actions from iron and chromium porphyrins to olefins.[17] OMo(TPP)X complexes represent the first example of metalloporphyrins able to catalyze selective and specific oxidation of olefins by peroxy-bond heterolysis. With other transition metals like iron or cobalt, free radical chain processes are observed for the oxidation of olefins,[17,18] giving only extremely low selectivity to epoxide,[19] or the hydroxylation of saturated hydrocarbons.[20] This oxomolybdenum porphyrin–*tert*-butyl hydroperoxide system may be considered as a simple chemical model for activation of hydroperoxides by cytochrome P-450 dependent monooxygenases.[21] These fascinating enzymes, involved in the biological oxidation of hydrocarbons and olefins according to the following equation

$$S + O_2 + 2H^+ + 2e^- \rightarrow SO + H_2O$$

contain an iron porphyrin in their active center. Until recently only speculative mechanisms have been proposed for the crucial step of oxygen activation and transfer to the substrate. The discovery that organic hydroperoxides, in the absence of both the reducing agent and molecular oxygen, were able to generate oxidizing species of close reactivity[22] required new simple chemical models. Until now, successful analogues of these unprecedented reactions have been only achieved by using iodosylbenzene as the oxidizing agent.[17,23]

In conclusion, the catalytic activity of molybdenum porphyrins strongly supports the mechanism of olefin epoxidation proposed by Sheldon[2a] and Sharpless:[2b] direct attack of the olefin on the electrophilic oxygen of the activated hydroperoxide, without requiring coordination to the metal center. This metalloporphyrin-catalyzed peroxy-bond heterolysis is the first example of a simple chemical model for hydroperoxide-supported oxidation of a substrate by cytochrome P-450. Mechanistic studies and scope of the synthetic applications of this reaction, as well as further characterization of the species observed in the presence of *t*-BuOOH, are in progress.

Acknowledgment. We thank Dr. I. Tkatchenko and Dr. K. B. Sharpless for extremely valuable suggestions and comments, Dr. M. Bonnet for experimental advice, the Société Chalonnaise de Peroxydes Organiques for a generous gift of alkyl hydroperoxide samples, and the Centre National de la Recherche Scientifique for financial support.

---

(17) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033. Groves, J. T.; Kruper, W. T. *Ibid.* **1979**, *101*, 7613–7615. Groves, J. T.; Kruper, W. T.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169–177.

(18) Ohkatsu, Y.; Tsutura, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 188–191. Fuhrhop, J.-H.; Baccouche, M.; Grabow, H.; Arzoumanian, H. *J. Mol. Catal.* **1980**, *7*, 245–256. Fuhrhop, J.-H.; Baccouche, M.; Penzlin, G. J. *J. Mol. Catal.* **1980**, *7*, 257–266.

(19) Paulson, D. R.; Ullman, R.; Sloane, R. B. *J. Chem. Soc., Chem. Commun.* **1974**, 186–187.

(20) Mansuy, D.; Bartoli, J. F.; Chottard, J.-C.; Lange, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 909–910.

(21) For recent reviews, see: (a) Hayaishi, O. "Mechanisms of Molecular Oxygen Activation"; Academic Press: New York, 1974. (b) Griffin, B. W.; Peterson, J. A.; Werringloer, J.; Estabrook, R. W. *Ann. N. Y. Acad. Sci.* **1975**, *244*, 107–131. (c) Gunsalus, I. C.; Pederson, T. C.; Sligar, S. G. *Annu. Rev. Biochem.* **1975**, *44*, 377–407. (d) Debrunner, P. G.; Gunsalus, I. C.; Sligar, S. G.; Wagner, G. C. in *Met. Ions Biol. Syst.* **1976**, *7*, Chapter 6. (e) Lu, A. Y. H. *Fed. Proc. Fed. Am. Soc. Exp. Biol.* **1976**, *35*, 2460–2463. (f) Cooper, Y.; Rosenthal, O.; Snyder, R.; Witmer, C. "Cytochromes P_{450} and b_5"; Plenum Press: New York, 1977. (g) Jerina, D. M. *ACS Symp. Ser.* **1977**, *No. 44*. (h) Ullrich, V. *Top. Curr. Chem.* **1979**, *83*, 67–104. (i) Groves, J. T. "Advances in Inorganic Biochemistry"; Eichhorn, G. L.; Marzilli, C. G., Eds.; Elsevier North Holland: Amsterdam, 1979; Vol. 1, Chapter 4. (j) "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1980.

(22) Kadlubar, F. F.; Morton, K. C.; Ziegler, D. M. *Biochem. Biophys. Res. Commun.* **1973**, *54*, 1255–1261. Rahimtula, A. D.; O'Brien, P. J. *Ibid.* **1974**, *60*, 440–47; **1975**, *62*, 268–275. Ellin, A.; Orrenius, S. *FEBS Lett.* **1975**, *50*, 378–381. Hrycay, E. G.; Gustafsson, J. A.; Ingelman-Sundberg, M.; Ernster, L. *Eur. J. Biochem.* **1976**, *61*, 43–52 and references therein. Nordblom, G. D.; White, R. E.; Coon, M. J. *Arch. Biochem. Biophys.* **1976**, *175*, 524–533. Akhrem, A. A.; Usanov, S. A.; Dvornikov, S. S.; Metelisa, D. I. *React. Kinet. Catal. Lett.* **1977**, *6*, 187–194. Capdevila, J.; Estabrook, R. W.; Prough, R. A. *Arch. Biochem. Biophys.* **1980**, *200*, 186–195.

(23) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413–3415.

Electron Spin Resonance and Electron Spin Echo Studies of Photoproduced Tetramethylbenzidine Cation Radical in Frozen Aqueous Micellar Solutions: Cation Surroundings and Retention of Micellar Structure in Frozen Solutions

P. A. Narayana, A. S. W. Li, and Larry Kevan*

Department of Chemistry, University of Houston
Houston, Texas 77004

Received January 30, 1981

The key aspect of any photoredox reaction for solar energy utilization is to achieve net charge separation. Optical studies have demonstrated that photoionization of aromatic molecules such as pyrene is much more efficient in anionic micelles than in homogeneous solution.[1-3] Solubilization sites of solutes in micelles have been studied by NMR[4] and fluorescence intensities.[5] However, information is lacking about the location of *cations* produced in micelles.

We have shown how ESR and electron spin echo (ESE) modulation can deduce the surrounding structure of paramagnetic species in frozen solutions.[6-11] Here we apply these techniques to *N,N,N′,N′*-tetramethylbenzidine (TMB) in anionic micelles. TMB was chosen because it undergoes monophotonic photoionization and has a long-lived cation.[12] We also show that the micellar structure is retained in frozen solutions.

TMB was solubilized to 0.1 mM in deoxygenated 0.1 M sodium dodecyl sulfate (SDS) by stirring at 60 °C for 3 h. Samples were irradiated in 2-mm Suprasil quartz tubes with 366-nm light from a high pressure mercury lamp with a No. 760 Corning filter at a flux of 10^5 erg/cm^2. A Varian E-4 ESR, Beckman 26 spectrophotometer and home-built ESE spectrometer[9] were used.

TMB dissolved in SDS in H_2O forms a pale yellow solution which freezes to a white polycrystalline solid. No ESR spectrum is observed before irradiation. After irradiation at 295 K the ESR spectrum in Figure 1a is seen and is stable for 12 h. Figure 1b shows the same sample at 77 K; the *g* factors at 77 and 295 K are identical within experimental error. Thawing the frozen sample regenerates the spectrum in Figure 1a. Irradiation at 4.2, 77, and 295 K gives identical ESR spectra when the sample is warmed to 295 K.

The optical spectrum after photoirradiation exhibits peaks at 475 and 460 nm characteristic of TMB$^+$[14] so the ESR spectrum is assigned to TMB$^+$. To show that TMB was solubilized by the micelles, benzene and nitrobenzene solvents were also used. Irradiation produced no spectra at 295 K and 50-fold weaker ESR spectra than in micelle solutions at 77 K.

The ESE decay envelopes of TMB$^+$ in H_2O and D_2O micellar solutions at 4.2 K are shown in Figure 2a,b. Proton modulation appears in Figure 2a and both proton and deuteron modulation in Figure 2b.

---

(1) Wallace, S. C.; Gratzel, M.; Thomas, J. K. *Chem. Phys. Lett.* **1973**, *23*, 359–362.

(2) Gratzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 2248–2254.

(3) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133–138.

(4) Gratzel, M.; Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 7869–74.

(5) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1974**, *99*, 2039–2044.

(6) Kevan, L.; Bowman, M. K.; Narayana, P. A.; Boeckman, R. K.; Yudanov, V. G.; Tsvetkov, Yu. D. *J. Chem. Phys.* **1975**, *63*, 409–416.

(7) Schlick, S.; Narayana, P. A.; Kevan, L. *J. Chem. Phys.* **1976**, *64*, 3153–3160.

(8) Ichikawa, T.; Kevan, L.; Narayana, P. A. *J. Chem. Phys.* **1979**, *71*, 3795.

(9) Ichikawa, T.; Kevan, L.; Narayana, P. A. *J. Phys. Chem.* **1979**, *83*, 3378–3381.

(10) Narayana, M.; Kevan, L. *J. Chem. Phys.* **1980**, *72*, 2891–2892.

(11) Ichikawa, T.; Kevan, L. *J. Chem. Phys.* **1980**, *72*, 2295–2299.

(12) Alkaitis, S. A.; Gratzel, M. *J. Am. Chem. Soc.* **1976**, *98*, 3549–3554.

(13) Bolton, J. R.; Carrington, A.; Dos Santas-Veiga, J. *Mol. Phys.* **1962**, *5*, 615–621.

(14) Kutter, P.; Schmitt-Fuiman, W. W.; Bachmann, L. Presented at the Sixth European Congress on Electron Microscopy, Jerusalem, 1976; pp 119–121.

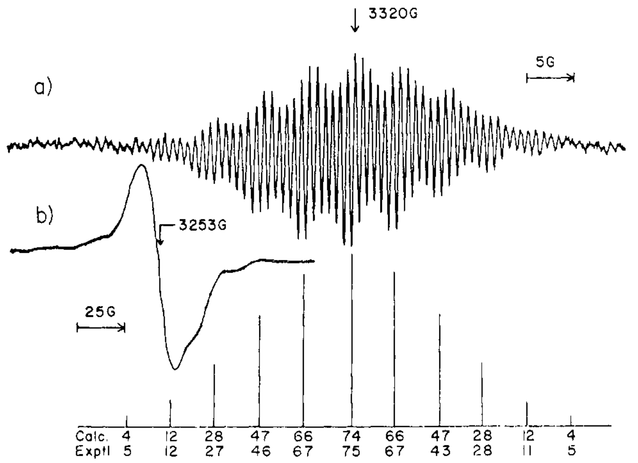


Figure 1. ESR spectrum of TMB^+ in aqueous micellar solution of sodium dodecyl sulfate. (a) Spectrum recorded at 295 K at 9.5 GHz, (b) spectrum recorded at 77 K at 9.3 GHz, and (c) calculated stick diagram for the multiplet groups. Numbers given denote the relative intensities. In cases a and b the sample was irradiated at 295 K with 366 nm light.

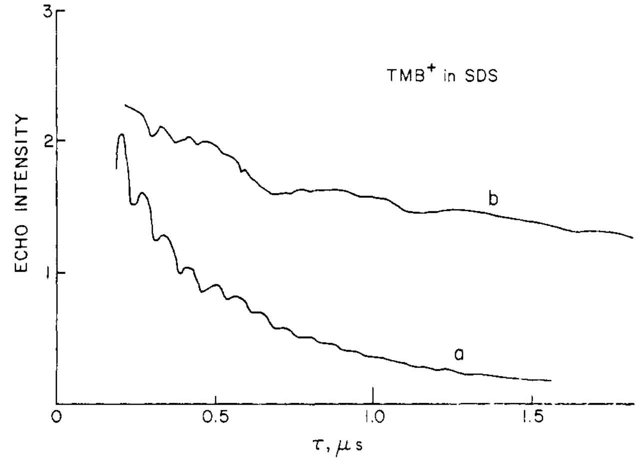


Figure 2. Two-pulse electron spin echo envelope of TMB^+ in (a) SDS prepared in H_2O and (b) SDS prepared in D_2O. Spectra were recorded at 4.2 K.

The ESR spectrum of TMB^+ in Figure 2a consists of 11 multiplets split by 4.8 G with a multiplet splitting of 0.85 G. We interpret the main splitting as due to nearly equivalent N and $H(CH_3)$ hyperfine splitting as is the case for the structurally similar Wurster's blue cation.[13] This would give 17 multiplets of which we observe only the central 11. Figure 1 shows that the observed and calculated intensities agree well with this model. The smaller multiplet splitting is attributed to ring-proton interactions.

Photoionization of TMB in benzene at 295 K or SDS aqueous solutions below the critical micelle concentration produces no observable ESR spectra, indicating that charge recombination is rapid in nonmicellar solutions. Thus the observation of TMB^+ at 295 K after freezing and thawing the micelle solution and after irradiation at 4.2 and 77 K indicates that the micellar structure is retained in the frozen solution and upon thawing. If it were not, rapid charge recombination would remove the cation. This conclusion is further supported by the identity of the ESE modulation of TMB^+ at 4.2 K for irradiations at 77 and 295 K. Electron microscope studies[14] of spray frozen micellar solutions also indicate that micellar structure is retained in frozen solutions.

The modulation of the ESE decay envelope of TMB^+ arises primarily from dipolar interaction between the unpaired electron and surrounding nuclei.[15] The modulation period identifies the interacting nucleus, and the modulation depth is related to the number and distance of the closest interacting nuclei. In Figure 2a the modulation period indicates that the interacting nuclei are protons on the alkyl chains of the surfactant molecules or on solvent water molecules. If the modulation arises from water protons, the proton modulation should be replaced by deuterium modulation when the micellar solution is prepared in D_2O. Deuterium and proton modulation are easily distinguished by the difference in their magnetic moments. Deuterium modulation is also more prominent, since the modulation depth increases with nuclear spin. In Figure 2b we observe both proton and deuterium modulation and that deuterium modulation arises at the expense of proton modulation. This suggests that the cation interacts with protons of both alkyl chains and solvent water. From the modulation depth the cation to water distance is 0.4–0.5 nm.

There is current controversy regarding micellar structure.[16] To suggest a probable region of cation localization in frozen micellar solutions, we assume a spherical micelle with a polar exterior and nonpolar interior.[17,18] For this model we suggest that TMB^+ is located in a weakly polar region of alkyl groups adjacent to polar headgroups of the surfactant, since weak D_2O interactions are observed. Also, since identical ESE data are found for TMB^+ produced at 295 K and then frozen as for TMB^+ produced in frozen solution, it appears that TMB^+ has not moved much relative to its precursor TMB.

If a more open micellar structure[16,19] is assumed, the cation location becomes more uncertain. Further experiments concerning this with different length surfactants are under way.

Acknowledgment. This work was supported by the Department of Energy under Contract DE-A505-80ER10745. We thank Professor J. Fendler for bringing ref 14 to our attention.

---

(15) Kevan, L. In "Time Domain Electron Spin Resonance"; Kevan, L., Schwartz, R. N., Eds; Wiley-Interscience: New York, 1979; Chapter 8.

(16) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111-117.

(17) Fendler, J. M.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.

(18) Hartley, G. S. *Trans. Faraday Soc.* **1935**, *31*, 31. *Q. Rev. Chem. Soc.* **1948**, *2*, 152.

(19) Fromherz, P. *Chem. Phys. Lett.* **1981**, *77*, 460-466.

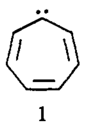
The Cycloheptatrienylidene–Cycloheptatetraene Problem. A MNDO Investigation[1]

Edward E. Waali

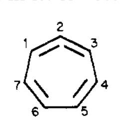
Department of Chemistry, University of Montana
Missoula, Montana 59812

Received January 12, 1981

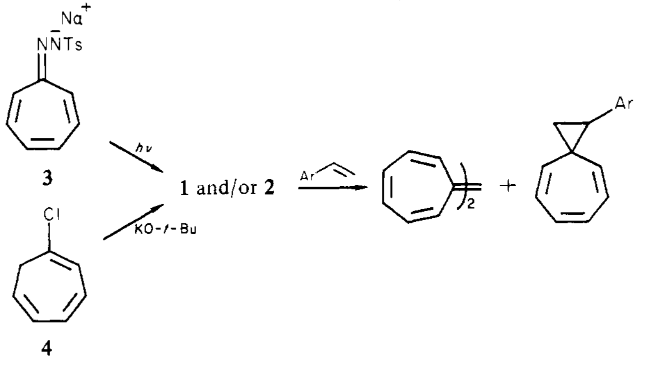
Cycloheptatrienylidene (**1**) is of prime importance to carbene chemistry, since it is a classical example of a carbocyclic, nucleophilic, aromatic carbene when in its lowest energy singlet state.



1



2



---

(1) A partial account of this work was presented at the Fifth IUPAC Conference on Physical Organic Chemistry, Santa Cruz, CA, Aug 1980.

0002-7863/81/1503-3604$01.25/0 © 1981 American Chemical Society