Light-Induced Simultaneous Photooxidation and Photoreduction of Zinc Tetraphenylporphyrin Radical Cation

Sir:

In the past it was shown that porphyrin and metalloporphyrin compounds undergo reversible one- and two-electron oxidation.[1] Rabinowitch[2] and Goedheer[3] showed that oxidation of chlorophyll *a* by Fe(III) salts is a reversible process by which the original compounds can be restored on addition of reductants. Mauzerall et al.[4] showed that metallooctaethylporphyrins can be oxidized by a variety of oxidants such as halogens as well as ferric salts. Stanienda[5] investigated oxidation of porphyrins and metalloporphyrins by using voltammetry technique with rotating platinum electrode. By this technique he determined the first and the second oxidation potential for a variety of porphyrin compounds in butyronitrile as a solvent. Fajer et al.[6] reported the first and second electrooxidation potential of ZnTPP as well as magnesium octaethylporphyrin in dry CH_2Cl_2 as solvent. They proved that the product obtained by two-electron oxidation is the dication; i.e., on addition of neutral porphyrin to the product of the two electron oxidation, they observed the regenerate cation radical via the coproportionation reaction.

Seely[7,8] reported one-electron photooxidation of pyrochlorophyll by a nitro compound forming the corresponding radical cation and anion. Tollin[9] showed that at low temperature photooxidation of chlorophyll by Fe^{3+} resulted in a complex formation such as [chlorophyll$^{+}\cdot$$Fe^{2+}$]. In a recent study[10] we showed that Eu^{3+} can be used as oxidant for zinc tetraphenylporphyrin (ZnTPP) and magnesium tetraphenylporphyrin (MgTPP) triplets. The oxidation products were shown to be the corresponding radical cations. Mauzerall et al.[11] showed that metalloporphyrin cation radicals, such as zinc octaethylporphyrin, form a diamagnetic dimer in a methanol-chloroform mixture.

Understanding of the chemical and photochemical behavior of metalloporphyrins in biological processes is very important. For example, it was postulated[12] that chlorophyll *a* cation radical decays by second-order kinetics with respect to its radical cation, where one of the products was the parent compound. Therefore it was assumed[12] that one of the intermediates was the dication formed owing to the disproportionation reaction.

In this work we report for the first time an example of light-induced oxidation and reduction of ZnTPP radical cation to the corresponding dication and the parent molecule.

Oxidation of ZnTPP im methylene chloride by chemical means was carried by contacting a solution of ZnTPP with $Fe(ClO_4)_3$ solid. Intermittently the optical spectrum of the reaction mixture was recorded and can be seen in Figure 1. As the oxidation reaction progressed, the gradual disappearance of ZnTPP (λ_{max} 419 nm) and the appearance of $ZnTPP^{+}\cdot ClO_4^{-}$ (λ_{max} 409 nm) were evident from observing their corresponding optical absorption spectra. It is interesting to note the isosbestic points as λ 412 and 430 nm indicating stoichiometrical conversion of the reactant into product without detectable amounts of intermediates. Using the known extinction coefficients of ZnTPP[6,14] the extinction coefficient of $ZnTPP^{+}\cdot ClO_4^{-}$ was calculated and found to be in good agreement with the one previously reported.[6,15] The radical cation formed was stable for at least 2 days without any noticeable change in absorption spectra.

The one electron oxidation of ZnTPP by $Fe(ClO_4)_3$ was carried out in the bulk solution almost to completion. From the spectrum of the radical cation obtained by this oxidation reaction and the available[6,14,15] extinction coefficients at the maximum wavelengths of the absorption of ZnTPP, $ZnTPP^{+}\cdot ClO_4$, and $ZnTPP^{2+}2ClO_4^{-}$, a table of extinction coefficients at selected wavelengths was constructed (see Table I). The photolysis of $ZnTPP^{+}\cdot ClO_4^{-}$ was done in a 1- or 10-cm quartz flashed cell. The solvent was distilled from the bulk to the flash cell and then 1 drop from the bulk solution was added until the OD in the flashed cell was adjusted between 1 and 2. In the case of the 1-cm cell the flashed solution included a small concentration of ZnTPP which was not greater than 1.7×10^{-8} M, whereas the concentration of the radical cation was $\sim 5 \times 10^{-6}$ M.

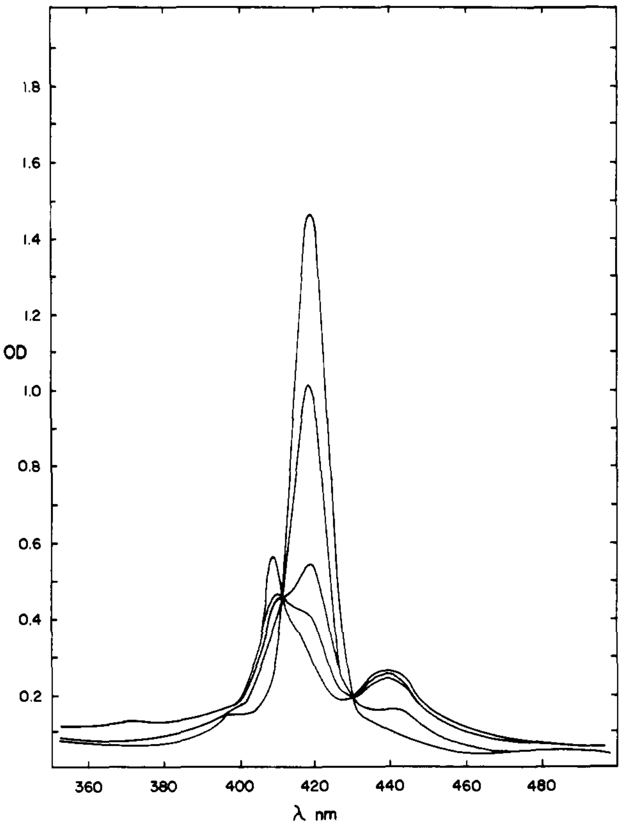

Figure 1. Progressive oxidation of ZnTPP to $ZnTPP^{+}\cdot ClO_4$ by $Fe(ClO_4)_3$ in CH_2Cl_2.

Table I. Extinction Coefficients of $ZnTPP^{+}\cdot ClO_4$, $ZnTPP^{2+}2ClO_4^{-}$, and ZnTPP at a Selected Wavelength (CH_2Cl_2)

λ, nm	ε(ZnTPP), M^{-1} cm^{-1}	ε($ZnTPP^{+}\cdot ClO_4^{-}$), M^{-1} cm^{-1}	ε($ZnTPP^{2+}2ClO_4^{-}$), M^{-1} cm^{-1}
350	0.10×10^5	$0.17 \times 10^5 \pm 0.05 \times 10^5$	0.59×10^5 ^{a,b}
409	0.99×10^5	1.90×10^5 ^{a,b}	0.19×10^5 ^{a}
419	5.60×10^5 ^{b,c}	0.87×10^5	0.18×10^5 ^{a}

[a] Reference 6. [b] Maximum. [c] Reference 14.

The photochemical processes occurring during the light period leading to the chemical processes observed during the dark period require some comments. From the stoichiometry of the disproportionation reaction it is clear that the photolysis of $ZnTPP^{+}\cdot ClO_4^{-}$ results in bleaching of $ZnTPP^{+}\cdot ClO_4^{-}$ and to the formation of ZnTPP and $ZnTPP^{2+}2ClO_4^{-}$ in a ratio of 2:1:1. This is evident from observing the differential spectrum obtained 300 μs after the flash (Figure 2). The ratio of ΔOD at the wavelength of maximum absorption of ZnTPP, $ZnTPP^{+}\cdot ClO_4^{-}$, and $ZnTPP^{2+}2ClO_4$ is given below:

$$[\Delta OD^{419}_{ZnTPP}]:[\Delta OD^{409}_{ZnTPP^{+}\cdot ClO_4^{-}}]:[\Delta OD^{350}_{ZnTPP^{2+}2ClO_4^{-}}] = 0.0202:0.0136:0.0020$$

The change in the concentration of the species involved in the disproportionation reaction can be calculated by using the effective extinction coefficients (ϵ^{λ}_{ef}). These coefficients can be estimated by using Table I, i.e.,

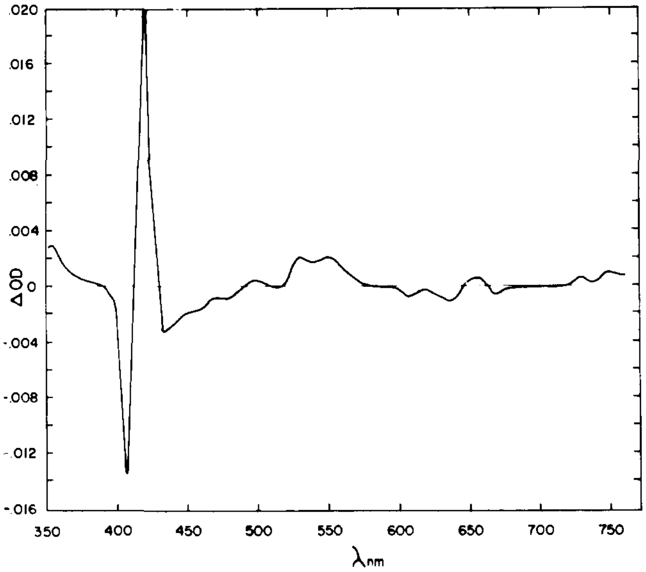

Figure 2. Flash photolysis of $ZnTPP^{+}\cdot/CH_2Cl_2$ (spectrum taken after 300 μs): $[ZnTPP^{+}\cdot]_e = 5.25 \times 10^{-6}$ M; $[ZnTPP]_3 \leq 1.7 \times 10^{-8}$ M.

$$\epsilon^{419}_{ef(ZnTPP)} = \epsilon^{419}_{(ZnTPP)} - 2\epsilon^{419}_{(ZnTPP^{+}\cdot ClO_4^{-})} + \epsilon^{419}_{(ZnTPP^{2+}2ClO_4^{-})} = 4.0 \times 10^5$$

$$\epsilon^{409}_{ef(ZnTPP^{+}\cdot ClO_4^{-})} = \epsilon^{409}_{(ZnTPP^{+}\cdot ClO_4^{-})} - \tfrac{1}{2}\epsilon^{409}_{(ZnTPP)} - \tfrac{1}{2}\epsilon^{409}_{(ZnTPP^{2+}2ClO_4^{-})} = 1.31 \times 10^5$$

$$\epsilon^{350}_{ef(ZnTPP^{2+}2ClO_4^{-})} = \epsilon^{350}_{(ZnTPP^{2+}2ClO_4^{-})} - 2\epsilon^{350}_{(ZnTPP^{+}\cdot ClO_4^{-})} + \epsilon^{350}_{(ZnTPP)} = 0.35 \times 10^5$$

Therefore, the change of the concentrations 300 μs after the flash is as follows: $\Delta[ZnTPP^{+}\cdot ClO_4^{-}] = -10.38 \times 10^{-9}$; $\Delta[ZnTPP] = 4.9 \times 10^{-9}$; $\Delta[ZnTPP^{2+}2ClO_4^{-}] = 5.7 \times 10^{-9}$ M. The uncertainty is in the effective extinction coefficient of the dication at 350 nm. The above calculations show that the stoichiometry of the disproportionation reaction is maintained.

One possibility by which the disproportionation reaction might be induced is the oxidation or reduction of an excited radical cation by another unexcited one, i.e.,

$$[ZnTPP^{+}\cdot ClO_4^{-}]^{*} + [ZnTPP^{+}\cdot ClO_4^{-}] \rightarrow ZnTPP + ZnTPP^{2+}2ClO_4^{-}$$

An alternative way to form the dication is by excitation of the dimeric radical cation which might exist in equilibrium with the radical cation through the following equation:

$$2(ZnTPP^{+}\cdot ClO_4^{-}) \rightleftarrows (ZnTPP^{+}\cdot ClO_4^{-})_2 \qquad K_{dim}$$

The existence of a dimer aggregate in the case of zinc octaethylporphyrin radical cation ($ZnOEP^{+}\cdot ClO_4^{-}$) in a mixture of methanol–chloroform was previously reported by Führhop et al.[11] They calculated the equilibrium for this system at room temperature to be $K = 2.6 \times 10^4$ M^{-1}. They also calculated the forward rate constant of dimerization to be 1.3×10^8 s^{-1} M^{-1}. The advantage of proposing that the photochemical reaction occurred in a dimeric form of radical cation is that there is no diffusion process involved in the oxidation reduction reactions. It will be hard to explain a high percent of bleaching of the radical cation if the reaction is due to oxidation or reduction of the excited radical cation by unexcited one because of the short time of the single excited state (10^{-8}–10^{-9} s). However, the bleaching of the radical cation due to the photolysis reaction did not exceed 2%. Therefore it is hard to distinguish between those two alternatives.

The appearance of ZnTPP and $ZnTPP^{2+}2ClO_4^{-}$ following the disappearance of the transient causes the disproportionation equilibrium that exists prior to the flash to be disturbed. Therefore the return to equilibrium may be monitored during the dark period. The simultaneous formation of radical cation and the disappearance of ZnTPP can be seen in Figure 3. The concentrations of the species involved in the disproportionation reaction at any time are

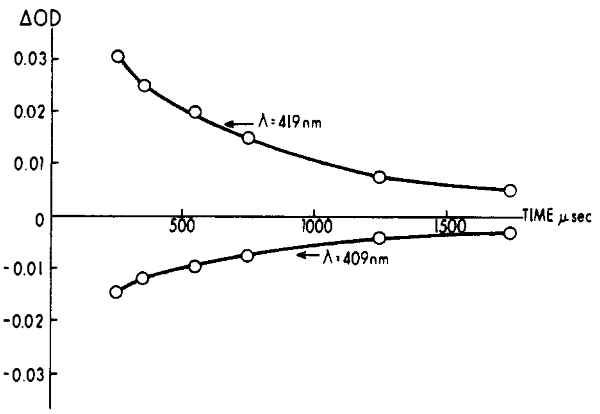

Figure 3. Formation of $ZnTPP^{+}\cdot$ and disappearance of ZnTPP as function of time.

Table II. Flash Photolysis Experiments of the Equilibrium Mixture of ZnTPP, $ZnTPP^{+}\cdot ClO_4^{-}$, and $ZnTPP^{2+}2ClO_4^{-}$

	expt 1	expt 2
ZnTPP, M	2×10^{-8}	8.79×10^{-9}
$ZnTPP^{+}\cdot$, M	5×10^{-6}	1.18×10^{-5}
$ZnTPP^{2+}$, M	1×10^{-8}	1.31×10^{-7}
slope, s^{-1}	4.79×10^2	2.68×10^3
k_{-1}, M^{-1} s^{-1}	1.4×10^{10}	1.9×10^{10}
k_1, M^{-1} s^{-1}	1.2×10^5	1.5×10^5

$$(ZnTPP)_t = (ZnTPP_e) + x = (a_e + x)$$

$$(ZnTPP^{+}\cdot)_t = (ZnTPP^{+}\cdot_e) - 2x = (b_e - 2x)$$

$$(ZnTPP^{2+})_t = (ZnTPP^{2+}{}_e) + x = (c_e + x)$$

where e indicates equilibrium concentration and x is the concentration of ZnTPP and $ZnTPP^{2+}$ over and above their equilibrium concentration. The following disproportionation reaction takes place,[6]

$$2(ZnTPP^{+}\cdot) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ZnTPP^{2+} + ZnTPP$$

where

$$K_e = \frac{k_1}{k_{-1}} = 8.27 \times 10^{-6}$$

The mathematical treatment of the rate equation is presented below:

$$\tfrac{1}{2}\frac{d(ZnTPP^{+}\cdot)_t}{dt} = K_1(ZnTPP^{+}\cdot)_t{}^2 - k_{-1}(ZnTPP^{2+})_t(ZnTPP)_t$$

Substitution of the concentrations at time t of ZnTPP, $ZnTPP^{+}\cdot$, and $ZnTPP^{2+}$ in the above equation and integrating the differential equation will give the following relation:

$$\frac{1}{a_e + c_e + 4K_eb_e}\ln\frac{(a_e + c_e + 4K_eb_e) + (1 - 4K_e)x}{x} = k_{-1}t + \text{constant}$$

Two experiments with different concentrations of ZnTPP, $ZnTPP^{+}\cdot$, and $ZnTPP^{2+}$ were carried out (see Table II).

A plot of $\ln\{[(a_e + c_e + 4K_eb_e)/x] + 1\}$ against time is seen in Figure 4 (expt 1) from which the slope was calculated and

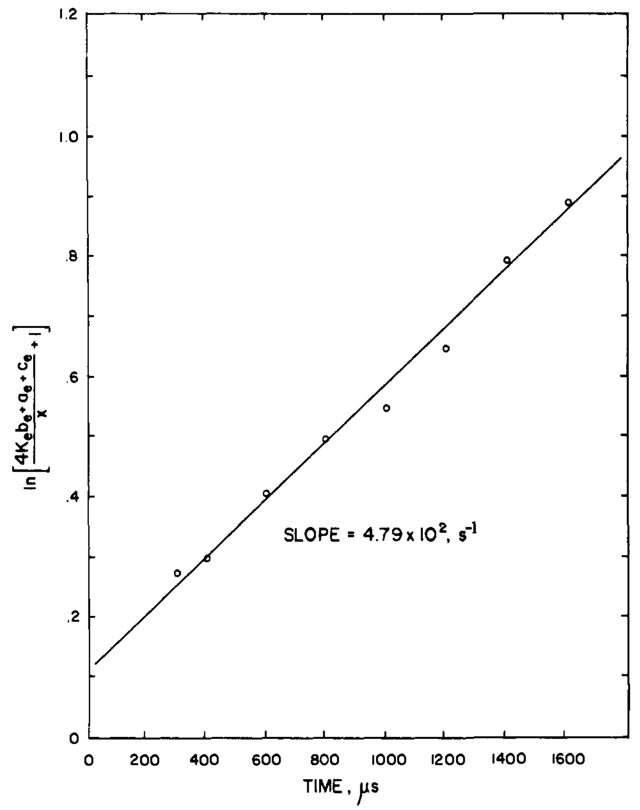

Figure 4. Kinetic of the disproportionation reaction: λ 409 nm, 1-cm cell.

found to be 479 s^{-1}. In the same way the slope was found to be 2680 s^{-1} for expt 2. Using the slopes and the equilibrium constant the forward and backward rate constants were calculated. The summary of this calculation is found in Table II.

It is worthwhile to mention, before we conclude, that, according to our assumptions, the equilibrium between the radical cation and the dimeric radical cation is also disturbed owing to the disappearance of the dimer. However, if we assume that the rate constant of dimerization is similar to the one obtained by Führhop,[14] i.e., $k_d = 1.0 \times 10^8$ M^{-1} s^{-1}, then the return to the equilibrium will be in the range of 4 μs and the complication resulting from the two simultaneous reactions is avoided.

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References and Notes

(1) J. H. Führohp in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975.
(2) E. Rabinowitch and J. Weiss, *Proc. R. Soc. (London), Ser. A*, **162**, 251 (1937).
(3) J. C. Goedheer in "The Chlorophylls", L. P. Vernon and G. R. Seely, Eds., Academic Press, New York, 1966, p 164.
(4) J. H. Führohp and D. Mauzerall, *J. Am. Chem. Soc.*, **90**, 3875 (1968); **91**, 4174 (1969).
(5) A. Stanienda, *Z. Phys. Chem., Neme Folge*, **52**, 254 (1967).
(6) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. H. Felton, *J. Am. Chem. Soc.*, **92**, 3451 (1970).
(7) G. R. Seely, *J. Phys. Chem.*, **73**, 117 (1969).
(8) G. R. Seely, *J. Phys. Chem.*, **73**, 125 (1969).
(9) G. Tollin and F. Rizzuto, *Chem. Photiol.*, **27**, 487 (1978).
(10) W. Potter and G. Levin, *Photochem. Photobiol.*, **30**(2), 225 (1979).
(11) J. H. Führohp, P. Wasser, D. Riesner, and D. Mauzerall, *J. Am. Chem. Soc.*, **94**, 7996 (1972).
(12) D. C. Borg, J. Fajer, R. H. Felton, and D. Dolphin, *Proc. Acad. Sci. U.S.A.*, **67**, 813 (1970).
(13) G. Levin, *J. Phys. Chem.*, **82**, 1584 (1978).
(14) L. Pekkarinen and H. Linschitz, *J. Am. Chem. Soc.*, **82**, 2407 (1960).
(15) A Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(16) G. Levin and M. Szwarc, *Chem. Phys. Lett.*, **30**, 116 (1975).

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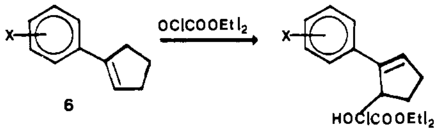
Synthesis of Allylcarboxylic Acids from Olefins with Diethyl Oxomalonate, an Enophilic Equivalent of Carbon Dioxide

Sir:

Control of the sites of C—C bond formation and C—H bond cleavage is important for synthetic exploitation of allylic activation in carbon skeletal construction. Ene reactions[1] of diethyl oxomalonate[2] (**2**), constrained by a pericyclic mechanism to occur with allylic transposition of the C=C bond, substitute an α-hydroxymalonyl group for allylic hydrogen (**1** → **3**). Conversion of this group into carboxyl allows olefin functionalization equivalent to an ene reaction of carbon dioxide (Scheme I).

We now show that **2** is indeed a synthetically valuable enophilic equivalent of carbon dioxide. Catalysis not only allows ene reactions of **2** under mild conditions, but also modifies the relative reactivities of olefins. Moreover, cerium(IV) oxidatively bisdecarboxylates α-hydroxymalonic (tartronic) acid intermediates (**4** → **5**).

Mono-, di-, and trisubstituted olefins listed in Table I afforded ene adducts with diethyl oxomalonate upon heating at 145-180 °C for 1-3 days. In each case only a single isomer was isolated by simple short-path distillation from the ene reaction mixture.[3] The selectivity of these ene reactions is primarily steric in origin, although small electronic effects are also operative. Thus, C—C bond formation occurs exclusively at the least substituted terminus of the C=C bond in arylcyclopentenes (**6**) and electron-donating substituents enhance reactivity moderately[4] ($\rho = -1.2 \pm 0.2$). However, steric effects readily overbalance this electronic bias since monosubstituted olefin reacts more readily than trisubstituted (entry 9). Both steric and electronic factors favor C—C bond formation at the less substituted terminus of a trialkyl olefin (entry 4), whereas the selective reaction of a monosubstituted C=C bond in the presence of a disubstituted C=C bond (entry 8) is sterically determined.



Synthetic methods which achieve stepwise substitution of a carboxyl group for allylic hydrogen by oxidation or metalation followed by C—C bond formation can result in retention or migration of the C=C bond (Scheme II). Our interest in ene reactions of **2** was sparked by the prospect that a regio-

Scheme I