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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY
CHEMILUMINESCENCE OF ORGANIC PEROXIDES. THE CONVERSION OF GROUND-STATE (U)
APR 79 G B SCHUSTER

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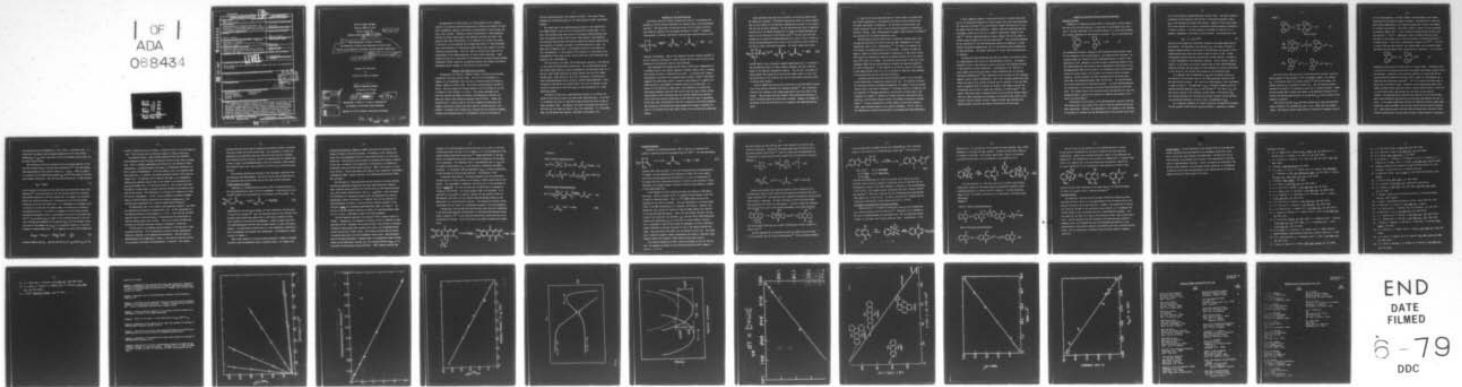
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A mechanism for thermal production of excited states is discussed. Electron transfer from an easily oxidized donor to a suitable organic peroxide followed by oxygen-oxygen bond cleavage generates radical ion intermediates. Subsequent chemical reaction followed by charge annihilation generates electronically excited state products. This sequence of reactions is called chemically initiated electron-exchange luminescence and is shown to be operating for diphenoyl peroxide, 1-phenylethylperoxy acetate, dimethyldioxetane, and 1,4-diphenyl-2,3-benzodioxin (0-xylylene peroxide).

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Chemiluminescence of Organic Peroxides.

The Conversion of Ground State Reactants to Excited State Products by the Chemically Initiated Electron-Exchange Luminescence.

by 9 Technical rept.,

10 Gary B. Schuster

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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? That query has been under investigation in our laboratory for the past four years. In particular, we have examined the distinguishing feature of these transformations; the conversion of a high energy content ground state reagent to an electronically excited product. With this report we describe the results of our investigation of the chemiluminescence of several organic peroxides. These studies have led to our postulation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism; an apparently general path leading from certain high energy content reagents to electronically excited states.

Chemical Light Generation in Solution

The generation of light by a chemical process in solution may be divided conceptually into three distinct steps. The first is the synthesis of a reagent, or an intermediate, that can react to liberate energy sufficient 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/mole on its way to product if such a photon is to result. This energy requirement both restricts severely the number of potential chemiluminescent reactions and makes the study of their mechanism sometimes 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-dioxetanes¹ and by our discovery of

efficient chemiluminescence from diphenyl peroxide.² The study of these compounds has contributed greatly to our understanding of chemi- and bioluminescence.

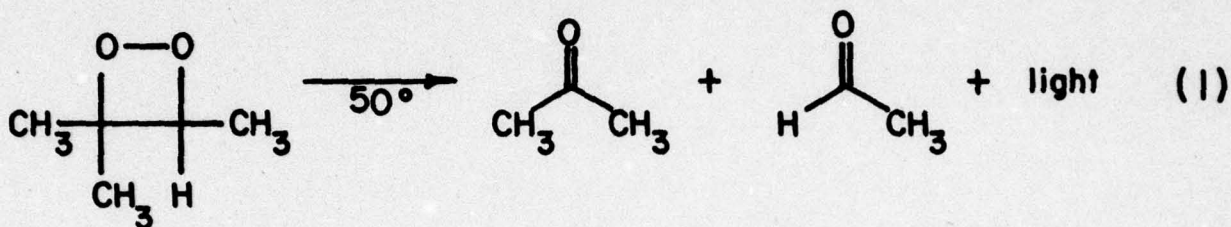
The second step of the chemiluminescence process is the conversion of the reagent formed in the first to an electronically excited state. It is this, the excitation step, that serves to distinguish chemiluminescent reactions that generate visible light from all other chemical transformations. The excitation step provides the mechanism whereby the energy released during the conversion of reactant to product is diverted from heat to light. As might well be imagined, there is considerable diversity in the details of this transformation. As the subject of this account is a description of our investigation of this step, we will discuss below the various mechanisms suggested for this transformation.

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. Quite naturally, the first circumstance is referred to as direct chemiluminescence and the second as indirect chemiluminescence. Identification of the emitter and classification, as direct or indirect, of the reaction is often one of the initial goals in the investigation of a light generating process.

The yield of light from a chemiluminescent process is, of course, the product of the yield of each of the three steps identified above. If our aim is to maximize the yield of light, then we must maximize the yield of each of these individual steps. Fortunately, the factors influencing the success of the first and last steps are, more or less, well understood. It is the middle step, the excitation step, wherein a good deal of the mystery lies.

Mechanism of the Excitation Step

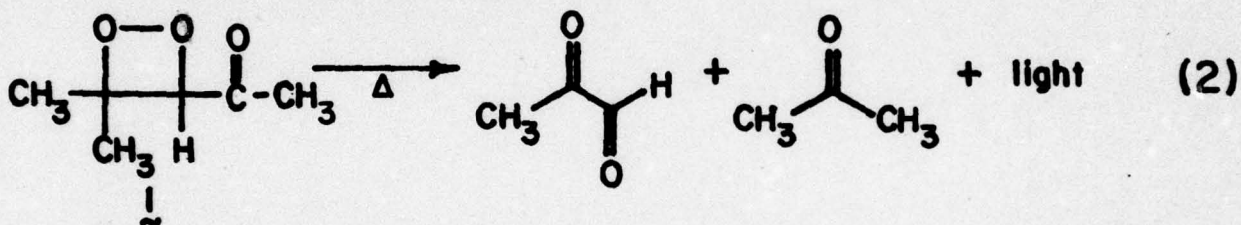
Well before they were actually prepared and isolated 1,2-dioxetanes were proposed as the key reactant responsible for numerous chemi- and bioluminescent reactions.³ The preparation and characterization of this originally elusive ring system was reported first by Kopecky and Mumford in 1969.^{1a} Subsequent investigations in numerous laboratories uncovered many revealing details of the



reactions of dioxetanes. Much of this chemistry has been reviewed recently⁴ so we will 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. McCapra⁵ and Kearns⁶ suggested that these bonds cleave in concert by what amounts to a symmetry forbidden pericyclic rearrangement to generate directly an excited state. To account for the observation, among others, that thermolysis of simply alkyl substituted dioxetanes yield more than fifty triplet for every singlet excited state produced, Turro⁷ elaborated upon the concerted mechanism by proposing a special spin-orbit coupling interaction as the transition state is approached. On the other hand, Richardson⁸ was the first to advocate an excitation mechanism that proceeds by rate determining oxygen-oxygen bond cleavage to generate initially a 1,4-biradical which then reacts further to give excited and ground state product.

Many experiments have been done to attempt to distinguish between these two mechanistic extremes.⁴ Richardson⁹ measured the effect of various substituents on the kinetics of the dioxetane fragmentation and found it to be consistent with the biradical mechanism. We have 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.¹⁰ We have found also that thermolysis of 3-acetyl-4,4-dimethyldioxetane (1) yields a ratio of triplet to singlet excited methylglyoxal much closer to the statistical limit of three to one than do simply substituted dioxetanes. The lowest singlet and triplet



excited states of the α -dicarbonyl compound methylglyoxal are, in contrast to the corresponding states in simply 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.¹² This calculation indicates that cleavage of the oxygen-oxygen bond is the first step in this process. They calculate that the biradical from unsubstituted dioxetane is about 14 kcal/mole above the ground state structure. However, no estimate of the height of the activation barrier for cleavage of the remaining bond was given.

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, and further discussion, we will refer to this excitation mechanism as unimolecular biradical cleavage. Other chemiluminescent reagents, Dewar benzene for example,¹³ may proceed by this excitation mechanism as well.

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.¹⁴ The radical ion reactants for this process are prepared typically at an electrode. Oxidation of some compound D, usually an aromatic hydrocarbon or heterocycle, to the radical cation ($D^{\dot{+}}$) occurs at an anode while reduction of another molecule (A) to the radical anion ($A^{\dot{-}}$) 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 respectively. 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 they annihilate.

Electronic excitation by the electron-transfer process is not restricted to the annihilation of oppositely charge radical ions. The reduction of molecular chlorine by sodium 9,10-diphenylanthracenide, for example, gives the excited singlet state of the neutral anthracene.¹⁵ Disproportionation of ruthenium (III) and ruthenium (I) complexes generates an electronically excited state of the ruthenium (II) product.¹⁶ Reaction of solvated electrons, generated by pulse radiolysis, with suitable radical cations also produces electronically excited states.¹⁷ In short, generation of excited states by sufficiently energetic simple redox processes appears to be a general phenomenon. We will refer to this mechanism for forming excited states as electrogenerated chemiluminescence.

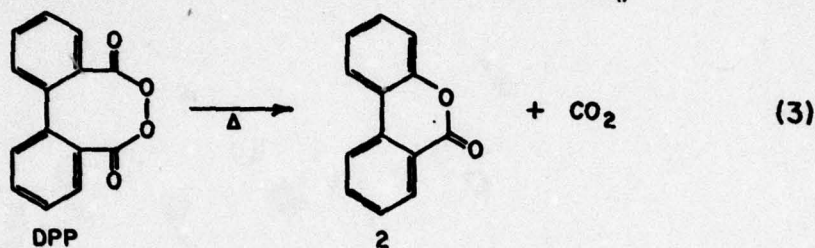
A third, apparently general, reaction that results in excited state products is the concerted elimination of singlet oxygen (1O_2) from certain peroxides. The relatively low energy of 1O_2 (23 kcal/mole) renders the emission of a visible photon from this state impossible. However, Kasha has discovered that the simultaneous transition of two 1O_2 is capable of generating a photon of red light.¹⁸ Indirect chemiluminescence by energy transfer from the 1O_2 dimer to suitable energy acceptors has also been postulated.¹⁹ 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 thermal generation of 1O_2 has found wide application in synthesis.

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.²⁰ 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 coworkers is that the fluor-escer is apparently able to catalyze the release of the energy stored in the intermediate and to direct it toward the formation of excited states.²¹ This special interaction stands in marked contrast to the excitation process responsible for simple dioxetanes and foreshadows our discovery of the specific, predictable, electron transfer reaction between suitable donor molecules and numerous organic peroxides that leads to electronically excited states.

Chemically Initiated Electron-Exchange Luminescence

Diphenyl Peroxide

Thermolysis of diphenyl peroxide (DPP) in dilute CH_2Cl_2 solution leads to the loss of CO_2 and the formation, in high yield, of benzocoumarin (λ), equation 3. We were interested in this reaction because it is sufficiently exothermic to permit generation of electronically excited λ . Also, we speculated that



the unimolecular biradical cleavage excitation mechanism might provide a path for the formation of the 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, unlike DBA, 9,10-diphenylanthracene (DPA) and DPP react to form efficiently the excited singlet state of DPA which we detect as bright chemiluminescence. This observation is not consistent with the excitation mechanisms we outlined above. The further study of this reaction revealed the operation of a new, and apparently general, path for the conversion of chemical bond energy to electronic excitation energy.²

Investigation of the kinetics of the chemiluminescent reaction of DPP and DPA revealed that it was cleanly 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 for the reaction of DPP and DPA is described by equation 4 where k_{obs} is the observed first order rate constant. Analysis of the kinetic behavior of this reaction for a series of activators plotted according to equation 4 is shown in Figure 1. The rate constant k_1 (intercept in Figure 1) is, as expected, independent of the nature of the activator. We attribute this rate

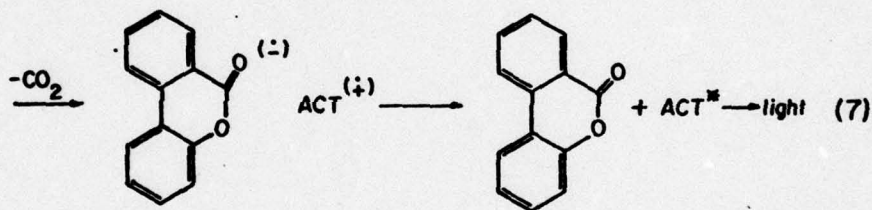
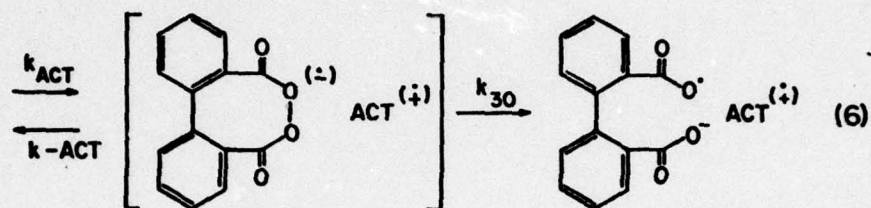
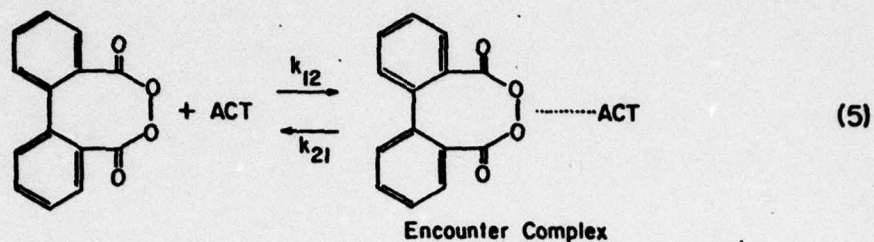
$$k_{\text{obs}} = k_1 + k_{\text{ACT}} [\text{ACT}] \quad (4)$$

constant to the unimolecular unassisted cleavage of the oxygen-oxygen bond of the peroxide. The bimolecular rate constants k_{ACT} (the slopes in Figure 1) obviously depend strongly on the nature of the activator; structurally similar rubrene and DPA have slopes that differ by about a factor of 150. Further investigation revealed that the electronically excited activator is formed as a direct consequence of the bimolecular reaction. Thus an analysis, shown in Figure 2, of the effect of activator concentration on total chemiluminescence intensity indicates that 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_{ACT} must be somehow related to a key feature of the excitation step for the chemiluminescent reaction of DPP with the various activators. The key to our understanding of this relationship is shown in Figure 3. The magnitude of k_{ACT} is predicted uniquely by the one electron oxidation potential (E_{ox}) of the activator.²² The lower is E_{ox} , the more easily oxidized is the activator, and the larger is the value of k_{ACT} . This finding indicates to us that the one electron transfer from the activator to the peroxide determines, at least in part, the magnitude of k_{ACT} .

As a convenient framework for further discussion, the mechanism we propose for the reaction of DPP with the various activators is presented in Scheme 1.

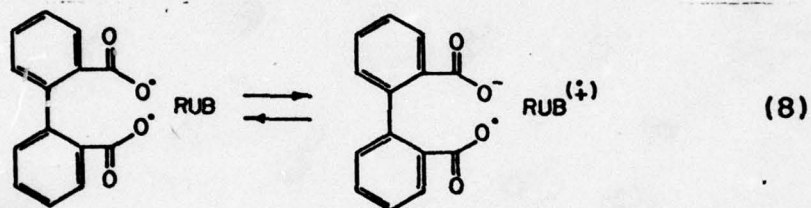
Scheme 1



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,²³ which we here adopt, the reverse reaction k_{21} is diffusion limited also. Thus the encounter complex identified in equation 5 is predicted to have only 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_{ox} of the activator in the presence of peroxide.

The electron transfer (k_{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 unactivated case, to give a new complex of activator and biradical. This path is shown in Figure 4 as the correlation of encounter complex (ACT --- O-O), through the dotted avoided crossing, with the state ACT --- [O[•] O[•]]. 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 4 as ACT^($\dot{+}$) --- [O⁻ O[•]]. In terms of DPP and some activator, say rubrene (RUB), we can associate these two states with the species shown in equilibrium in equation 8. It is of great



relevance to decide which of these states is of lower energy. Fortunately, this is not difficult to determine, and the electrochemical measurements needed to do so are available. Comparison of the oxidation potential of rubrene with the calculated oxidation potential of benzoate ion²⁴ (a model for the diphenate ion) shows that the zwitterionic state ACT^($\dot{+}$) --- [O⁻ O[•]] is some 18 kcal/mole lower in energy than the diradical state. Therefore, as the oxygen-oxygen bond of the complex stretches these states must avoid a crossing (dotted region in Figure 4), and this simple motion thus provides the activation for the electron transfer. An equivalent way of analyzing this reaction is to follow the movement of the antibonding σ_{O-O}^* orbital of the peroxide (the LUMO for the case in hand). As the oxygen-oxygen bond stretches the LUMO moves steadily toward lower energy and crosses the HOMO of the activator making electron transfer spontaneous. These analyses predict that the electron transfer gives directly a vibrationally excited radical ion pair which we show in square brackets in equation 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 ($k_{30} \gg k_{-ACT}$) and irreversibly to give the diphenate radical anion and activator radical cation.

The correlation of the rate constant with the oxidation potential of the activator follows directly from the above considerations.²⁵ The usual steady state approximations yield equation 9 where $K_{12} = k_{12}/k_{21}$. Shown in Figure 5 is an analysis of the relationship between k_{ACT} and the free energy of the electron transfer reaction ΔG° . When $\Delta G^\circ=0$ the activation barrier is ΔG_0^\ddagger (intersec-

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

tion of the two solid curves) and has been often associated with solvent reorganization.²⁶ If we now increase ΔG° for the electron transfer by increasing the oxidation potential of ACT by an amount $\Delta\Delta G^\circ$, for example, the activation barrier for reaction increases also, (intersection of the solid and dotted curves) but not by the full amount $\Delta\Delta G^\circ$. As a consequence of the geometry only a fraction (α) of the total free energy change is realized as an increase in the activation barrier. This factor is analogous to the well-known transfer coefficient and generally takes a value between 0.3 and 0.7 for electrode reactions.²⁷ We can express k_{obs} in terms of the oxidation potential of the activator, the reduction potential of the peroxide (E_{red}) and the coulombic attractive force of the charged ions (E_{coul}) as in equation 10 where k_1 is the rate constant for reaction when $\Delta G^\circ=0$. It is important to realize that changing the

$$\ln(k_{obs}) = \ln(k_1 K_{12}) + \frac{\alpha(E_{red} + E_{coul})}{RT} - \frac{\alpha E_{ox}}{RT} \quad (10)$$

activator affects only E_{ox} . Thus the semilog plot of k_{obs} against E_{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 3 with $\alpha=0.3$.

The electron transfer - bond cleavage sequence we have just described yields diphenate radical anion (\mathfrak{z}) and activator radical cation within a solvent cage. There is indirect experimental verification for the existence of these intermediates. As mentioned above, the product of unimolecular thermolysis of DPP is primarily benzocoumarin. Critically, diphenic acid is not detected under those conditions. In contrast, the rubrene catalyzed reaction yields about 5% diphenic acid. We interpret this to indicate that there is an intermediate formed by the catalyzed reaction that is not present in the unimolecular process, and we suspect that it is the radical anion \mathfrak{z} . Also, we have found that the yield of excited states is roughly inversely related to the dielectric constant of the solvent. This observation is consistent with formation of a radical ion pair intermediate. Finally, we have attempted to generate \mathfrak{z} independently by reacting diphenic anhydride with tert-butyl hydroperoxide. This reaction gives benzocoumarin by a route we presume passes through \mathfrak{z} .²

The penultimate step in the proposed light generating sequence is the familiar annihilation of oppositely charged radical ions. We have determined that the reduction potential of benzocoumarin is -1.92 V. Thus, with the activators shown in Figure 2, sufficient energy is released during the annihilation to form the excited singlet state directly. The yield of singlet excited state activator by the CIEEL path under favorable circumstance is about 30%.

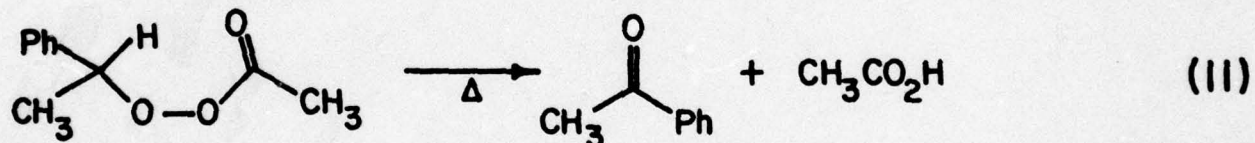
The last step in our proposed reaction mechanism is the emission of light by excited activator. For the hydrocarbon activators we have examined, this emission is identical to the photoexcited fluorescence. With the amines N-phenylcarbazole and triphenylamine, however, a new emission, which we ascribe to an exciplex of the amine and benzocoumarin, is observed. This finding

indicates that the entire reaction sequence, from electron transfer to annihilation, occurs within the initial solvent cage. This conclusion is further 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 represents a departure from the previously described pathways. We set out next to show the generality of this mechanism and to probe further each of the steps we have postulated.

1-Phenylethylperoxy Acetate

Thermolysis of 1-phenylethylperoxy acetate (PPA) in benzene solution at 95° gives quantitatively acetic acid and acetophenone. Group equivalent calculations²⁸ predict this transformation to be exothermic by 58 kcal/mole. Our



PPA

determination of the activation enthalpy for this unimolecular reaction gives a value of 33.2 kcal/mole.²⁹ Thus, the transition state of this reaction is 93 kcal/mole 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 2.

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 (Figure 6) without itself being consumed. The products of this reaction are acetic acid and acetophenone; which are formed quantitatively as in the uncatalyzed case. Electronically excited states are formed by the catalytic reaction as well and, in contrast to the unimolecular transformation, are detected as fluorescence from the excited singlet activator. DMAC is not unique in its catalytic ability. Similar observations were made for other phenazines, N,N-diphenyl-2-aminopyrene (DPAP), rubrene, perylene, 9,10-diphenylethynylanthracene (DPEA), DPA, and others.

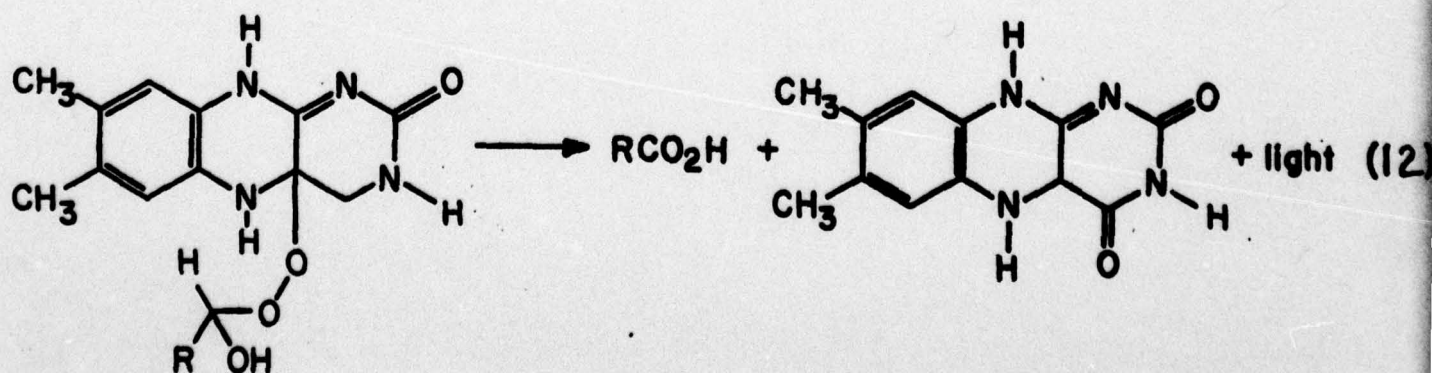
The efficiency of light generation from the reaction of various activators with PPA was determined by measuring the total chemiluminescence intensity under conditions where essentially all the PPA reacts by the unimolecular path (i.e. low activator concentration so that $k_1 \gg k_{ACT}[ACT]$). After correcting for differences in fluorescence quantum yield, and photomultiplier tube and monochromator spectral efficiency it is apparent that the only predictor of chemiluminescence efficiency is the one electron oxidation potential of the activator, ~~except~~ for N,N-dimethyldihydrophenazine (DMP); see Figure 7. 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 2. Conceptually, the sequence of reactions for PPA is identical to 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 deuterated at the methine hydrogen is employed there is no measurable primary isotope effect on the unimolecular reaction (k_1), the catalyzed reaction (k_{ACT}), 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 either for Path A or B of Scheme 2, or in the distribution of the product between ground and excited state.²⁹ Charge annihilation of the cage radical ions generates the excited activator which we detect by its characteristic luminescence. This mechanism leads to the prediction that $\ln k_{ACT}$ will be inversely proportional to E_{ox} of the activator; a prediction verified by experiment. In the general case, the magnitude of k_{ACT} is directly proportional to the efficiency of excited state generation. The exception is DMP.

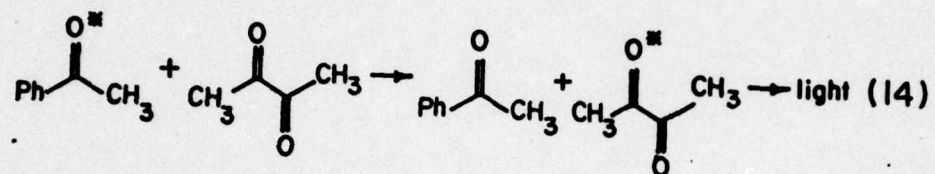
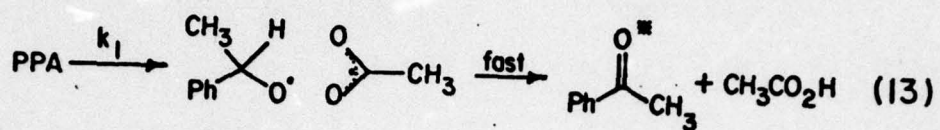
To generate light directly the energy released by the ion annihilation reaction must be at least as great as the energy of lowest singlet state of the emitter. This requirement is apparently fulfilled by all of the activators of Figure 7 ~~except~~ DMP. For this activator the ion annihilation is expected to release ca. 59 kcal/mole. The singlet energy of DMP is 72 kcal/mole. 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 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 equation 12.³⁰ In this case the dihydroflavin nucleus may serve as an intramolecular activator. We will have more to say about intramolecular systems below.

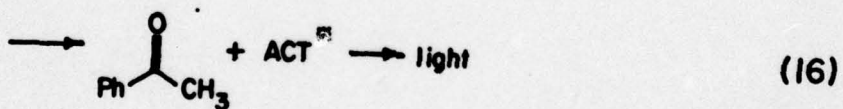
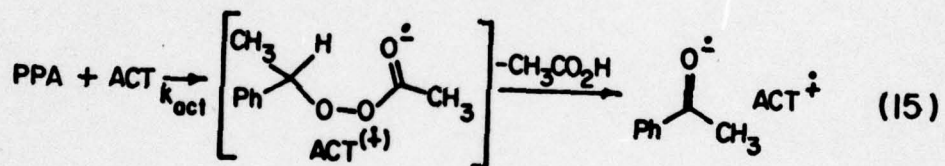


Scheme 2

Path A - Indirect Chemiluminescence

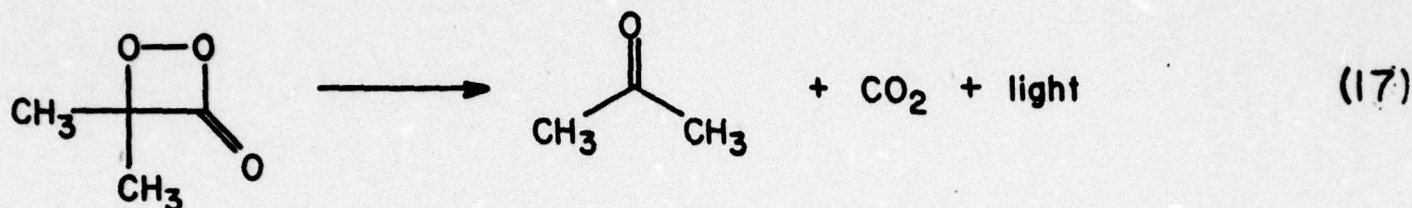


Path B - Activated Chemiluminescence



Dimethyldioxetanone

Thermolysis of dimethyldioxetanone (DDO) in CH_2Cl_2 or in benzene gives acetone in quantitative yield, (presumably) CO_2 , and light.³¹ The chemiluminescence



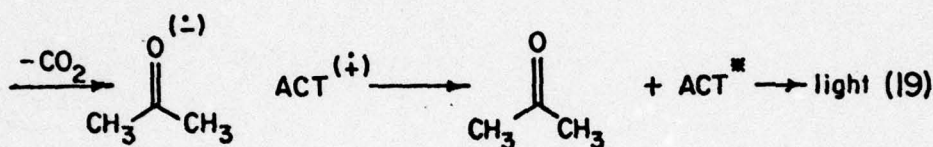
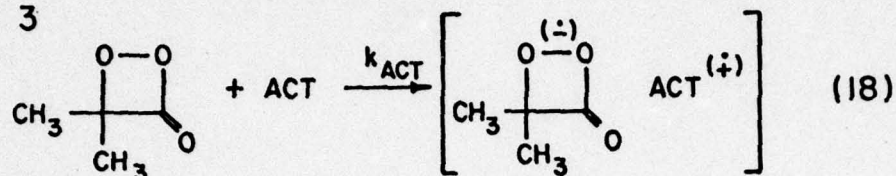
observed under these conditions is from the fluorescence and the phosphorescence of acetone. We have determined that thermolysis of DDO at 30° gives singlet and triplet excited acetone with efficiencies of 0.1 and 1.5% respectively.³² We suspect that this uncatalyzed excitation is similar to the reaction 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° in a benzene solution DDO has a half-life of about one thousand seconds. With $1 \times 10^{-3} \text{ M}$ DMAC present the half-life decreases to less than five seconds. This rate acceleration is directly proportional to the DMAC concentration as is apparent from Figure 8. Moreover, the bimolecular rate constant for reaction of DDO with DMAC predicts the intensity of the observed chemiluminescence. Other activators behave similarly; the magnitude of the bimolecular rate constant, k_{ACT} , and the initial chemiluminescence intensity are predicted by E_{ox} for activators of diverse chemical structure. This is displayed in Figure 9 which shows the dependence of initial chemiluminescence intensity on activator structure for over a two hundred thousand 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 formation of DMP singlet excited state directly.

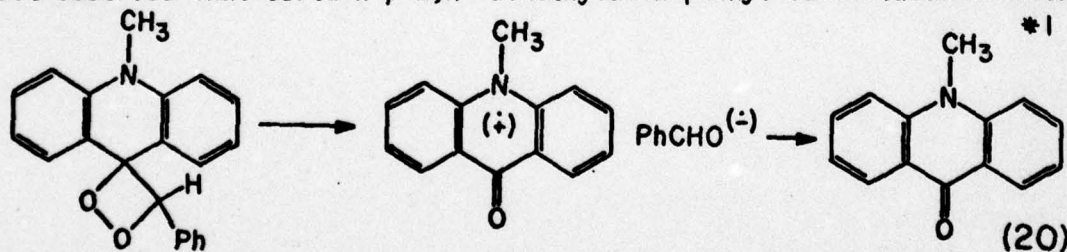
This reaction mechanism for DDO is entirely analogous to that for DPP and PPA. The sequence we propose for the activated excitation step is shown in Scheme 3. As in the

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 CO_2 leaves acetone radical anion.³³ Finally, charge annihilation generates the electronically excited activator which we detect by its characteristic emission.

Scheme 3



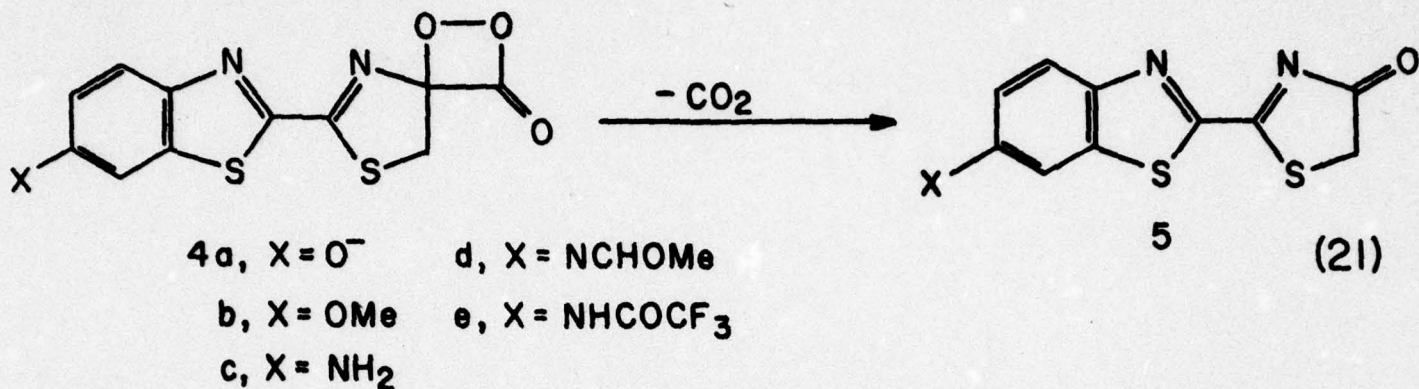
McCupra and coworkers have reported recently on their observation of a dioxetane that reacts to form singlet excited product with unusually high efficiency; equation 20.³⁴ They speculate that a mechanism conceptually similar to the CIEEL process is operating. The major difference is that the electron donor and the acceptor are within the same molecule. Similarly, Schaap and coworkers have observed that certain p-N,N'-dimethylaminophenyl substituted dioxetanes



give high singlet yields and have invoked intramolecular electron transfer to explain this.³⁵

We have suggested that intramolecular electron transfer may be involved in the excitation step of firefly bioluminescence.³⁶ After considerable debate

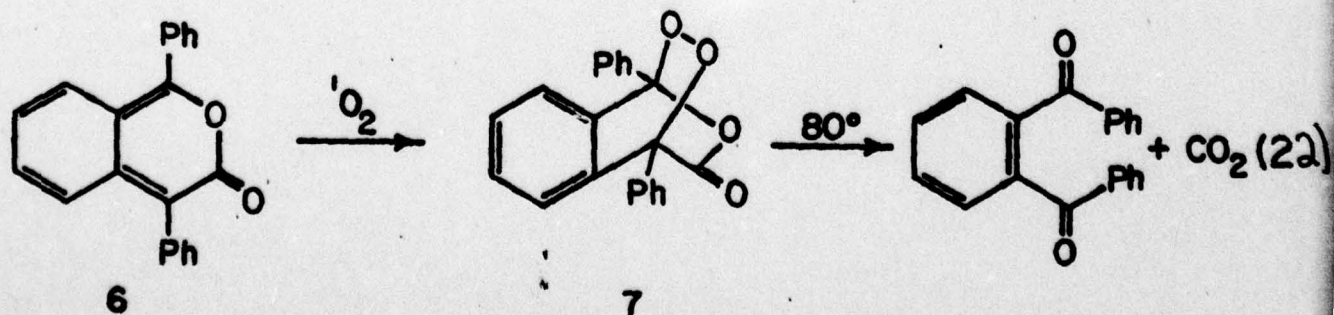
it has now been widely accepted that the key transformation in this excitation process is the conversion of dioxetanone $4a$ to amide $5a$.³⁷ The discovery of



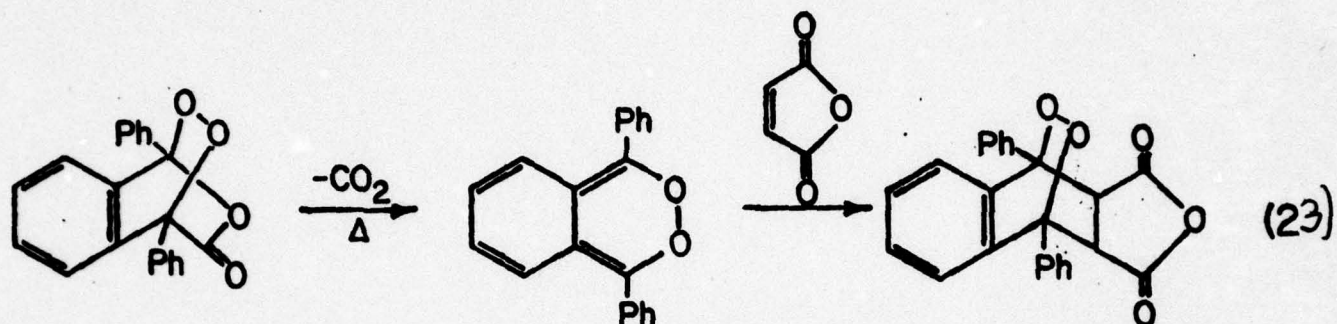
activated chemiluminescence of simple dioxetanones, and finding that intramolecular electron transfer generates singlets has led us to speculate that an intramolecular version of the CIEEL mechanism is operating in the bioluminescence of the firefly. This proposal neatly rationalizes some early findings of White and coworkers.³⁸ Their work indicates that the dioxetanones $4a$ and $4c$ generate light whereas $4b$, d , and e do not. Of course, we now quickly recognize that $4a$, c have good intramolecular electron donors while $4b$, d , e do 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.³⁹ Thermolysis of 7 in benzene at 80° gives o-dibenzoylbenzene and (presumably) CO_2 . With an appropriate energy acceptor, or activator, this reaction generates light. Interestingly, if the



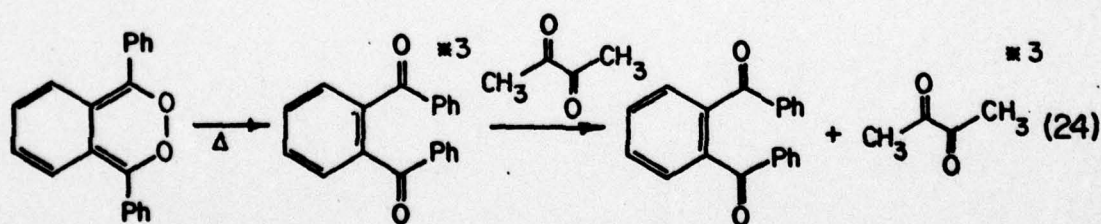
thermolysis of λ is carried out in the presence of maleic anhydride, then o-dibenzoylbenzene is no longer the major product. Instead, the Diels-Alder adduct β is isolated in 70% yield. This finding, among others, leads us to postulate o-xylylene peroxide (OXP) as an intermediate in the thermolysis of λ .



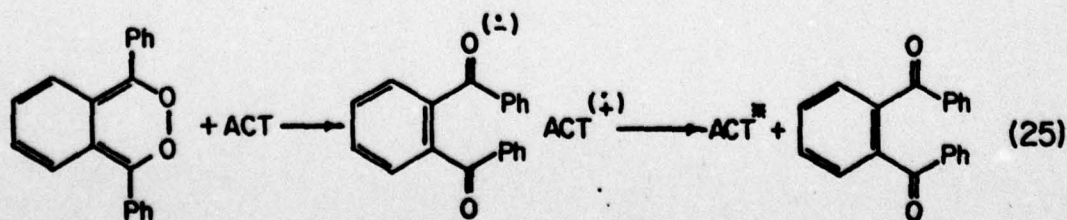
Our data show that it is OXP that gives rise to excited state products. Unimolecular cleavage of the oxygen-oxygen bond apparently generates triplet o-dibenzoylbenzene as is shown as Path A of Scheme 4. The CIEEL mechanism, shown as Path B in Scheme 4, accounts for our observation of activated chemiluminescence.

Scheme 4

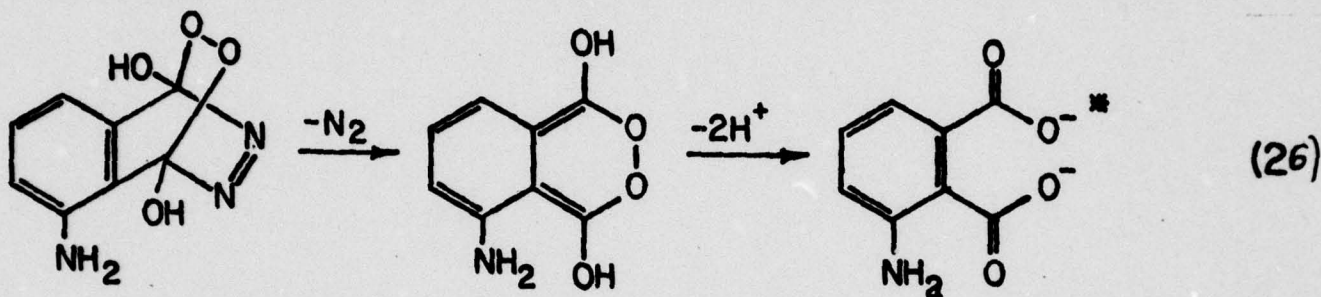
Path A - Indirect Chemiluminescence :



Path B - Activated Chemiluminescence :



The OXP results may be applicable to the chemiluminescence of luminol. The key reactive intermediate in the luminol system has not been identified unambiguously. However, most informed speculation centers on the endoperoxy azo compound δ .⁴⁰ The resemblance of this structure to endoperoxide λ is apparent immediately and suggests that a similar mechanism may be operating; equation 26. 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.⁴¹

Concluding Remarks

The chemically initiated electron-exchange luminescence mechanism we have described provides a fabric for the understanding of the excitation step for peroxides of diverse structure and properties. Moreover, the 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 widespread applicability in the understanding of the reactions numerous electrophiles with easily oxidized electron donors. We are continuing to investigate these and other aspects of chemical reactivity.

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Captions for Figures

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: coronene, DPA, perylene, naphthacene, and rubrene.

Figure 2 - Reciprocal plot of chemiluminescent intensity for DPP and DPA in CH_2Cl_2 at 32°C .

Figure 3 - Correlation of the magnitude of k_{ACT} with the one electron oxidation potential of the hydrocarbon activators. In order of increasing E_{ox} the points are: rubrene, naphthacene, perylene, DPA, coronene, pyrene.

Figure 4 - State correlation diagram for the activated electron transfer with simultaneous cleavage of the oxygen-oxygen bond.

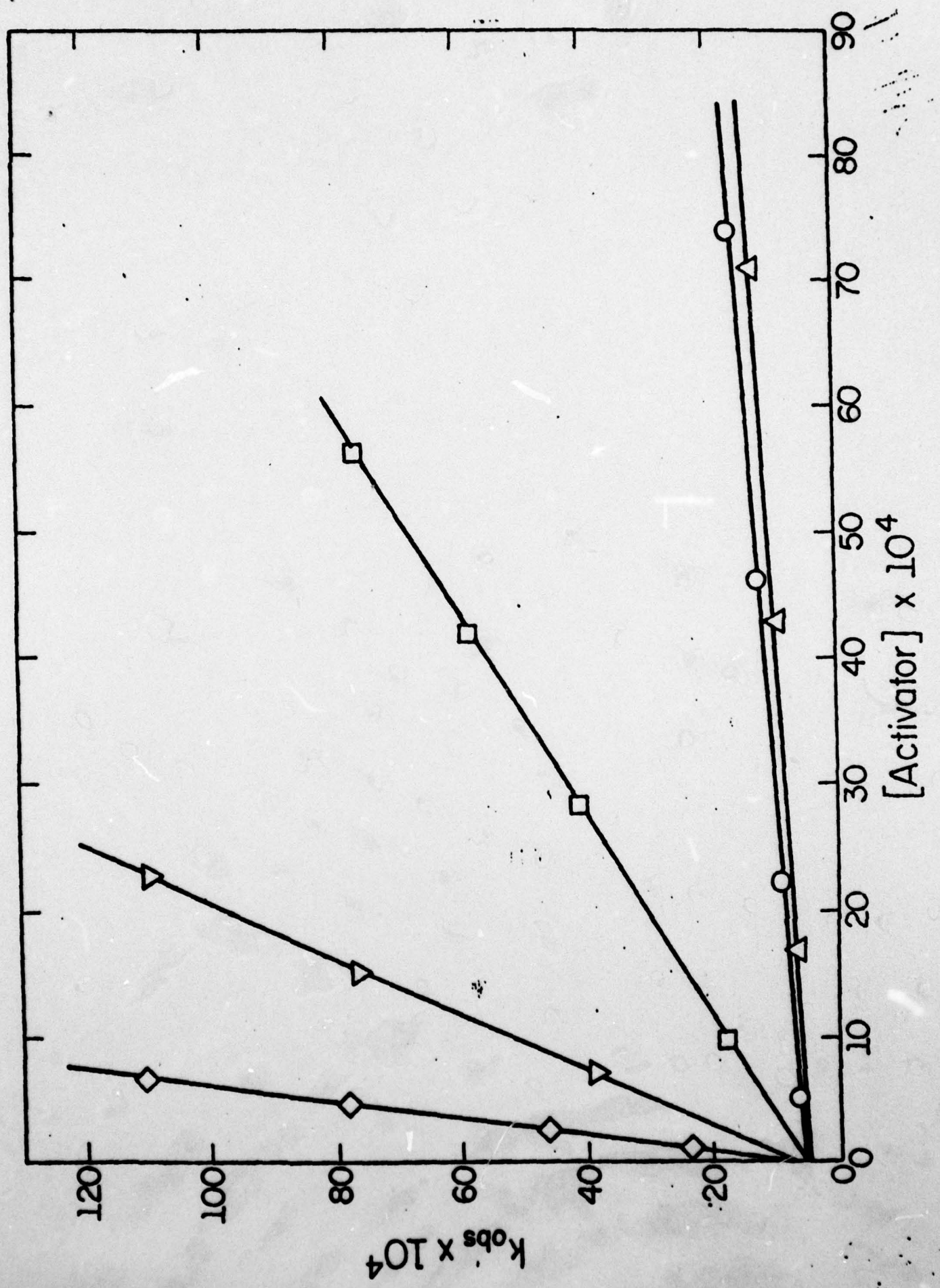
Figure 5 - Origin of the factor α in the semilog plot of k_{ACT} against E_{ox} .

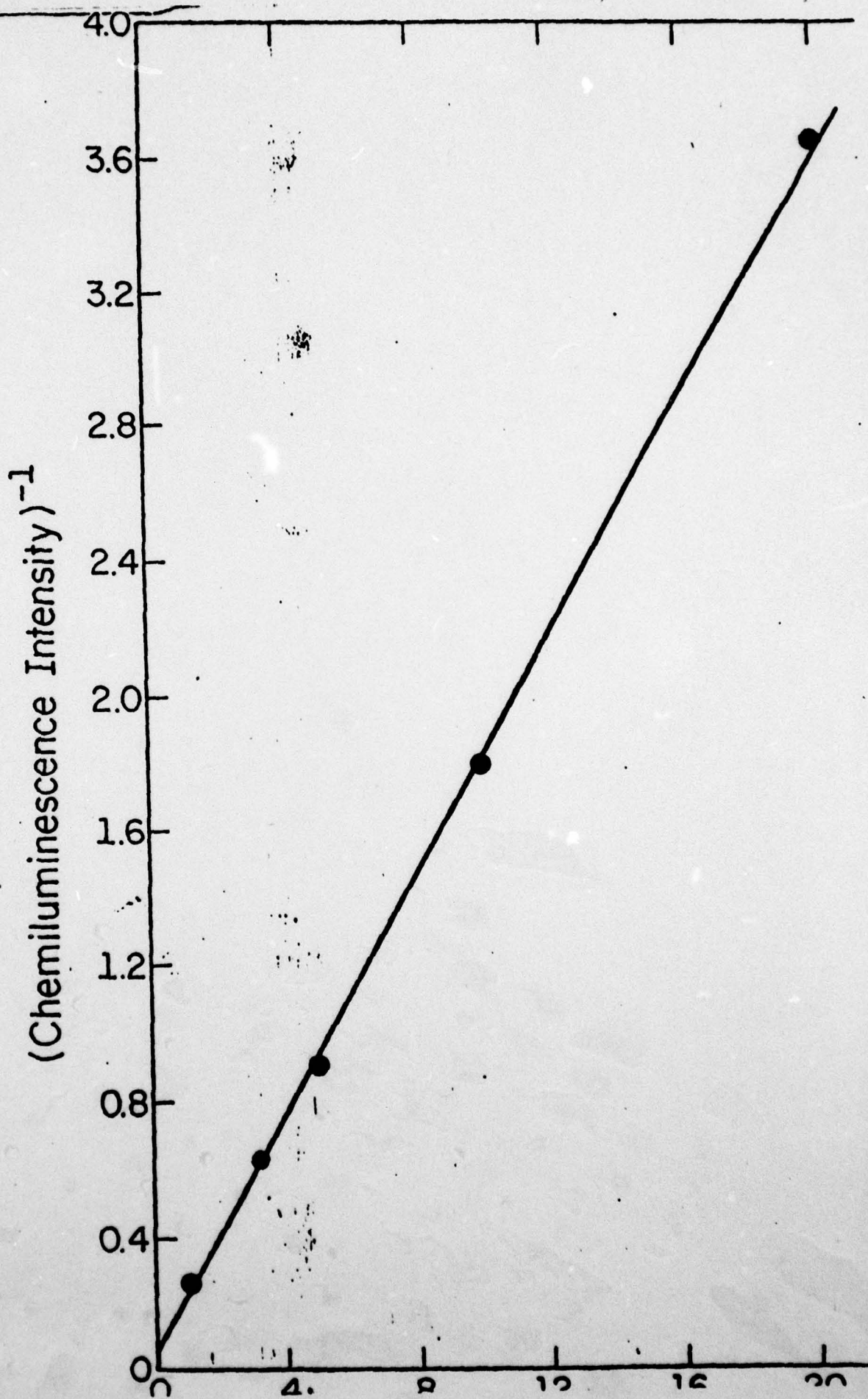
Figure 6 - Dependence of the observed first order rate constant for reaction of PPA with DMAC in benzene solution at 99°C .

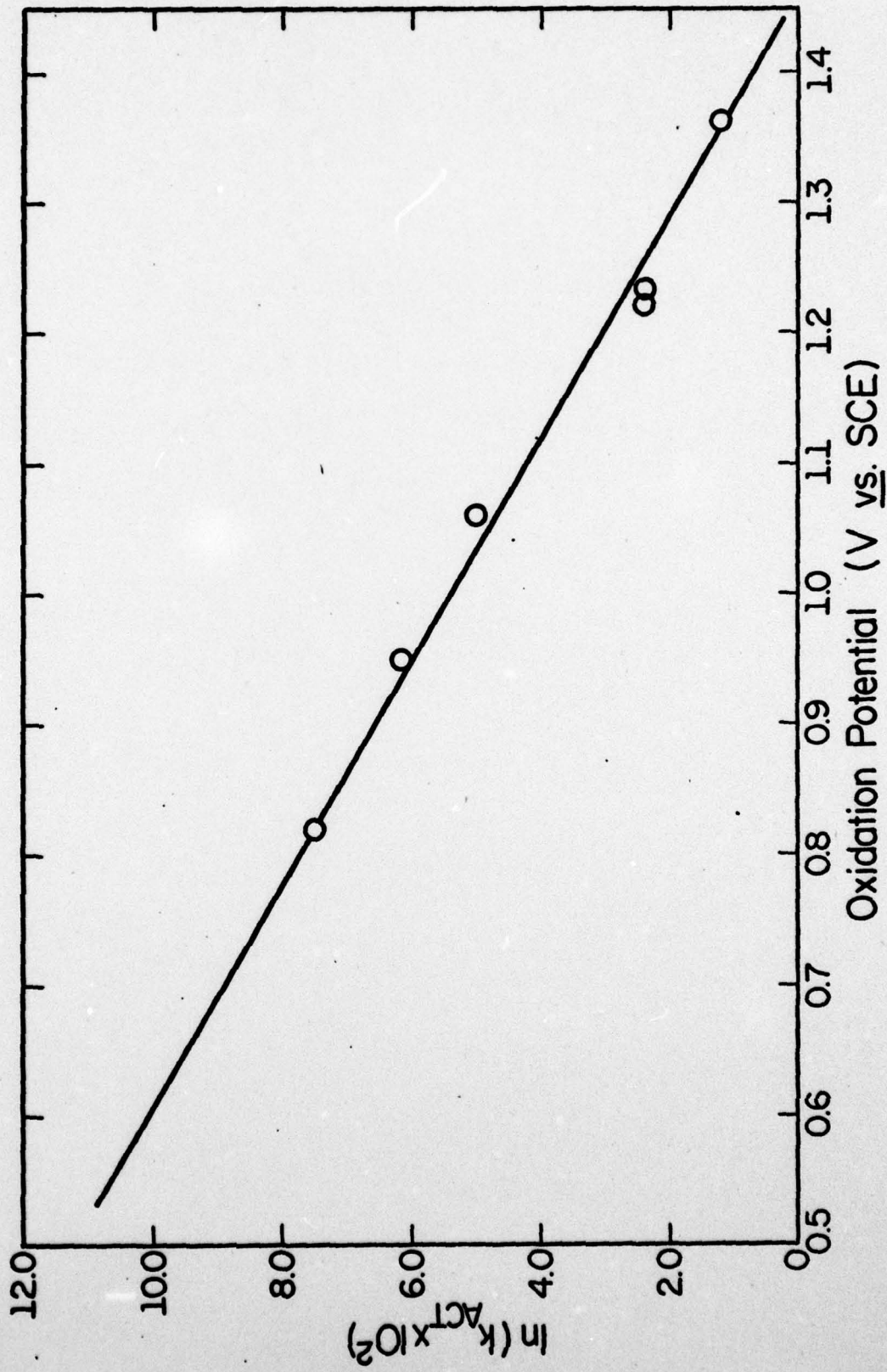
Figure 7 - Correlation of the total chemiluminescent intensity of PPA with oxidation potential of various activators in benzene solution at 99°C .

Figure 8 - Dependence of the observed first order rate constant for reaction of DDO with DMAC in benzene at 24° .

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

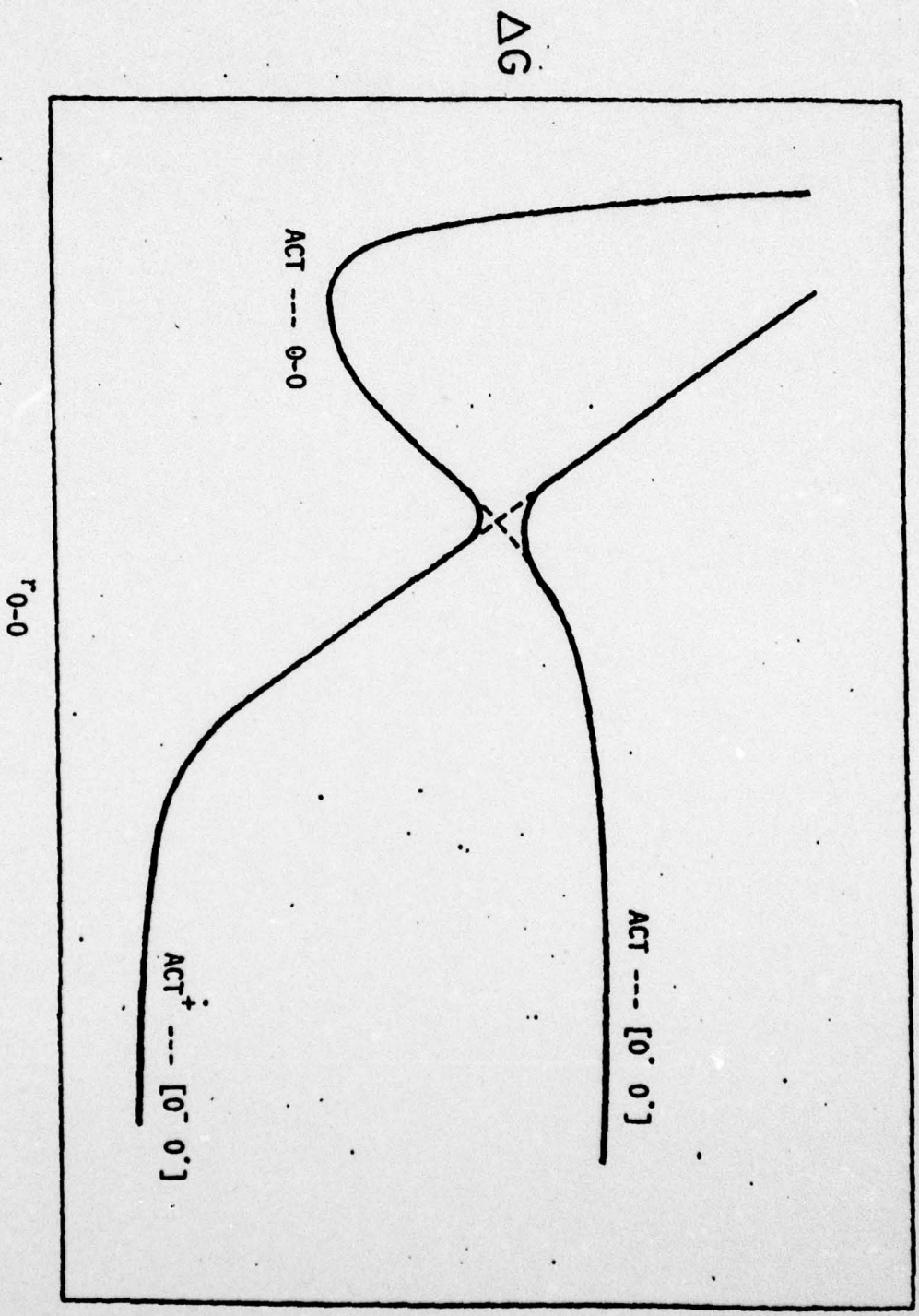


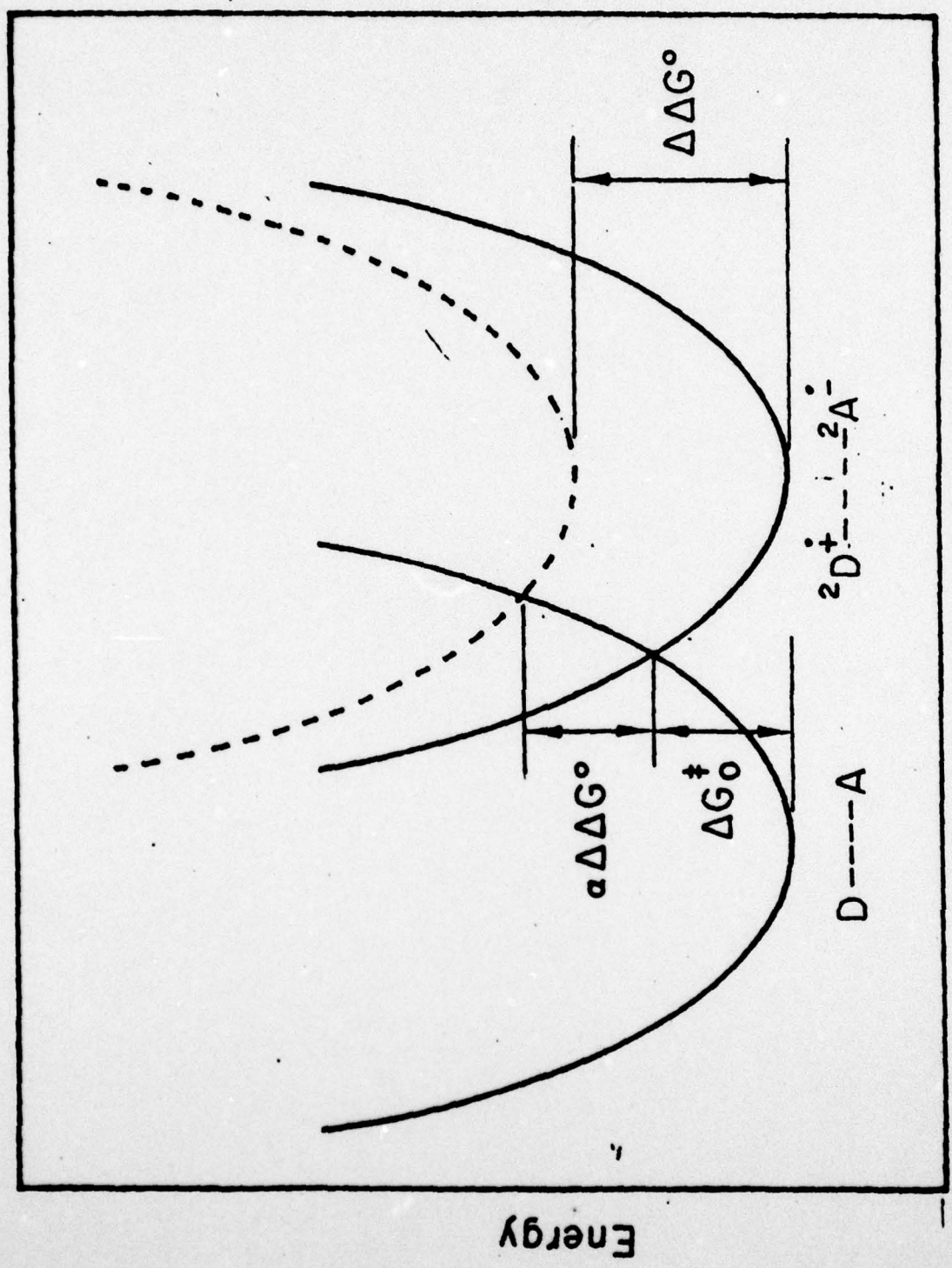




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Fig. 4





Reaction Coordinate

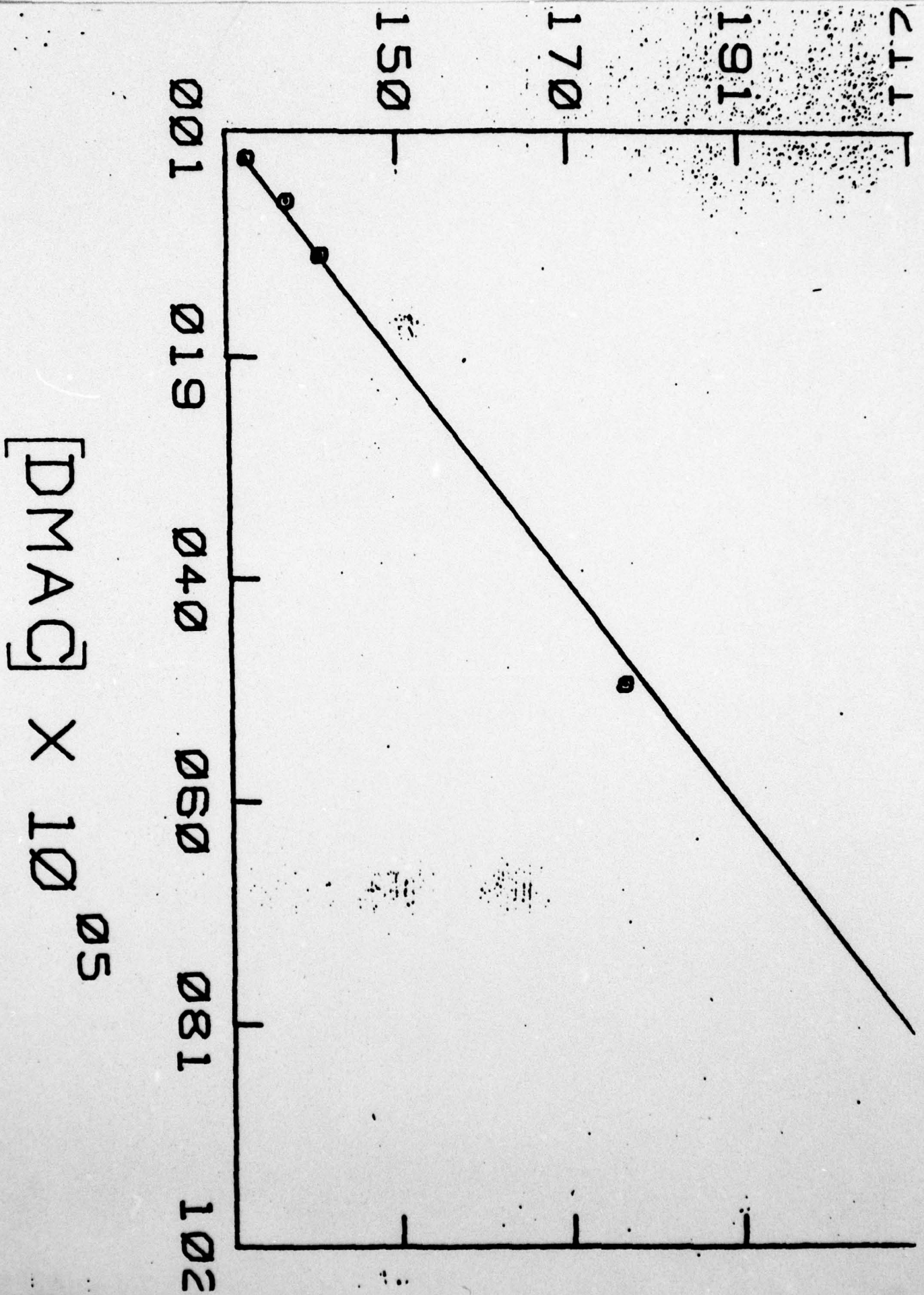
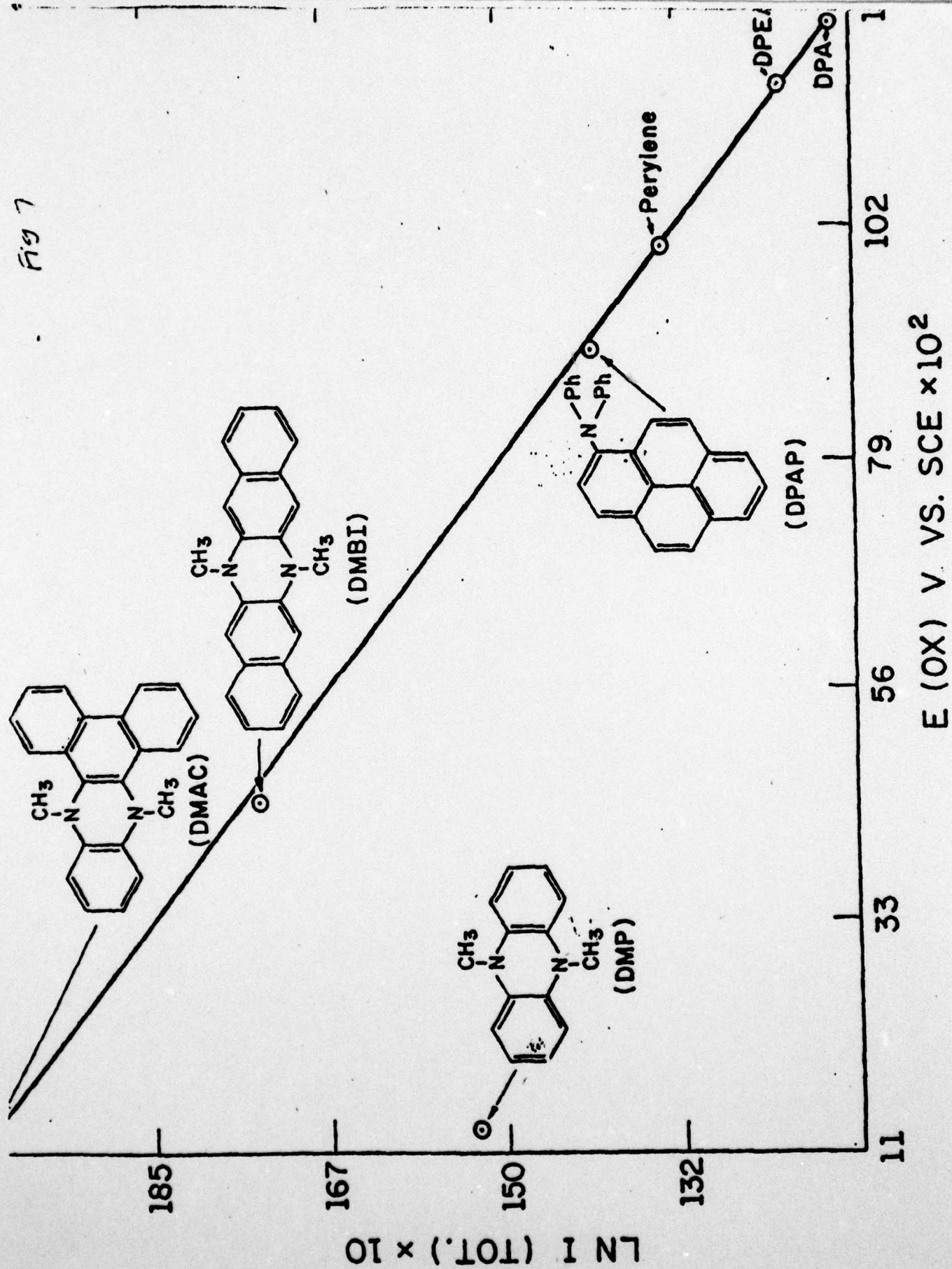
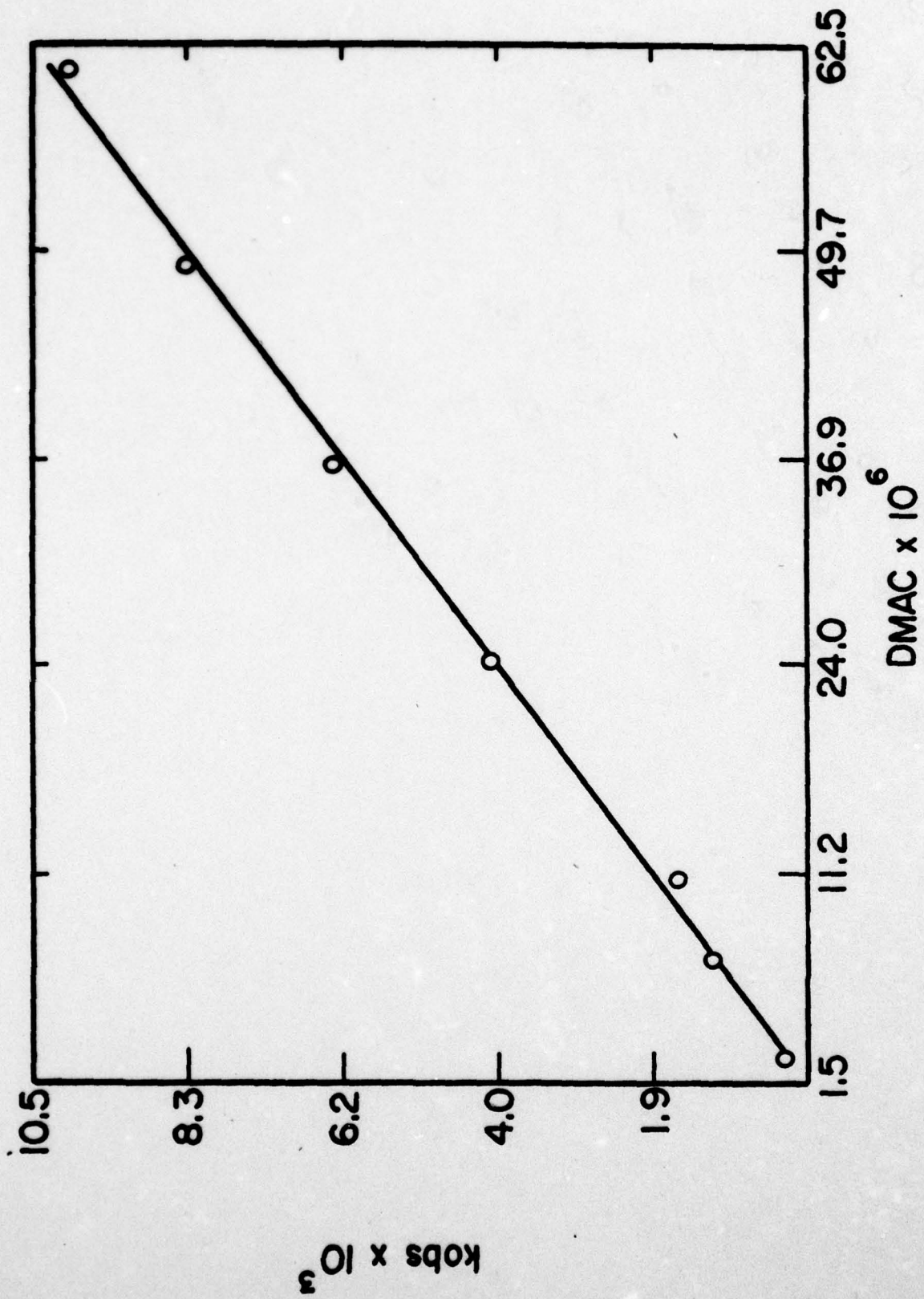
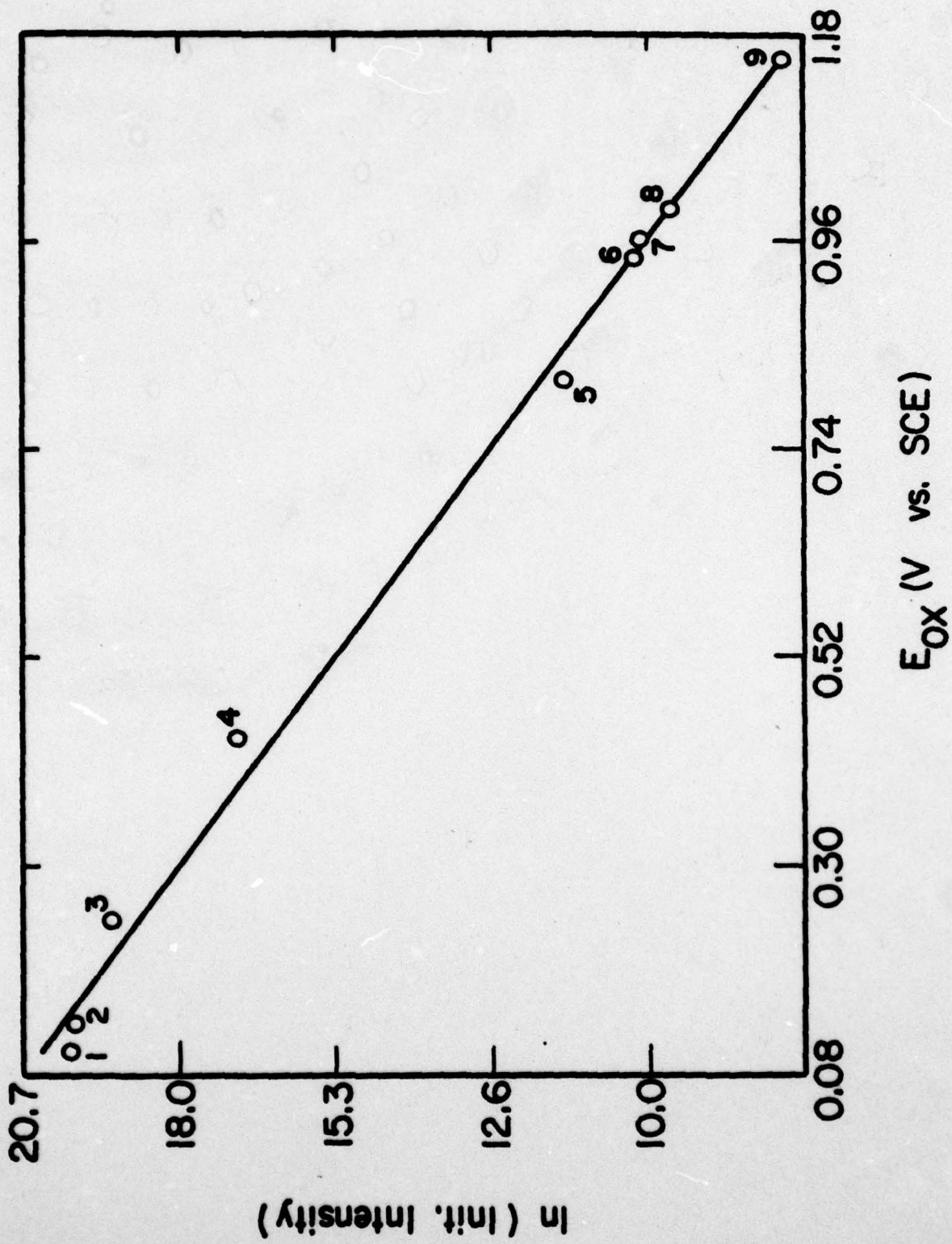


Fig 7







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