_3\text{F}_3$	$22.3 \pm .3^d$	$25.6 \pm .1$
CCl_4	$21.3 \pm .3^e$	$24.5 \pm .5$
PhH	$21.8 \pm .1^e$	$24.9 \pm .4$
CH_2Cl_2	$20.8 \pm .1^e$	$24.8 \pm .4$

^aAir saturated solutions, $\sim 5 \times 10^{-4}$ M in I_2 . ^bTypical range of temperature over which rate constants were determined is 15 to 40°. ^cTypical range of temperature over which chemiluminescence intensity was determined -1 to 14°. ^dEyring activation enthalpy: $\Delta H^\ddagger = 21.7$ kcal/mol; activation entropy, $\Delta S^\ddagger = 0 \pm 1$ eu. ^eSolutions contained 5% Na_4EDTA .

Captions for Figures

Figure 1. Unimolecular chemiluminescence of high energy organic molecules.

Figure 2. Electrogenenerated chemiluminescence.

Figure 3. Effect of DPA concentration on the rate of reaction of diphenoyl peroxide in THF at 32°.

Figure 4. The effect of activator structure and activator concentration on the observed first order decay of diphenoyl peroxide. In order of decreasing slope the activators are: rubrene; naphthacene; perylene; DPA; pyrene.

Figure 5. Correlation of the magnitude of k_2 with the oxidation potential of the activators. The points are: rubrene; naphthacene; perylene; DPA; coronene; pyrene.

Figure 6. Mechanism of Chemically Initiated Electron Exchange Luminescence for diphenoyl peroxide.

Figure 7. Photochemical and chemielectronic generation of exciplex emission from benzocoumarin and diphenoyl peroxide.

Figure 8. Limiting reaction mechanisms for thermal unimolecular fragmentation of dimethyldioxetanone to acetone and CO_2 . Part A represents the concerted process with two transition states; Part B shows a path proceeding through an intermediate biradical with at least two exit channels.

Figure 9. Dependence of the chemiluminescence intensity by the CIEEL path on oxidation potential of the activator. In order of increasing oxidation potential the points are: rubrene; perylene; 9,10-diphenylethynylanthracene; and DPA.

Figure 10. Chemically initiated electron exchange path of generation of activator excited states from dimethyldioxetanone.

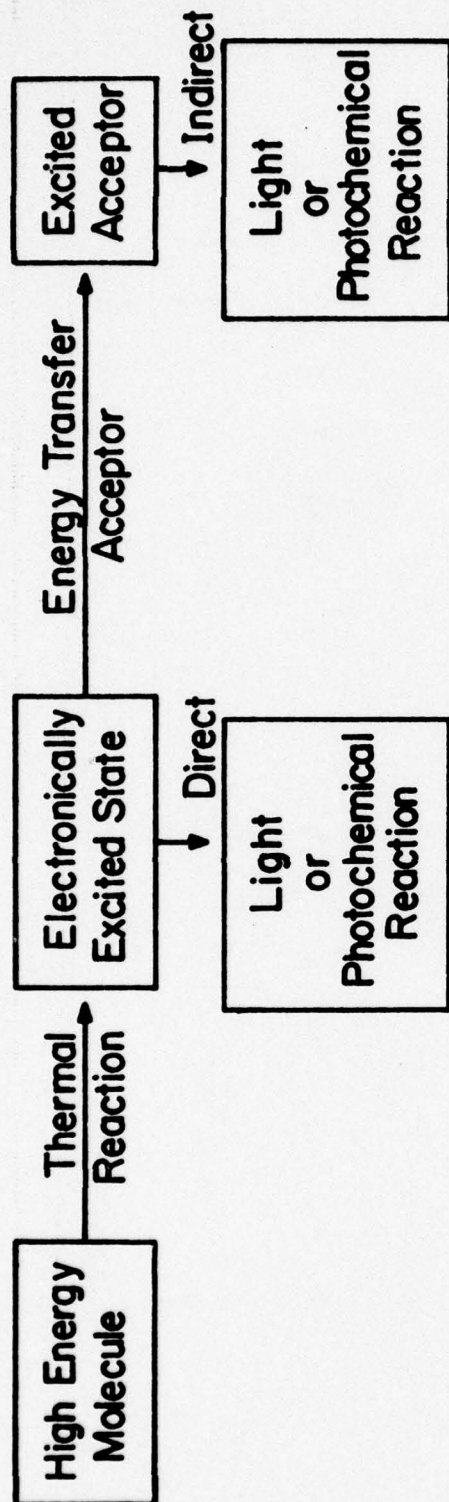
Figure 11. Correlation of structure and bioluminescent activity for a series of substituted luciferins.

Figure 12. Pathways for the thermal decomposition of the diphenylbenzopyranone endoperoxide.

Figure 13. Mechanisms for light generation from o-xylylene peroxide. Path A represents the unimolecular chemiluminescence route. Path B is the chemically initiated electron exchange route.

Figure 14. Mechanism for generation of electronically excited acetophenone from the thermolysis of secondary peresters.

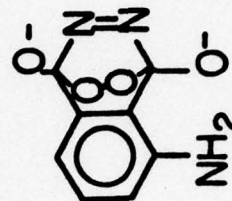
Conventional Chemiluminescence of Organic Molecules



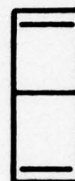
Examples:



a) 1,2-Dioxetanes



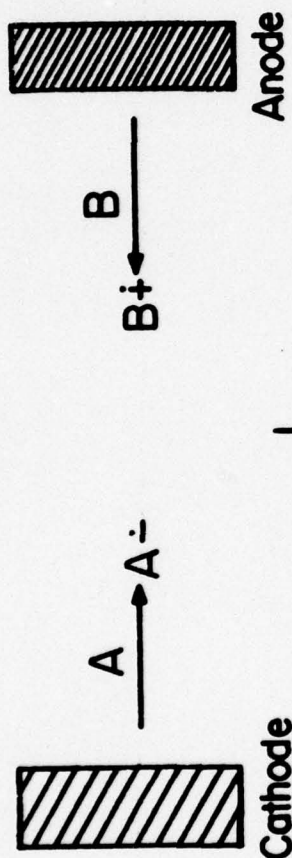
b) Luminal



c) Dewar Benzene

Figure 1.

Electrogenerated Chemiluminescence (ECL)



Annihilation

$(A^{\bullet+} B^{\bullet-})^{\ddagger}$ electronically excited (A, B, or Exciplex)

MO - Picture

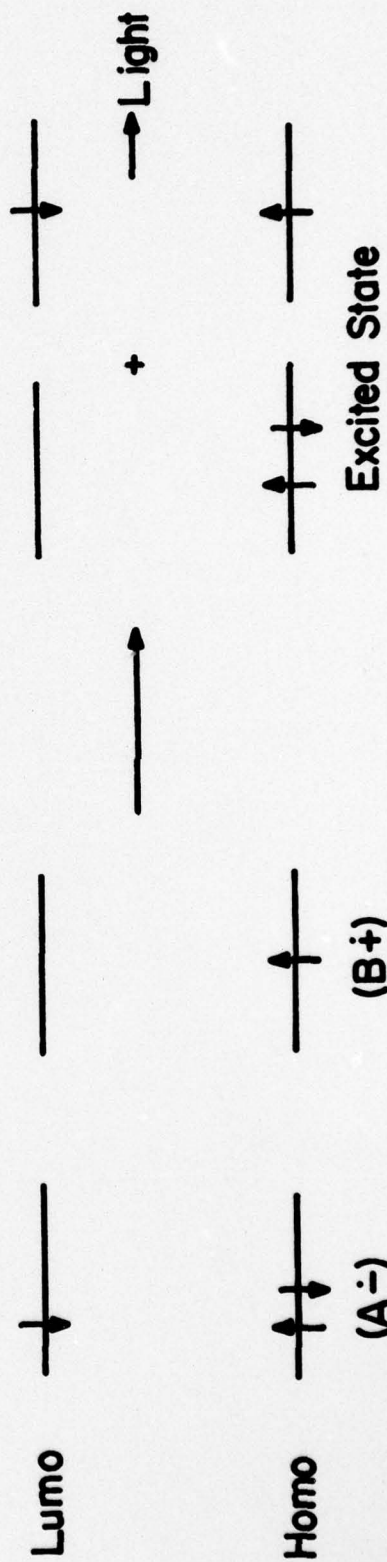


Figure 2.

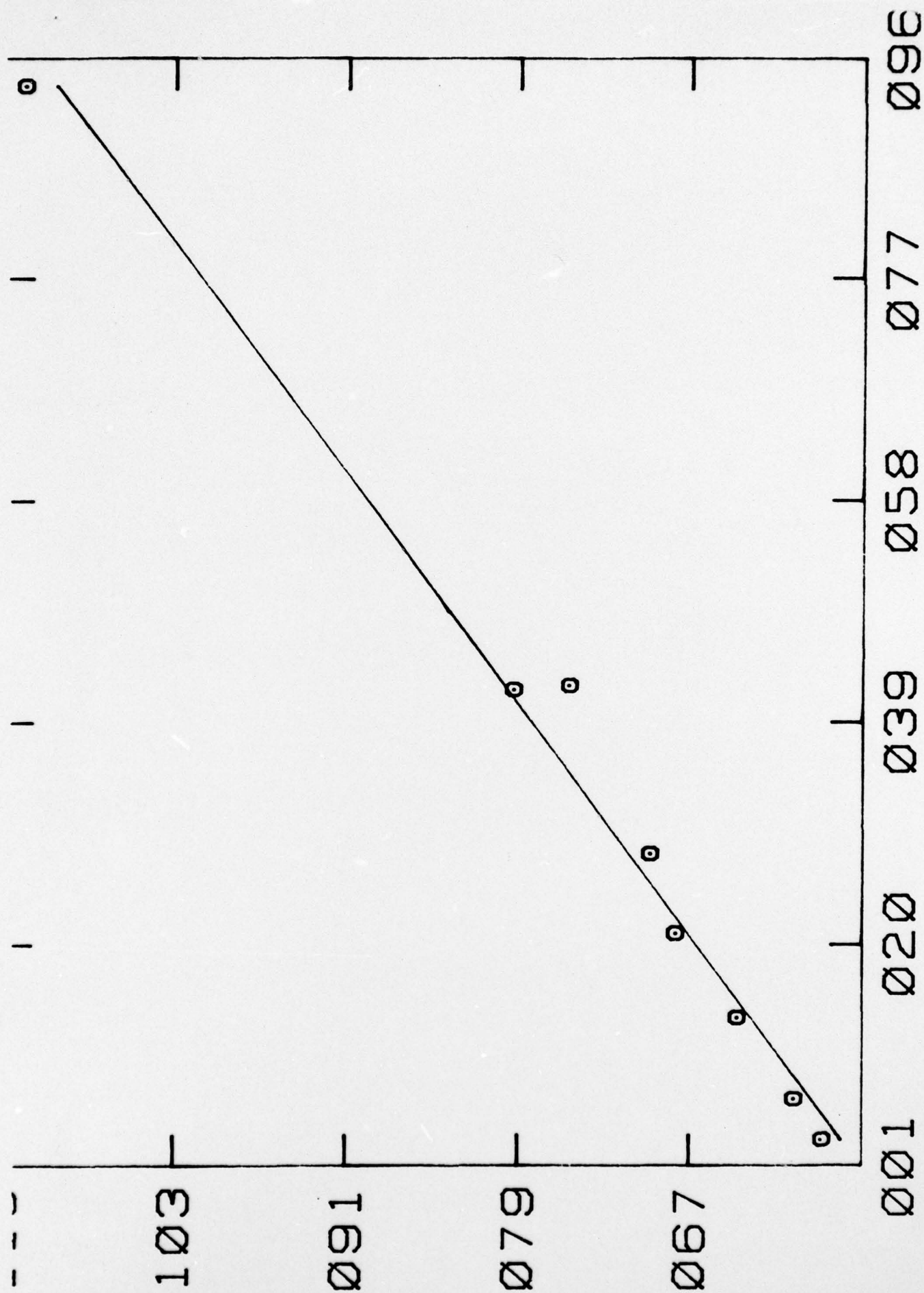


Figure 3.

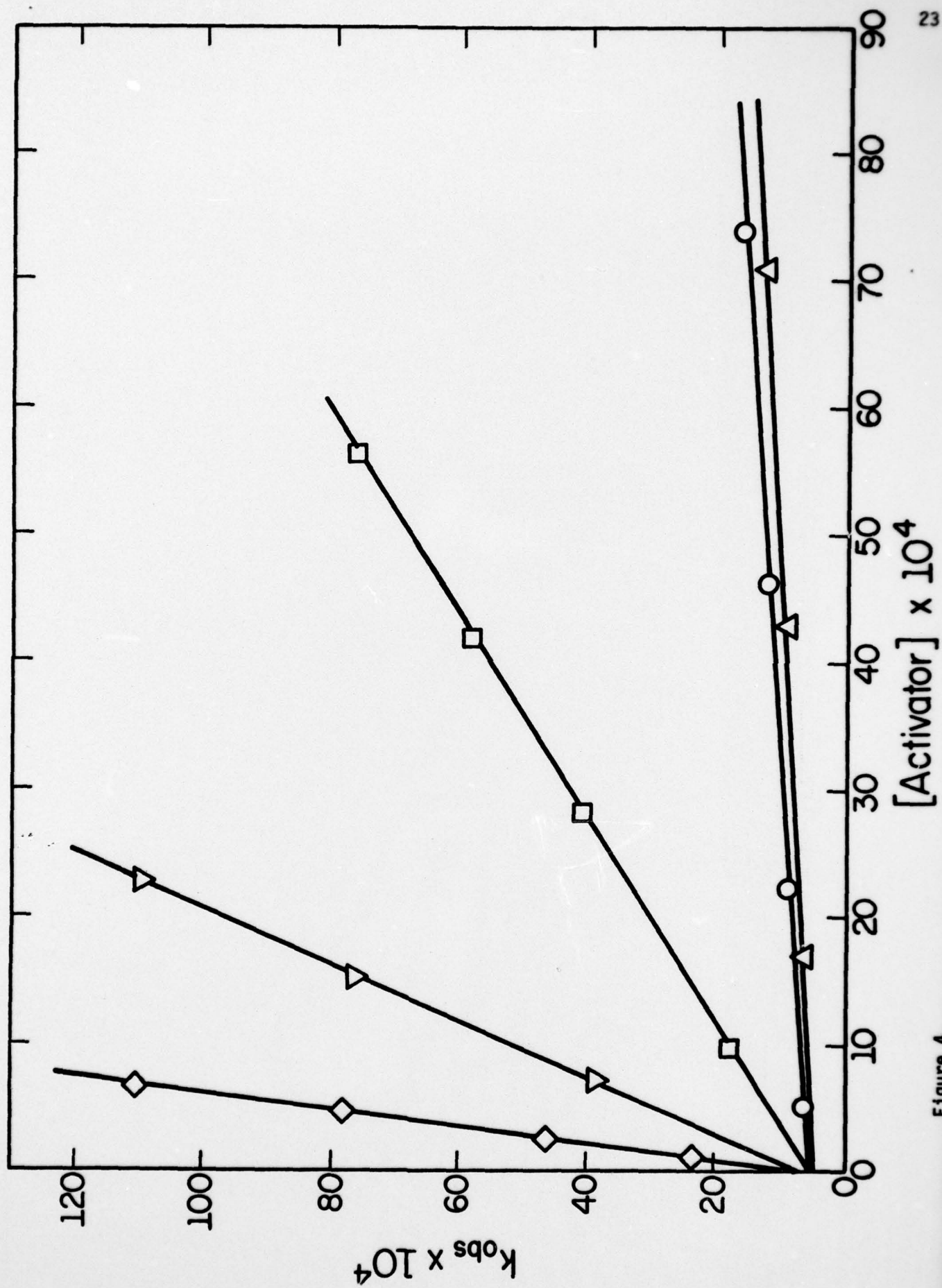


Figure 4.

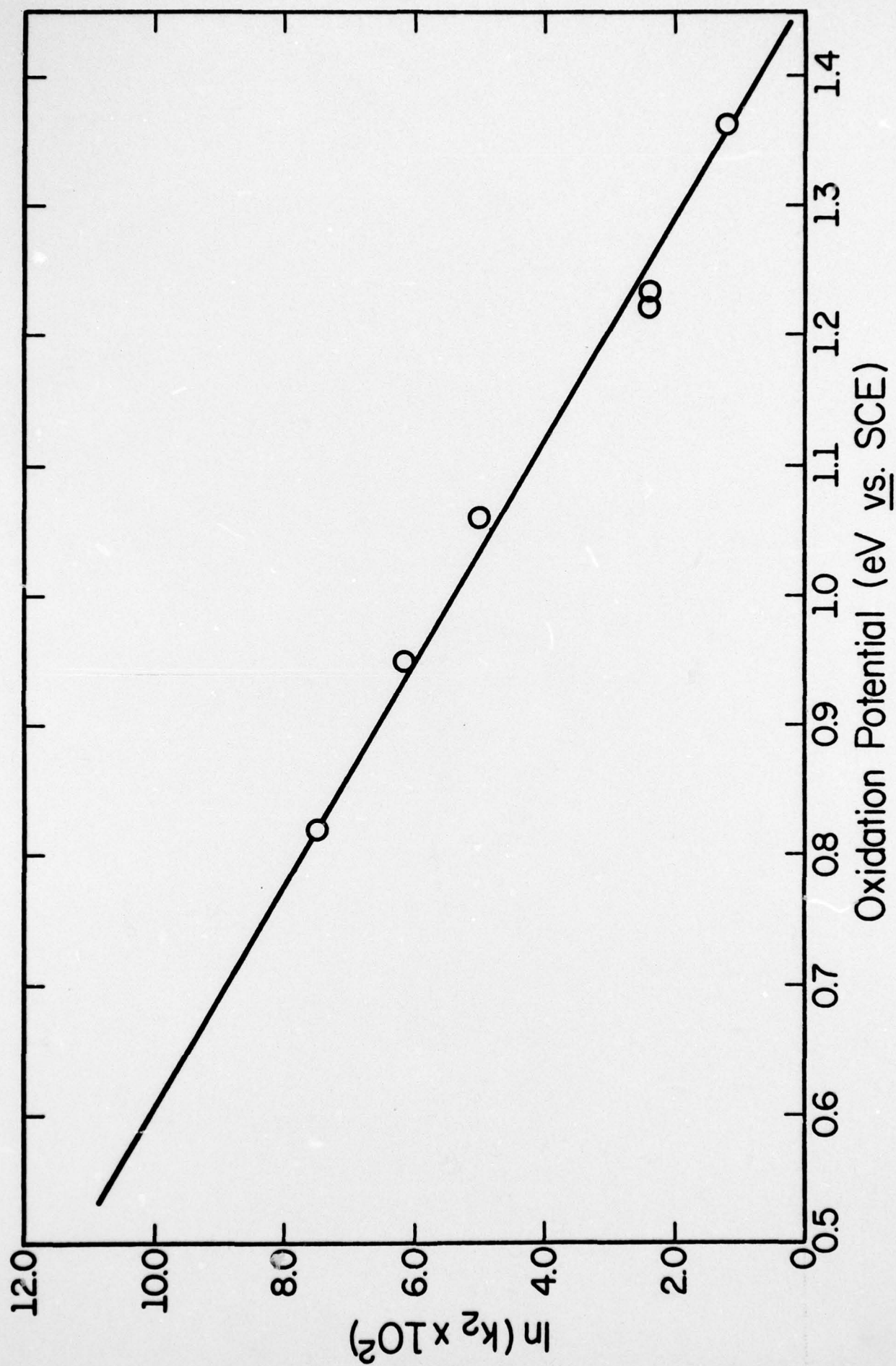


Figure 5.

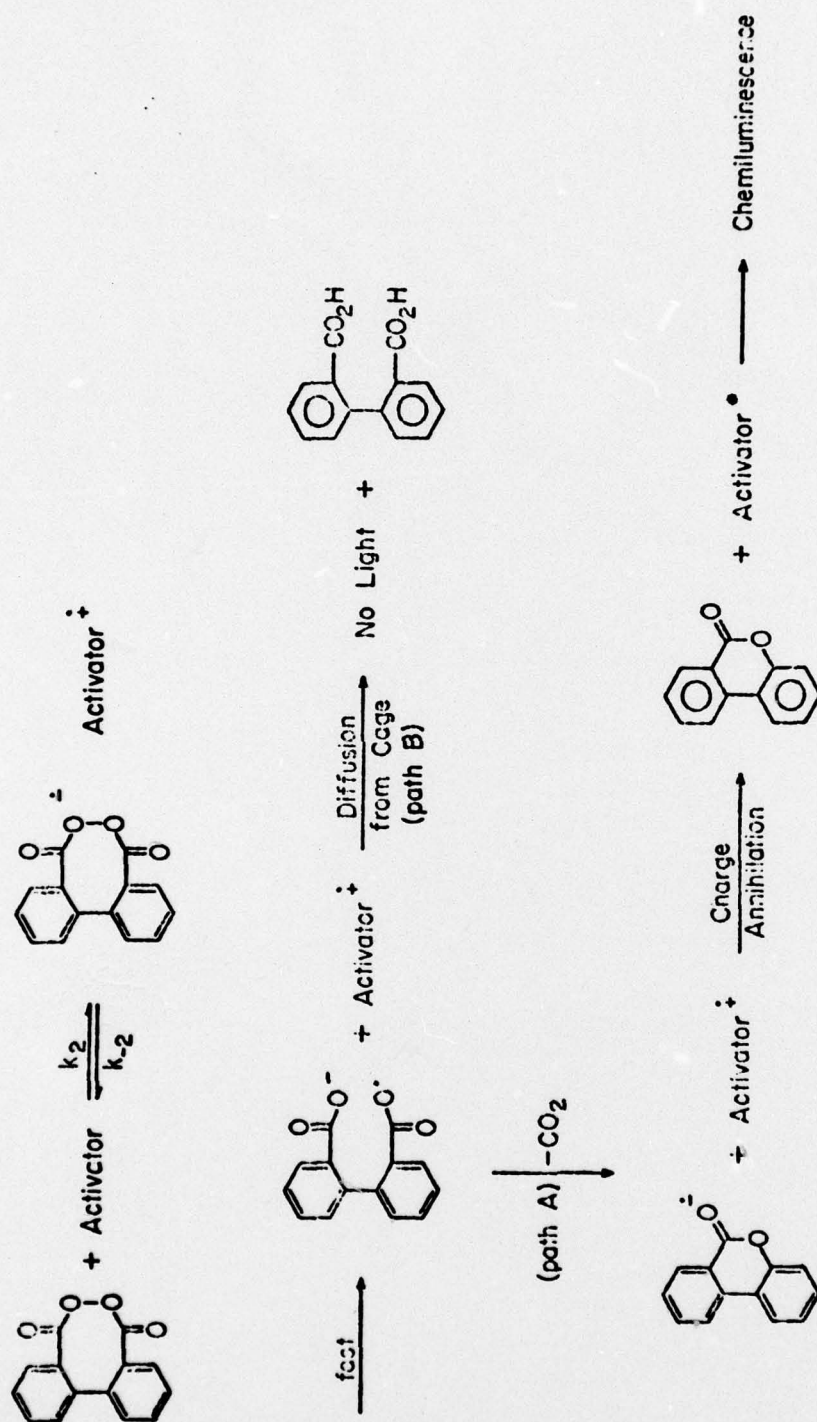


Figure 6.

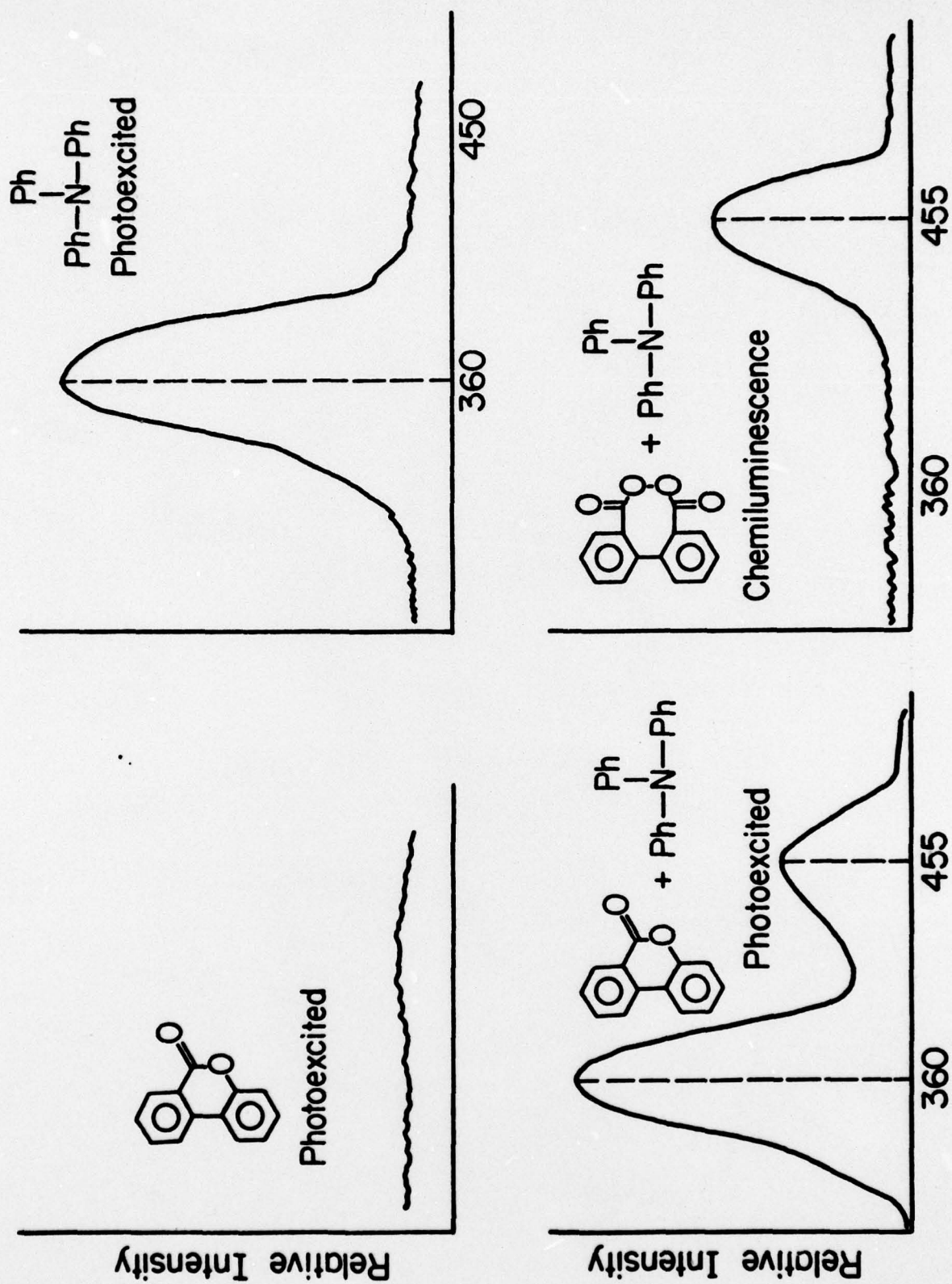


Figure 7.

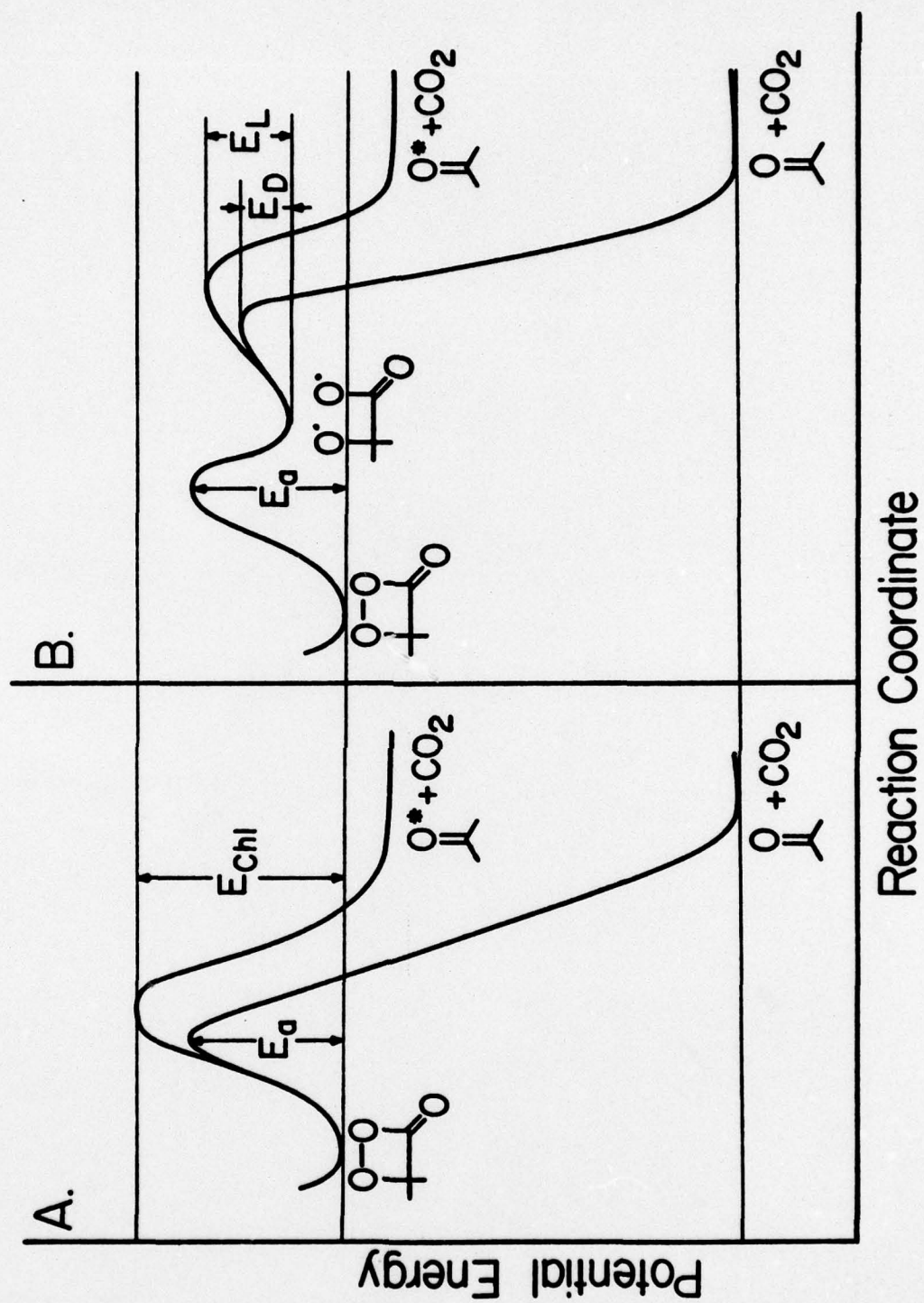


Figure 8.

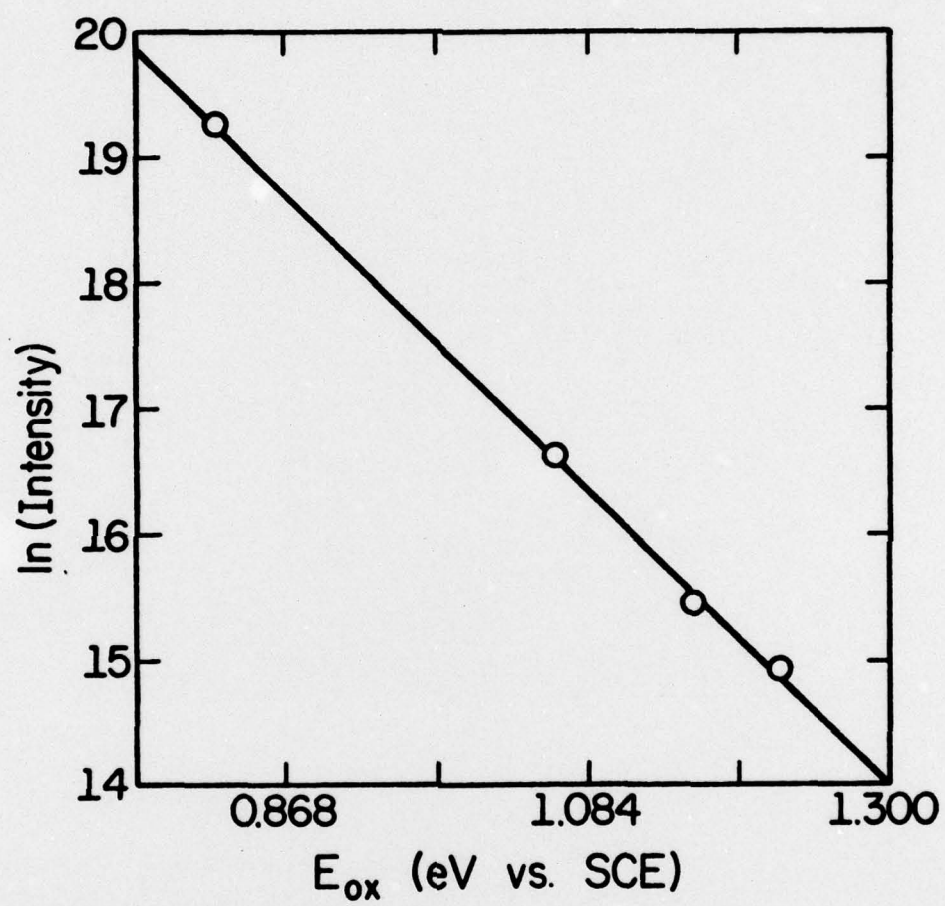


Figure 9.

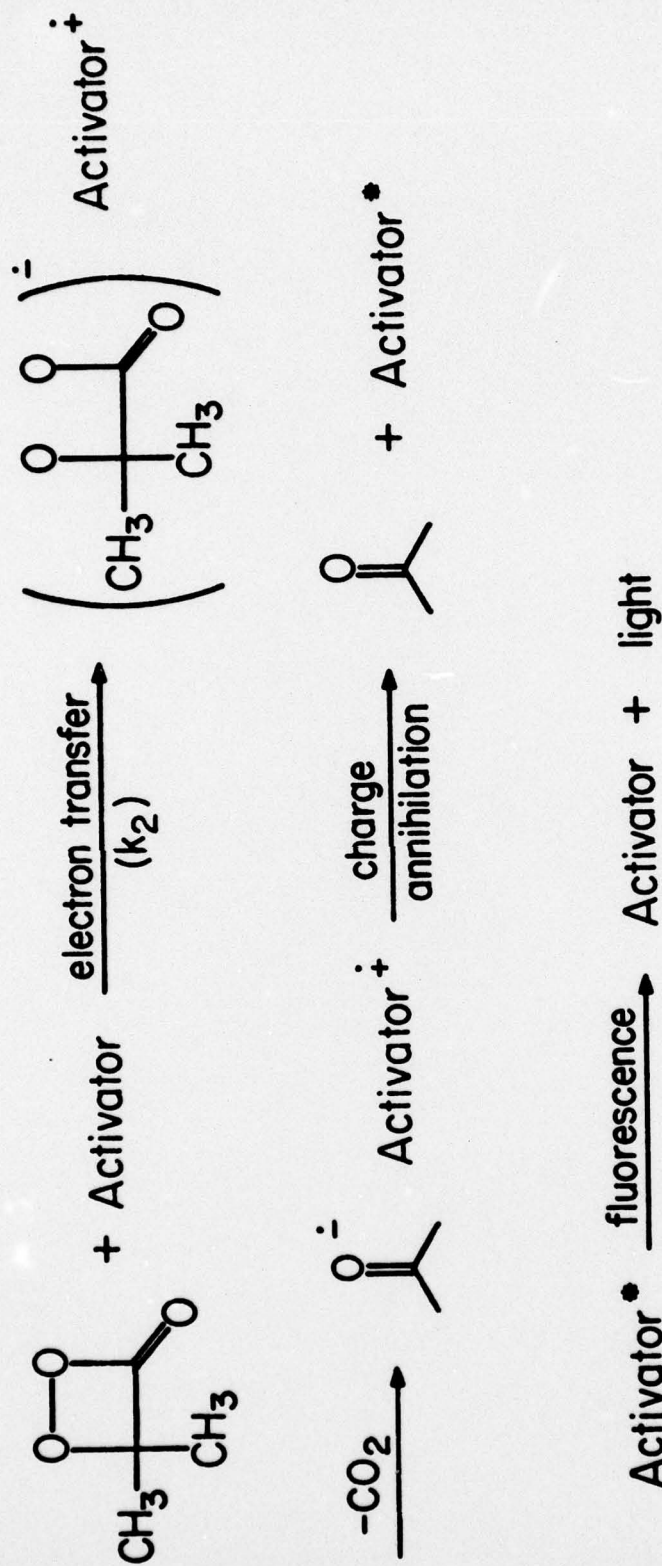
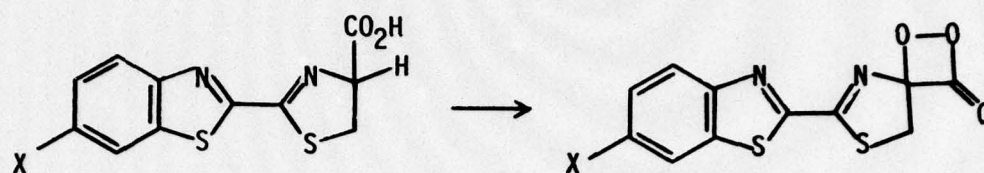


Figure 10.



Bioluminescent

$X = \text{OH}, \text{NH}_2$

Non-bioluminescent

$X = \text{OCH}_3, \text{NHCO}_2\text{CH}_3, \text{NHCO}_2\text{CF}_3$

Figure 11.

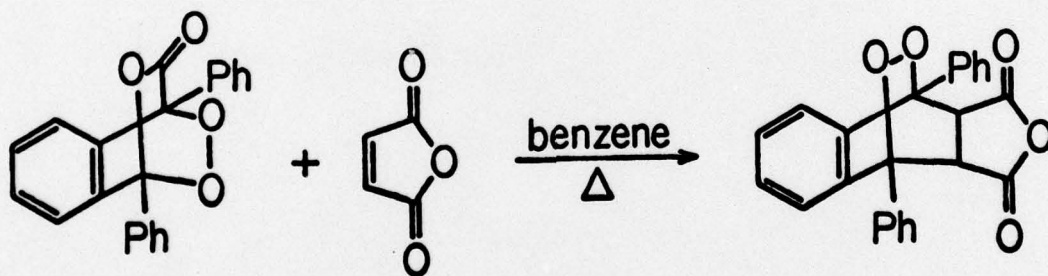
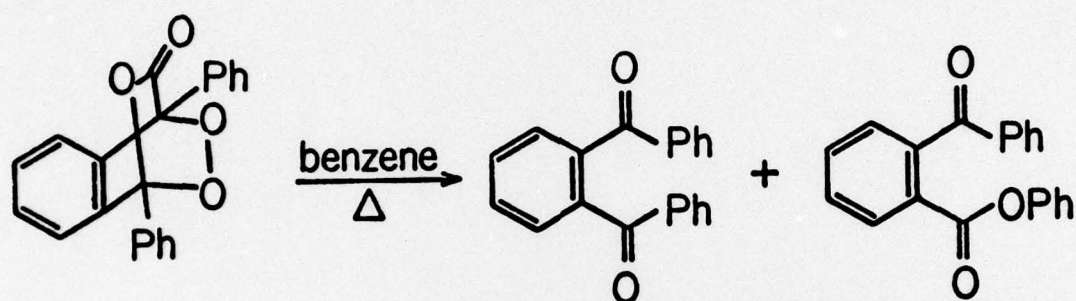
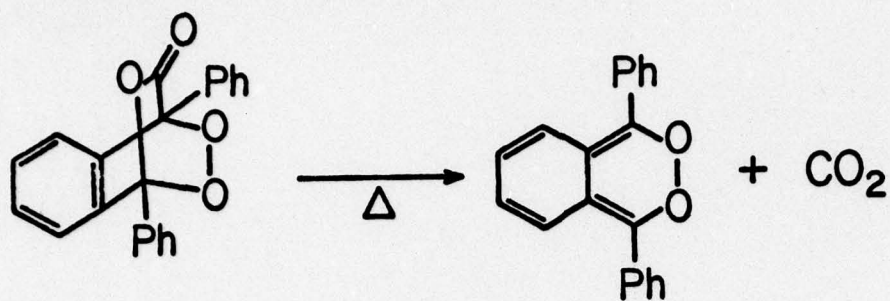


Figure 12.

SCHEME 1

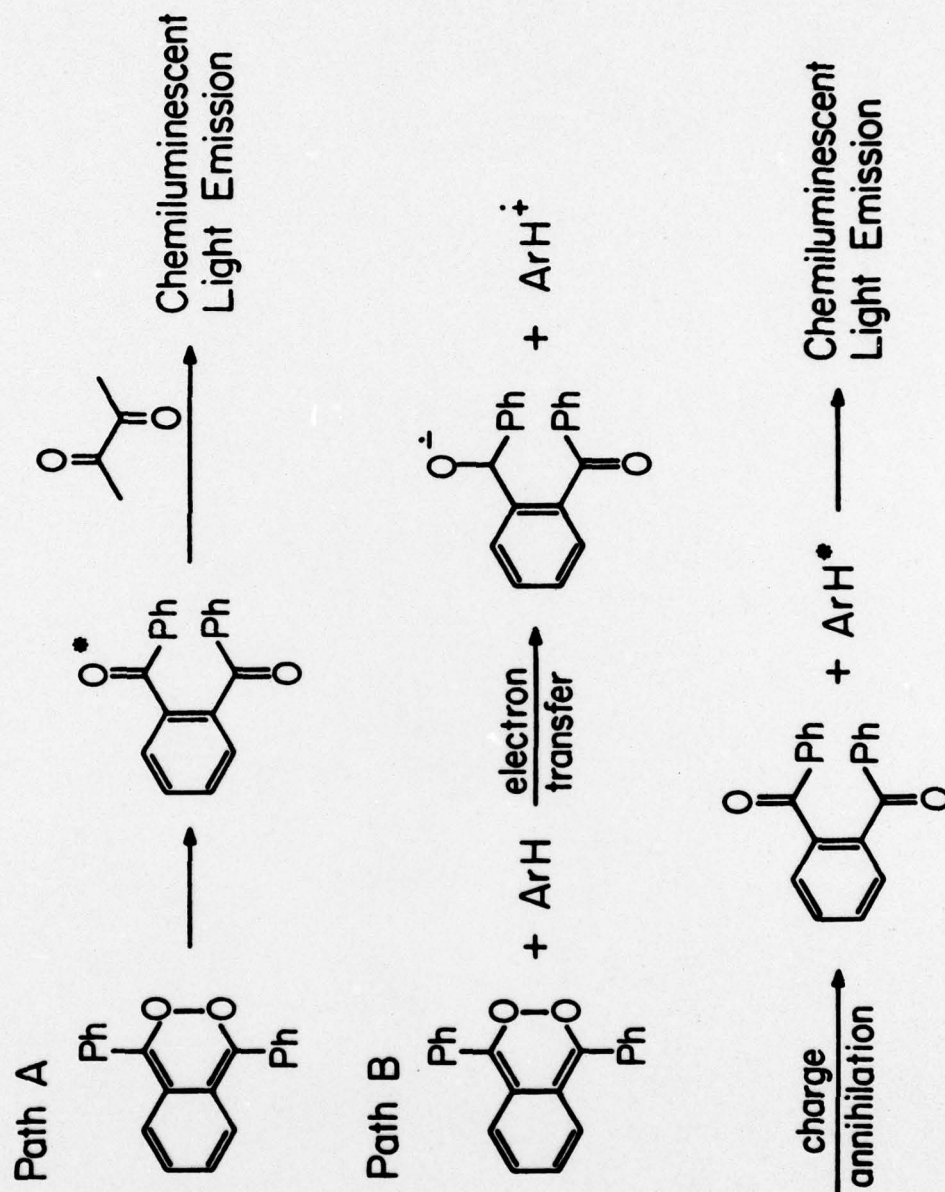


Figure 13.

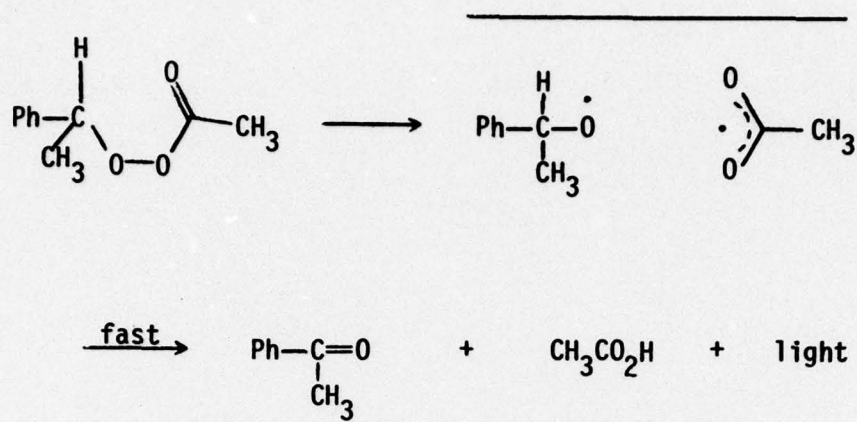


Figure 14.

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