$$C(E) = E \log_2 E - \sum_i E_i \log_2 E_i \quad (4)$$

where the E_i are the number of atoms of element i, and E is the total number of atoms. The total complexity is $C_T = C(\eta) + C(E)$. When all the atoms are the same, $C(E) = 0$ and the total complexity, C_T, is equal to $C(\eta)$, the complexity due to connectivity. Although a number of "branching" indexes and "topological" indexes have been advanced,[8,11,12] C_T is the first measure of molecular complexity that is completely general.

Now that it is possible to calculate a number for any molecule which measures its complexity, it is possible to calculate the change in complexity, ΔC_T (hereafter symbolized as Δ), upon going from reactant to product in the course of a chemical reaction. The increases in complexity for the Diels–Alder reaction between butadiene and *p*-benzoquinone and the Weiss reaction[13] of glyoxal with dimethyl 3-ketoglutarate are calculated in Figure 1. This example shows that it is still possible to invent powerful synthetic reactions[14] and the calculation of complexity can aid in recognizing them. For a *functional group interchange*[1] such as the conversion of cyclohexene to cyclohexanol ($\Delta = 1.1$), the change in complexity is small. The process of calculating Δ can be repeated for all the steps in a synthetic sequence, thus providing a means to gauge progress toward a complex target molecule.

Thus by equating the complexity of a molecule with that of its molecular graph, formulating a new equation to measure this quantity, and applying this equation to the appropriate graph-theoretical invariant (connections), the first general index of molecular complexity has been constructed and shown to be applicable to synthetic analysis.

Acknowledgment. I thank D. Slepian and G. Smolinsky for their helpful advice.

(12) Hosoya, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2332–2339. Merrifield, R. E.; Simmons, H. E. *Theor. Chim. Acta* **1980**, *55*, 55–75. Randić, M. *J. Am. Chem. Soc.* **1975**, *97*, 6609–6615. Wiener, H. *Ibid.* **1947**, *69*, 17–20. Randić, M.; Brissey, G. M.; Spencer, R. B.; Wilkins, C. L. *Comput. Chem.* **1979**, *3*, 5–13.

(13) Weiss, U.; Edwards, J. M. *Tetrahedron Lett.* **1968**, 4885–4887. Mitschka, R.; Cook, J. M.; Weiss, U. *J. Am. Chem. Soc.* **1978**, *100*, 3973. Bertz, S. H.; Cook, J. M.; Gawish, A.; Weiss, U. *Org. Synth.* in press.

(14) A Weiss reaction is the key step in a synthesis of modhephene under way in Professor J. M. Cook's laboratories. Another Weiss reaction has been used to synthesize isocomene; see: Dauben, W. G.; Walker, D. M. *J. Org. Chem.* **1981**, *46*, 1103–1108.

Selective Epoxidation of Olefins by Molybdenum Porphyrin Catalyzed Peroxy-Bond Heterolysis

Henry J. Ledon,* Patrick Durbut,† and François Varescon

Centre National de la Recherche Scientifique
Institut de Recherches sur la Catalyse
69626 Villeurbanne Cédex, France

Received July 8, 1980
Revised Manuscript Received April 9, 1981

The selective epoxidation of olefins with tertiary alkyl hydroperoxides, catalyzed by molybdenum complexes, is a synthetic reaction of great significance which is used to produce industrial organic chemicals.[1] However, the nature of the actual oxidizing species is not clearly established. In particular, the requirement for olefin activation through its coordination to the metal center prior to the oxygen-transfer step is still a matter of controversy.[1,2]

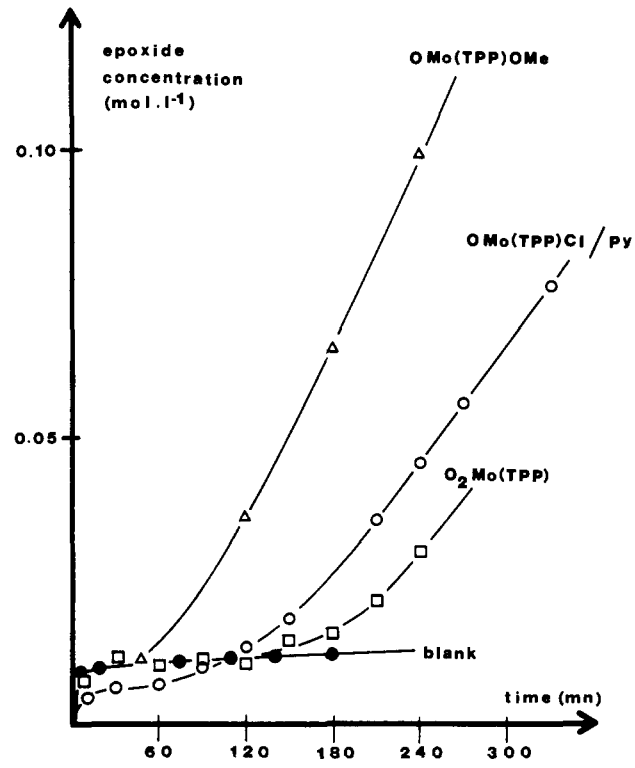

Figure 1. Cyclohexene epoxidation with *t*-BuOOH catalyzed by several molybdenum porphyrin complexes.

Our current interest in the reactivity of molybdenum porphyrins[3-7] led us to study their catalytic properties. Owing to the steric hindrance of the macrocyclic ligand, the coordination, at the same time, of the olefin and the hydroperoxide to the metal center would be unlikely. Here we report on the selective epoxidation of olefins with *tert*-butyl hydroperoxide catalyzed by (5,10,15,20-tetraphenylporphyrinato)molybdenum(V) complexes [OMo(TPP)X].[8,9]

In a typical experiment, OMo(TPP)OMe[6] (ca. 4 mg; 5×10^{-6} mol) was dissolved in dry oxygen-free benzene (13 mL). Then cyclohexene (2.5 mL; 24.6 mmol) and *n*-decane (used a GC internal standard) were added. The accurate catalyst concentration was measured by UV–visible spectrophotometry, and the mixture was heated to 80 ± 2 °C under argon. After equilibration, *t*-BuOOH (0.5 mL; 5 mmol) was added, and aliquots were periodically taken for GC analysis and recording of the UV–visible spectra.[10]

A high selectivity to cyclohexene oxide was obtained *at total conversion* of the hydroperoxide (Table I). Figure 1 shows the rates of appearance of cyclohexene oxide according to the nature

†On leave from Université de Liège, Laboratoire de Chimie Macromoléculaire et de Catalyse Organique, Sart-Tilman B 4000, Liège, Belgique.

(1) For recent reviews, see: (a) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* **1976**, *25*, 272–413. (b) Lyons, J. E. *Aspects Homogeneous Catal.* **1977**, *3*, 1–136. (c) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243–270. (d) Sheldon, R. A. *Ibid.* **1980**, *7*, 107–126. (e) "Chemical and Physical Aspects of Catalytic Oxidation"; Portefaix, J. L., Figueras, F., Eds.; Editions du C.N.R.S.: Lyon, 1980.

(2) (a) Sheldon, R. A.; Van Doorn, J. A. *J. Catal.* **1973**, *31*, 427–437. (b) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1587–1590. (c) Mimoun, H. *J. Mol. Catal.* **1980**, *7*, 1–29. (d) Mimoun, H.; Charpentier, R.; Mitschler, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047–1054.

(3) Ledon, H.; Bonnet, M.; Lallemand, J.-Y. *J. Chem. Soc., Chem. Commun.* **1979**, 702–704.

(4) Ledon, H.; Bonnet, M. *J. Mol. Catal.* **1980**, *7*, 309–313.

(5) Mentzen, B. F.; Bonnet, M. C.; Ledon, H. J. *Inorg. Chem.* **1980**, *19*, 2066–2069.

(6) Ledon, H. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1978**, *287*, 59–61. Ledon, H. J.; Bonnet, M. C.; Brigandat, Y.; Varescon, F. *Inorg. Chem.* **1980**, *19*, 3488–3491.

(7) Ledon, H.; Mentzen, B. *Inorg. Chim. Acta* **1978**, *31*, L393–L394.

(8) Oxygenation of cyclohexene in a complex mixture containing both iron and molybdenum (or vanadium) octaethylporphyrin was claimed to produce cyclohexene oxide and 2-cyclohexen-1-ol in a 1:1 ratio, but very few experimental details were given. See: Baccouche, M.; Ernst, J.; Fuhrhop, J.-H.; Arzoumanian, H. *J. Chem. Soc., Chem. Commun.* **1977**, 821–822.

(9) Part of this work has been presented at the 2nd International Symposium on Homogeneous Catalysis, Sept 1–3, 1980, Düsseldorf, Federal Republic of Germany: Ledon, H.; Durbut, P.; Bonnet, M. "Abstracts of Papers", p 186.

(10) Concentrations of OMo(TPP)X complexes were monitored by measuring the absorbance at 454 nm after conversion into OMo(TPP)OMe by addition of methanol.

0002-7863/81/1503-3601$01.25/0

Table I. Cyclohexene Epoxidation by *t*-BuOOH in the Presence of Various Molybdenum Complexes[a]

complex	[Mo] × 10^4, M	induction period, min	*t*,[b] h	selectivity to cyclohexene oxide[c]
none		5	19	6
$Mo(CO)_6$	1.5	40	7	98
OMo(TPP)Cl/Py	3.6	80	17	68[d]
OMo(TPP)OMe	3.0	40	17	84
cis-O_2Mo(TPP)	3.5	140	24	85

[a] Reaction conditions: benzene, 80 °C, under argon. Relative molar ratio Mo/*t*-BuOOH/cyclohexene = $1:10^3:5 \times 10^3$. [b] Time needed for total conversion of *t*-BuOOH. [c] Epoxide selectivity based on *t*-BuOOH introduced and calculated at total conversion of the hydroperoxide. [d] Small amounts of *tert*-butyl-2-cyclohexenyl peroxide were also identified by ^{1}H NMR and GC-MS.

of the molybdenum porphyrin complex initially added. After an induction period, depending on the catalyst, a phase of epoxide formation at constant rate is observed. A similar feature has been reported by Sheldon[11] for cyclohexene epoxidation with *t*-BuOOH catalyzed by a dioxomolybdenum(VI) phthalocyanine. The induction period was attributed to the transformation of O_2MoPc into the related dioxobis(diolato)molybdenum(VI) complex, responsible for the catalytic activity of the system. Very recently, another example of porphyrin demetalation under oxidizing conditions has been observed for OW(TPP)OMe.[12] However, several molybdenum complexes have been reported to survive in the presence of hydroperoxides,[13] and we have evidence that catalysis by species arising from demetalation or destruction of OMo(TPP)X during the induction period could be ruled out as the main route of cyclohexene oxidation. The rates of epoxide formation, expressed as the turnover number of the catalyst, are, respectively, $Mo(CO)_6$ 283 and OMo(TPP)OMe 51 h^{-1}. Therefore, to account for the reactivity observed with molybdenum porphyrins, about 15–20% of the complex initially added should have been destroyed during the induction period.[14] Monitoring the reaction by UV–visible spectrophotometry revealed a complicated spectrum evolution during that stage. However, after a time of reaction corresponding to three times the duration of the induction period, i.e., when the reaction had reacted its stage of full catalytic activity, the concentration of molybdenum(V) porphyrin complexes in solution is still 98–100% of the initial one, measured before addition of *t*-BuOOH.[10] Moreover, no increase of the rate of epoxidation was observed with time, as could be expected if the porphyrin complex was destroyed during the reaction.

If OMo(TPP)Cl[7] or OMo(TPP)Cl/pyridine (1:0.8 molar ratio) was used as a catalyst, the diol complex OMo(TPP)$OC_6H_{10}OH$, formed at the expense of cyclohexene oxide,[15] was the first intermediate identified in the reaction mixture. This is in agreement with the lower concentration of cyclohexene oxide found at the very early stage of the reaction, compared to the blank. The release of chloride ion in the reaction mixture, by chloro–alkoxo axial ligand exchange may account for the lower final selectivity to cyclohexene oxide, as it is known that free chloride anion induces radical decomposition of hydroperoxides.[11] No axial ligand exchange was observed when OMo(TPP)Cl was treated with an excess of *t*-BuOOH. The different induction periods found for OMo(TPP)Cl and OMo(TPP)OMe can then be simply explained by the required formation of a molybdenum porphyrin complex with an alkoxo axial ligand to exhibit a catalytic activity. Further evolution of the spectra revealed the formation of a small amount of the hydroxo complex OMo(TPP)OH[6] (λ_{max} 464 nm) and a new compound exhibiting a broad absorption at 480 nm, which involves coordination of *t*-BuOOH to the OMo(TPP)OR complex, presumably OMo(TPP)OO-*t*-Bu. In fact, when a benzene solution of OMo(TPP)OMe was titrated with strictly anhydrous *t*-BuOOH, a new spectrum was obtained: λ_{max}, nm ($\epsilon \times 10^{-3}$, L mol^{-1} cm^{-1}) 652 (8.9), 607 (11.3), 480 (54), 344 (39) with isosbestic points at λ 627, 614, 548, 469 and 415 nm. Electron spin resonance spectrum of this solution exhibited the characteristic pattern for a molybdenum(V) porphyrin complex,[6] and the UV–visible spectrum of OMo(TPP)OMe could be fully restored upon addition of methanol, which advocates for a simple axial ligand exchange. However, attempts to isolate this complex in the solid state were invariably frustrated by precipitation of the μ-oxo dimer $[OMo(TPP)]_2O$. This is not surprising due to the extremely low solubility of this complex in benzene,[6] and at the end of the epoxidation reaction, the molybdenum porphyrin complexes could be quantitatively recovered as the μ-oxo dimer, apart from a small amount of the cis dioxo O_2Mo(TPP).[3,5] As shown in Table I, O_2Mo(TPP) exhibits an unexpectedly long induction period which corresponds to the formation of a molybdenum(V) species, as shown by the appearance of the characteristic ESR spectrum. Thus this complex is not an intermediate in the catalytic oxidation of cyclohexene.

Table II. Relative Rates of 2-Hexene Epoxidation Measured by a Competitive Method[a]

olefin	relative rates: $Mo(CO)_6$[b]	relative rates: OMo(TPP)Cl[c]
trans-2-hexene	1.0	1.0
cis-2-hexene	2.0	3.5

[a] Reaction conditions: benzene, 65 °C, under argon; [olefin] = 0.44 M, [*t*-BuOOH] = 0.43 M. [b] $[Mo(CO)_6] = 4 \times 10^{-4}$ M. [c] $[OMo(TPP)Cl] = 18 \times 10^{-4}$ M.

Using similar conditions, the OMo(TPP)Cl catalyzed epoxidation of *cis*- and *trans*-2-hexene was found to be highly stereospecific, affording, respectively, 97 and 99% of the corresponding *cis*- and *trans*-2-epoxides. Relative rates of formation of *cis*- and *trans*-2-hexene oxide are significantly different whether $Mo(CO)_6$ or OMo(TPP)OMe was used as catalyst, showing again a specific behavior of the porphyrin complex (Table II). The higher rate of formation observed for *cis*-2-hexene oxide indicates a more efficient steric control as expected if the bulky rigid porphyrin ligand is present in the activated complex. This effect is clearly evidenced in the case of 2-methylbutadiene (isoprene) where 3-methyl-3,4-epoxy-1-butene and 2-methyl-3,4-epoxy-1-butene corresponding, respectively, to the epoxidation of the di- and monosubstituted double bond are obtained in a 4:1 ratio by using $Mo(CO)_6$[16] compared to 0.7:1 with OMo(TPP)OMe. Similar steric effects have been reported for the oxidation of phosphines with cis dioxo O_2Mo(TPP)[4] and the oxo-transfer re-

(11) Sheldon, R. A. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 253–266, 367–373.

(12) Fleischer, E. B.; Chapman, R. D.; Krishnamurthy, M. *Inorg. Chem.* **1979**, *18*, 2156–2159.

(13) Yamada, S.; Mashiko, T.; Terashima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988–1990. Jacobson, S. E.; Muccigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921–923. Westland, A. D.; Haque, F.; Bouchard, J.-M. *Inorg. Chem.* **1980**, *19*, 2255–2259.

(14) It is not possible to strictly rule out that a very small amount of the leached Mo species is a more active catalyst than the one produced in the $Mo(CO)_6$ system. However, this is very unlikely as Sheldon has shown that after an induction period, the rate of cyclohexene epoxidation by *t*-BuOOH was independent of the nature of the molybdenum complex used as catalyst. See ref 11.

(15) When a benzene solution of OMo(TPP)Cl was treated, at room temperature, with a large excess of cyclohexene oxide (epoxide/Mo ca. 250) a very slow evolution of the UV–visible spectra was observed with isosbestic points at 655, 631, 545, 480 and 324 nm. The final spectrum was identical with that of OMo(TPP)$OC_6H_{10}OH$ prepared by an independent method: λ_{max} nm ($\epsilon \times 10^{-3}$ L mol^{-1} cm^{-1}) 624 (16.1), 584 (22.4), 456 (177).

(16) Sheng, M. N.; Zajacek, J. G. *J. Org. Chem.* **1970**, *35*, 1839–1843. Sheng, M. N.; Zajecek, J. G. US Patent 3 538 124 (to Atlantic Richfield Co.); *Chem. Abst.* **1971**, *74*, 22683.

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 Sociêtê 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.

0002-7863/81/1503-3603$01.25/0