Electrochemiluminescence of Perylene. The Role of Direct Excimer Formation[1a]

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Received August 2, 1969

Abstract: The electrochemiluminescence (ecl) of perylene was investigated with an image intensifier spectrograph using single-pulse excitation. The component of perylene ecl at wavelengths longer than perylene fluorescence was found to be dependent on solvent and on the direction of polarity change of the potential pulse. Such behavior is not consistent with the previous assignment of this long-wavelength component to a perylene excimer. In acetonitrile, the amount of the longer wavelength component is greater than in benzonitrile. Since cation radical stability appears to be greater in the latter solvent, the long-wavelength components in perylene ecl can be attributed to cation decomposition products. At higher concentrations ($>10^{-3}$ *M*), the behavior of the perylene cation reduction wave is abnormal. This behavior is reflected in the difference in ecl intensity *vs.* time curves for cation-to-anion and anion-to-cation excitation.

The direct formation of excimers in the electrochemiluminescence (ecl) of aromatic hydrocarbons has been a subject of recent interest.[2-5] Hoytink's calculations indicate that excimer formation from electron transfer reactions should not be a favorable process.[2b] However, several workers have suggested direct excimer formation to explain ecl occurring at wavelengths to the red of hydrocarbon fluorescence, one such example being perylene.[2a] In fact, reported spectra show most of the ecl emission at wavelengths longer than perylene fluorescence, suggesting that direct excimer formation is a highly favorable pathway. Perylene excimer formation *via* the normal photoexcited mechanism is not an efficient process; in fluorescence quenching studies[6] and in triplet–triplet annihilation, it is weak or absent.[7] Chandross, *et al.*, postulated a charge-transfer excimer unique to the ecl mechanism and capable of more efficient fluorescent emission than the normal photoexcited excimer to explain the discrepancy.[2a]

Several workers have studied the ecl spectra of anthracene derivatives where emission also is observed at wavelengths longer than hydrocarbon fluorescence.[2a,3-5] It has been demonstrated[4,5] that in several cases this long-wavelength emission is due to compounds formed by reactions of the aromatic hydrocarbon cation radical, rather than by excimer formation. Anthracene radical cations are unstable by electrochemical criteria, and reactions of these species under ecl conditions lead to fluoresent products.[4,5] 9,10-Dimethylanthracene is reasonably stable by electrochemical criteria, but reaction products are not fluorescent. Therefore, we have reinvestigated the ecl spectra of perylene which, by analogy with anthracene, should form fluorescent decomposition products, but which is also moderately stable by electrochemical criteria.

We have studied perylene ecl spectra using an image intensifier spectrograph.[8] Measurements of perylene ecl spectra as a function of solvent and which radical is generated first showed direct perylene excimer formation to be less efficient than previously suggested. Other mechanisms, such as energy transfer or mixed annihilation reactions involving cation decomposition products, are more likely causes of the long-wavelength ecl component. Some anomalous electrochemical behavior of the perylene cation and of perylene ecl as a function of concentration and time of generation are also reported.

Experimental Section

Perylene obtained from Aldrich Chemical Co. was vacuum sublimed twice before use. Spectral grade acetonitrile from Matheson Coleman and Bell was distilled from P_2O_5 after standing over $CuSO_4$ and Na_2SO_4 for several days. Matheson Coleman and Bell spectral grade benzonitrile was used without purification.

Tetra-*n*-butylammonium perchlorate (TBAP) was used as supporting electrolyte. It was prepared from G. Frederick Smith reagent grade 70% $HClO_4$ and Southwestern analytical grade tetra-*n*-butylammonium hydroxide. Required amounts of TBAP were put in small bottles and placed in a drying pistol for 24–48 hr to ensure minimum water content.

The potentiostat used for both current-voltage curves and for ecl excitation was composed of a Heath Model EUA-19A operational amplifier and Model EUA-19A polarography module. Readout for current-voltage data was on a Mosley 7035B X-Y recorder. The cell used for all electrochemical and ecl measurements was of the three-electrode type, consisting of platinum counter and working electrodes and a $Ag|Ag^+$ (0.01 *M* in acetonitrile or in benzonitrile) reference electrode separated from the solution by a Vycor plug. All solutions were 0.1 *M* in TBAP.

Ecl spectra were taken on an image intensifier spectrograph. Details of the spectrograph operation are given elsewhere.[8] The ecl spectra were recorded on Type 107 Polaroid film (ASA 3000) which produced a positive print. Negatives were made from these prints for readout on a Leeds and Northrup recording microphotometer, Model 6700-A2. The great sensitivity of this spectrograph (gain ~70,000) enables one to obtain an ecl spectrum with minimum electrolysis. In addition, the ecl spectra on the cation-

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[1] (a) This work was supported in part through funds provided by the United States Atomic Energy Commission under Contract No. AT(30-1)-905; (b) National Institutes of Heath Predoctoral Fellow, 1967–1968; (c) Massachusetts Institute of Technology; (d) address all correspondence to this author at the University of Georgia.

[2] (a) E. A. Chandross, J. W. Longworth, and R. E. Visco, *J. Amer. Chem. Soc.*, 87, 3259 (1965); (b) G. J. Hoytink, *Discuss. Faraday Soc.*, 14 (1968).

[3] C. A. Parker and G. D. Short, *Trans. Faraday Soc.*, 63, 2618 (1967).

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[6] J. B. Birks and L. G. Christophorou, *Proc. Roy. Soc., Ser. A*, 271, 571 (1964).

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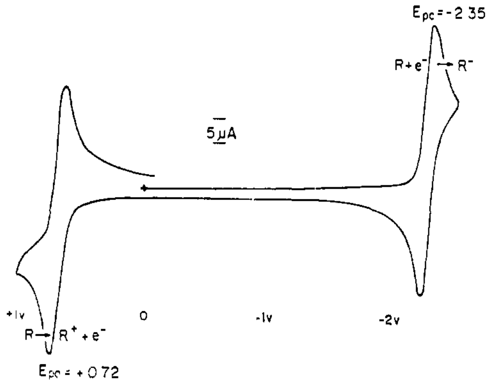

Figure 1. Current–voltage curve of perylene in benzonitrile: $C = 7.6 \times 10^{-4}$ *M*, electrode area = 0.10 cm², reference electrode = AgAg⁺ (0.01 *N*) in $C_6H_5(N)$, ν = 166 mV/sec, + = 0 V, 0 μA.

to-anion (+ to −) and anion-to-cation (− to +) cycles can be obtained independently by use of single-pulse excitation.

A three-electrode cell of tubular design was used in the ecl experiments. The cell consisted of a piece of 18-mm (o.d.) Pyrex tubing to which were attached four standard-taper outer joints, holding the three electrodes and a nitrogen bubbler. This design eliminated interference from counter-electrode emission. The test electrode (area = 0.10 cm²) was placed as close as possible to the spectrograph slit. Solutions were thoroughly deoxygenated.

Ecl excitation was obtained by use of a pulse generator capable of applying a single square-wave signal of adjustable length.[9] Ecl spectra were taken with a potential range from *ca.* 60 mV past the peak of one redox process to *ca.* 60 mV past the peak of the other. The procedure was to generate one ion for 1 sec and then switch to the potential of the second ion. Spectra could be obtained on one to five of these pulses with a spectral band pass of *ca.* 100 Å. Monitoring the reference electrode during ecl excitation with a Tektronix 502A oscilloscope showed that potential overshoot was negligible.

Fluorescence spectra of perylene in acetronilite and in benzonitrile were taken on the image intensifier for comparison with ecl spectra. All spectra were calibrated with mercury lines from an Ultra-Violet Products Inc. Pen-ray lamp. The relative intensities of the vibronic components for both ecl and fluorescence spectra are dependent on exposure time—an artifact of photographic recording. All image intensifier spectra are averages of several normalized spectra.

A WaveTek Model 110 signal generator was used to continuously excite ecl for the ecl *vs.* time measurements. Ecl was detected by an RCA 1P21 photomultiplier powered by a Kepco Model ABC power supply operated at 750 V. The photomultiplier signal was amplified by a Consolidated Electronics Corp. Type 1-165 DC amplifier, and read out on two channels of a Consolidated Electronic Corp. Type 5-124 recording oscillograph.

Results

Electrochemistry. The electrochemical oxidation and reduction curves for perylene in benzonitrile are shown in Figure 1. Both redox processes have large reverse waves, indicating the perylene cation and anion are moderately stable over the period of measurement. The ratio of the current of the reverse reaction (i_r) to that of the forward reaction (i_f) for both perylene oxidation and reduction is 0.85–0.95 at v = 33–333 mV/sec. The presence of a second oxidation and reduction wave beyond the initial cation and anion waves makes location of the base line somewhat uncertain.

Unusual behavior of the perylene oxidation wave is apparent from Figure 2. At concentrations greater than 10^{-3} *M*, the cation reduction wave becomes diffuse, as though other reduction processes were occurring at nearly the same potential. No corresponding change is noted in the oxidation wave of the perylene anion.

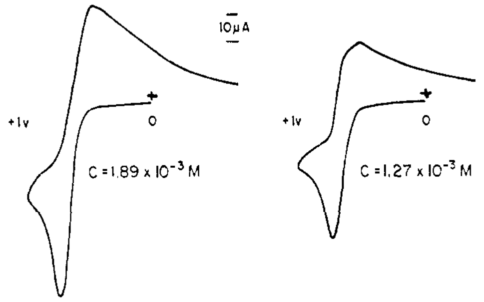

Figure 2. Oxidation of perylene in benzonitrile at 1.89 and 1.27 × 10^{-3} *M*: electrode area = 0.10 cm², reference electrode = Ag|Ag⁺ (0.01 *N*) in $C_6H_5(CN)$, ν = 166 mV/sec, + = 0 V, 0 μA.

Ion radical reactivity is reflected in the value of $i_p/\nu^{1/2}C$ as a function of ν.[10] Calculated results for $i_p/\nu^{1/2}C$ (K_a) and $i_{pc}/\nu^{1/2}C$ (K_c) for perylene in benzonitrile are listed in Table I. The data are given for concentrations where the cation reduction wave appears normal (5.4×10^{-4} *M*) and where it is diffuse (1.7×10^{-3}). The peak potential of the hydrocarbon oxidation wave (P → P⁺) did not show a significant shift as a function of concentration in the region where this wave became diffuse.

Table I. Values of $i_p/\nu^{1/2}C$ as a Function of ν for Perylene in Benzonitrile

C, *M*	ν, mV/sec	K_A[a]	K_C[a]
1.7×10^{-3}	333	2.85	
	167	2.96	
	83	3.04	
	33	3.22	
	17	3.27	
		ΔK_A = 0.42	
5.4×10^{-4}	333	2.85	2.91
	167	2.94	3.02
	83	3.03	3.16
	33	3.09	3.20
	17	3.05	3.22
		ΔK_A = 0.24	ΔK_C = 0.31

[a] $K = i_p/\nu^{1/2}C \times 10^3$ (A = anodic wave, C = cathodic).

In acetonitrile the oxidation (E_{pa} = 0.66 V) and reduction (E_{pc} = −2.30 V) waves of perylene also indicate the formation of relatively stable ion radicals. However, the concentration at which the cation reduction wave becomes diffuse is lower than in benzonitrile. At concentrations greater than 5×10^{-4} *M* the cation reduction wave behaves similarly to that shown in Figure 2 for perylene in benzonitrile. Values of $i_p/\nu^{1/2}C$ *vs.* ν are tabulated in Table II for perylene oxidation and reduction. Included in the table are values for $i_p/\nu^{1/2}C$ *vs.* ν for the addition of 110 mmol/l. of water to the acetonitrile solution.

When solutions (10^{-3} *M*) of perylene in benzonitrile or in acetonitrile were subjected to square-wave electrolysis (0.1 cps) for several hours, under conditions similar to ecl production, decomposition was evident. The final solution was discolored and showed new fluorescence spectra having maxima in the 500–550-nm region. Current–voltage curves showed decreased perylene ion radical stability and a buildup of decom-

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(9) The pulse generator was built in the Laboratory of Nuclear Science electronics shop from specifications supplied by Professor D. K. Roe.

(10) R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 705 (1964).

Table II. Values of $i_p/\nu^{1/2}C$ as a Function of ν for Perylene in Acetonitrile

C, M	ν, mV/sec	K_A[a]	K_C[a]
1.1×10^{-3}	333	3.35	3.90
	166	3.66	4.09
	83	3.79	3.85
	33	3.86	4.03
	17	4.06	4.06
		$\Delta K_A = 0.61$	$\Delta K_C = 0.24$
	With 0.11 mol of H_2O Added		
1.1×10^{-3}	333	3.55	3.90
	166	3.95	3.87
	83	3.95	3.99
	33	4.26	4.42
	17	3.40	4.73
		$\Delta K_A = 0.85$	$\Delta K_C = 0.83$

[a] $K = i_p/\nu^{1/2}C \times 10^3$ (A = anodic wave, C = cathodic).

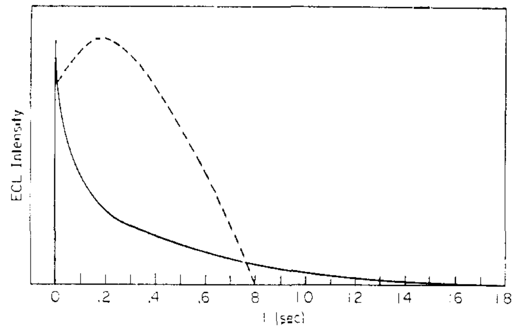

Figure 3. Ecl intensity *vs.* time for perylene in benzonitrile for one pulse of excitation: $C = 3.1 \times 10^{-3}$ M; $f = 0.1$ cps; ——, anion-to-cation excitation; - - - - -, cation-to-anion excitation.

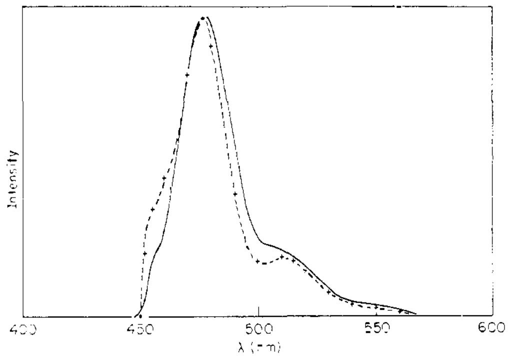

Figure 4. Comparison of fluorescence and ecl spectra of perylene in benzonitrile (anion-to-cation pulse): —, fluorescence (*ca.* 10^{-3} M, 365-nm excitation); +- - -+, ecl (*ca.* 10^{-3} M).

position products. The test electrode was coated with a dark substance at the end of the experiment.

Ecl Spectra. The ecl of perylene in benzonitrile was observed as a function of time for concentrations from 0.7 to 3.1×10^{-3} M. The potential range for excitation of ecl was from 60 mV past the peak of cation formation to 60 mV past the peak of anion formation. Greater sweep ranges resulted in less intense ecl. At 1 cps excitation, ecl on both the cation-to-anion (+ to −) and anion-to-cation (− to +) potential steps was a sharp pulse which decayed exponentially. For concentrations greater than 1.6×10^{-3} M, where the diffuse cation reduction wave is observed, the ecl output with time at 0.1 cps depended on the direction of the pulse. Figure 3 shows intensity *vs.* time curves for single ecl pulses for − to + and + to − excitation. The + to − ecl no longer shows a maximum at $t = 0$, and the pulse decay is not exponential. In acetonitrile, at concentrations where the cation reduction is not normal, ecl *vs.* time data observed are similar to those of Figure 3.

Spectra for perylene fluorescence and ecl (− to + pulse) in benzonitrile are compared in Figure 4. Ecl maxima are virtually identical with perylene fluorescence maxima. The slight difference at the shorter wavelength end of the spectrum is simply a result of differences in self-absorption.

Figure 5 shows an ecl spectrum obtained by + to − potential step excitation of perylene in benzonitrile. The ecl spectrum on the + to − cycle contains a greater long-wavelength component than either perylene fluorescence or ecl from the − to + cycle. The relative amount of long-wavelength ecl component was not found to be concentration dependent from 0.7 to 2.2×10^{-3} M.

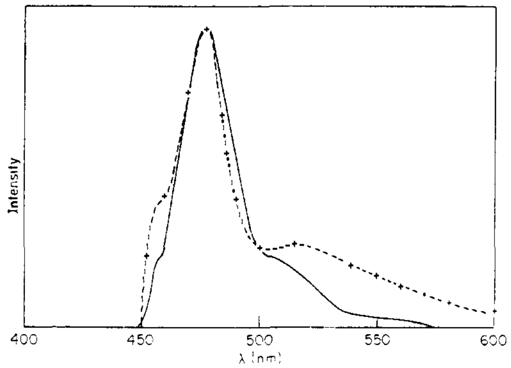

Figure 5. Comparison of fluorescence and ecl spectra of perylene in benzonitrile (cation-to-anion pulse): ——, fluorescence (*ca.* 10^{-3} M, 365-nm excitation); +- - -+, ecl (*ca.* 10^{-3} M).

Representative ecl spectra of perylene in acetonitrile for both − to + and + to − steps are compared with perylene fluorescence in Figures 6 and 7, respectively. More long-wavelength component is observed than for either perylene fluorescence or ecl in benzonitrile. No spectral dependence on the range of the potential pulse was observed in acetonitrile. The maximum intensity was attained with a pulse range from 60 mV past the initial ion peak to 60 mV past the second ion peak. When this range was increased, the ecl intensity decreased, but the spectral appearance did not change.

Discussion

Comparison of ecl spectra in benzonitrile and acetonitrile in Figures 4, 5, 6, and 7 demonstrates dependence of the spectrum on solvent and direction of polarity change of the potential step. On the − to + step in benzonitrile, the ecl spectrum is a good match for perylene monomer fluorescence; thus on the − to + step the emitter is almost exclusively the perylene singlet. On the + to − step in benzonitrile, and for both directions of the potential step in acetonitrile, the presence of a long-wavelength component indicates emitters other than perylene.

The dependence of ecl on the solvent and on the direction of polarity change is inconsistent with the suggestion that long-wavelength emission arises from direct

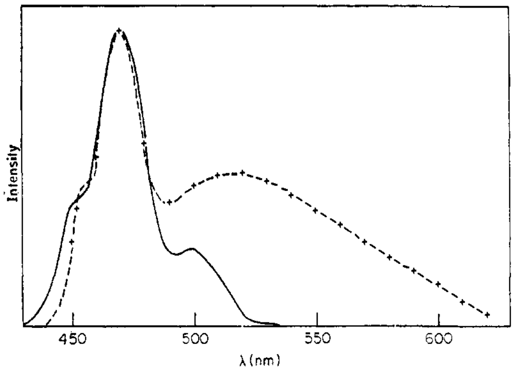

Figure 6. Comparison of fluorescence and ecl spectra of perylene in acetonitrile (anion-to-cation pulse): —, fluorescence (*ca.* 5 × 10^{-4} *M*, 365-nm excitation); +- - -+, ecl (ca. 5 × 10^{-4} *M*).

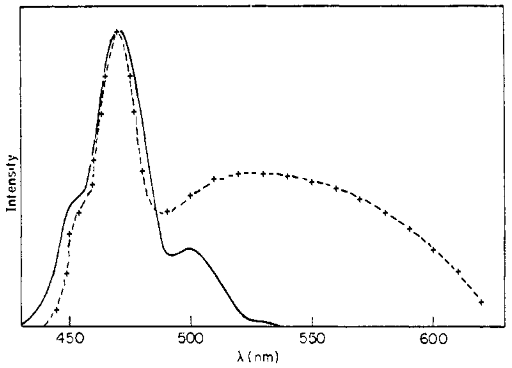

Figure 7. Comparison of fluorescence and ecl spectra of perylene in acetonitrile (cation-to-anion pulse): —, fluorescence (*ca.* 5 × 10^{-4} *M*, 365-nm excitation); +- - -+, ecl (*ca.* 5 × 10^{-4} *M*).

excimer formation. Formation of an excimer in the annihilation reaction cannot depend on which ion is generated first. The large difference in the amount of the long-wavelength component in the two solvents is not consistent with Birks' data, which show excimer formation to be solvent independent in solvents of similar viscosities.[11] Therefore, the annihilation reaction does not lead to significant amounts of direct excimer formation, which is in line with Hoytink's prediction.[2b]

The long-wavelength component of the single-pulse ecl spectra of perylene in acetonitrile, Figures 6 and 7, is virtually identical with that of the long-term ecl spectra reported for perylene earlier.[2a] That these spectra fail to match the spectrum of the crystalline excimer of perylene[2a] constitutes additional evidence that origin of the emission is not the perylene excimer.

The excellent match of perylene fluorescence and ecl spectra on the − to + pulse in benzonitrile suggests that this case represents the simplest ecl mechanism. All other cases must include some modification of the ecl mechanism, whereby emitters besides the perylene singlet are formed. The exact nature of these other emitters has not yet been determined, but by analogy to anthracene,[4,5] hydroxy and other substituted perylenes are good possibilities.

Badger has proposed that "excimers" may be formed by reaction of cation dimers with the anion radical.[12] Since the perylene excimer has a low fluorescence efficiency, a large amount of cation dimer would be required to account for the intensity of the long-wavelength component of ecl emission. Differences in the electrochemical behavior in the two nitrile solvents do not seem great enough to rationalize the solvent dependence of the ecl spectrum on the basis of greater cation dimer formation, particularly at low concentrations. An even stronger argument against excimer emission resulting from reaction of a cation dimer is the observation that the relative intensities of perylene fluorescence and the long-wavelength emission are independent of perylene concentration for a given pulse direction in a given solvent.

Excited-state charge-transfer complexes between perylene and various electron donors have broad structureless emission bands with maxima *ca.* 5000 cm^{-1} to the red of the perylene fluorescence.[13] It is possible that ecl could be produced by reaction of a perylene ion radical and the electrochemical product (I) of some species present at low concentrations in the solvent, to form a radiative complex. The reduction potential of I would have to be equal to or less than the reduction potential of perylene for the reaction to occur in the potential range employed. Current–voltage curves for the solvent did not show large oxidation or reduction peaks between the solvent cutoff regions. Consequently, the reduced form of any impurities present will be at lower concentrations than the perylene radical anion formed on the negative potential step. Complex formation would not be able to compete for the cation with the diffusion-controlled annihilation reaction. In addition, Weller, *et al.*, have shown that for solvents having a dielectric constant greater than 30, the emission from complexes is quenched by dissociation of the complex.[14]

The following ecl mechanism is proposed for perylene. Although all steps of the mechanism cannot be proven unambiguously, it is consistent with all of the electrochemical, spectroscopic, and kinetic data currently available for perylene.

Because the ecl behavior of perylene in benzonitrile is more complicated when the radical cation is generated first, this mechanism will be considered. During the anodic step three reactions occur (where P = perylene)

$$\mathrm{P} \longrightarrow \mathrm{P}^{\cdot +} + \mathrm{e} \qquad (1)$$

$$\mathrm{P}^{\cdot +} \longrightarrow \begin{cases} \mathrm{A} \\ \mathrm{B} \end{cases} \qquad (2)$$

$$\mathrm{A} \longrightarrow \mathrm{C} + \mathrm{e} \qquad (3)$$

Step 1 is the oxidation of perylene to the radical cation, step 2 represents slow reactions of the radical cation to form at least two products, and in step 3 one product from (2) is electroactive at the applied potential.

On the cathodic step, perylene will be reduced to the radical anion

$$\mathrm{P} + \mathrm{e} \longrightarrow \mathrm{P}^{\cdot -} \qquad (4)$$

and one or more of the products from the cation reactions above will be reduced, at a potential slightly more negative than for $\mathrm{P}^{\cdot +}$. During the cathodic step,

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(11) J. Birks, M. Lamb, and I. Munro, *Proc. Roy. Soc., Ser. A*, **280**, 289 (1964).

(12) B. Badger and B. Brocklehurst, *Nature (London)*, **219**, 263 (1968).

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light emission will occur, determined by the following reactions

$$\mathrm{P}\cdot^{+} + \mathrm{P}\cdot^{-} \longrightarrow {}^{1}\mathrm{P}^{*} + \mathrm{P} \qquad (5)$$

$$\mathrm{P}\cdot^{-} + \mathrm{A} \longrightarrow {}^{1}\mathrm{P}^{*} + \mathrm{Q} \qquad (6)$$

$${}^{1}\mathrm{P}^{*} \longrightarrow \mathrm{P} + h\nu_{\mathrm{f}} \qquad (7)$$

$${}^{1}\mathrm{P}^{*} + \mathrm{B} \longrightarrow \mathrm{P} + {}^{1}\mathrm{B}^{*} \qquad (8)$$

$${}^{1}\mathrm{B}^{*} \longrightarrow \mathrm{B} + h\nu_{\mathrm{f}}' \qquad (9)$$

$${}^{1}\mathrm{P}^{+} + \mathrm{Q} \longrightarrow \mathrm{X} + \mathrm{P} \qquad (10)$$

Step 5 represents a radical in annihilation to form the perylene singlet, step 6 the reaction of the perylene anion with the intermediate from (2) to form a perylene singlet, (7) the fluorescence of perylene, step 8 energy transfer from the perylene singlet to a product from (2), (9) fluorescence different from perylene, and step 10 the product from (6) reacting with the perylene cation.

A qualitative comparison of the stabilities of the perylene radical ions in the two nitriles can be obtained from the data of Tables I and II. Values of K as a function of sweep rate generally increase with decreasing ν. Compared to the deviations of K for compounds showing extensive follow-up reactions,[15] the deviations of Tables I and II are not severe. Thus these data are consistent with moderate stability of the radical ions in these solvents, and reactions 1, 4, 5, and 7 represent the major pathway for light emission.

A rough measure of radical ion stability can be obtained from ΔK, the difference between the maximum and minimum values of K. The addition of small amounts of water to acetonitrile caused an increase in ΔK for both the perylene oxidation and reduction waves. No similar effect was observed for benzonitrile. The instability in acetonitrile is, by analogy with anthracene,[5] due to nucleophilic attack of water on the radical cation and probably to protonation effects on the radical anion.[16] The lack of an effect in benzonitrile relates to the low solubility of water in this solvent.[17] In general, perylene radical cations seem to be less stable in acetonitrile, which correlates with the findings of others.[18]

For perylene in benzonitrile the value of ΔK is larger at $1.7 \times 10^{-7}\ M$ than at $5.4 \times 10^{-4}\ M$. This also correlates with the appearance of the diffuse cation reduction wave shown in Figure 2. These data are consistent with reactions 1, 2, and 4 of the proposed mechanism. The perylene radical cation reacts slowly from a product *via* reaction 2, which is reduced at potentials slightly more negative than required for the reduction of $\mathrm{P}\cdot^{+}$. The product does not form in sufficient quantity to be observed at the lower concentration but does so at *ca.* $2 \times 10^{-3}\ M$. Thus one would expect to see more nearly ideal behavior at higher sweep rates. Such is observed. For $1.27 \times 10^{-3}\ M$ solutions of perylene, the reverse peak of the $\mathrm{P}\cdot^{+}$ reduction is seen at $\nu = 10$ V/min, but occurs only as a shoulder at $\nu = 2$ V/min. The fact that the perylene cation reduction wave becomes diffuse in acetonitrile at concentrations lower than in benzonitrile correlates with the greater stability of $\mathrm{P}\cdot^{+}$ in the latter solvent.

Prolonged electrolysis gave products having fluorescence spectra quite similar to the long-wavelength ecl emission. This implies that the long-wavelength emitter is the stable product of a radical cation reaction. This is consistent with the behavior of anthracene.[4,5,19] It is unlikely this product is the one responsible for the diffuse cation reduction wave, although it could be the product of this reduction. It is quite clear that decomposition products accumulate in solution during electrolysis because of the decreased radical stability in electrolyzed solutions and the stable fluorescence of these solutions.

That the ecl spectra are identical with perylene fluorescence when the radical anion is generated first (− to + cycle) is consistent with the proposed mechanism. During the cathodic cycle only reaction 4 will proceed. When the electrode is switched anodic reaction 1 will occur first, since (2) and (3) are assumed slow relative to (1). As the perylene cation radicals diffuse away from the electrode surface, they will immediately encounter anion radicals and react. All other processes will occur to a very small extent under these conditions.

When the radical cation is generated first, reactions 1, 2, and 3 will all proceed during the time of generations (1–10 sec). When the electrode is made anodic, the radical anion diffusing away from the electrode can encounter A, B, or C, all of which will have concentration profiles overlapping that of $\mathrm{P}\cdot^{+}$. In the diffusion layer near the electrode surface, concentrations of species such as A, B, and C will be of the same order of magnitude as that of $\mathrm{P}\cdot^{+}$, permitting any of reactions 5–10 to proceed.

The reason that energy transfer, reaction 8, has been suggested as the excitation mechanism for the long-wavelength emission is the lack of dependence of the ecl spectrum on concentration over the ranges studied. It is possible that some species, Y, could react with $\mathrm{P}\cdot^{-}$ ($\mathrm{P}\cdot^{-} + \mathrm{Y} \rightarrow \mathrm{Y}^{*}$) to give an excited state directly, but such a process should be very concentration dependent.

The proposed mechanism also correlates with the ecl emission of perylene in acetonitrile. That long-wavelength components of the spectra are observed both for + to − and − to + reflects the lesser stability of ion radicals in that solvent. When water is added to acetonitrile the overall ecl intensity is diminished, corresponding to enhanced rates for reactions 2 and 3 and subsequently smaller amounts of $\mathrm{P}\cdot^{+}$ available for reaction 5.

We have also reexamined some ecl spectra of rubrene in DMF[20] and found a spectral dependence on pulse direction. When the rubrene anion was generated first, spectra were normal. When the rubene cation was generated first, a shift of the ecl maximum to longer wavelengths was observed. Rubrene forms no radiative excimers and hence its ecl behavior probably parallels that of perylene.

Figure 3 indicates there is a difference in the ecl mechanism depending on the direction of excitation, *i.e.*, + to − *vs.* − to +. This difference is observed only for perylene concentrations greater than $1.5 \times 10^{-3}\ M$ and for low frequencies of excitation, *i.e.*, 0.1 cps. For lower concentrations and higher frequencies (1 cps) decay of a pulse is exponential. This behavior is consistent with the proposed mechanism.

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At high concentrations the exponential decay on the − to + cycle results from having only reactions 1, 4, 5, and 7 participating in the ecl process. On the + to − cycle, when the radical anion diffuses away from the electrode surface it can encounter $P\cdot^+$, A, B, or C. Because B and C are not electroactive, they will have simple exponential distributions from the electrode into the solution. The concentrations of both $P\cdot^+$ and A will be zero at the electrode surface and go through a maximum at some distance from the electrode surface. The concentration of $P\cdot^+$ near the electrode surface will be greater than that of A because of moderate cation stability. But at distances further out into solution, the relative concentration of A will increase. As $P\cdot^-$ diffuses away from the electrode it will first encounter mostly $P\cdot^+$ giving reaction 5, but with increasing amounts of A, giving reaction 6. This could easily cause an increase in luminescence intensity with time. However, Q, the product of reaction 6, will start to accumulate in solution and will be available to quench the reaction, resulting in the abrupt decrease in intensity as shown in Figure 3.

At higher excitation frequencies the concentration distance profiles of all species will be compressed. There will be less time for reactions 2 and 3 to occur and the probability of $P\cdot^-$ encountering $P\cdot^+$ as it diffuses away from the electrode surface will be increased.

Acknowledgments. This work was supported in part through funds provided by the U. S. Atomic Energy Commission under Contract No. AT (30-1)-905. T. C. W. thanks the National Institutes of Health and the Proctor and Gamble Company for fellowship support. We thank L. N. Klatt for helpful discussions.

Medium Effects on the Activation Parameters for A-1 Dioxolane Hydrolysis in Water–Glycerol Mixtures[1]

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Abstract: Kinetic data for the A-1 hydrolysis of 2,2-dimethyl-1,3-dioxolane (**1**), 2-isopropyl-2-methyl-1,3-dioxolane (**2**), and 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (**3**) in 0, 10, 20, 30, and 40 wt % aqueous glycerol at temperatures from 20 to 45° have been collected. The partial molar free energy and enthalpy of transfer of **1** from water to 40% glycerol have been measured, permitting the medium effects on the activation parameters to be dissected into ground- and transition-state contributions. It is found that both contributions are important. The directions of these changes are discussed in terms of the effects of glycerol, cations, and the nonpolar residues of organic solutes upon the structure of liquid water. The significance of these results with respect to the entropy criterion of mechanism is discussed. The partial molar enthalpy of transfer of **3** from water to 40% glycerol has been determined and the medium effect upon its enthalpy of activation dissected.

Kinetic solvent effects upon organic reactions taking place in aqueous media are not well understood. This is largely because the properties of liquid water, and the often dramatic changes in those properties which occur upon the addition of solutes, defy rigorous theoretical description. Although the Hughes–Ingold theory of solvent effects[3] is often able to predict the direction and approximate magnitude of medium effects on free energies of activation, $\delta_M \Delta G^*$, it has proven totally inadequate in dealing with enthalpies and entropies of activation, which parameters are not only more sensitive to solvent changes but are correspondingly more informative. The failure of electrostatic theory has been shown to be due in part to neglect of neutral solute–water interactions which can be more important energetically than ion–water interactions.[4–6]

To learn more about the part played by the aqueous solvent in the activation process, we have initiated a study of kinetic solvent effects on simple acid-catalyzed reactions in water–glycerol mixtures. Unlike the monohydric alcohols, which behave as "soluble hydrocarbons" in dilute solution in water,[7] glycerol forms relatively ideal aqueous mixtures.[8] The available evidence[9] indicates that the structure of liquid water is gradually disrupted with the addition of increasing amounts of glycerol. Glycerol is also a good ionizing solvent, the dielectric constants at 25° of pure and 50 wt % glycerol being 40 and 64, respectively.[10]

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