Electrogenerated chemiluminescence. 29. The electrochemistry and chemiluminescence of chlorophyll a in N,N-dimethylformamide solutions

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Electrogenerated Chemiluminescence. 29. The Electrochemistry and Chemiluminescence of Chlorophyll a in *N,N*-Dimethylformamide Solutions

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Abstract: The electrochemistry and ecl of chlorophyll a (Chl a) have been studied in highly purified DMF solutions. Cyclic voltammetric and coulometric experiments demonstrate that both the radical anion, (Chl a)$^{-}\cdot$, and the dianion, (Chl a)$^{2-}$, are fairly stable even under bulk electrolysis conditions in the absence of proton donors and oxygen. The protonation of (CHl a)$^{-}\cdot$ and (Chl a)$^{2-}$ by hydroquinone was also studied. Luminescence was observed for the reduction of Chl a in the presence of oxygen, but not for the Chl a anion–cation annihilation in the absence of oxygen. Chemiluminescence on mixing a solution of (Chl a)$^{-}\cdot$ and oxygen was also observed.

Chlorophyll a (Chl a) plays an important role in photosynthesis in the initial redox events following the absorption of light. Thus the nature and reactions of the oxidized and reduced forms of Chl a and the potentials associated with the electron-transfer processes of this molecule have been the subject of a number of investigations. Several authors have discussed the electrochemical behavior of Chl a.[1-7] The oxidation[5-7] of Chl a in aprotic solvents (e.g., CH_2Cl_2) occurs with the reversible formation of the radical cation which is stable even for time scales characteristic of bulk electrolysis. The reduction, which has been studied at a mercury electrode, shows two one-electron waves, similar to those observed with other metal porphyrins.[8,9] These latter results suggested that the radical anion formed at the first wave [(Chl a)$^{-}\cdot$] was not very stable. Thus Berg and Kramarčzyk[3] observed some reoxidation of (Chl a)$^{-}\cdot$ in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (Me_2SO) using the Kalousek commutator technique and estimated the half-life of the radical anion as between 0.01 and 0.1 s. The second reduction wave for Chl a was irreversible. Similarly, Kiselev et al.[4] reported, by using cyclic voltammetry, that the first reduction wave of Chl a in DMF was quasireversible and the second wave was irreversible. Felton et al.[2] reported that controlled-potential coulometric reduction of Chl a at a Pt electrode in Me_2SO at potentials of the first wave yielded an n_{app} value of 1.1 to 1.3. However, the solution produced by reduction could neither be reduced further at potentials of the second wave nor oxidized at potentials at the foot of the first wave. Spectroscopic examination of the reduced solution suggested that (Chl a)$^{-}\cdot$ decomposed by loss of a hydrogen atom (at the 10 position) to form the phase test intermediate; the hydrogen atom acceptor was not identified. The instability of (Chl a)$^{-}\cdot$ and (Chl a)$^{2-}$ as compared with the relative stability of the reduced forms of other metalloporphyrins and the free porphins[8-11] suggested that further investigation of the electrochemical reduction of chlorophyll be undertaken.

The question of ecl in chlorophyll systems is also of interest. Radical ion annihilation luminescence has been observed for α, β, γ, δ, tetraphenylporphin (TPP),[10] and for PtTPP and PdTPP.[11] Fairly extensive experiments in our laboratories failed to show ecl from Chl a in several solvents with careful purification and deaeration.[12] However, Krasnovskiĭ and Litvin[13] reported studies of Chl a in DMF with LiCl supporting electrolyte in which ecl was observed both upon cycling the potential of a Pt electrode between the oxidation and reduction waves (i.e., radical ion annihilation ecl) and upon reduction of Chl a in the presence of oxygen.

In this paper we describe experiments which demonstrate that both (Chl a)$^{-}\cdot$ and (Chl a)$^{2-}$ are quite stable in purified DMF and discuss the conditions for observing chemiluminescence in (Chl a)-containing systems.

Experimental Section

Chlorophyll a Separation.[14-15] Chl a was isolated from spinach leaves. After extraction with 80% acetone, the pigments were adsorbed on talc, eluted with ethyl ether, and separated by chromatography on a column of fine powdered sugar. To remove yellow compounds, the adsorbed pigments were washed with 1:1 *n*-pentane:benzene. Chl a and Chl b were further separated chromatographically by washing with *n*-pentane containing 0.5% 1-propanol. The Chl a zone was eluted with ethyl ether and dried on a vacuum line for 1 day, then stored in a drybox under a helium atmosphere. The final separation was carried out under subdued light, and the Chl a was stored in the dark.

Reagents. DMF was first purified by stirring for several days over molecular sieves and then using the procedure reported previously, method A.[16] For further purification, the solvent containing supporting electrolyte was treated with neutral alumina as recommended

Table I. Cyclic Voltammetry Results for Chlorophyll a[a]

Scan rate, mV/s	$E_{1/2} = -1.14$ V			$E_{1/2} = -1.61$ V		
	$i_p/(v^{1/2}C)^b$	i_{pa}/i_{pc}	ΔE_p, mV	$i_p/(v^{1/2}C)^b$	i_{pa}/i_{pc}	ΔE_p, mV
500	2.1	1.0	61	2.1	1.0	68
200	2.2	0.9	59	2.2	0.9	68
100	2.2	1.0	60	2.3	0.9	65
50	2.1	0.9	63	2.3	0.8	63
20	2.4	1.0	58	2.2	0.8	62
10	2.2	1.0	60			

[a] The solution was 0.48 mM chlorophyll a and 0.1 M TBAP in DMF at 25 °C. $E_{1/2}$ = half-wave potential vs. SCE. [b] μa, $s^{1/2}$; $V^{1/2}$, mM^{-1}; electrode area, cm^2.

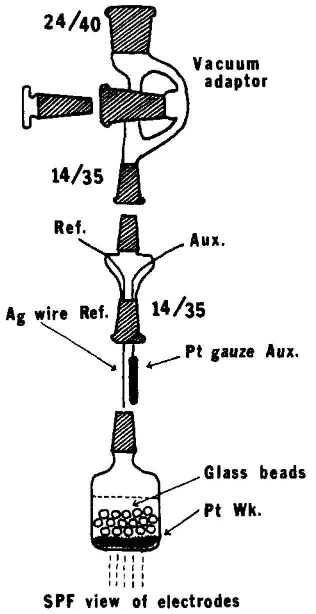

Figure 1. Ecl cell used for studying the chlorophyll emission.

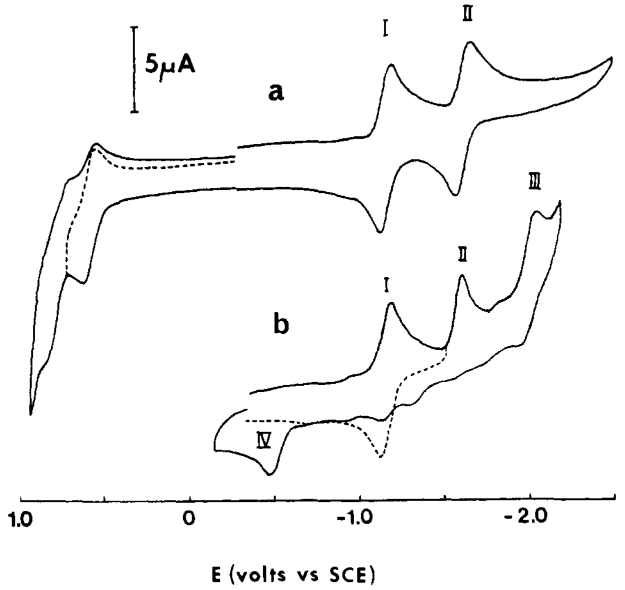

Figure 2. Cyclic voltammograms of 0.5 mM Chl a in 0.1 M TBAP-DMF at Pt electrode; scan rate, 200 mV/s; (a) without hydroquinone; (b) with the addition of 2 mM hydroquinone. Very similar behavior is observed for DMF not treated with alumina.

by Parker and co-workers.[17,18] Neutral alumina (10 g) was added to 50 mL of DMF containing supporting electrolyte in the glovebox, and the mixture was stirred overnight. The alumina was allowed to settle, and the solution was decanted. This was used to prepare the test solution. This treatment frees the solvents of proton donors and other electrophilic impurities. The neutral alumina (ROC/RIC Chemical Co., Belleville, N.J.) was dried before use under vacuum at 150 °C. Tetra-*n*-butylammonium perchlorate (TBAP), used as the supporting electrolyte, was polarographic grade (Southwestern Analytical Chemicals, Austin, Tex.). The TBAP was recrystallized from ethyl acetate, dried in vacuo for 24 h at 100 °C, and then stored in the glovebox.

Apparatus. The cell used for ecl studies is shown in Figure 1. The platinum gauze working electrode was placed very close to the glass cell wall to prevent absorption of any emission by the highly colored solution. The ecl was detected with an RCA 4832 photomultiplier tube. Since the intensity of ecl was too weak to detect using the monochromator of the Aminco-Bowman spectrophotofluorometer, a circular graded filter (Barr & Stroud Limited Co.) with a bandwidth of 20 nm was used to determine the ecl spectrum. The general techniques and cells used in the electrochemical studies have been described in previous papers in this series.[19]

Results and Discussion

Cyclic Voltammetry. A cyclic voltammogram of Chl a at Pt in DMF purified with neutral alumina shows two well-defined reduction waves with half-wave potentials of −1.14 and −1.61 V vs. saturated calomel electrode (SCE) and two oxidation waves at +0.59 and +0.8 V. Clear reversal peaks for the two reduction waves and the first oxidation waves were observed even with scan rates as slow as 20 mV/s (Figure 2a). The cyclic voltammetric parameters for the reduction waves, i.e., peak current ratio of the cathodic wave to the reverse anodic wave (i_{pc}/i_{pa}), peak potential separation (ΔE_p), and $i_p/v^{1/2}C$ values given in Table I show that these two reduction waves are reversible, one-electron processes and that (Chl a)$^{-}\cdot$ and (Chl a)$^{2-}$ are stable on this time scale in pure DMF. The first oxidation wave is also a reversible, one-electron process. When purified DMF which was not treated with neutral alumina was used, the reversal peak of the second wave disappeared and was only observed at low temperature (0 to −50 °C). Under these conditions two other waves appeared at −2.0 (III) and −0.4 V (IV) in this voltammogram (as in Figure 2b). Wave IV does not appear when the reversal potential of the sweep is more positive than the potential of the second wave. The ratios of the peak currents of waves III and IV to that of wave I decrease as the scan rate increases. These results indicate that the compound oxidized at −0.4 V is the product of a reaction between (Chl a)$^{2-}$ and an impurity in the solvent (probably water). This conclusion is supported by the experiments in the presence of proton donors described later. The half-wave potential separation between the first and the second reduction waves, 0.47 V, is the largest reported, compared with the values of others (Table II). The smaller values can probably be attributed to a positive shift of the second reduction wave because of a reaction of (Chl a)$^{2-}$ with impurities.

The reduction processes, Chl a to (Chl a)$^{-}\cdot$ and to (Chl a)$^{2-}$, can be attributed to electron transfer to the porphyrin ring[9] rather than to the central metal atom. The half-wave potential separation of 0.47 V compares well with that of a series of

Table II. Reported Half-Wave Potentials for Oxidation and Reduction of Chlorophyll a

Author	Solvent	Supporting electrolyte	Oxidation[e]		Reduction[e]		
			$E_{1/2}^{\mathrm{Ox}}(1)$	$E_{1/2}^{\mathrm{Ox}}(2)$	$E_{1/2}^{\mathrm{R}}(1)$	$E_{1/2}^{\mathrm{R}}(2)$	$E_{1/2}^{\mathrm{R}}(1) - E_{1/2}^{\mathrm{R}}(2)$
Felton et al.[a]	Me_2SO	0.1 M TPAP			−1.12	−1.54	0.42
Stanienda[b]	EtCN	0.1 M $LiClO_4$	+0.52	+0.77			
Berg et al.[c]	Me_2SO	0.04 M LiCl			−0.85[f]	−1.3[f]	
Kiselev et al.[d]	DMF	0.2 M LiCl			−1.12	−1.56	0.44
Present authors	DMF	0.1 M TBAP	+0.59	+0.8	−1.14	−1.61	0.47

[a] Reference 2. [b] Reference 5. [c] Reference 3. [d] Reference 4. [e] E/V vs. SCE. [f] E/V vs. mercury pool.

metalloporphyrins, 0.42 ± 0.03 V.[8] If the central metal ion were involved, one would not expect this agreement when the metal is changed. In general, the polarograms for reduction of metalloporphyrins show three or four reduction steps. With Chl a, the third and fourth reduction waves are not observed up to −2.8 V vs. SCE. The half-wave potential separation for the second and third waves, in metal porphyrins, is generally 0.75 ± 0.06 V,[8] so that the third wave of Chl a should be observed at about −2.4 V vs. SCE. This suggests that the energy level of the second lowest vacant orbital is higher for Chl a than those of other metalloporphyrins.

Effect of Proton Donors. The effect of addition of 2 mM hydroquinone (HQ) on the cyclic voltammogram of Chl a is shown in Figure 2b. Two new waves appear at −2.0 and −0.4 V. The first reduction wave (I) remains reversible even when 0.2 M HQ is added. The second wave is completely irreversible, and E_p of the second wave shifts to more positive potentials with increasing concentrations of HQ. The wave at −0.4 V does not appear when the reversal potential of the sweep is more positive than the potential of the second wave. Since the two new waves which appear on addition of HQ show the same E_p values and $i_p v$ dependence as those in the cyclic voltammogram of a solution not treated with neutral alumina, the instability of $(\mathrm{Chl\ a})^{2-}$ can be attributed to its reaction with proton donors in both cases, and the oxidation wave at −0.4 and reduction wave at −2.0 V can be assigned to one or more products of this reaction.

Controlled Potential Coulometry. Coulometric experiments were undertaken to study the long-term stability of $(\mathrm{Chl\ a})^{-\cdot}$ and $(\mathrm{Chl\ a})^{2-}$ under bulk electrolysis conditions. Coulometric reduction of 0.42 mM Chl a in 0.1 M TBAP-DMF with a Pt electrode held at −1.3 V give an $n_{\mathrm{app}} = 0.97$ for a 1-h experiment, where n_{app} is the number of faradays per mole of Chl a. The reduced product in solution is yellow-green. A cyclic voltammogram taken after controlled-potential electrolysis at −1.3 V compared with one before electrolysis is shown in Figure 3. The peak current of the wave I system was about 70% of the preelectrolysis wave I (Figure 3a). On the other hand, the peak current of wave II was almost the same as that of Figure 3a. Two new small waves appear at −0.2 (wave V) and −2.0 V (wave III). In another experiment, however, i_p of wave I was almost the same as that of wave II and of those before electrolysis; waves IV and V were absent. In this latter experiment, the Chl a solution was purified by stirring with neutral alumina for 1 day. The results of this experiment demonstrate that the species $(\mathrm{Chl\ a})^{-\cdot}$ is very stable, but is capable of reacting with traces of impurities (probably water) to form new species. The fact that i_p for wave II was unchanged upon electrolytic reduction and was larger than that for wave I in the experiment of Figure 3 suggests that the reaction product is reducible at the same potentials as $(\mathrm{Chl\ a})^{-\cdot}$. The new wave at −2.0 V is similar to that attributed to reaction of $(\mathrm{Chl\ a})^{2-}$ in the CV experiments with HQ, but the wave at −0.2 V is shifted slightly from wave IV in Figure 2b. There is no evidence in our experiments for loss of a hydrogen atom from $(\mathrm{Chl\ a})^{-\cdot}$, as observed by Felton et al.,[2] and we suspect that reaction of the radical anion with water may have occurred in those experiments.

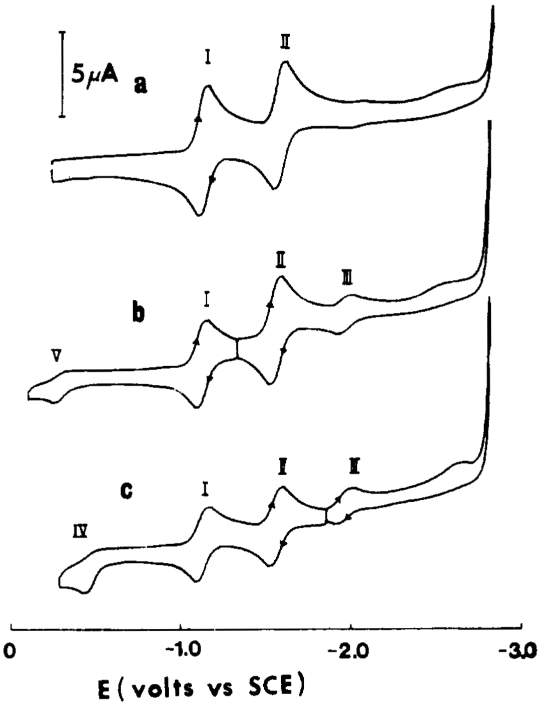

Figure 3. Cyclic voltammograms during various stages of reduction of 0.42 mM Chl a in 0.1 M TBAP-DMF at Pt electrode; scan rate, 200 mV/s; (a) before reduction; (b) after reduction at −1.3 V vs. SCE; (c) after reduction at −1.75 V.

Further coulometric reduction of the solution at −1.75 V gave an n_{app} of 0.90 producing a dark-brown colored solution. The reduced product was stable as shown by the cyclic voltammograms of this solution (Figure 3c). The peak potentials of the waves I and II of this figure are the same as those of the original Chl a solution, demonstrating that the reduction product was $(\mathrm{Chl\ a})^{2-}$. A new oxidation wave appeared at −0.4 V (wave IV), replacing wave V; this potential is the same as that of wave IV in the CV protonation experiments. Coulometric reoxidation of this solution at −1.3 and −0.6 V give $n_{\mathrm{app}} = 0.57$ and 0.51, respectively.

Ecl Experiments. The fluorescence spectrum of dilute (10^{-6} to 10^{-5} M) DMF solutions of Chl a shows a main band at 680 nm with a shoulder at about 730 nm (Figure 4a), in agreement with previous results in other solvents.[20-22] In a more concentrated solution (0.3 mM), the main band shows an apparent shift toward longer wavelengths (700 nm) and the intensity decreases. However, when the excitation path length is minimized (0.02 mm), the main band wavelength is the same as that of the dilute solution, so that the apparent concentration dependence of the fluorescence spectrum is due to self-absorption by Chl a and not dimerization.[22] The wavelength of the absorption maximum of Chl a (660 nm)[23] is almost the

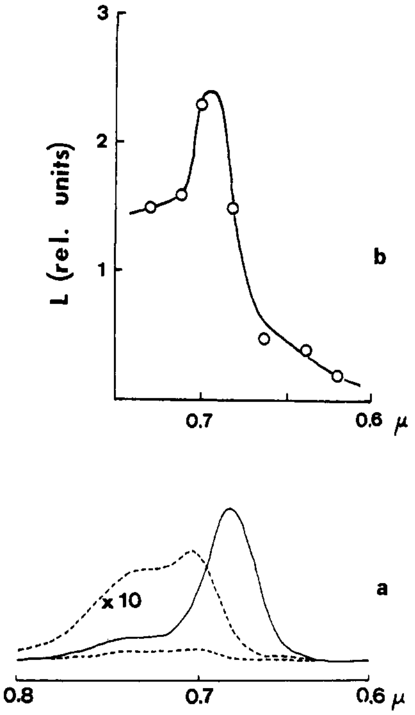

Figure 4. (a) Fluorescence spectra of Chl a in DMF with 430-nm excitation: (—) 0.004 mM, (- - -) 0.3 mM. (b) Ecl spectrum of 1 mM Chl a in 0.1 M TBAP-DMF under 1 atm O_2 using circular graded filter with transmission half-width of 20 mm. The intensity measured after electrolysis at −1.3 V during 1.0 s.

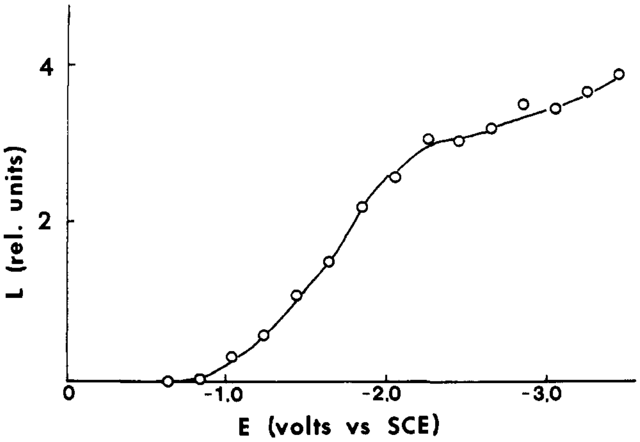

Figure 5. Ecl intensity vs. electrode potential for 1 mM Chl a in 0.1 M TBAP-DMF. Ecl intensity measured after electrolysis during 0.5 s.

same as the wavelength of the fluorescence main band (680 nm).

With the usual ecl cell, where the working electrode is immersed in the central part of the solution, no emission is observed on pulsing between potentials on the reduction and oxidation waves of Chl a either in the presence or absence of oxygen. When the ecl cell of Figure 1, where a platinum gauze working electrode is in contact with the cell wall, is used, ecl is observed on reduction of Chl a in the presence of oxygen. Even with this cell, however, no emission is found with pulsing between potentials on the reduction and oxidation waves of Chl a in the absence of oxygen. Figure 5 shows the relationship between the ecl intensity and electrode potential in the presence of oxygen at a pressure of 1 atm. Emission is observed at potentials more negative than −1.0 V, with the intensity increasing until about −2.2 V, where a plateau is observed. Taking account of the reduction potentials of Chl a, (Chl a)$^{-}\cdot$, and oxygen (ca. −0.8 V),[24] we can attribute the emission to a reaction between (Chl a)$^{-}\cdot$ and oxygen or between Chl a and $O_2^{-}\cdot$. The intensity of emission increases approximately linearly with the pressure of oxygen up to 300 Torr (Table III). The ecl spectrm, extending from 650 to 750 nm with the maximum at 690 nm (Figure 4b), is nearly identical with the fluorescence spectrum of Chl a. The apparent red-shift of the maximum and the relatively large shoulder at about 730 nm can be attributed to self-absorption. The ecl spectrum reported by Krasnovskii et al.[13] showed an additional peak at 640 nm. This peak may be due to a reaction with impurity. When we used 0.2 M LiCl in place of the 0.1 M TBAP as supporting electrolyte, the same peak at 640 nm was observed. The shape of the emission intensity (*L*)-time transient when the platinum electrode was pulsed from 0 to −1.3 V for 0.2 s is shown in Figure 6a. The rise time of the emission is slow compared with other ecl processes; a decay in *L* begins soon after the pulse terminates, but emission continues for some time after the pulse. The log-plot analysis of the transient decay (Figure 6b) is linear with time, and the time for *I* to decay to half-intensity is independent of oxygen pressure (Table III). These results suggest that the emission process is a first-order reaction with a rate constant of 1.3 s^{-1} determined from the time of half-intensity and 1.4 s^{-1} from the log-plot analysis.

Table III. Effect of Oxygen Pressure on Intensity and Decay Rate of Chlorophyll a Emission[a]

O_2 pressure, cm Hg	Emission intensity, rel unit	Half-decay time,[b] $t_{1/2}$, s
3.7	9.4	0.48
11.2	15.5	0.46
17.5	20.9	0.50
23.2	27.3	0.55
27.5	29.3	0.50
30.8	31.6	0.49
34.4	30.9	0.48
39.4	30.0	0.51
51.5	30.7	0.55
61.7	32.3	0.52
76.0	29.5	0.55

[a] 1 mM Chl a and 0.1 M TBAP in DMF; Pt electrode pulsed from 0 to −1.3 V; pulse duration, 0.5 s. [b] Measured from the time that the emission peak is observed.

We could not observe an oxidation wave for Chl a with a DMF solution containing 1 mM Chl a and 0.2 M LiCl, the conditions of ref 13, because of the large oxidation wave of chloride ion. However, pulsing between the reduction wave and oxidation limit in DMF-0.2 M LiCl did not produce ecl in the absence of oxygen. In the presence of oxygen, emission was again observed on reduction of Chl a.

The results obtained here, as well as our previous studies,[12] demonstrate that ecl does not occur upon reaction of (Chl a)$^{-}\cdot$ and (Chl a)$^{+}\cdot$. Thermodynamic reasoning suggest that formation of the triplet state (^{3}Chl a) but not the singlet state (^{1}Chl a*) should be possible upon radical ion annihilation. The enthalpy of the cation-anion annihilation reaction can be estimated from the peak potentials obtained from electrochemical measurements:[25]

$$-\Delta H° = E_p(R/R^+) - E_p(R/R^-) - 0.16\ (\text{eV}) \qquad (1)$$

These values, listed in Table II, suggest that the enthalpy of reaction between (Chl a)$^{+}\cdot$ and (Chl a)$^{-}\cdot$, 1.63 eV, is smaller than the energy needed to populate the first excited singlet state (1.82 eV), but sufficient to populate the triplet state (1.40 eV).[26] Emission by triplet-triplet annihilation might be possible.[25,27] The ecl found with Pd(TPP) and Pt(TTP) was ascribed to direct emission from the triplet state.[11] Phospho-

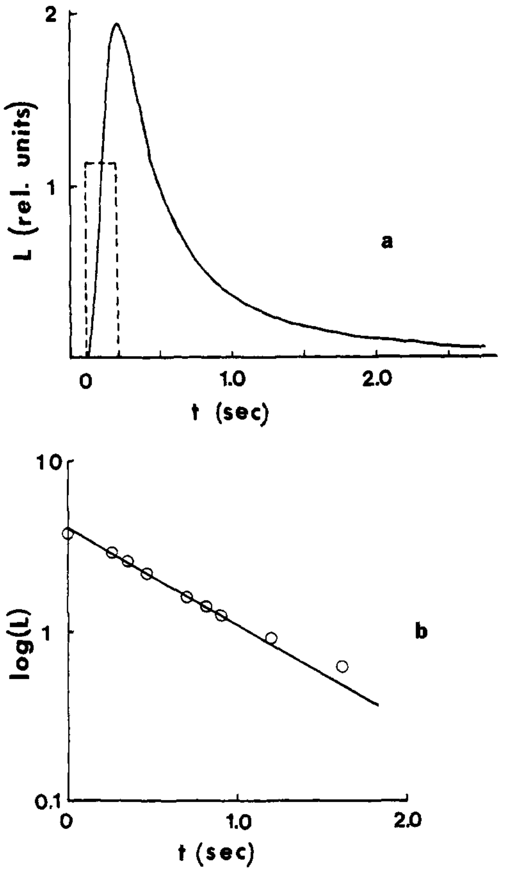

Figure 6. (a) Ecl intensity of 1 mM Chl a in 0.1 M TBAP-DMF under 520 Torr O_2 vs. time. The intensity measured after electrolysis at −1.3 V during 0.2 s: (—) ecl intensity, (- - -) electrode potential. (b) Plot of log (L) vs. time for 1 mM Chl a in 0.1 M TBAP-DMF under 520 Torr O_2; L, intensity of emission. Time measured from peak of intensity.

rescence of Chl a is usually not observed in fluid solution.[28] Delayed fluorescence of Chl has been reported,[28] however, and triplet-triplet annihilation was proposed as the mechanism of TPP ecl.[10] However, the intensity of ecl for both the TPP and M(TPP) systems was rather weak, and this was ascribed to quenching of the triplet state by the ground-state species via the formation of a triplet excimer. This same effect may be contributing to the quenching of the ecl of Chl a. Alternately, ^{3}Chl a may be very effectively quenched by radical ions.

When the Chl a is excited by light to the first excited singlet state, the small reaction enthalpy of the anion-cation annihilation reaction favors the following disproportionation reaction to the extent of about 4.6 kcal:

$$ {}^1\text{Chl a}^* + \text{Chl a} \rightarrow (\text{Chl a})^{+\cdot} + (\text{Chl a})^{-\cdot} \qquad (2) $$

$(\text{Chl a})^{+\cdot}$ has been proposed as an intermediate in photosynthetic processes.[7] $(\text{Chl a})^{-\cdot}$ may also play a role as the initial reductant in photosynthesis. Formation of both $(\text{Chl a})^{+\cdot}$ and $(\text{Chl a})^{-\cdot}$ has been observed by pulse radiolysis of glasses,[29] and the electron-transfer reaction of $(\text{Chl a})^{-\cdot}$ with vitamin K_3, phenazine methosulfate, and flavin mononucleotide was shown to be rapid, probably much faster than the reaction with proton donors.

Chemiluminescent Reaction of $(\text{Chl a})^{-\cdot}$ and Oxygen. To determine the reaction products of the chemiluminescence reaction, an experiment involving mixing of bulk $(\text{Chl a})^{-\cdot}$ and O_2 was undertaken. A solution of 0.2 mM Chl a and 0.1 M TBAP in alumina-treated DMF was placed in an electrolysis cell. After the cell was evacuated, a solution of 0.2 mM (Chl a)$^{-\cdot}$ was prepared by controlled-potential electrolysis at −1.3 V. When dry air was introduced into the cell, and the solution stirred, chemiluminescence which increased and then decreased with time was observed (Figure 7a). After the reaction was completed and the cell was evacuated again, the cyclic voltammogram of the above solution showed four waves (Figure 7b). The half-wave potentials of the two larger waves at −1.14 and −1.61 V agree with those of Chl a. The peak currents of these were 80% of those of the solution before electrolytic reduction and reaction. Two small new waves at −0.9 and −1.4 V appeared. The peak height of the new wave at −0.9 V was larger and those of the −1.14 and −1.61 V waves were smaller when the solution was not degassed completely. A small diffusion-controlled prewave at about −0.9 V was also found in the polarographic studies of Kiselev et al.[4] and Berg.[3] The former authors ascribed this prewave to Chl a dimers. This prewave in deaerated Chl a solutions has a height of about 3% of the −1.14 V wave. Although the chlorophylls are known to form aggregates in very low dielectric constant solvents (e.g., CCl_4, benzene, hydrocarbons),[30] we feel the prewave is more reasonably assigned to an O_2-Chl a adduct.

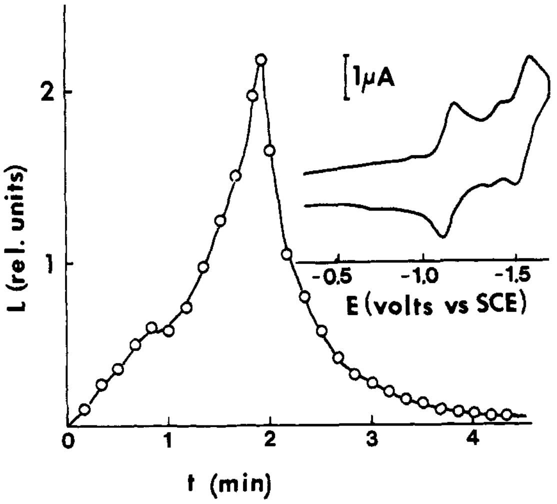

Figure 7. (a) The intensity of chemiluminescence between 0.2 mM (Chl a)$^-$ in 0.1 M TBAP-DMF and dry air vs. time. (b) Cyclic voltammogram of the solution after the reaction is completed and degassed again; scan rate, 200 mV/s.

Many weak chemiluminescent reactions involving molecular oxygen are known,[31] and peroxide intermediates are often proposed as precursors to the excited state. Such intermediates, e.g., formed by the reaction of small amounts of $O_2^{-\cdot}$ with protons, followed by further reduction and reaction with Chl a, are possible. Very weak chemiluminescence upon reaction of O_2 and photoreduced chlorophyll (formed by irradiation of chlorophyll solutions in pyridine containing ascorbic acid)[32] and upon reaction of chlorophyll, probably with peroxides, in boiling tetralin,[33] has been reported.

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Bimolecular Decay Routes in the Singlet Quenching of Naphthalenes by Chloroacetonitrile

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Abstract: The fluorescence of naphthalene, 2-methoxynaphthalene, 2,6-dimethoxynaphthalene, and 1,4-dimethoxynaphthalene is quenched by chloroacetonitrile in acetonitrile solution. Quenching rate constants span almost three orders of magnitude. Excited triplet states result from quenching three of the naphthalenes and photochemical reaction is also observed. Radical cations of 2,6- and 1,4-dimethoxynaphthalene were observed by flash spectroscopy. The quantum yields for quenching induced triplet formation and limiting yields of photoproducts (as measured by HCl formation) permit elucidation of the consequences of the quenching process.

A topic of current interest in organic photochemistry is the quenching of electronically excited states by compounds not able to accept energy by classical energy transfer. One aspect of this problem with which we and others have been concerned is the quenching of electron rich aromatics by compounds containing an activated C–Cl or similar bond.[3,4] In particular, we were interested in gaining more specific information as to the precise pathways and consequences of singlet quenching in these systems.

We recently reported a method for the determination of intersystem crossing quantum yields of benzene derivatives which is also useful for other systems in which aromatic triplet–triplet absorption cannot be conveniently measured.[5] The method is based on the enhancement of intersystem crossing in the aromatic by a heavy atom additive such as xenon and determination of increased triplet formation by a chemical "triplet counter". For xenon the only effect of quenching aromatic singlets is assumed to be formation of the aromatic triplet. We pointed out, however, that for other quenchers triplet formation might be only one of the consequences of singlet quenching and that the method could be extended to the determination of the fraction of quenching events which produce triplets if the intersystem crossing quantum yield of the aromatic were independently known. We now report the measurement of triplet formation associated with the singlet quenching of naphthalenes by chloroacetonitrile which, with other results, clarifies the effects of methoxy substitution on the bimolecular decay modes of the naphthalene–chloroacetonitrile system.

Results

Rate constants for chloroacetonitrile quenching of the fluorescence of naphthalene and three methoxy-substituted naphthalenes in acetonitrile solution were determined according to usual Stern–Volmer kinetics and are given in Table I. The agreement of quenching rate constants determined from fluorescence intensities and from fluorescence lifetimes indicates that the quenching we are observing is indeed a dynamic process. Although they increase with increasing methoxy substitution and span almost three orders of magnitude, these values by themselves tell us little about the ultimate consequences of the quenching act.

Preliminary experiments indicated that triplets, photoproducts (including HCl), and ions were produced upon irradiation of these systems. Our initial interest, therefore, was in determining whether quenching-induced triplet formation occurred and, if so, the quantum yield for this process. On the basis of the mechanism outlined in eq 1–11 and under the condition of constant light dose, this fraction can be obtained from relative fluorescence intensities of the aromatic (A) and relative conversions of a triplet counter as a function of quencher (Q) concentration. The triplet counter used in these experiments was *cis*-piperylene (*cis*-P) and the appearance of *trans*-piperylene (*trans*-P) was monitored by GLC. The relationship between these quantities is expressed in eq 12, the derivation of which has been outlined previously.[5] The symbol β is used for the ratio $k_7/(k_7 + k_8)$. Since the fluorescence quenching rate constant (k_q) equals $[k_6(k_7 + k_8)]/(k_{-6} + k_7$