Electrogenerated chemiluminescence. X. .alpha.,.beta.,.gamma.,.delta.-Tetraphenylporphine chemiluminescence

Nurhan E. Tokel, Csaba P. Keszthelyi, and Allen J. Bard

J. Am. Chem. Soc., **1972**, 94 (14), 4872-4877• DOI: 10.1021/ja00769a012 • Publication Date (Web): 01 May 2002

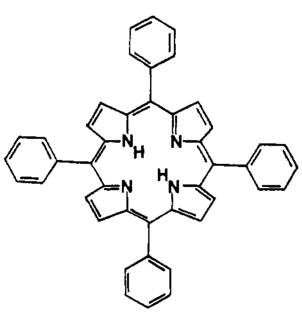
Electrogenerated Chemiluminescence. X. $\alpha,\beta,\gamma,\delta$-Tetraphenylporphin Chemiluminescence

Nurhan E. Tokel, Csaba P. Keszthelyi, and Allen J. Bard*

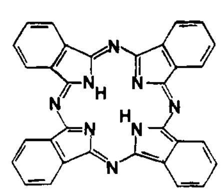
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received January 11, 1972*

Abstract: Electrogenerated chemiluminescence (ecl) resulting from the reaction of $\alpha,\beta,\gamma,\delta$-tetraphenylporphin (TPP) anion radical with the cation radical of TPP, rubrene, or 10-methylphenothiazine in methylene chloride solutions is described. The ecl emission is the same as that observed in TPP fluorescence and a mechanism is proposed for the process involving production of triplet TPP in the radical ion electron-transfer process followed by triplet–triplet annihilation to yield excited singlet TPP. Ecl is also observed upon the simultaneous reduction of TPP and 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene.

The original work on annihilation electrogenerated chemiluminescence (ecl) in which polycyclic aromatic hydrocarbons are the emitting species has been extended over the past several years to include heterocyclic compounds of oxygen (isobenzofurans),[1] nitrogen (oxadiazoles),[2] and sulfur (thianthrene).[2] In this paper we extend studies of ecl to macrocyclic compounds and report here the results of the investigation of the electrochemistry, fluorescence, and ecl of systems containing $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, I (TPP), and $\alpha,\beta,\gamma,\delta$-tetraazatetrabenzoporphin (phthalocyanine or Pc), II, as well as mixed systems containing TPP



I



II

and rubrene, 10-methylphenothiazine (10-MP), or 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$). The metalloporphyrins are important in biological processes and, for example, the cation radical of chlorophyll *a* has been identified as an intermediate in photosynthetic processes.[3] Moreover, there has been much interest in the spectroscopy of porphyrins[4] and the nature and energetics of the processes forming excited state species and their deactivation. The ecl studies were undertaken to obtain a better understanding of the behavior of the radical ion and excited species of this class of compounds and to provide an alternate method of producing excited states of the porphyrins.

(1) A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Amer. Chem. Soc.*, **89**, 4091 (1967).
(2) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *ibid.*, **94**, 1522 (1972).
(3) D. C. Borg, J. Fajer, R. H. Felton, and D. Dolphin, *Proc. Nat. Acad. Sci. U. S.*, **67**, 813 (1970).
(4) M. Gouterman, *J. Mol. Spectrosc.*, **6**, 138 (1961); L. Edwards, D. H. Dolphin, M. Gouterman, and A. D. Adler, *ibid.*, **38**, 16 (1971), and references cited therein.

Experimental Section

The general techniques for purification of solvents and supporting electrolyte followed previous publications in this series. Methylene chloride (MC), spectroscopic grade, Fisher Scientific Co., was either used as received or dried over Linde Type 4A molecular sieve followed by distillation. TPP was obtained from Mad River Chemical Co., Yellow Springs, Ohio, and was used without further purification. No impurities were detected by absorption spectrophotometric, fluorescence, or electrochemical analysis. Pc was Baker Grade (Lot No. 1-1150) and was used as received. Rubrene, puriss, was obtained from Aldrich Chemical Co. and 10-MP from Eastman Organic Chemicals. The 10-MP was recrystallized three times from 95% ethanol before use. $DPACl_2$ was prepared from 9,10-diphenylanthracene (DPA) (Aldrich Analyzed, Lot No. 120207) by bubbling dry chlorine gas into a CH_2Cl_2 solution of DPA and subsequently evaporating the solvent under reduced pressure.[5]

The ecl cells used in most experiments are shown in Figure 1. These employed a silver wire reference electrode[2,6] and a platinum auxiliary electrode. In most of the experiments the reference and auxiliary electrodes were contained in separate tubes connected to the test solution *via* fritted glass disks. Electrochemical measurements given in Table I were performed in a cell equipped with a saturated calomel electrode (sce). Fluorescence measurements employed either a 1-cm quartz cuvette or the cell shown in Figure 1a with the electrodes removed. Test solutions were prepared on a vacuum line and were deaerated by freeze–pump–thaw techniques as previously described.[2] Electrochemical experiments were performed with a Princeton Applied Research Corp. Model 170 electrochemistry system (PAR) and optical measurements were made on an Aminco-Bowman spectrophotofluorometer (SPF) employing a Hamamatsu TV Corp. R456 photomultiplier tube with uv-improved S-20 response and operated at 1100 V to increase sensitivity. In fluorescence measurements where laser excitation was employed, the 632.8-nm line of a Spectraphysics Model 132 He–Ne laser was used, with the laser positioned above the SPF sample chamber and the exciting beam passing vertically into the sample cuvette in line with the slits of the emission detector.

Results

Spectroscopic Data. The fluorescence spectrum of TPP in methylene chloride (MC) shows two emission maxima at 651 and 703 nm (Figure 2a) in agreement with previous results in other solvents.[7] The ratio of the intensities of the two emission peaks as well as the apparent absolute intensity of each depends upon the TPP concentration and the method of determining the fluorescence spectrum. Besides the inner filter effects of increasing absorption of the excitation beam with increasing TPP concentration and absorption of

(5) E. A. Chandross and F. I. Sonntag, *J. Amer. Chem. Soc.*, **88**, 1089 (1966).
(6) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971).
(7) F. Bar, E. Schnabel, and H. Kuhn, *Z. Elektrochem.*, **65**, 346 (1961).

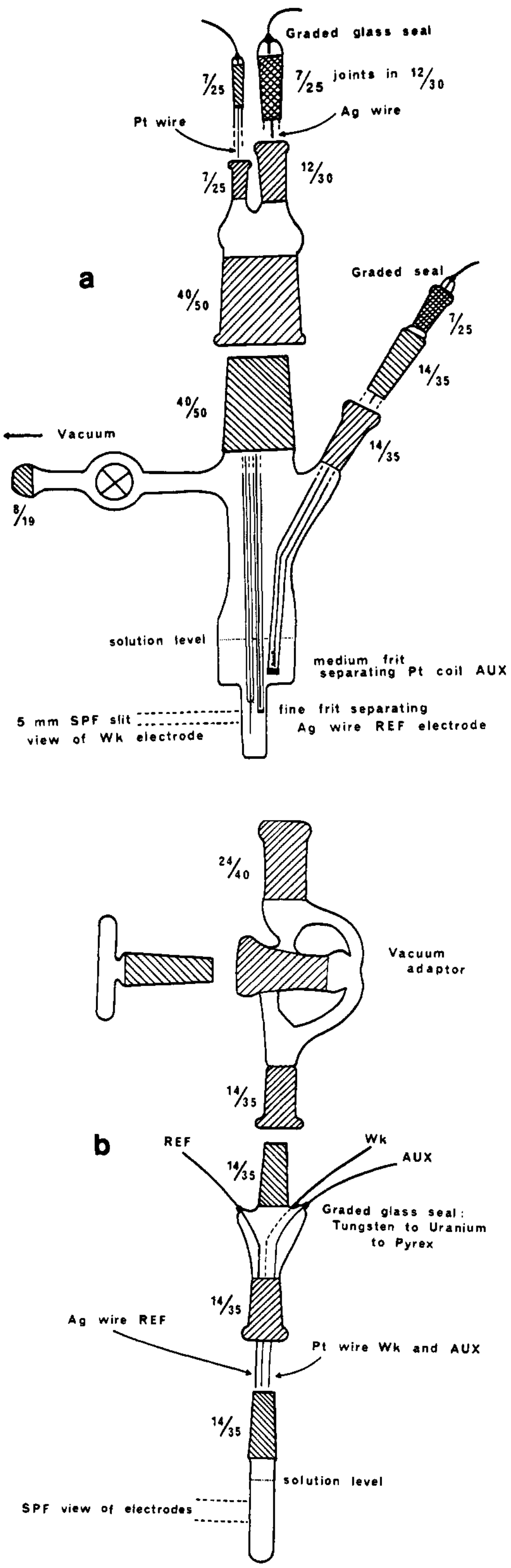


Figure 1. Ecl cells: (a) general purpose cell; (b) the ecl cell used for studying the concentration and frequency effects.

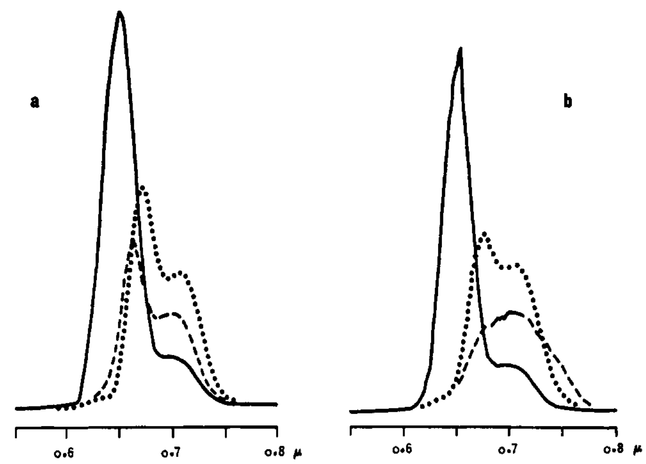


Figure 2. Laser excited fluorescence of TPP: (a) vertical excitation at the geometric center of the cuvette (···) 1.00 mM, (---) 0.100 mM, and (——) 0.0100 mM TPP solutions in CH_2Cl_2; (b) vertical excitation positioned for maximum (*ca.* 7 mm) (··· and ---) and minimum (*ca.* 1 mm) (——) emission path length in the cuvette; the concentrations and SPF multiplier settings were (——) 1.00 mM, 3×; (···) 1.00 mM, 30×; (---) 2.00 mM, 100×.

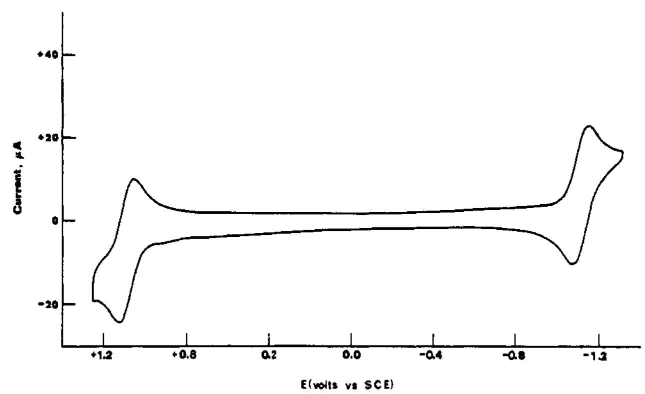


Figure 3. Cyclic voltammogram of TPP at a platinum electrode. The solution contained 1 mM TPP and 0.2 M TBAP in MC. The scan rate was 100 mV/sec.

fluorescence emission, especially in the vicinity of the 650-nm peak, by TPP (self-absorption), self-quenching may also occur. These effects are illustrated in Figure 2, where the fluorescence of several concentrations of TPP in MC with excitation with the 632.8-nm line of a He–Ne laser for different emission path lengths are shown. Note that as the emission path length is decreased (Figure 2b) the ratio of the intensities of the 650–700 peaks increases because of decreased self-absorption. When the excitation path length is minimized the fluorescence intensity increases with increasing concentration, although not linearly, probably because of residual inner filter effects.

Electrochemical Data. A typical cyclic voltammogram of a MC solution containing 1 mM TPP and 0.2 M tetra-n-butylammonium perchlorate (TBAP) at a platinum electrode is shown in Figure 3. Peak potentials for these waves and data for other compounds employed in the ecl experiments are given in Table I. The values for $E_p - E_{p/2}$ and $E_{pa} - E_{pc}$ as well as i_{pa}/i_{pc} ratios near 1 demonstrate that the half-reactions are nernstian and that the anion and cation radicals of TPP are stable in MC for the duration of the cyclic voltammetric experiment. The deviations of the ΔE_p from the nernstian value of 58 mV probably reflect incomplete compensation of the resistance between the reference electrode tip and working electrode in this fairly high resistance solution (the dielectric constant of MC is only about 9.1 at 25°). Rubrene and 10-MP also undergo reversible one-electron oxidations to stable cation radicals in the MC–0.2 M TBAP solution.

Table I. Electrochemical and Spectroscopic Data[a]

Compd (R)	$E_p(R^+/R^{2+})$, V	ΔE_p, mV	$E_p(R/R^+)$, V	ΔE_p, mV	$E_p(R/R^-)$, V	ΔE_p, mV	$E_p(R^-/R^{2-})$, V	ΔE_p, mV	$E(^1R^*)$, eV	$E(^3R^*)$, eV
TPP	+1.30	65	+1.05	70	−1.26	70	−1.66	95	1.90	1.57[d]
TPP[b]			+1.12[c]	62	−1.06	60				
Rubrene			+0.90	70					2.20	1.25[e]
10-MP			+0.84	57	NR[g]				3.4	2.4[f]

[a] Methylene chloride solvent used unless specified otherwise; see reference electrode; $\Delta E_p = E_{pc} - E_{pa}$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials. [b] DMF solvent. [c] Presumably an ece type oxidation. [d] G. D. Dorough, J. R. Miller, and F. Huennekens, *J. Amer. Chem. Soc.*, **73,** 4315 (1951). [e] Estimated from triplet level value for naphthacene: S. P. McGlynn, M. R. Padhye, and M. Kasha, *J. Chem. Phys.*, **23,** 593 (1955). [f] Estimated from value of phenothiazine: J. M. Lhoste and J. B. Merceille, *J. Chim. Phys. Physicochim. Biol.*, **65,** 1889 (1968). [g] NR = no reduction.

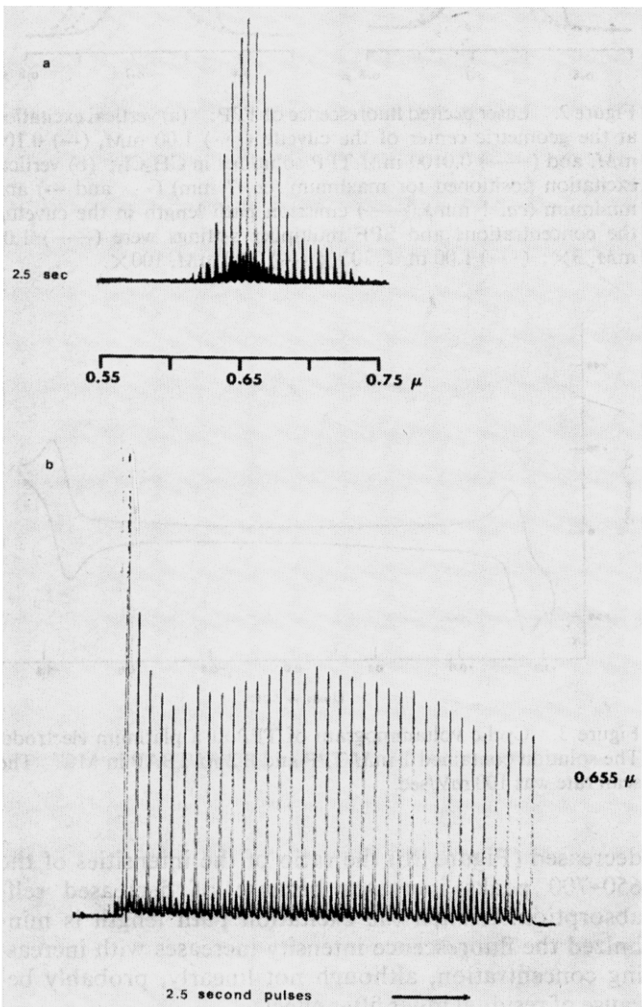


Figure 4. (a) Ecl spectrum resulting from pulsing at platinum electrode at a frequency of 0.2 Hz between +1.05 ($TPP\cdot^+$ production) and −1.26 V ($TPP\cdot^-$ production) in a MC solution containing 0.1 m*M* TPP and 0.2 *M* TBAP; (b) ecl intensity with time, solution as in a.

However, the reduction of rubrene in the presence of TPP in MC gives an ill-defined wave.

In DMF–0.1 *M* TBAP, TPP undergoes a clean one-electron reduction to the anion radical, as has previously been reported.[8] The oxidation wave under the same conditions is twice as large as the one-electron reduction wave, suggesting a rapid decay of the TPP^+ cation radical to a substance oxidizable at these potentials (an ece reaction) following the arguments given by Nelson.[9] Acetonitrile did not appear to be a useful solvent for ecl studies of TPP because of apparent filming of the electrode upon oxidation of TPP.

Ecl of TPP. When the potential of a platinum electrode immersed in a MC solution containing 0.1 m*M* TPP and 0.2 *M* TBAP is stepped between potentials on the reduction and oxidation waves of TPP at a frequency of 0.2 Hz, ecl emission with maxima at 655 and 705 nm is observed (Figure 4a). The intensity of this emission is quite weak and is less than about one-hundredth that of a 9,10-diphenylanthracene (DPA) solution under similar conditions. Comparable results were obtained when operating in the "two-electrode mode" with a square wave of ±1.90–±2.50 V applied between the working and counter electrodes. The positions of the ecl emission maxima correspond closely to those observed in fluorescence studies, so the emitting species is the first excited singlet of TPP ($^1TPP_1$). The intensity of the ecl emission upon continuous cycling at 0.2 Hz is quite steady (Figure 4b), with the light spikes alternating between a larger one during an oxidation half-cycle and a smaller one during the reduction half-cycle. This observed alternation of emission pulse heights is usually ascribed to instability of one of the radical ion reactants (in this case it would be the cation radical) and also is associated with an overall decrease of the envelope of the emission pulses.[10] Although a decrease is observed for the first few pulses, this behavior of TPP, especially since the cation radical appears quite stable in MC, probably is caused by different factors. The variation of ecl emission with concentration and frequency of applied square wave is shown in Figure 5. This concentration dependence is also different than the behavior usually observed[10,11] where intensity increases with increasing concentration of the radical ion parent molecule. Emission was never observed in these solutions upon stepping to only the reduction or oxidation peak or upon cycling from the anodic or cathodic peak to potentials where the other radical ion was not formed (preannihilation emission).

Ecl of Mixed Systems. To gain further insight into the nature of the ecl process, experiments in which a second radical ion generating component was added to the system (10-MP or rubrene) were undertaken. 10-MP is oxidized more easily than TPP, so that reaction between electrogenerated $10\text{-MP}\cdot^+$ and $TPP\cdot^-$ occurs upon cycling between the first oxidation and reduction waves. Typical emission from a solution containing 1 m*M* 10-MP, 0.1 m*M* TPP, and 0.2 *M* TBAP in MC is shown in Figure 6a. In this case the

(8) D. W. Clack and N. S. Hush, *J. Amer. Chem. Soc.*, **87,** 4238 (1965); G. P. Heiling and G. S. Wilson, *Anal. Chem.*, **43,** 550 (1971).
(9) R. F. Nelson, *J. Electroanal. Chem.*, **18,** 329 (1968).
(10) S. A. Cruser and A. J. Bard, *J. Amer. Chem. Soc.*, **91,** 267 (1969).
(11) S. A. Cruser and A. J. Bard, *Anal. Lett.*, **1,** 11 (1967).

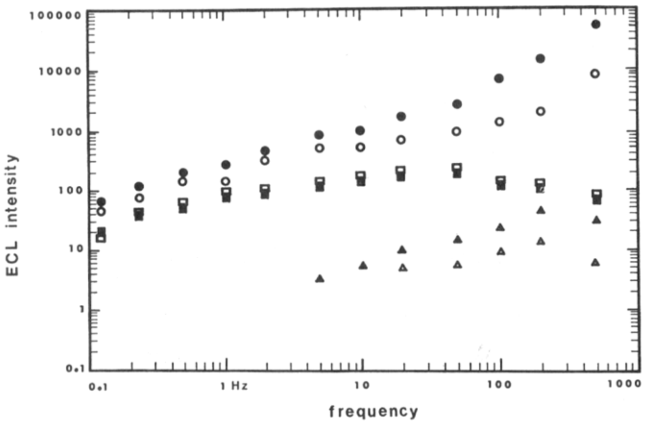


Figure 5. Variation of TPP ecl intensity with concentration and frequency of applied square wave: □ and ■, 1.0 mM; ○ and ●, 0.10 mM; △ and ▲, 0.010 mM TPP; filled points represent emission at about 650 nm, open points, emmission at about 700 nm (emission monochromator adjusted for maximum intensity). Intensities are corrected for wavelength response of the photomultiplier.

emission always occurs on the reduction cycle, and the emission maxima occur at 653 and 701 nm. Lower emission intensity is also observed when the electrode is pulsed between potentials corresponding to formation of the following species: (a) 10-MP$\cdot^+$ and TPP^{2-}, (b) TPP$\cdot^+$ and TPP$\cdot^-$, and (c) TPP$\cdot^+$ and TPP^{2-}. Although the emission from the solution containing 1 mM 10-MP with the electrode cycled between potentials for 10-MP$\cdot^+$ and TPP$\cdot^-$ formation was about four times that of a solution containing only 0.1 mM TPP, the ecl emission from a solution containing 0.1 mM 10-MP and 0.1 mM TPP was about half that of a 0.1 mM TPP solution (Table II). In no case was emission attributable to 10-MP or its products observed.

Table II. Relative Intensities of Ecl Emission for Several Mixed Systems[a,b]

Added component	Potential program, V	Rel intensity	$\Delta H°$[c], eV
None	+1.00 to −1.40	1.0	2.15
10^{-4} M 10-MP	+0.86 to −1.22	0.5	1.94
10^{-3} M 10-MP	+0.85 to −1.31	4.4	1.94
10^{-4} M rubrene	+0.99 to −1.20	1.4	2.00
10^{-3} M rubrene	+0.99 to −1.15	13.1	2.00

[a] Solution contained 10^{-4} M TPP and 0.1 M TBAP in methylene chloride. [b] Potentials given *vs.* Ag reference electrode. [c] Calculated from E_p values of Table I and eq 1.

Similar experiments were carried out with rubrene–TPP mixtures. Rubrene (R) is also oxidized to the radical cation more easily than TPP, but unlike 10-MP its excited states are of much lower energy (Table I) and ecl from rubrene itself is often observed. When a platinum electrode immersed in a MC solution containing 1 mM rubrene, 0.1 mM TPP, and 0.1 M TABP was cycled between potentials corresponding to formation of R$\cdot^+$ and TPP$\cdot^-$ (ΔE = 2.14 V), emission corresponding to both rubrene and TPP is observed (Figure 6b). Under these conditions the intensity of emission of the TPP is about 13 times larger than that of a 0.1 mM TPP alone solution (Table II). The intensity

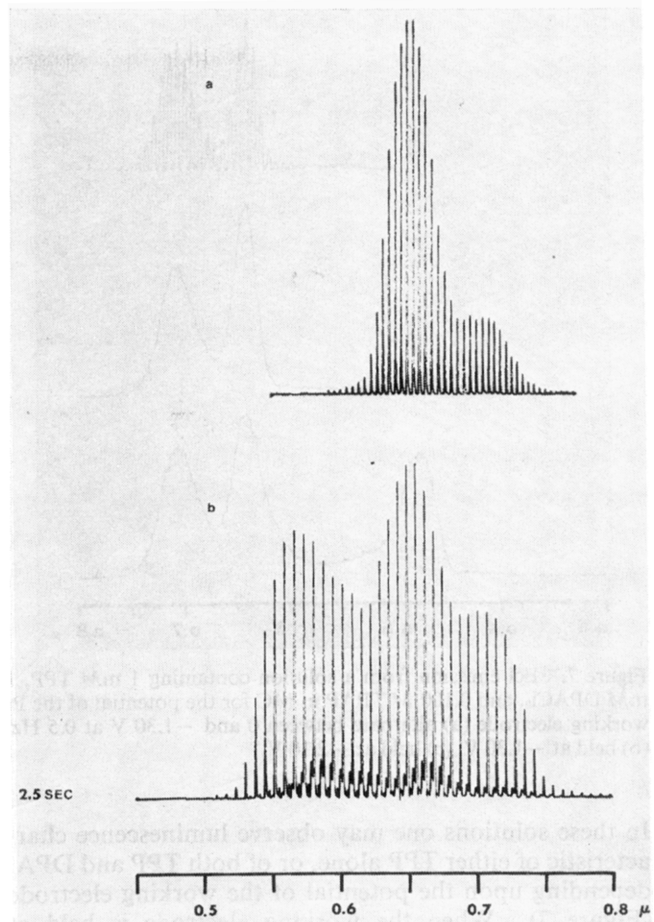


Figure 6. (a) Ecl of TPP–10-MP mixture. The solution contained 1 mM 10-MP, 0.1 mM TPP, and 0.2 M TBAP in MC. Pt electrode cycled at 0.2 Hz between +0.84 (10-MP$\cdot^+$ production) and −1.26 V (TPP$\cdot^-$ production). (b) Ecl of TPP–rubrene mixture. The solution contained 1 mM rubrene, 0.1 mM TPP, and 0.2 M TBAP in MC. Pt electrode cycled at 0.2 Hz between +0.90 R$\cdot^+$ production) and −1.26 V (TPP$\cdot^-$ production).

of rubrene emission under these conditions is very much smaller than that for a 1 mM rubrene solution with the electrode cycled between R$\cdot^+$ and R$\cdot^-$ formation. When the rubrene–TPP solution is cycled to these potentials, a large increase in the rubrene emission is observed, with the TPP emission now seen as a long wavelength shoulder on the rubrene emission peak. The larger light pulses from the R$\cdot^+$–TPP$\cdot^-$ reaction arise on stepping the electrode to the negative potentials, just as they do in the 10-MP–TPP system. When both the rubrene and TPP are at 0.1 mM concentration, the ecl intensity at 650 nm is somewhat larger than that of 0.1 mM TPP alone solution.

Ecl of TPP–$DPACl_2$ Mixtures. Siegel and Mark[12] have reported that the simultaneous reduction of 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) and an aromatic hydrocarbon such as DPA or rubrene leads to emission characteristic of that hydrocarbon and that the intensity of this emission is often much larger than that obtained by the same hydrocarbon in the usual radical ion annihilation ecl mode. Following this concept, we investigated the luminescence obtained upon reduction in MC solutions containing 1 mM TPP, 1 mM $DPACl_2$, and 0.1 M TBAP.

(12) T. M. Siegel and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **93**, 6281 (1971).

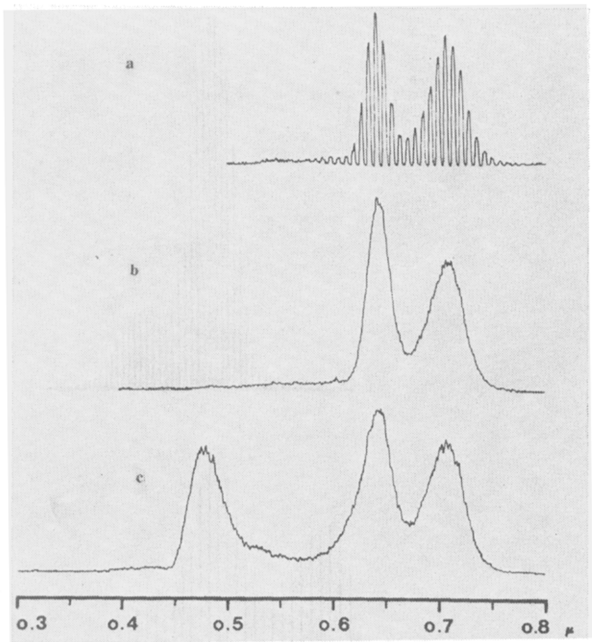


Figure 7. Ecl emission from a solution containing 1 m*M* TPP, 1 m*M* $DPACl_2$, and 0.100 *M* TBAP in MC for the potential of the Pt working electrode (a) alternate between 0 and −1.30 V at 0.5 Hz, (b) held at −1.30 V, (c) held at −2.10 V.

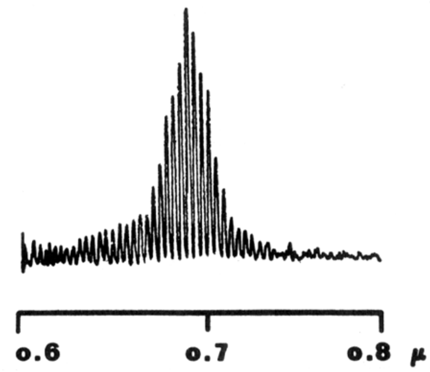


Figure 8. Ecl of phthalocyanine. Solution contained 0.3 m*M* Pc and 0.100 *M* TBAP in MC. Pt electrode cycled between +1.40 and −1.70 V at 1 Hz.

In these solutions one may observe luminescence characteristic of either TPP alone, or of both TPP and DPA, depending upon the potential of the working electrode (Figure 7). When the working electrode is held at potentials between −1.25 and −1.65 V *vs.* sce, or pulsed between 0 V and these potentials, the emission is only that characteristic of TPP (curves a and b). For potentials between −1.65 and −2.15 V (the reduction limit in MC) the emission contains components from both DPA and TPP. The DPA emission peak which normally occurs at 428 nm is distorted by absorption by the large Soret band of TPP. The DPA peak intensity is, at all potentials, less than those of the TPP peaks; the TPP peak intensity is comparable with that found in the annihilation ecl experiments in solutions containing 1 m*M* rubrene and 0.1 m*M* TPP.

Ecl of Phthalocyanine. When a platinum electrode immersed in a solution containing 0.3 m*M* phthalocyanine (Pc) and 0.1 *M* TBAP in MC is stepped between +1.40 and −1.70 V *vs.* Ag reference electrode, very weak emission, less than one-fiftieth of that of 0.1 m*M* TPP ecl, is observed (Figure 8). The observed emission, with an intensity maximum at 695 nm, corresponds closely to that of Pc fluorescence. Because of the very low intensity of this emission, the ecl of Pc was not investigated further.

Ecl of TPP in Other Solvents. When propylene carbonate solutions of 0.1 m*M* TPP and 0.1 *M* TBAP are employed for ecl studies, weak ecl was observed upon cycling of the electrode between potentials for generation of $TPP\cdot^-$ and $TPP\cdot^+$. Although the spectral characteristics of the emission were the same as those of the fluorescence of TPP, the low intensity of the emission discouraged further studies in this solvent. Ecl experiments were also conducted in DMF solutions. For a solution containing 3 m*M* TPP and 0.1 *M* TBAP cycling the working electrode at 0.2 Hz between +1.12 and −1.06 V *vs.* sce results in low intensity ecl emission at 662 and 702 nm. These values are close to the intensity maxima observed for the fluorescence of TPP in DMF, 657 and 702 nm. The ecl intensity increases when the positive potential step is decreased to +1.07 V. The low intensity observed in DMF is probably connected with the instability of $TPP\cdot^+$ in this solvent. Ecl emission characteristic of TPP is also seen for DMF solutions containing 1.0 m*M* 10-MP, 1.0 m*M* TPP, and 0.2 *M* TBAP upon cycling between potentials for formation of $10\text{-}MP\cdot^+$ and $TPP\cdot^-$

Discussion

Two main routes have been proposed for ecl reactions: (1) the direct production of excited singlet species by reaction of the electrogenerated radical ions and (2) initial production of a triplet species upon the reaction of the radical ions followed by triplet–triplet annihilation to form the emitting singlet species. A necessary condition for the first mechanism is that the enthalpy of the radical ion reaction is greater than that of the excited singlet produced (an "energy-sufficient" reaction). The enthalpy of the radical ion annihilation reaction between $TPP\cdot^-$ and oxidant ($TPP\cdot^+$, $10\text{-}MP\cdot^+$, or $R\cdot^+$) can be estimated from the peak potentials obtained from electrochemical measurements from eq 1.[13] These values, listed in Table II, suggest

$$-\Delta H^\circ = E_p(R'/R'\cdot^+) - E_p(R/R\cdot^-) - 0.16 \text{ (eV)} \quad (1)$$

that the reaction involving $TPP\cdot^-$ and $TPP\cdot^+$ has sufficient energy to populate the first excited singlet state directly (an energy sufficient reaction) while the reactions involving $10\text{-}MP\cdot^+$ and $R\cdot^+$ are marginal (within the uncertainty of calculations based on eq 1). The lowest TPP triplet state is accessible to all three redox processes. Although the $TPP\cdot^-$–$TPP\cdot^+$ reaction is energy sufficient, the experimental results are better described by the T route to ecl, involving formation of triplets in the electron transfer step followed by triplet–triplet annihilation.[13,14] This route would account

$$TPP\cdot^- + TPP\cdot^+ \longrightarrow {}^3TPP + TPP \quad (2)$$

$$2\,{}^3TPP \longrightarrow {}^1TPP^* + TPP \quad (3)$$

$${}^1TPP^* \longrightarrow TPP + h_\nu \quad (4)$$

(13) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, **94**, 691 (1972).

(14) See, for example, (a) R. Bezman and L. R. Faulkner, *ibid.*, **94**, 3699 (1972); (b) D. J. Freed and L. R. Faulkner, *ibid.*, **93**, 2097, 3565 (1971); (c) A. Weller and K. Zachariasse, *Chem. Phys. Lett.*, **10**, 197 (1971), and references cited therein.

for the very low efficiency of TPP ecl. The fluorescence yield, ϕ_f, of TPP is 0.11 and most of the $^1TPP^*$ produced crosses to the accessible triplet state rather than emit (the natural radiative lifetime and the radiationless decay time in benzene solution are about 100 and 16 nsec, respectively).[15] However, this ϕ_f value would not account for the low ecl emissions, unless quenching of the $^1TPP^*$ was unreasonably high or the yield of $^1TPP^*$ from the charge-transfer step was much lower than that of say, $DPA\cdot^-$ and $DPA\cdot^+$. Moreover, the ecl emission intensity is of the same order as that from the $TPP\cdot^-$ and $10\text{-}MP\cdot^+$ which is more likely to proceed *via* the T route. Finally, the variations in the heights of the reduction and oxidation pulses in the absence of instability of either reactant and the variation of intensity with concentrations is more like a known energy deficient system, $DPA\cdot^-$ and the tetramethyl-*p*-phenylenediamine radical cation where this behavior was ascribed to quenching of triplet species by radical ions,[16] rather than a system proceeding by the singlet route. There are several possibilities in the $TPP\cdot^-$–$R\cdot^+$ system for production of excited species. The reaction enthalpy is sufficient to produce either triplet TPP or triplet rubrene. Formation of excited singlet rubrene by triplet–triplet

$$TPP^- + R\cdot^+ \longrightarrow {}^3TPP + R \qquad (5)$$

$$TPP^- + R\cdot^+ \longrightarrow TPP + {}^3R \qquad (6)$$

annihilation can occur, as has been observed in, for example, the reaction of $R\cdot^+$ and benzoquinone anion radical,[13,17] while $^1TPP^*$ forms *via* the reaction in eq 3.

$$2\,{}^3R \longrightarrow {}^1R^* + R \qquad (7)$$

Aside from the quenching of the intermediate triplets by the radical ions, two other energy-transfer reactions can be envisioned as shown in eq 8 and 9.

$${}^3TPP + R \longrightarrow TPP + {}^3R \qquad (8)$$

$${}^1R^* + TPP \longrightarrow {}^1TPP^* + R \qquad (9)$$

Fluorescence experiments we have carried out demonstrate that TPP is an effective quencher of R fluorescence with a half-quenching concentration of TPP (for a 0.1 mM R solution) of about 0.01 mM. Attempts at observing increases in TPP emission upon excitation of R singlet and producing sensitized delayed fluorescence of R by excitation of TPP *via* reactions 7 and 8 were unsuccessful because of difficulties in selecting the proper excitation wavelength to observe these effects unambiguously and because of an apparent photochemical reaction between TPP and R which is currently under investigation. The mechanism proposed here for the production of $^1TPP^*$ is based on triplet–triplet annihilation of TPP. To our knowledge no delayed fluorescence of TPP has been observed, although sensitized delayed fluorescence of chlorophyll has been described.[18] Magnetic field effect studies on the ecl and delayed fluorescence of TPP systems would be useful in demonstrating the validity of the T-route mechanism. The ecl of TPP during the simultaneous reduction of TPP and $DPACl_2$ probably arises by the same route as that found for $DPACl_2$–aromatic hydrocarbon systems.[12] Reduction of $DPACl_2$ produces an oxidant (such as $DPACl\cdot$) which reacts with $TPP\cdot^-$ to form the excited state.

Acknowledgment. The support of this research by the U. S. Army Research Office, Durham, is gratefully acknowledged.

(15) P. G. Seybold and M. Gouterman, *J. Mol. Spectrosc.*, **31**, 1 (1969); A. T. Gradyushko, A. N. Sevchenko, K. N. Solov'ev, and M. P. Tsvirko, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **34**, 636 (1970).

(16) J. T. Bowman, Ph.D. Dissertation, University of Texas at Austin, 1970.

(17) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1968).

(18) C. A. Parker and T. A. Joyce, *Photochem. Photobiol.*, **6**, 395 (1967).