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ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY
CHEMILUMINESCENCE OF DIPHENOYL PEROXIDE. PULSED LASER SPECTROPH--ETC(U)
JUL 79 G B SCHUSTER, K A HORN

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6 Chemiluminescence of Diphenoyl Peroxide.
Pulsed Laser Spectrophotometric Detection of
Radical Ion Intermediates on the CIEEL Path.

by

10 Gary B. Schuster and Keith A. Horn

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Abstract

The reactions of diphenoyl peroxide with a series of electronically excited state hydrocarbon reactants was investigated by pulsed laser spectrophotometry. It was found that the primary reaction between the excited state and the peroxide is electron transfer to generate a radical ion pair. The ions were detected by their characteristic absorption spectra. The reaction kinetics were measured and used to verify the generation of radical ion intermediates in the chemically initiated electron-exchange luminescence (CIEEL) mechanism for the chemiluminescence of organic peroxides.

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Sir:

Our investigation of the chemiluminescence of diphenoyl peroxide (DPP) led us to postulate the chemically initiated electron-exchange luminescence (CIEEL) mechanism for that,¹ and later, for numerous other peroxides.² The key feature of the CIEEL mechanism is the rate limiting single electron transfer to peroxide to generate radical ion intermediates from the neutral, ground-state, closed-shell reactants. These ions may undergo further chemical transformations before they finally annihilate to form electronically excited states. The primary evidence for the intermediacy of the radical ions in this sequence has been the correlation of reaction kinetics with the redox properties of the reactants. We report herein the results of our pulsed laser spectrophotometric³ study of the reaction of DPP with several electronically excited electron donors (activators). Pulse excitation enables us to identify the intermediate reaction products by their characteristic absorption spectra and to measure simultaneously the rate of the reaction. These experiments show unambiguously that radical ions are formed in the reaction of DPP with the chemiluminescence activators, and that generation of caged ions precedes the formation of electronically excited products in the chemiluminescence process.

The fluorescence of excited singlet pyrene ($\text{Py}^{\ast 1}$), in acetonitrile solvent, is quenched by DPP which forms eventually benzocoumarin (BC) in 60% yield as the only volatile product detected. When $\text{Py}^{\ast 1}$ is generated by irradiation with a nitrogen laser it is possible to record the absorption spectrum of the transient products that result from its reaction with the peroxide. The spectrum we observe 200 nsec after the excitation of the pyrene, shown in Figure 1, is identical to that which has been attributed previously to pyrene radical cation ($\text{Py}^{\dot{+}}$).⁴ The yield of cage escaped $\text{Py}^{\dot{+}}$ can be determined simply by measuring the optical density of its characteristic absorption after all of the $\text{Py}^{\ast 1}$ has reacted. Comparison of the yield of $\text{Py}^{\dot{+}}$ from the several systems we investigated is particularly revealing.

Weller has shown that the quenching of $\text{Py}^{\ast 1}$ by p-dicyanobenzene (DCB) in acetonitrile occurs by electron transfer from $\text{Py}^{\ast 1}$ to generate $\text{Py}^{\dot{+}}$.⁵ We have

measured the yield of cage escaped $\text{Py}^{\dot{+}}$ in this system to be 67% of the $\text{Py}^{\star 1}$ that reacts with DCB. The remaining 33% of the $\text{Py}^{\star 1}$ must be converted to ground or triplet state pyrene, apparently, by in cage ion annihilation. When phthaloyl peroxide⁶ (PP) reacts with $\text{Py}^{\star 1}$ we have determined that the yield of cage escaped $\text{Py}^{\dot{+}}$ is 48%. However, when DPP is the electron acceptor the yield of escaped $\text{Py}^{\dot{+}}$ is only 5%. It should be noted also that, in comparison to DPP, phthaloyl peroxide is not chemiluminescent.⁷ The CIEEL mechanism provides a convincing explanation for the different behavior of phthaloyl and diphenoyl peroxides.

One electron reduction of DPP by $\text{Py}^{\star 1}$ generates, after oxygen-oxygen bond cleavage, diphenic acid radical anion. Rapid decarboxylation and ring closure of this species produces a powerful reducing agent, benzocoumarin radical anion ($\text{BC}^{\dot{-}}$), presumably within the same solvent cage as $\text{Py}^{\dot{+}}$. The radical ion pair, $\text{Py}^{\dot{+}} \text{BC}^{\dot{-}}$, has several energetically possible reaction channels available. Annihilation within the cage can generate singlet, or triplet, excited pyrene, or pyrene ground state.⁸ In competition with annihilation, diffusion into bulk solution generates the low yield of escaped $\text{Py}^{\dot{+}}$ that we observe. On the other hand, one electron reduction of PP generates phthalate radical anion. The structure of this species precludes its efficient rearrangement to a reducing agent. The cage annihilation reactions that consume the $\text{BC}^{\dot{-}} \text{Py}^{\dot{+}}$ pair from DPP do not occur with PP because electron transfer from phthalate radical anion to $\text{Py}^{\dot{+}}$ is endergonic. As a result, diffusion competes more effectively with in cage reactions and we observe a relatively high yield of escaped $\text{Py}^{\dot{+}}$.⁹ These reactions are summarized in Scheme 1.

Confirmation of the notion that reaction of $\text{Py}^{\star 1}$ with DPP can eventually regenerate $\text{Py}^{\star 1}$ comes from an analysis of the reaction kinetics and from measurement of the reaction quantum efficiency. Pyrene singlet reacts with PP with a diffusion limited rate constant of $1.67 \pm (0.01) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, and consumes peroxide with a quantum efficiency of 0.81 ± 0.05 . In contrast, DPP reacts with $\text{Py}^{\star 1}$ with an apparent rate constant of only $1.02 \pm (0.007) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ but with a quantum efficiency of 1.56 ± 0.15 . These observations can be reconciled

if, as we suggest in Scheme 1, Py^{*1} is, to some extent, regenerated from the cage radical ion pair resulting from its reaction with DPP but not from its reaction with PP. Indeed, the extent of Py^{*1} regeneration calculated from the quenching results is in agreement with the efficiency of Py^{*1} production we have determined for the chemiluminescent reaction of ground state pyrene with DPP. Of course, the $\text{Py}^{\dot{+}} \text{BC}^{\dot{-}}$ radical ion pair should be the same regardless of whether it is formed from ground or excited state pyrene.

Finally, we have established a kinetic link between the chemiluminescence of DPP and its reactions with electronically excited states. According to the CIEEL mechanism, the predictor of the rate constant for reaction between a peroxide and an activator is the one electron oxidation potential of the activator. If this is correct, then the rate constant for reaction of electronically excited, as well as ground state, activators should be predicted equally well by their oxidation potentials. The oxidation potential of Py^{*1} is $-2.00 \text{ V (vs. SCE)}$.¹⁰ Extrapolation of the ground state chemiluminescence data to the oxidation potential of Py^{*1} (Figure 2) predicts a bimolecular rate constant of $1.2 \times 10^{16} \text{ M}^{-1} \text{ s}^{-1}$. Of course, this is much greater than the diffusion limit, and the rate we observe indicates, essentially, a diffusion controlled reaction.

The oxidation potential of triplet anthracene is calculated to be -0.47 V . This activator is expected, therefore, to react with a rate constant slower than the diffusion limit. We have measured the rate of reaction of triplet anthracene with DPP by monitoring the triplet-triplet absorption spectrum following laser excitation. The rate constant for this reaction was found to be $1.44 \pm (0.03) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The excellent correlation of this rate constant with the previously determined ground state activator rate data is shown in Figure 2. This correlation demands that the rate determining step for the ground and excited state reactions of DPP with the various activators is the same, namely, electron transfer from the activator to the peroxide.

In conclusion, this investigation, and our other studies of the CIEEL mechanism, permit a fairly detailed sketch of the reaction coordinate. Electron transfer from the activator (which may be in its ground, or an electronically excited state) occurs, with a rate constant determined by the activator oxidation potential, to generate a pair of oppositely charged radical ions. These ions may diffuse from the solvent cage or they may undergo further rapid chemical transformation. Annihilation of ion pairs which are sufficiently energetic form electronically excited product. We have investigated this sequence of reactions primarily for reagents capable of giving excited products. We suspect, however, that rate limiting electron transfer may underlie the mechanism of many strictly ground state reactions as well. We are continuing to investigate this, and other, aspects of these reactions.

Acknowledgment We thank Mr. James Wehmer for his valuable assistance in the design, construction, and operation of the laser apparatus and Dr. Joseph Zupancic for the preparation of phthaloyl peroxide. This work was supported in part by the Office of Naval Research and in part by the National Science Foundation. The laser apparatus was constructed with funds supplied by NSF.

References and Notes

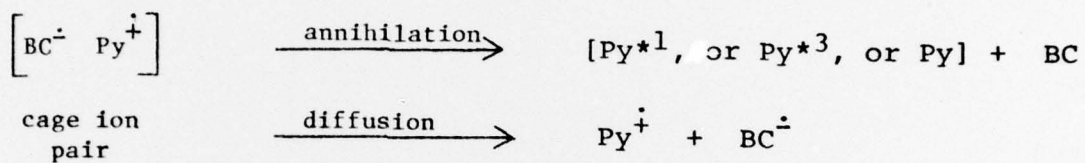
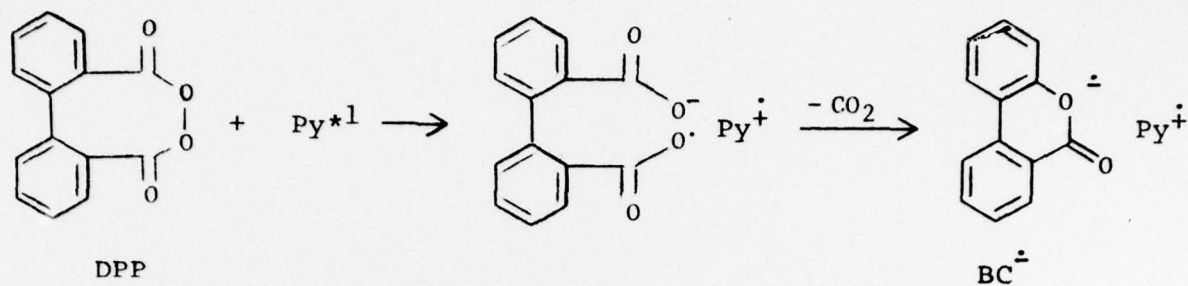
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8. The energy released on annihilation can be estimated by subtracting the reduction potential of the anion from the oxidation potential of the cation and correcting for the coulombic stabilization energy of the ion pair.
9. The chemistry of phthaloyl peroxide with ground and excited state electron donors is the subject of a forthcoming publication from this laboratory.
10. The oxidation potential of an excited state can be estimated by subtracting the excitation energy from the ground state oxidation potential: Rehm, D.;

Weller, A. Isr. J. Chem., 8, 259 (1970). This is strictly true only if the stokes shift is negligible, which can be verified for singlet states but not easily for triplets.

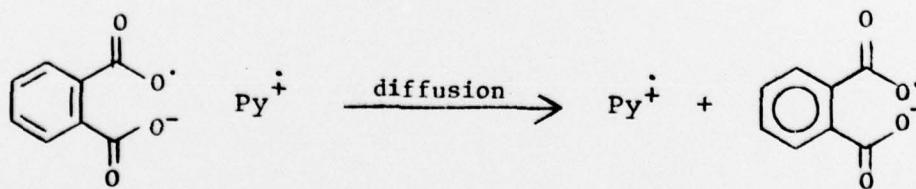
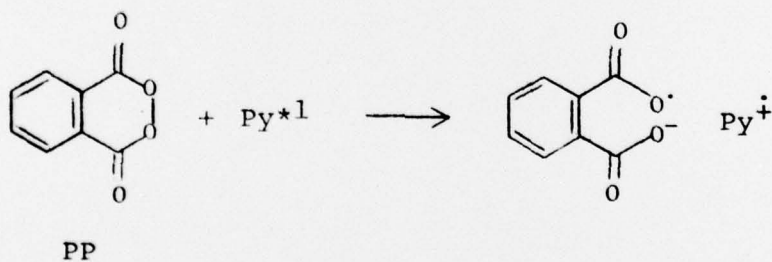
11. Fellow of the Alfred P. Sloan Foundation 1977-79.

Scheme 1

Diphenoyl Peroxide



Phthaloyl Peroxide



Captions for Figures

Figure 1. Absorption spectrum of pyrene radical cation recorded 200 nsec after excitation. The solvent is acetonitrile, pyrene concentration is 3.04×10^{-5} M and DPP concentration is 2.4×10^{-3} M.

Figure 2. Correlation of reaction kinetics for reaction of DPP with ground and excited state activators. The data for the ground state activators come from reference 1b.

Figure 1

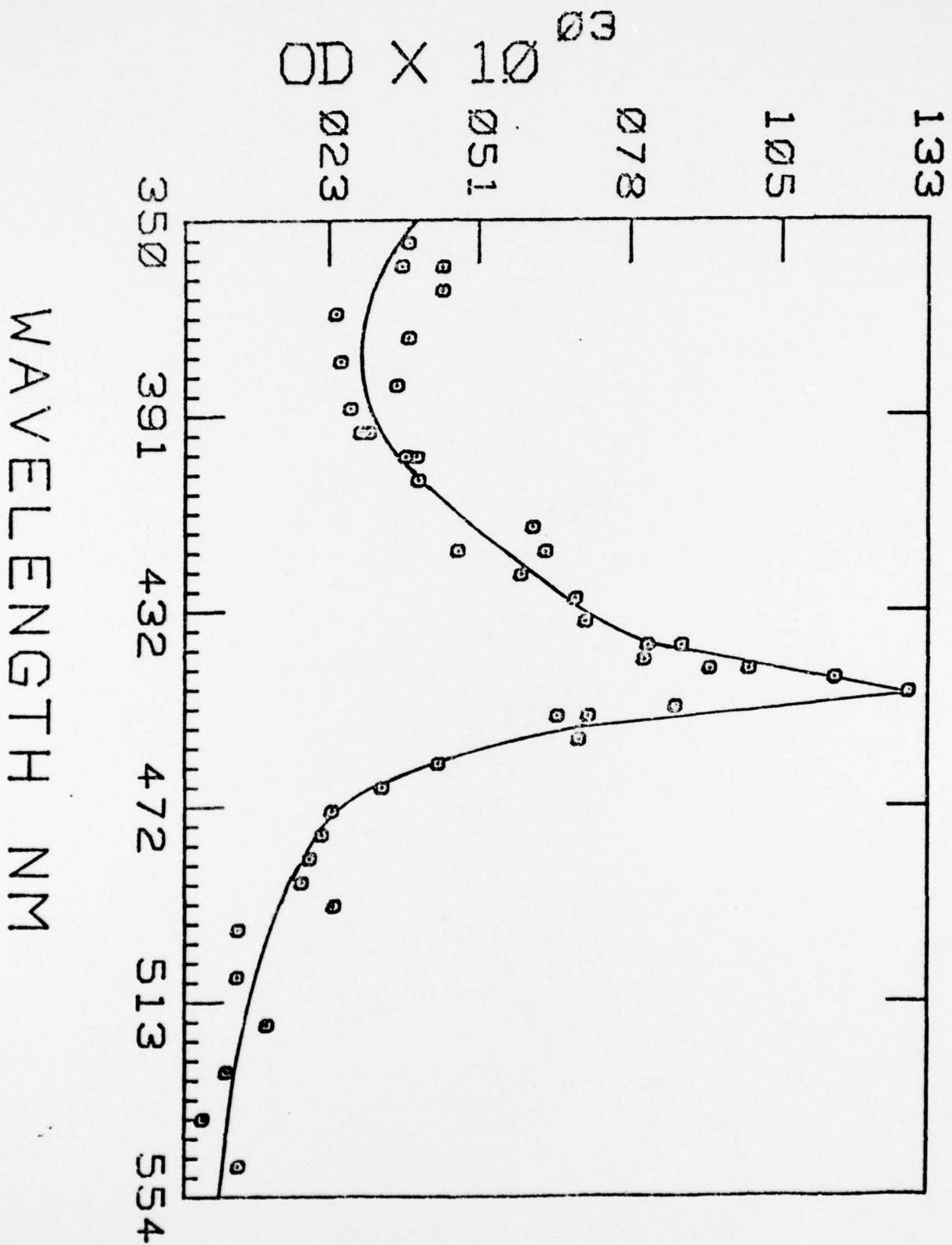
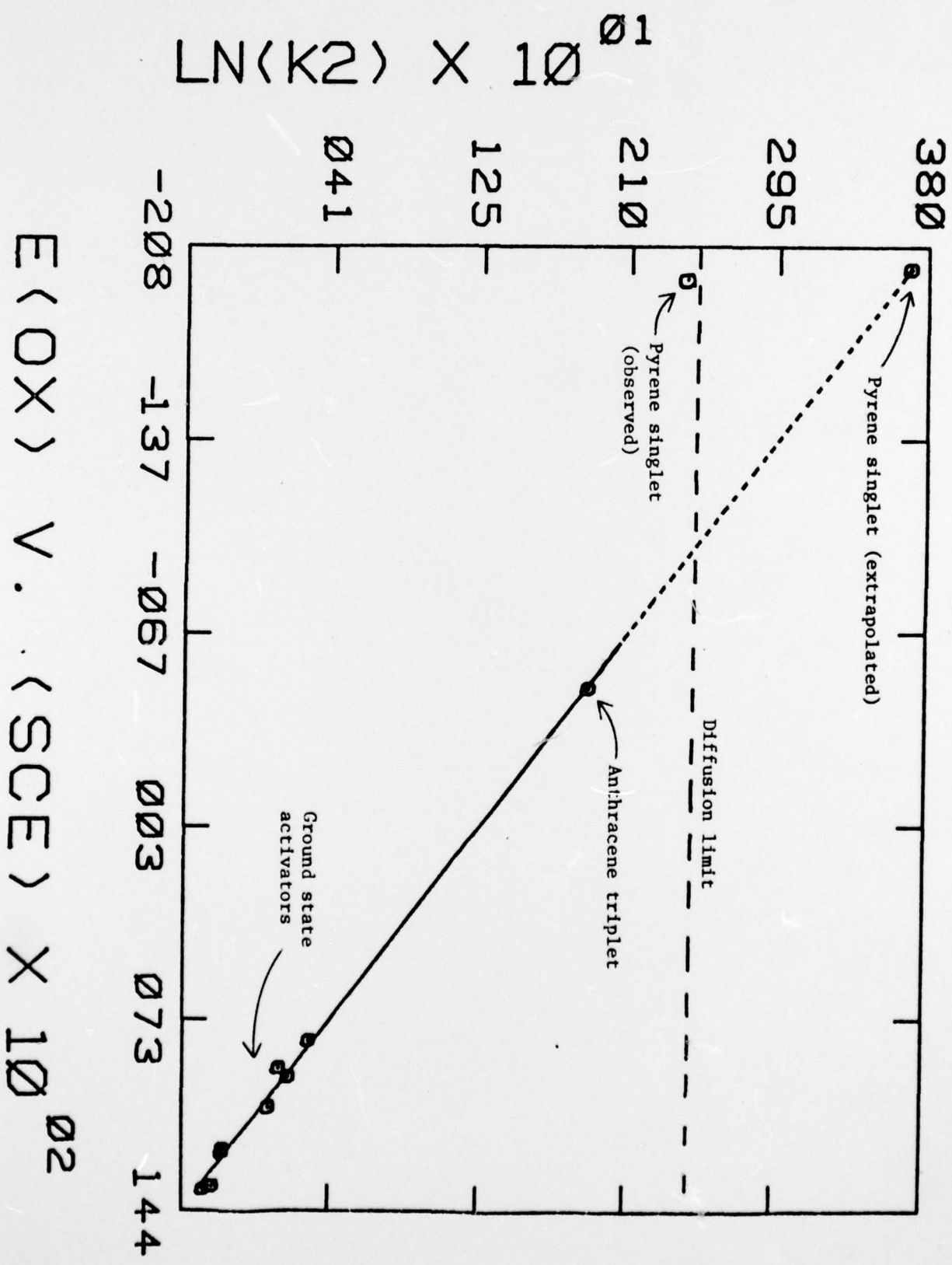


Figure 2



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