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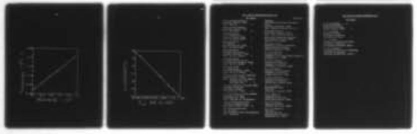

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The chemiluminescence of dimethyldioxetanone (1) in the presence of easily oxidized aromatic hydrocarbons was studied. It was observed that the rate of reaction of 1 depends upon the nature and concentration of the aromatic hydrocarbon. The efficiency of light production was correlated with the one electron oxidation potential of the hydrocarbon. These results are interpreted in terms of the recently described chemically initiated electron exchange luminescence.

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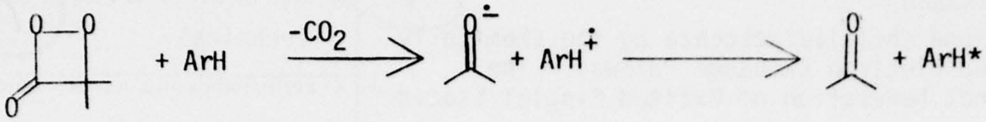

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by

(10) Steven P. Schmidt ~~and~~ Gary B. Schuster

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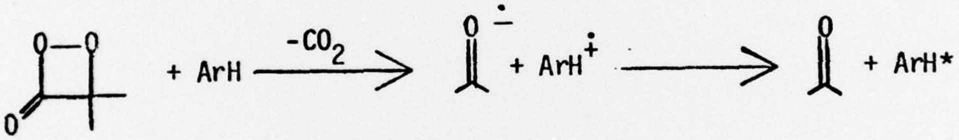
Dioxetanone Chemiluminescence by the Chemically Initiated Electron Exchange Pathway. The Efficient Generation of Excited Singlet States.[1]

Abstract: The chemiluminescence of dimethyldioxetanone (**1**) in the presence of easily oxidized aromatic hydrocarbons was studied. It was observed that the rate of reaction of **1** depends upon the nature and concentration of the aromatic hydrocarbon. The efficiency of light production was correlated with the one electron oxidation potential of the hydrocarbon. These results are interpreted in terms of the recently described chemically initiated electron exchange luminescence.



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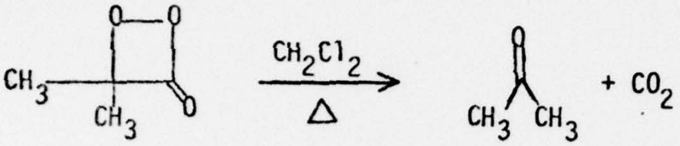
Sir:

Many recent studies of chemiluminescence from organic molecules have centered on the reactions of the strained four membered ring peroxides known as dioxetanes.[2] These molecules have been identified or implicated in many of the most efficient chemi- and bioluminescent reactions. In particular, a carbonyl substituted dioxetane (dioxetanone) has been identified as the key high energy molecule responsible for light production in the firefly.[3] In this paper we report our findings on the mechanism of light production from simply substituted dioxetanones. Our studies show that the most important light forming path for reaction of dioxetanone 1 is the bimolecular route we have recently identified as chemically initiated electron exchange luminescence (CIEEL).[4] Moreover, we have found that under conditions favoring CIEEL the fraction of reacting dioxetanone molecules that generate a photon of light approaches the most efficient bioluminescent reactions known. In addition, by analogy, it appears that the initiating reaction in firefly bioluminescence is an intramolecular electron transfer akin to the observed intermolecular reaction reported herein.[5]

Dimethyldioxetanone (1) was prepared and purified according to the procedure of Adam.[6] Thermolysis of 1 in CH_2Cl_2 at 24.5° leads to the quantitative generation of acetone and to light emission.[7] The observed chemiluminescence under these conditions is a result of acetone emission. It has been reported previously that the addition of certain aromatic hydrocarbons to solutions of dioxetanone 1 results in the generation of hydrocarbon luminescence and markedly increases the light yield.[8] 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 (catalytic chemiluminescence activator), as is shown for rubrene in Figure 1.



(1)

Also, the observed rate acceleration is dependent on the structure of the activator. These findings are inconsistent with the previously proposed unimolecular pathway for excited state production. In the original mechanism, thermal reaction of the dioxetanone generated electronically excited acetone which, in a subsequent step, transferred energy to the hydrocarbon. If this scheme was operative, the rate of reaction of the dioxetanone would be independent of the structure and concentration of the added hydrocarbon. This is contrary to our results.

To probe the nature of the interaction between dimethyldioxetanone (1) and the catalytic chemiluminescence activator, the efficiency of generation of light with various activators was examined. We observed that at identical hydrocarbon concentrations there is nearly a hundred fold range in the ability of the different activators to catalyze excited state formation.[9] This finding indicates that it is the bimolecular reaction between the dioxetanone and the activator that is responsible for the major fraction of the hydrocarbon chemiluminescence. Critically, the only predictor of activator efficiency is the one electron oxidation potential of the hydrocarbon, as is shown in Figure 2. This result is required if electron transfer from the activator to the dioxetanone is the rate determining step for formation of the activator excited singlet state. These findings are entirely consistent with excited state production from dioxetanone 1 by the mechanism we have recently identified as chemically initiated electron exchange luminescence.[4]

The efficiency of production of excited singlet activator by the induced decomposition of 1 was investigated by measuring the absolute chemiluminescence yield.[10] When rubrene was employed as the activator in CH_2Cl_2 solution at 24.5° it was found that 17 ± 5% of the dioxetanone molecules that proceed through the bimolecular path generate an excited rubrene singlet state. Even though this system is unoptimized, the remarkably high efficiency approaches that of the known bioluminescent reactions.[12]

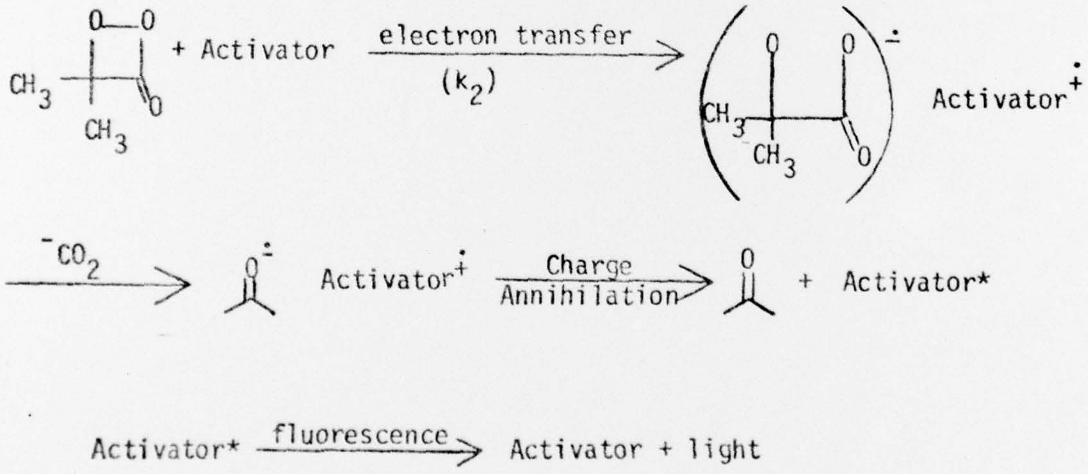
The proposed mechanism for formation of the emitting singlet state of the chemiluminescence activator by the CIEEL path is shown in Scheme 1. The first step is a one electron transfer from the activator to the dioxetanone. The rate of this process, of course, depends upon the activation barrier for the reaction which is determined, in part, by the oxidation potential of the activator. Similiar electron transfer reactions have been postulated, for example, to account for the catalytic induced decomposition of peroxides by transition metals and amines.[13] The activation energy for the electron transfer is also dependent upon the reduction potential of the peroxide. For dioxetanone 1 the bimolecular rate constant for the CIEEL path (k_2) in CH_2Cl_2 at 24.5° with rubrene is $0.44\ \underline{M}^{-1}\ s^{-1}$. This compares to a value of $8\ \underline{M}^{-1}\ s^{-1}$ determined for diphenoyl peroxide under similar conditions.[4] The difference in the catalytic rate constants for these two peroxides is predicted by their reduction potentials.[14] The electron withdrawing carbonyl groups flanking the oxygen-oxygen bond of the diacyl peroxide results in more facile reduction and concomitantly a larger k_2 for diphenoyl peroxide.

The next step along the chemiluminescence path is the rapid loss of CO_2 from the reduced dioxetanone. This generates the radical anion of acetone within the same solvent cage as the radical cation of the activator.[15]

Subsequent charge annihilation of the cage radical ions results in electronically excited state generation.[16] One explanation for the observed 17% singlet yield is that the decarboxylation and charge annihilation are competitive with spin equilibration. Thus, the dioxetanones that react by the CIEEL path, but do not generate an excited singlet activator, may be generating the undetected triplet excited state of the hydrocarbon. The final step in the sequence is light emission from the excited activator, which we detect as chemiluminescence.

In competition with the CIEEL path, uncatalyzed unimolecular decomposition of the dioxetanone generates electronically excited acetone. The combination of these two excitation mechanisms accounts for all of the experimental observations on the chemiluminescence of dioxetanone **1**.

Scheme I



In summary, we have shown that an efficient CIEEL pathway is the major light generating process from dioxetanone **1** with any one of several easily oxidized activators. This is the third example of efficient chemiluminescence by this route.[4,17] We are continuing our investigation of the chemiluminescence of dioxetanones to further establish the details of the mechanism in this case. We are also investigating other chemiluminescent systems that appear to react by the CIEEL path.

Acknowledgment

This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund administered by the American Chemical Society. We wish to thank Mr. William Wokas for the preparation of 9,10-diphenylethynylanthracene.

Steven P. Schmidt and Gary B. Schuster*[18]

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1. These results were presented in part at the 1977 annual meeting of the American Chemical Society, Chicago, Illinois, August 28, 1977.
2. For leading references see: T. Wilson, *Int. Rev. Sci.: Phys. Chem., Ser. Two*, **9**, 265 (1976).
3. E. H. White, J. D. Miano, and M. Umbreit, *J. Am. Chem. Soc.*, **97**, 198 (1975).
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6. W. Adam and O. Cueto, *J. Org. Chem.*, **42**, 38 (1977); W. Adam and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2894 (1972); W. Adam, A. Alzerreca, J.-C. Liu, and F. Yany, *J. Am. Chem. Soc.*, **99**, 5768 (1977).
7. Typical conditions; [**1**] = 10^{-4} *M* in CH_2Cl_2 at 24.5°. Light was detected by the photon counting technique. Spectral resolution was achieved with a Jarrel-Ash 0.25 M monochromator.
8. W. Adam, G. A. Simpson, and F. Yany, *J. Phys. Chem.*, **78**, 2559 (1974).
9. The intensity was determined at 2×10^{-5} *M* in activator in CH_2Cl_2 solution at 24.5° under low resolution conditions so that the emission spectra were Gaussian. The intensities were corrected for photomultiplier tube and monochromator efficiencies according to data supplied by the manufacturers. All solutions contained 20 μl of 5% aqueous Na_4EDTA to suppress metal catalyzed reactions.
10. The yield of light was determined relative to tetramethyldioxetane (TMD) using 9,10-dibromoanthracene as the acceptor. The yield of acetone triplet was taken to be 30%,[11a] the triplet-singlet energy transfer efficiency at 40%,[11b] and the fluorescence quantum yield to be 10%.

11. a) T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976); b) R. Schmidt, H. Kelm, and H.-D. Brauer, *Ber. Bunsenges Phys. Chem.*, **81**, 402 (1977).

12. Firefly bioluminescence is claimed to be 80% efficient; W. D. McElroy, *Fedn. Proc. Fedn. Am. Soc. Exp. Biol.*, **19**, 941 (1960).

13. For example see: J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, 1862 (1965).

14. Peroxyesters typically have reduction potentials of *ca.* -0.9 eV while diacyl peroxides reduce at *ca.* -0.1 eV versus the saturated calomel electrode: L. S. Silbert, L. P. Witnauer, D. Swern, and C. Ricciati, *J. Am. Chem. Soc.*, **81**, 3244 (1959).

15. Air saturated solutions were nearly as efficient as argon purged solutions. Free radical anions should react rapidly with O_2.

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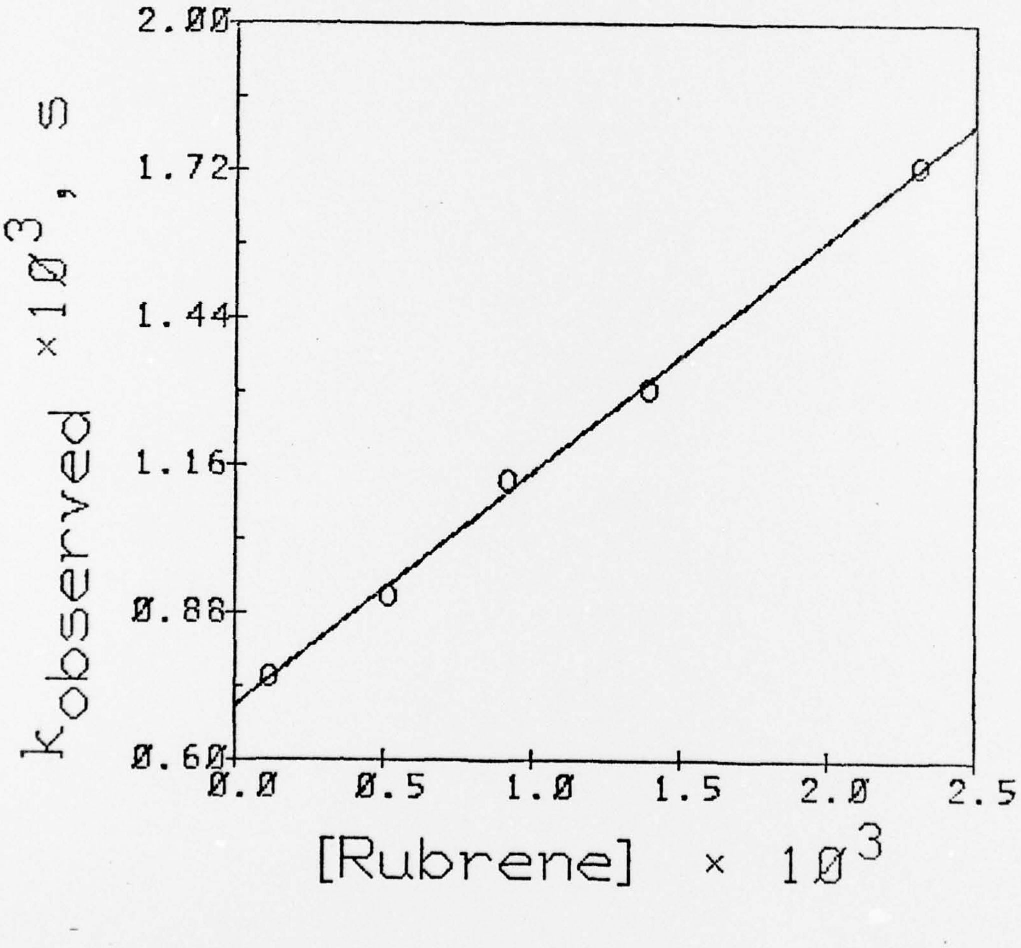
18. Fellow of the Alfred P. Sloan Foundation.

Captions for Figures

Figure 1. Observed dependence of rate of reaction for dioxetanone on the rubrene concentration. Note that the extrapolated zero rubrene concentration rate agrees, within experimental error, to the independently determined value.

Figure 2. Dependence of the chemiluminescence intensity by the CIEEL path on oxidation potential (E_{ox}) of the activator. In order of increasing oxidation potential the points are: rubrene, perylene, 9,10-diphenylethynylanthracene, and 9,10-diphenylanthracene.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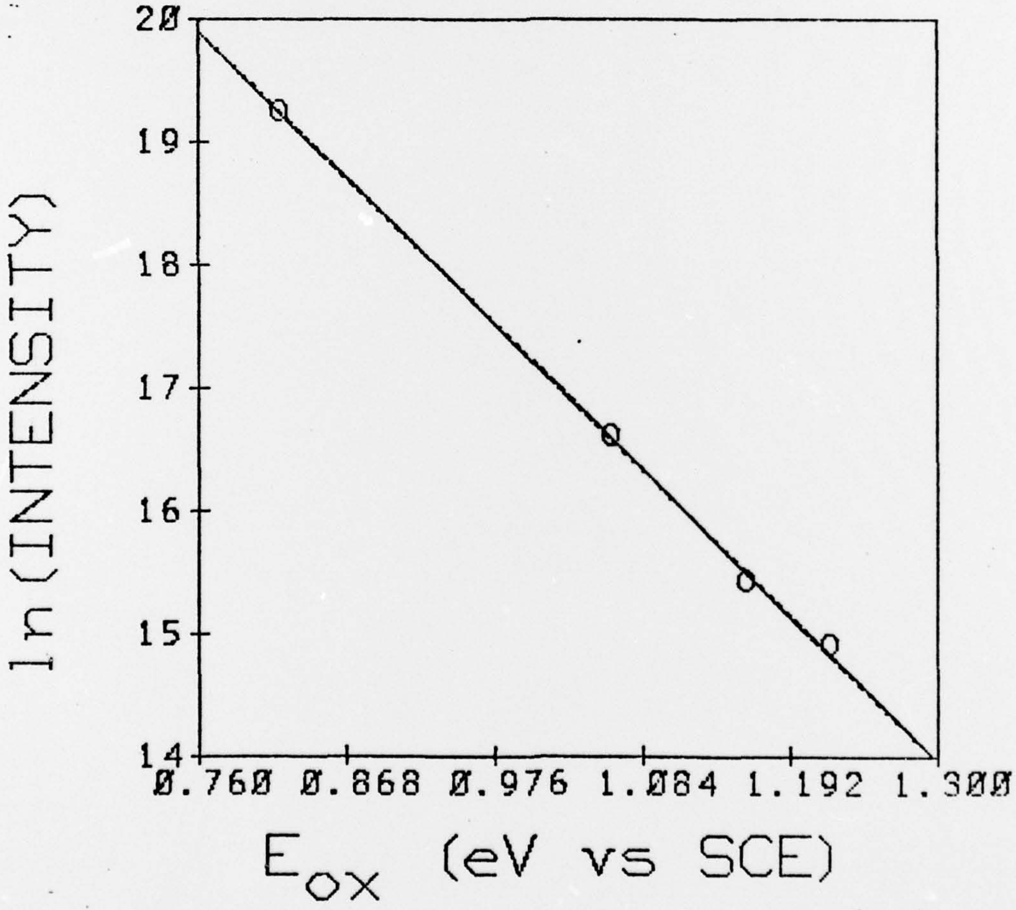
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