Anomalous Metalloporphyrin and Chlorophyll a Activated Chemiluminescence of Dimethyldioxetanone. Chemically Initiated Electron-Exchange Luminescence

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Abstract: A wide range of fluorescent electron donors catalyze the chemiluminescence of dimethyldioxetanone (**1**) by the chemically initiated electron-exchange luminescence (CIEEL) pathway. In general, the magnitude of the catalytic rate constant and the efficacy of excited-state generation correlate well with the one-electron oxidation potential of the donor. Exceptions to this correlation are several zinc and magnesium porphyrins, including chlorophyll a, for which their chemiluminescent catalysis is much greater than predicted by their oxidation potentials. The critical role of the central metal atom in eliciting this unusual behavior was evaluated by determining the catalytic rate constants and the initial chemiluminescence intensitities of several nonmetallated as well as differently metallated porphyrins. These results suggest that formation of a ground-state complex between **1** and certain metalloporphyrins is the cause of the unusual catalysis. This analysis is supported by studies of the inhibition of the anomalous catalysis by the addition of competitive complexing agents. In addition, spectroscopic evidence of a ground-state complex between zinc tetraphenylporphyrin (ZnTPP) and tetramethyldioxetane, a model for **1**, has been obtained.

The chemistry of the dioxetane ring system has been under active investigation for the past decade.[2] In a recent report[3] we described our discovery of the operation of the chemically initiated electron-exchange luminescence (CIEEL) mechanism[4] in the chemiluminescence of dimethyldioxetanone (**1**). The involvement of this mechanism was indicated primarily by the correlation of the excited state generating effectiveness of a wide range of electron donors with the one-electron oxidation potential (E_{ox}) of the donor. In that report we noted that zinc tetraphenylporphyrin (ZnTPP) is an apparent exception to this correlation. The initial chemiluminescent light intensity from ZnTPP is about 100 times greater than is predicted simply from its one-electron oxidation potential. Moreover, the observed rate constant for catalysis of the decomposition of **1** by ZnTPP is much larger than is predicted by its oxidation potential.

Unusual chemiluminescent phenomena have been reported previously for metalloporphyrins. Linschitz observed emission from the thermolysis of tetralin hydroperoxide in the presence of ZnTPP or chlorophyll.[5] He noted that the free-base porphyrin, unlike ZnTPP, has no catalytic effect on the rate of reaction of tetralin hydroperoxide. Moreover, the free-base reaction is not chemiluminescent. More recently, McCapra reported chemiluminescence from the reaction of a variety of peroxides with ZnTPP.[6] Again the metal is an absolute requirement.

In this report we describe our investigation of the interaction of ZnTPP and other metallo- and free-base porphyrins with dioxetanone **1**. The results of this investigation show conclusively for the first time that the unusual behavior of ZnTPP is consistent with the CIEEL mechanism and that this behavior is due to the formation of a ground-state complex between the peroxide and the metalloporphyrin.

Scheme I

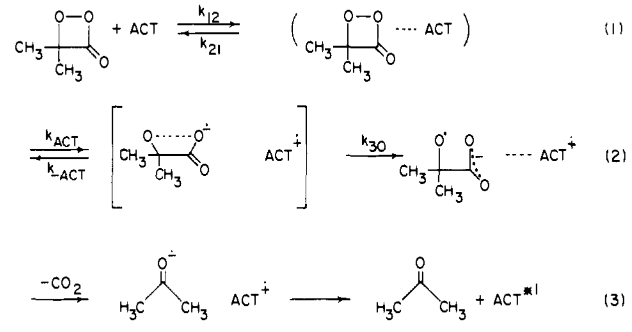

Table I. Oxidation Potentials of Activators and Rate Constants for Their Catalysis of the Reaction of Dioxetanone I

activator	E_{ox},[a] V	k_{CAT},[b] M^{-1} s^{-1}
chlorophyll a	0.52[c]	$(1.5 \pm 0.1) \times 10^3$
MgTAP	0.54	$(2.6 \pm 0.2) \times 10^4$
MgTPP	0.60	$(1.0 \pm 0.1) \times 10^4$
AgTPP	0.59[d,e]	1.1 ± 0.2
CdTPP	0.64[f]	$(2.7 \pm 0.2) \times 10^3$
ZnTAP	0.66[g]	$(1.3 \pm 0.1) \times 10^3$
ZnTPP	0.73	$(7.0 \pm 0.2) \times 10^2$
CoTPP	0.77[d]	$>10^5$ [h]
H_2TAP	0.80[g]	0.67 ± 0.03
rubrene	0.82	0.44 ± 0.02

[a] This work, measured in CH_2Cl_2, unless otherwise noted. For details see Experimental Section. [b] Measured in CH_2Cl_2 solution at 24.5 °C. All errors are standard deviations. [c] A. Standienda, *Naturwissenschaften,* 50, 731 (1963); *Z. Phys. Chem.* (*Leipzig*) 229, 257 (1965). [d] Metal centered oxidation $M^{II}TPP \rightarrow M^{III}TPP$. [e] 0.60 V in pyridine. [f] A. Standienda and G. Biebl, *Z. Phys. Chem.* (*Wiesbaden*), 52, 254 (1967). [g] Reference 7c. [h] Estimated rate constant.

Results and Discussion

In our previous report[3] we concluded that the mechanism for electron donor (activator, ACT) catalyzed chemiluminescence of dioxetanone **1** proceeds by a rate-limiting electron transfer from ACT to the peroxide generating eventually acetone radical anion and ACT radical cation. Annihilation of these oppositely charged radical ions forms the excited state of ACT which we detect by it characteristic luminescence. This mechanism and the appropriate rate constants are shown in Scheme I. Our results[3] indicate that the kinetics of the activator-catalyzed reaction conforms to eq 4, where k_{obsd} is the rate constant for the observed net first-order

$$k_{obsd} = k_1 + k_{CAT}[ACT] \qquad (4)$$

consumption of dioxetanone **1**, k_1 is the rate constant for reaction

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[1] Fellow of the Alfred P. Sloan Foundation, 1977–1979, and the Dreyfus Foundation, 1979–1984.

[2] K. A. Horn, J.-y. Koo, S. P. Schmidt, and G. B. Schuster, *Mol. Photochem.*, **9**, 1 (1978–79). P. D. Bartlett and M. E. Landis in "Singlet Oxygen", H. H. Wasserman and R. W. Murray, Eds., Academic Press, New York, 1979. W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977); T. Wilson, *Int. Rev. Sci.: Phys. Chem., Ser. Two*, **9**, 265 (1976).

[3] S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, **102**, 306 (1980).

[4] (a) G. B. Schuster, *Acc. Chem. Res.*, **12**, 366 (1979). (b) J.-y. Koo and G. Schuster, *J. Am. Chem. Soc.*, **100**, 4496 (1978).

[5] H. Linschitz in "Light and Life", McElroy and Glass, Eds.; Johns Hopkins Press, Baltimore, Md., 1961, p 173.

[6] F. McCapra and P. D. Leeson, *J. Chem. Soc., Chem. Commun.*, 114 (1979).

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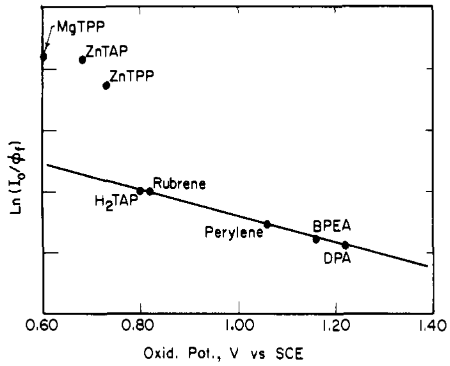


Figure 1. Relationship between the initial chemiluminescence intensity in dichloromethane at 24.5 °C, corrected for fluorescence efficiency (ϕ_f) and photomultiplier tube and monochromator response, and the one-electron oxidation potential of the activator: DPA = 9,10-diphenylanthracene, BPEA = 9,10-bis(phenylethynyl)anthracene.

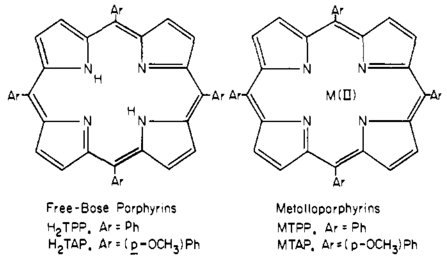
of **1** in the absence of ACT, and k_{CAT} is the rate constant for the bimolecular reaction of **1** and ACT. It is the bimolecular interaction that is primarily responsible for the chemiluminescence.[3]

The ratio of initial chemiluminescence intensity (I_0) to the fluorescence efficiency of ACT (ϕ_f) can be related to the magnitude of k_{CAT} and the initial concentrations of **1** and ACT according to eq 5. Thus under conditions where the concentrations

$$I_0/\phi_f = k_{CAT}[\mathbf{1}]_0[\mathrm{ACT}] \qquad (5)$$

of **1** and ACT are constant during the time required for the experiment, I_0/ϕ_f is directly proportional to k_{CAT}. We have measured I_0/ϕ_f under these conditions for a wide variety of ACT. In general, for amine and aromatic hydrocarbon ACT their E_{ox} accurately predict the magnitude of I_0/ϕ_f. The exceptions to this correlation are some metalloporphyrins (Figure 1). The measured values of k_{CAT} for a variety of ACT are presented in Table I. It should be noted that the exceptionally large values I_0/ϕ_f for the zinc and magnesium porphyrins are consistent with the independently measured values for k_{CAT}.

In order to determine if the unusual catalytic ability of the zinc and magnesium porphyrins is due to the metal ion or to the porphyrin ring system, we investigated the behavior of some free-base porphyrins. In particular, we determined I_0/ϕ_f and k_{CAT} for tetraanisylporphyrin (H_2TAP). As can be seen from Figure 1 and Table I, H_2TAP does not behave unusually. That is, its E_{ox} is a reliable predictor of both I_0/ϕ_f and k_{CAT}. Similarly, tetraphenylporphyrin (H_2TPP) does not appear to catalyze the decomposition of **1** or its chemiluminescence beyond that which would be predicted by its E_{ox}. Evidently, the metal ion plays a crucial role in causing the unusually efficient catalysis by MgTPP and ZnTPP.



Free-Base Porphyrins
H_2TPP, Ar = Ph
H_2TAP, Ar = (p-OCH_3)Ph

Metalloporphyrins
MTPP, Ar = Ph
MTAP, Ar = (p-OCH_3)Ph

To probe further the mechanism of this metal ion dependent catalysis, we examined the effect of changing the metal ion on I_0/ϕ_f and k_{CAT} for tetraphenyl- and tetraanisylporphyrins. Cyclic voltammetric measurements have revealed that for zinc, cadmium, and magnesium porphyrins the first oxidation is ligand centered.[7] On the other hand, for silver and cobalt porphyrins the first oxidation is metal centered.[7,8] Interestingly, zinc, cadmium, cobalt, and magnesium porphyrins (including chlorophyll a) exhibit the unusually effective catalysis, but AgTPP does not. The magnitude of k_{CAT} for AgTPP is simply predicted by its E_{ox} (Table I). Evidently, the identity of the metal ion matters greatly for the catalysis. Compare, for example, AgTPP (E_{ox} = 0.59 V vs. SCE) which exhibits a k_{CAT} of 1.1 $M^{-1}\,s^{-1}$ and MgTPP (E_{ox} = 0.60 V vs. SCE) whose k_{CAT} is nearly 10 000 times larger. But, the catalysis can occur with metalloporphyrins that undergo either metal- or ligand-centered oxidation. Apparently, it is some feature other than the site of oxidation of the metalloporphyrin that engenders the remarkable chemiluminescent catalysis.

It is quite well-known that certain metalloporphyrins form stable complexes with nitrogen bases such as pyridine.[9] Moreover, it is known that free-base porphyrins do not form these complexes.[10] Recently the results of a thermodynamic study of the complex formation of ZnTPP with several neutral donors were reported.[11] In this study the equilibrium constant for the complex was estimated by following the shift of the maximum of the porphyrin Soret absorption band as a function of the concentration of added donor. For metalloporphyrins it has been observed that the maximum of the Soret band shifts to longer wavelengths upon complex formation. For simple ester donors the limiting shift in cyclohexane solution is observed to be ca. 5 nm, and for alkyl ethers it is observed to be ca. 6 nm. We investigated the possibility that the formation of a ground-state complex between dioxetanone **1** and certain metalloporphyrins is the cause of the unusual catalysis.

Addition of ZnTPP or MgTPP to cyclohexane solutions of dioxetanone **1** causes such a rapid reaction that it is difficult for us to measure the absorption spectrum of the mixture before most of the peroxide has reacted. Also, acetone, which is inevitably present in dioxetanone solutions, is known[11] to coordinate to ZnTPP and shift its Soret band. Finally, since it has not been possible to prepare dioxetanone as other than a rather dilute solution, the concentration typically needed to obtain a measurable shift in the Soret band is not readily achieved. To circumvent these problems, we used tetramethyldioxetane (**2**) as a model for **1**. The reactions of **2** are not particularly sensitive to metalloporphyrin catalysis, presumably because its reduction potential is far more negative than that of **1**. In cyclohexane solution the maximum of the Soret band for ZnTPP is at 416.0 nm. In the presence of 0.35 M **2** this maximum shifts to 417.2 nm. A similar result is obtained with MgTPP. Interestingly, AgTPP, which does not readily expand its coordination sphere[12] and for which no special catalysis is observed, does not give evidence of complex formation with dioxetane **2**. This is in line with out observation that even pyridine does not shift the absorption maximum or oxidation potential of this metalloporphyrin. Evidently the ability of the metalloporphyrin to form detectable complexes with dioxetane **2** and other donors predicts reliably the unusual catalytic behavior.

The magnitude of k_{CAT} is related to several of the rate constants specified in Scheme I. Our previously reported[3] data indicate that $k_{30} \gg k_{-ACT}$. Thus simple analysis of the kinetics shows that

$$k_{CAT} = K_{12}k_{ACT} \qquad (6)$$

where K_{12} (k_{12}/k_{21}) is the equilibrium constant for complex formation.[13] For the amine and aromatic hydrocarbon activators K_{12} is evidently independent of the structure of ACT and probably depends, as in the Weller model,[14] only on diffusion. However,

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(7) (a) D. G. Davis, *Porphyrins*, **5**, Chapter 4 (1978); (b) R. H. Felton, *ibid.*, **5**, Chapter 3 (1978); (c) A. Wolberg, *Isr. J. Chem.*, **12**, 1031 (1974).

(8) (a) A. Antipas, D. Dolphin, M. Gouterman, and E. C. Johnson, *J. Am. Chem. Soc.*, **100**, 7705 (1978); (b) F. A. Walker, D. Beroiz, and K. M. Kadish, *ibid.*, **98**, 3484 (1976); (c) L. A. Truxillo and D. G. Davis, *Anal. Chem.*, **47**, 2260 (1975); (d) J. Manassen, *Isr. J. Chem.*, **12**, 1059 (1974). (e) K. M. Kadish and L. A. Bottomley, *Inorg. Chem.*, **19**, 832 (1980).

(9) (a) P. Hambright, *Coord. Chem. Rev.*, **6**, 247 (1971); (b) C. B. Storm, A. H. Corwin, R. R. Arellano, M. Martz, and R. Weintraub, *J. Am. Chem. Soc.*, **88**, 2525 (1966); (c) C. H. Kirksey, P. Hambright, and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969); (d) C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

(10) J. R. Miller and G. D. Dorough, *J. Am. Chem. Soc.*, **74**, 3977 (1952).

(11) G. C. Vogel and J. R. Stahlbush, *Inorg. Chem.*, **16**, 950 (1977).

(12) The equilibrium constant for pyridine complexation of MgTPP is at least 4 × 10^4 times greater than that for AgTPP.[10]

(13) G. B. Schuster, *J. Am. Chem. Soc.*, **101**, 5851 (1979).

Table II. Effect of Diethyl Ether on the Rate Constant and the Initial Chemiluminescence Intensity of the MgTPP-Catalyzed Reaction of Dioxetanone 1 in CH_2Cl_2 at 24.5 °C

$[Et_2O]$, M	$10^2 k_{obsd}$,^{a} s^{-1}	I_0^{a,b}
0	1.53 ± 0.03	46 ± 8
0.2	0.31 ± 0.03	4.6 ± 0.8
0.5	0.19 ± 0.02	2.0 ± 0.1
1.0	0.16 ± 0.01	1.0 ± 0.1

[a] The MgTPP concentration was 1.6×10^{-6} M. Errors are standard deviations of several determinations. [b] Relative initial chemiluminescence intensity in arbitrary units. The fluorescence efficiency of MgTPP was not measurably affected by Et_2O at these concentrations.

ZnTPP, MgTPP, CoTPP, CdTPP, etc. form ground-state complexes with peroxide **1** and the magnitude of k_{CAT} is therefore the product of K_{12} for the complex and k_{ACT}. Indeed, if we assume that complexation does not affect k_{ACT}, then we can estimate the magnitude of K_{12} from the measured value of k_{CAT} and an interpolated (from the E_{ox} vs. I_0/ϕ_f plot) value for k_{ACT}. The K_{12} of ZnTPP is thereby estimated to be 100 M^{-1}, a value consistent with equilibrium constants reported by others for complexes of metalloporphyrins with various oxygen donors.[11]

The anomalous metalloporphyrin catalysis of the reaction of **1** may be inhibited by the addition of donor molecules capble of competitive complexation, thus confirming the involvement of the ground-state complex with **1** on the catalytic chemiluminescence pathway. Data for the inhibition of the MgTPP catalysis by diethyl ether are summarized in Table II. Two related effects are to be noted. First, the observed rate constant for reaction of **1** is decreased markedly by the addition of ether and is decreased further as the ether concentration is increased. Since the rate constant k_1 for the reaction of **1** in the absence of activator is not appreciably affected by ether at these concentrations and since the bimolecular path predominates at this MgTPP concentration, clearly it is the bimolecular component, k_{CAT}[ACT], which is being affected by ether. Second, the initial chemiluminescence intensity is decreased markedly by the addition of ether and likewise is decreased further as the ether concentration is increased. These two effects are internally consistent as predicted by eq 5. Similar results are obtained with pyridine. The competitive inhibition of MgTPP catalysis by pyridine is more dramatic than that by diethyl ether, however. Only approximately 2×10^{-4} M pyridine is required to achieve an effect similar to that of 0.2 M diethyl ether.

This inhibition of catalysis apparently derives from complexation of the diethyl ether or pyridine to MgTPP. Pyridinate complexes of MgTPP have been extensively investigated[9b,d] and are known to be quite stable. Thermodynamic studies[11] have shown that equilibrium constants for complex formation of metalloporphyrins with neutral oxygen donors such as diethyl ether are several orders of magnitude smaller than those of nitrogen bases; this relative stability is reflected in the markedly different concentrations of added donor required to achieve similar effects. Importantly, the addition of 0.2 M diethyl ether had no measurable effect on the initial chemiluminescence intensity with H_2TAP. Since the nonmetallated porphyrin does not form a complex with donor molecules,[10] this confirms the involvement of an ether–MgTPP or pyridine–MgTPP complex in the catalysis inhibition. Thus, when the MgTPP coordination site is occupied by diethyl ether or pyridine, the metalloporphyrin is not nearly as effective a catalyst of dioxetanone chemiluminescence.

The potential of the first oxidation of certain metalloporphyrins such as CoTPP or FeTPP for which the lowest oxidation is metal centered and which form stable complexes is lowered by the addition of bases such as pyridine.[8b,c,e] In general, the oxidation potentials of metalloporphyrins which have ligand-centered first oxidations such as ZnTPP or MgTPP are much less affected by added base.[8d] We have determined experimentally that the oxidation potential of MgTPP in CH_2Cl_2 is shifted positive 70 mV by the addition of 1.0 M of Et_2O. This change in oxidation potential should cause only a slight change in k_{CAT} and I_0/ϕ_f; compare, for example, MgTAP and MgTPP (Table I) which differ in E_{ox} by 60 mV. We conclude that the 45-fold inhibition by 1.0 M ether of the catalytic chemiluminescence is a result of competitive complexation of the metalloporphyrin. The added donor competes with **1** for the formation of the weak ground-state complex, thereby inhibiting the otherwise effective catalysis.

The electron-transfer reactions of chlorophyll a (Chl a) continue to be of general interest due to their intimate involvement in the initiating steps of photosynthesis. In connection with their study of the electrochemistry of Chl a, Saji and Bard reported their observation of the electrogenerated chemiluminescence of Chl a in the presence of oxygen.[15] In our system Chl a behaves much like the synthetic magnesium and zinc porphyrins in eliciting efficient chemiluminescence from **1** by the electron-exchange pathway. The magnitude of the Chl a catalytic rate constant is comparable to that of magnesium tetraphenylporphyrins (Table I), suggesting that ground-state complex formation with peroxide **1** is important for Chl a as well. It is likely therefore that other Chl a–peroxide systems might also be chemiluminescent, the result of an analogous complexation–electron-transfer sequence. As noted by others,[15] for example, weak chemiluminescence has been observed from the reaction of O_2 with photoreduced chlorophyll.[16]

While the magnesium and zinc porphyrins are among the most effective activators of chemiluminescence for **1** which we have found, they are quite ineffective in catalyzing chemiluminescence with diphenoyl peroxide (DPP). This might be surprising initially in light of the established involvement of the CIEEL pathway for the chemiluminescence of DPP in the presence of aromatic hydrocarbons.[4] In fact, bimolecular rate constants for the catalyzed decomposition of DPP are generally several orders of magnitude larger than for **1** under comparable conditions, a consequence of the more facile reduction of DPP and diacyl peroxides in general than that of **1** and peroxyesters in general.[3] The metalloporphyrin, however, is consumed in the reaction with DPP. We suspect, therefore, that two-electron reduction of DPP is occurring. The second oxidation potentials of these metalloporphyrins are relatively low,[7] in comparison to those of the typical aromatic hydrocarbons which catalyze light formation with DPP. The aroyloxy radical intermediate produced from the one-electron reduction and O–O bond cleavage of DPP is more easily reduced than the alkoxy radial derived from the one-electron reduction and O–O bond cleavage of **1**.[17] Relative rates of decarboxylation may also contribute to the different behavior of **1** and DPP. In any event, further reduction of DPP radical anion effectively removes this species from the light-generating path.

Finally, we would like to point out the remarkable sensitivity of the metalloporophyrin activated chemiluminescence as an analytical technique. The unusually large values of k_{CAT} for the complex forming metalloporphyrins and the emissive properties of ZnTPP and MgTPP conspire to make possible the detection of incredibly small amounts of the metal ions. For example, we have been able to detect unambiguougly ca. 1 ppb zinc in solutions of PdTPP and ZnTPP by using dioxetanone **1**.

Conclusion

The chemical reactions of dimethyldioxetanone with a variety of fluorescent electron donors have revealed new features of the CIEEL mechanism. In this report we have described our detection of a ground-state complex between this peroxide and several metalloporphyrins. The complex evidently involves an interaction between the metal ion and the peroxide. In all of the cases, and only in those cases, for which complex formation is detected we observe an increase in both I_0/ϕ_f and k_{CAT}. This finding indicates that the complex is on the reaction path leading to eventual light generation. This remarkably enhanced chemiluminescence catalysis should prove valuable in the detection of trace quantities of these metal ions and in increasing the yield of light when the

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(14) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

(15) T. Saji and A. J. Bard, *J. Am. Chem. Soc.*, **99**, 2235 (1977).

(16) F. F. Litvin, J. A. Vladimirov, and A. A. Kransnovskii, *Usp. Fiz. Nauk*, **71**, 149 (1960).

(17) L. Eberson, *Acta. Chem. Scand.*, **17**, 2004 (1963).

CIEEL path is in competition with a rapid unimolecular decomposition of the key chemiluminescent intermediate.

Experimental Section

General Data. All chemiluminescence measurements were made by the photon-counting technique as previously described.[3] Photoexcited fluorescence spectra were obtained on a Farrand Mark V spectrofluorometer or by photon counting for direct comparison with chemiluminescence emission spectra. UV–VIS absorption spectra were recorded on a Beckman Acta MVI or Cary 14 instrument. Solvents used in the chemiluminescence experiments were purified as previously described.[3]

Cyclic Voltammetry. Cyclic voltammetry was done in argon saturated dichloromethane solution at 23 ± 2 °C with 0.1 M tetra-*m*-butylammonium perchlorate as supporting electrolyte. A three-electrode system, consisting of a platinum working electrode, a counterelectrode, and saturated calomel reference electrode (SCE), was used. Scans were made typically at 0.5 V/s. The E_{ox} values were measured as that potential lying midway between the oxidation and reduction peaks for a given couple.

Peroxides. Dimethyldioxetanone,[3,18] tetramethyldioxetane,[19] and phenoyl peroxide[4b] were prepared and purified as described elsewhere.

Porphyrins. The porphyrin free-bases H_2TPP and H_2TAP were kindly provided by Professor Larry Faulkner. PdTPP was a gift from Professor David Whitten. They were purified by treatment with dichlorodicyanobenzoquinone (DDQ) in refluxing chloroform, as described by Barnett et al.[20] The porphyrins were shown to be chlorin free by visible absorption spectroscopy.[21]

ZnTPP (Sigma) was also purified by treatment with DDQ.

Other metalloporphyrins were prepared by reaction of the appropriate divalent metal salt with the porphyrin free base in refluxing dimethylformamide according to the general procedure of Adler et al.[22] The magnesium porphyrins and CdTPP were recrystallized from benzene–hexane. ZnTAP was purified by dry column chromatography on Al_2O_3, eluting with chloroform, followed by several recrystallizations from chloroform–methanol. CoTPP and AgTPP were purified by dry column chromatography on Florisil, eluting with chloroform, followed by recrystallization from chloroform–methanol.

All porphyrins gave satisfactory elemental analyses and had visible absorption spectra consistent with literature data.[21,23]

Chlorophyll a (Sigma) was used as received.

Acknowledgment. This research was supported by the Office of Naval Research and the National Science Foundation. S.P.S. is a University of Illinois Fellow, 1976–1980.

Supplementary Material Available: Listings of observed rate constants for the porphyrin-catalyzed reaction of **1** (Table III), representative plots of the first-order decay of the chemiluminescence intensity for this reaction (Figure 2), and plots of the effect of activator identity and activator concentration on the observed first-order rate constants (Figure 3) (12 pages). Ordering information is given on any current masthead page.

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(18) W. Adam and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2894 (1972); W. Adam, A. Alzerreca, J.-C. Liu, and F. Yany, *ibid.*, **99**, 5768 (1977).

(19) K. R. Kopecky, J. E. Filby, C. Mumford, P. A. Lockwood, and J.-Y. Ding, *Can. J. Chem.*, **53**, 1103 (1975).

(20) G. H. Barnett, M. F. Hudson, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1401** (1975).

(21) G. M. Badger, R. A. Jones, and R. L. Laslett, *Aust. J. Chem.*, **17**, 1028 (1964).

(22) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

(23) G. D. Dorough, J. R. Miller, and F. M. Huenneckens, *J. Am. Chem. Soc.*, **73**, 4315 (1951).

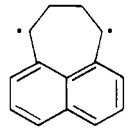
Communications to the Editor

Photolytic Generation of a 1,8-Naphthoquinodimethane Biradical. Time-Resolved and Polarization Electron Spin Resonance Studies

Sir:

The study of biradicals has been quite extensive in the last few years, owing to their real or imagined intermediacy in a large number of thermal and photochemical processes. A wide variety of chemical and physical techniques have been used to characterize the biradicals themselves and the modes of their formation and decay, but despite its obvious suitability time-resolved electron paramagnetic resonance (EPR) has hardly been exploited. To our knowledge, only one study has thus far been reported. Doetschman[1] determined, by a spin-echo method, the initial populations of the spin eigenstates of diphenylmethylene following its formation by photolysis of diphenyldiazomethane in a single-crystal host at 1.2 K.

We report here a study by continuous monitoring of the EPR response at short-time resolution (less than 0.1 μs) of the formation of **1** by photolysis of **2**.[2] In addition, we report the magnetic and optical anisotropy of **1** when it is produced in rigid media by photolysis with plane-polarized light.[3]



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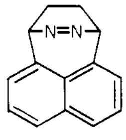

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The experiments on transient magnetization were performed at 77 K in hexafluorobenzene, octafluorotoluene, or 2-methyltetrahydrofuran. The results are independent of the solvent. Photolysis was accomplished by pulsed irradiation from a nitrogen laser (λ = 337 nm, pulse energy <1 mJ, pulse duration ~6 ns). The experimental methods for detection of the pulses of magnetization have been described.[4] The continuous wave (CW) EPR spectrum of **1** is characteristic of a triplet molecule with axial symmetry of the distribution of the interspin vector ($|D| = 0.018$ cm^{-1}, $|E| < 0.003$ cm^{-1}). Maximum transient magnetization is observed at the positions of the XY peaks (static field perpendicular to symmetry axis). The initial magnetization of the low-field XY peak is absorptive and that of the high-field XY peak emissive[5] (Figure 1). The rise time of the magnetization is of the order of 0.1 μs and that of the decay time on the order of 5 μs.[6]

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(1) Doetschman, D. C.; Botter, B. J.; Schmidt, J.; Van Der Waals, J. H. *Chem. Phys. Lett.* **1976**, *38*, 1. Doetschman, D. C. *J. Phys. Chem.* **1976**, *80*, 2167.

(2) For earlier work on **1**, see: Gisin, M.; Rommel, E.; Wirz, J.; Burnet, M.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216, and references cited therein.

(3) Optical dichroism has been noted previously. See ref 2.

(4) Kim, S. S.; Weissman, S. I. *Rev. Chem. Intermed.* **1979**, *3*, 107–120.

(5) The observation of enhanced magnetization in **1** is related to the intersystem crossing (isc) step. The three mechanisms, $^{1}2^{*} \xrightarrow{\text{isc}} {}^{3}\mathbf{1} + N_2$; $^{1}2^{*} \xrightarrow{\text{isc}} {}^{3}2 \rightarrow {}^{3}1 + N_2$; and $^{1}2^{*} \rightarrow N_2 + {}^{1}\mathbf{1} \xrightarrow{\text{isc}} {}^{3}1$, seem reasonable for the formation of triplet **1** (^{3}**1**). Trapping experiments with O_2 demonstrate that the last mechanism does not operate: Pagni, R. M.; Burnett, M. N., unpublished results. Nothing is known at present about the viability of the other two mechanisms.

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