absorption bands (KBr pellet): 3450 (w), 2980 (w), 1608 (m), 1140 (m), 1350 (m), 1282 (m), 1265 (m), 1210 (m), 1180 (s), 1100 (s), 1050 (s), 990 (s), 910 (s), 860 (w), 830 (m), 775 (m), 705 (m), 645 (m), and 620 (w) cm^{-1}.

Anal. Calcd for $C_7H_3Cl_6F$: C, 26.35; H, 0.94. Found: C, 26.63; H, 0.91.

5,6-*endo,endo*-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (2). The *cis*-1,2-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 65.6% yield, mp 157–158°. The fluorine spectrum is a typical AA'XX' multiplet centered at ~210 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3400 (m), 2990 (w), 1605 (s), 1355 (m), 1292 (m), 1258 (w), 1185 (s), 1160 (s), 1050 (s), 1015 (s), 915 (s), 888 (m), 825 (s), 730 (s), 698 (m), and 670 (s) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.99; H, 0.59.

***endo,exo*-5,6-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (3).** The *trans*-1,2-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 10.8% yield, mp 95–96°. Extensive *cis–trans* isomerization of the olefin occurred during the reaction since the adduct of the *cis*-1,2-difluoroethylene isomer was isolated in 83% yield. Careful chromatography using alumina and Skelly solvent A separated the isomeric adducts. Then fluorine nmr spectrum consisted of two octets centered at ~195 and ~202 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3340 (w), 3000 (3), 1615 (s), 1380 (m), 1350 (w), 1275 (s), 1185 (s), 1165 (w), 1130 (s), 1115 (s), 1065 (s), 1015 (m), 930 (s), 865 (m), 800 (s), 760 (w), 720 (s), and 650 (m) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.50; H, 0.57.

5,5-Difluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (4). The 1,1-difluoroethylene–hexachlorocyclopentadiene adduct was formed in 33.7% yield, mp 104–105°. The fluorine nmr spectrum was an intense octet with a pair of very weak wing quartets separated by ~200 Hz. The fluorine chemical shifts are 13.1 and 14.2 ppm upfield from 1,1,2,2-tetrafluoro-3,3,4,4-tetrachlorocyclobutane or ~95 and 96 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3450 (m), 1610 (s), 1438 (m), 1300 (s), 1240 (s), 1195 (s), 1125 (m), 1092 (m), 1075 (s), 1045 (s), 950 (s), 930 (m), 920 (m), 870 (w), 830 (s), 722 (s), 700 (s), 660 (w), and 622 (w) cm^{-1}.

Anal. Calcd for $C_7H_2Cl_6F_2$: C, 24.94; H, 0.59. Found: C, 24.94; H, 0.56.

***endo*-5,6,6-Trifluoro-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2-heptene (5).** The trifluoroethylene–hexachlorocyclopentadiene adduct was formed in 25.1% yield, mp 145–146°. The fluorine nmr spectrum contains three octets occurring at ~102, 114, and 214 ppm upfield from trichlorofluoromethane. Infrared absorption bands (KBr pellet): 3440 (s), 2990 (w), 1608 (s), 1360 (m), 1290 (s), 1230 (s), 1185 (s), 1160 (s), 1140 (m), 1070 (s), 920 (s), 827 (m), 765 (s), 712 (s), 695 (s), and 630 (w) cm^{-1}.

Anal. Calcd for $C_7HCl_6F_3$: C, 23.61; H, 0.28. Found: C, 23.31; H, 0.27.

Acknowledgments. Financial support by the University of Kentucky computer center is greatly appreciated. A. M. I. wishes to thank the Haggin Foundation for a fellowship. Use of the HA-100 spectrometer at Texas Christian University is also appreciated.

The Electrochemiluminescence of Anthracene and 9,10-Dimethylanthracene. The Role of Direct Excimer Formation[1a]

T. C. Werner,[1b] Jack Chang, and David M. Hercules[1c]

Contribution from the Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Received July 14, 1969

Abstract: Electrochemiluminescence (ecl) spectra have been obtained for anthracene and 9,10-dimethylanthracene (DMA) using an image intensifier spectrograph and single pulse excitation. Rapid decomposition of the anthracene cation during ecl production leads to formation of products (9-anthranol and 9,10-dihydroxyanthracene) which emit at longer wavelengths than anthracene. The long wavelength component of anthracene ecl, previously assigned to an anthracene excimer, is shown to arise from energy transfer or from a mixed annihilation reaction involving cation decomposition products. The ecl of DMA contains less "excimer" component than previously reported. Substitution at the 9 and 10 positions of anthracene protects the cation radical and prevents decomposition product participation in the ecl process. The small amount of long wavelength component observed for DMA may result from directly formed excimers or those formed by triplet–triplet annihilation.

The nature of the excited states formed during the electrochemiluminescence (ecl) of aromatic hydrocarbons has received considerable attention in recent years. One of the more controversial proposals has been direct formation of an excimer by the ecl annihilation reaction.

$$R^+ + R^- \longrightarrow R_2^* \longrightarrow 2R + h\nu_{ex}$$

Excimer formation was proposed to explain ecl emission observed at longer wavelengths than normal hydrocarbon fluorescence.[2]

Chandross, *et al.*, concluded that excimer formation during ecl is more efficient than excimer formation *via* photoexcitation.[2] It was suggested that a "charge-transfer" type excimer, isomeric to the normal photoexcited excimer, could be formed during ecl. If the charge-transfer excimer were capable of more efficient fluorescent emission than the photoexcited one, the discrepancy in the ecl and hydrocarbon fluorescence could be understood.[2]

---

(1) (a) Presented in part at the 155th Annual Meeting of the American Chemical Society, San Francisco, Calif., 1968; (b) National Institutes of Health Predoctoral Fellow, 1967–1968; (c) Department of Chemistry, University of Georgia, Athens, Ga. 30601. Address all correspondence to this author.

(2) E. A. Chandross, J. W. Longworth, and R. E. Visco, *J. Amer. Chem. Soc.*, **87**, 3259 (1965).

Parker and Short reported excimer emission in the ecl of 9,10-dimethylanthracene (DMA).[3] Based on a kinetic analysis, they concluded that appreciable excimer formation occurred directly from the annihilation reaction.

Theoretical considerations of Hoytink[4] indicate that direct excimer formation during ecl should be an inefficient process. Hoytink's calculations show that electron transfer between ion radicals can occur with unit probability at an intermolecular separation of 10 Å. At this distance, the interaction between the resulting excited and ground state molecules is less than kT and no significant excimer formation would be expected. Even if the two ion radicals approach within excimer formation distances (*ca.* 3.5 Å) before electron transfer occurred, an "isomeric" excimer seems unlikely. Any initially formed isomeric excimer should revert to the normal "sandwich" type excimer formed by photoexcitation before emission occurs.

While the present study was in progress, Bard and Faulkner[5] published data to show that the excimer component of anthracene ecl in DMF results from energy transfer to a cation decomposition product. This mechanism had also been suggested by the present authors in a preliminary report of this work.[1a]

In the present investigation the ecl spectra of anthracene and 9,10-dimethylanthracene (DMA) in acetonitrile have been examined to determine whether direct excimer formation is a major ecl pathway for these molecules. The data were obtained using an image intensifier spectrograph which has several unique advantages for ecl studies. Spectra can be obtained with few electrochemical cycles and the spectra of the anion to cation and cation to anion cycles can be studied independently.

The present results confirm the energy transfer mechanism of Bard, *et al.*,[5] for anthracene ecl. The data on DMA indicate significantly less direct excimer formation occurring than previously suggested.[2,3]

Experimental Section

Scintillation grade anthracene was used without further purification. 9,10-Dimethylanthracene obtained from the Aldrich Chemical Co. was recrystallized three times from ethanol before use.

Tetra-*n*-butylammonium perchlorate (TBAP) was used as electrolyte. It was prepared from G. Frederick Smith reagent grade 70% $HClO_4$ and Southwestern Analytical 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.

Matheson Coleman and Bell spectral grade acetonitrile, after standing for several days over $CuSO_4$ and Na_2SO_4, was distilled from P_2O_5 at normal pressure. The distillate was stored in a vacuum desiccator until used. Matheson Coleman and Bell N,N-dimethylformamide (DMF) was used without purification.

All absorption measurements were recorded on a Cary Model 14 spectrophotometer. Fluorescence spectra, except where otherwise noted, were obtained using a G. K. Turner Associater Model 310 "Spectro" absolute spectrofluorometer. Mass spectral data were taken on a Hitachi mass spectrometer.

The potentiostat used both for 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 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 test electrodes and a Ag|Ag$^+$ (0.01 M in acetonitrile) reference electrode separated from the solution by a Vycor plug. All solutions were 0.1 M in TBAP. After use, the cell and electrodes were washed with acetone and treated with HNO_3, and with a solution of ferrous ammonium sulfate in dilute H_2SO_4.

Ecl spectra were taken on an image intensifier spectrograph. Details of the spectrograph design, construction, and method of focusing are given elsewhere.[6] A Polaroid Land camera was focused on the P-11 phosphor anode of the image tube. Ecl spectra were recorded on Type 107 Polaroid film (ASA 3000) which produced a positive print. Negatives were made from these prints and read on a Leeds and Northrup recording microphotometer, Model 6700-A2.

Ecl spectra were taken using a 3-electrode cell of tubular design. The cell consisted of a piece of 18-mm (o.d.) Pyrex tubing to which were attached four standard taper $^{10}/_{30}$ outer joints. These joints were used to hold the three electrodes and nitrogen bubbler. This design eliminated interference from any counter electrode emission. The test electrode (area = 0.10 cm^2) was placed as close as possible to the spectrograph slit. Solutions were thoroughly deoxygenated before ecl measurement.

Ecl excitation was obtained by use of a pulse generator capable of applying a single square-wave signal of adjustable length.[7] Ecl spectra were taken with a potential range from *ca.* 70 mV past the peak of one redox process to *ca.* 70 mV past the peak of the other. Monitoring the reference electrode signal with a Tektronix 502A oscilloscope indicated that potential overshoot was negligible.

The anthracene ecl was produced by generating the anion for 1 sec and switching to cation formation. About 6–12 cycles were necessary to obtain a spectrum. The spectral bandpass was 100–180 Å. DMA ecl spectra were measured for both anion to cation (− to +) and cation to anion (+ to −) potential pulses. Each ion was generated for 1 sec. For DMA, the spectra could be obtained on 1–5 cycles with a bandpass of *ca.* 100 Å.

Fluorescence spectra of anthracene and DMA were taken on the image intensifier spectrograph for comparison with ecl spectra. Both fluorescence and ecl 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 reported are averages of several normalized spectra. This treatment also tends to cancel out baseline drift and spectral noise.

The anodic oxidation of anthracene in acetonitrile (10^{-3} M) was carried out in a three-electrode cell with an isolated counter electrode. The solution was thoroughly deoxygenated and held at the peak potential of anthracene oxidation for 4 hr. The final solution was concentrated using a rotary evaporator and chromatographed on a silica gel column (*ca.* 100 mesh) using hexane, benzene, ether, and ethanol as solvents. Fluorescence and absorption spectra were run on these fractions and, after combination of fractions containing similar components, they were evaporated for mass spectral analysis.

For exhaustive square-wave electrolysis, a 1.5×10^{-3} M solution of anthracene in acetonitrile was placed in a cell similar to the one used for electrochemical measurements. After deoxygenating, the solution was subjected to square-wave electrolysis at 0.02 cps for 2.5 hr. The potential range of the square wave was from *ca.* 80 mV past the peak potential of the cation formation to *ca.* 80 mV past the peak potential of anion formation. At the end of the experiment, current–voltage curves and absorption and fluorescence spectra were taken on the final solution while it was still deoxygenated. Air was then admitted to the cell, and spectra were run again on the final solution. A thin layer chromatographic (tlc) separation was performed on the final solution. The eluent was benzene, and the plates were Eastman Chromatagram sheets, Type 6060, with silica gel absorbent and a fluorescent indicator.

Results

Decomposition during Ecl. Although the anion radical of anthracene is known to be stable, the radical cation has a lifetime of several milliseconds in organic solvents.[8] This is explained by the high reactivity of

---

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

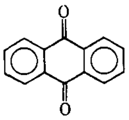
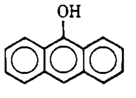
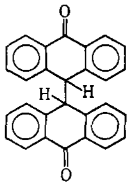
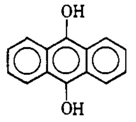
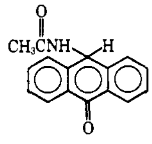
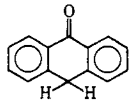
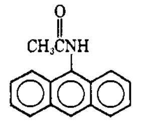
[4] G. J. Hoytink, *Discuss. Faraday Soc.*, 14 (1968).

[5] L. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).

[6] S. Ness and D. M. Hercules, *Anal. Chem.*, **41**, 1467 (1969).

[7] This pulse generator was built in the laboratory of Nuclear Science electronics shop from specifications supplied by Professor D. K. Roe.

Table I. Summary of Evidence for Products of Anthracene Cation Decomposition in Acetonitrile[a]

Compound name	Structure	Evidence	Compound name	Structure	Evidence
Anthraquinone		ms, cv, a	9-Anthranol		a, f
Bianthronyl		ms	9,10-Dihydroxyanthracene		f
Hydrogen ion	H^+	cv	9-Acetamido-10-anthrone		ms
Anthrone		cv, a	9-Acetamidoanthracene		ms

[a] ms = mass spectra, f = fluorescence spectra, a = absorption spectra, and cv = current-voltage curves.

the anthracene *meso* positions toward nucleophilic attack.[9] Ohnesorge, *et al.*,[10] have recently published a study of the controlled potential oxidation of anthracene. They suggest that reaction of the cation with residual water accounts for the short cation lifetime, while Aikens, *et al.*,[11] propose that cation decomposition results from rapid solvent attack.

A controlled potential oxidation and a long term square-wave electrolysis of anthracene have been carried out in this laboratory. The conditions for the latter are similar to those used for ecl excitation. Analysis of these solutions gave a complex mixture in both cases. Several products for which evidence has been obtained are shown in Table I along with the method of identification. Anthraquinone (AQ), bianthronyl, hydrogen ion, and anthrone have been detected previously in anthracene cation decomposition.[10] In the square-wave electrolysis experiments an air sensitive emission, shown in Figure 1, is observed immediately after electrolysis. This emission is in the region of 9-anthranol and 9,10-dihydroxyanthracene (9,10-DHA) fluorescence, also shown in Figure 1. When air is admitted the solution fluorescence is drastically reduced in this region. Such behavior is consistent with the rapid air oxidation of hydroxy anthracenes.[12]

The products detected are consistent with an ECEC mechanism involving water attack.[10] Initially, water attacks the anthracene cation producing 9-anthranol which rapidly reverts to anthrone.[13] Anthrone can be oxidized during solution work-up to bianthronyl.[10] Since 9-anthranol will be oxidized at potentials less positive than anthracene,[14] a second similar mechanism will produce 9,10-DHA. Oxidation of 9,10-DHA produces anthraquinone.

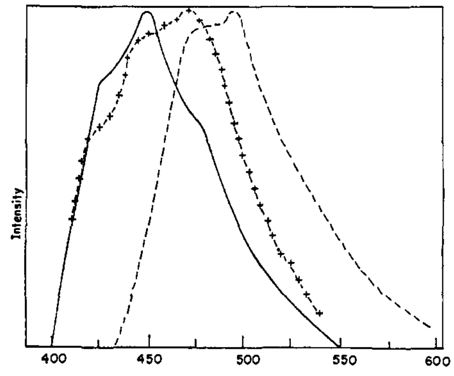


Figure 1. Comparison of the fluorescence of 9-anthranol and 9,10-dihydroxyanthracene with the fluorescence from an electrolyzed anthracene solution (solvent: CH_3CN): ——, 9-anthranol (excitation: 365 nm); - - -, 9,10-droxyanthracene (excitation: 365 nm); -+-+-+-, anthracene solution after 2.5 hr of electrolysis (*ca.* 10^{-3}, excitation 395 nm, deoxygenated).

Once anthraquinone (AQ) is formed, 9,10-DHA can also be generated on the negative half-cycle during square-wave electrolysis. At the potential of anthracene reduction, anthraquinone and hydrogen ion will be reduced by one or both of the following reactions.

$$AQ + 2e^- \longrightarrow AQ^{2-};\ AQ^{2-} + 2H^+ \longrightarrow 9{,}10\text{-DHA} \quad (1a)$$

$$H^+ + e^-/Pt \longrightarrow H\cdot/Pt;\ AQ + 2H\cdot/Pt \longrightarrow 9{,}10\text{-DHA} \quad (1b)$$

---

(8) M. E. Peover and B. S. White, *J. Electroanal. Chem.*, **13**, 93 (1967).

(9) T. A. Gough and M. E. Peover, "Polarography 1964," Proceedings of the 3rd International Polarography Congress, The Macmillan Co., London, 1965, p 1017.

(10) (a) E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *J. Amer. Chem. Soc.*, **90**, 633 (1968). (b) An ECEC mechanism constitutes an electron transfer step followed by a chemical reaction to produce an intermediate. The intermediate immediately undergoes a second electron transfer step, which is also followed by a chemical reaction.

(11) A. E. Coleman, H. H. Richtol, and D. A. Aikens, *J. Electroanal. Chem.*, **18**, 165 (1968).

(12) K. H. Meyer, *Ann. Chem.*, **379**, 37 (1911).

(13) Y. Bansho and K. Nukada, *Bull. Chem. Soc. Jap.*, **33**, 579 (1960).

(14) A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, **32**, 1322 (1967).

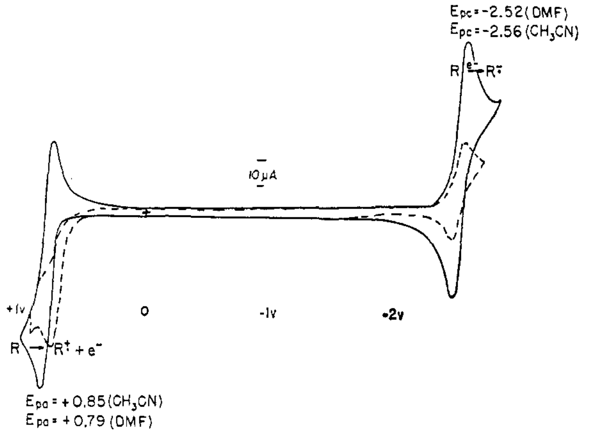


Figure 2. Current–voltage curves of DMA in acetonitrile, and in DMF; electrode area = 0.10 cm², V = 166 mV/sec; reference electrode = Ag|Ag⁺ (0.01 N in CH_3CN); + = 0 V, 0 μA: ——, in CH_3CN ($C = 9.0 \times 10^{-4}$ M); ---, in DMF ($C = 5.0 \times 10^{-4}$ M).

This was checked experimentally by holding a solution 10^{-3} M in AQ and H^+ at potentials more negative than H^+ reduction (more negative than −0.50 *vs.* Ag|Ag⁺ in acetonitrile). The characteristic blue-green fluorescence of 9,10-DHA appeared at the electrode.

Mass spectral data showed the presence of several species having high, odd numbered *m/e* peaks. These species did not appear to be fragment ions, but are more likely parent ions containing nitrogen from solvent participation in the decomposition mechanism. Two of the products were tentatively identified as 9-acetamidoanthracene (parent at *m/e* 235, fragments at *m/e* 192 and 43) and 9-acetamido-10-anthrone (parent at *m/e* 251, fragments at *m/e* 208, 180, and 43). These species are produced in considerably smaller quantities than the other products.

The complexity of the absorption, fluorescence, and mass spectral data demonstrates that several unidentified products are formed in the decomposition. These products are present in low concentrations and are not simple anthracene derivatives. No evidence was found for any dianthracene formation in the square-wave electrolysis.

From the products formed, it is difficult to evaluate the relative importance of water and solvent attack on the cation. Both mechanisms eventually lead to anthraquinone formation.[10,11] However, several observations suggest that water attack dominates. First, the cation is unstable in all solvents thereby suggesting a common decomposition pathway, such as water attack. Second, gas chromatographic analysis of solutions during controlled oxidation revealed large amounts of anthrone.[10] Third, water addition experiments are more consistent with the water attack mechanism. Values of i_a, the peak current for anthracene oxidation, increase by 20–30% on small additions of water (*ca.* 20 mmol/l.). Increased water content enhances the hydrolysis reaction producing more products capable of undergoing oxidation at the anthracene oxidation potential. In the solvent attack mechanism, hydrolysis occurs after initial solvent attack to produce a saturated middle ring derivative incapable of undergoing further oxidation at the anthracene oxidation potential.[11]

Unlike anthracene, DMA possesses relatively stable cation and anion radicals in acetonitrile. The current–voltage curves of DMA in acetonitrile and in DMF are shown in Figure 2. In DMF the cation is unstable during the time of measurement and behaves similarly to anthracene. DMF is oxidized at potentials near DMA oxidation, and the DMA cation radical probably oxidizes the solvent or reacts with a solvent oxidation product.[15]

Nucleophilic attack by water on the DMA cation in acetonitrile is drastically reduced by methyl groups at the *meso* position. Only a 10% increase in i_a is noted for DMA oxidation upon addition of 450 mmol/l. of water, and the cation reduction wave is still observed at normal sweep rates (166 mV/sec).

Solutions of DMA in acetonitrile (10^{-3} M), when subjected to long-term square-wave electrolysis (5–6 hr), showed less decomposition than anthracene. At the end of the experiment the cation reduction wave was still observed at normal sweep rates (166 mV/sec). Fluorescence analysis of the final solution showed weak emission in the 500–550-nm region, but tlc indicated that the major decomposition product was nonfluorescent. Methyl substitution not only protects the *meso* positions from attack but also determines the type of product expected from cation decomposition. For DMA, attack of a nucleophile at the 9,10 position and subsequent loss of a H^+ is not possible. Loss of CH_3^+ is unlikely, and therefore *meso* attack on the cation would lead to a product in which the large aromatic system is destroyed. Similarly, electrophilic attack on the anion radical will lead to products where the center ring resonance is not preserved. Therefore, the decomposition product detected on tlc is most likely a saturated middle ring derivative.

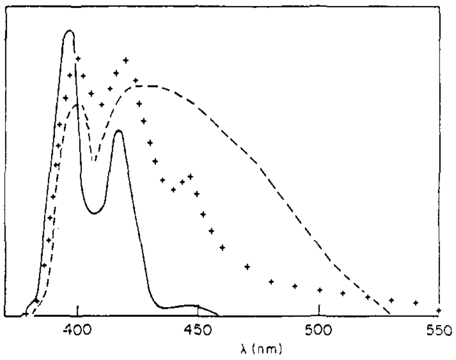


Figure 3. Comparison of the ecl and fluorescence of anthracene in acetonitrile: A = anthracene; B = benzonitrile; ——, fluorescence of A in acetonitrile (*ca.* 10^{-3} M, 365 nm excitation); ---, ecl from $A\cdot^- + A^+$ (*ca.* 10^{-3} M A); +++, ecl from $B\cdot^- + A^+$ (*ca.* 10^{-3} M A + *ca.* 5×10^{-2} M B).

Ecl Spectra. Anthracene. Ecl spectra of anthracene are compared with anthracene fluorescence in Figure 3. These spectra were taken on the image intensifier spectrograph by generating the anion radical for 1 sec and switching to cation radical production. Cation radical stability is to low to measure ecl under similar conditions for the cation to anion (+ to −) potential step. When the sweep range was increased to include dianion formation the ecl intensity was too low to be measured. The spectrum in Figure 3 from the anthracene annihilation reaction ($A\cdot^+ + A\cdot^-$) shows much long wavelength emission. When 5×10^{-2} M benzonitrile was added

---

[15] R. E. Visco and E. A. Chandross, *Electrochim. Acta*, **13**, 1187 (1968).

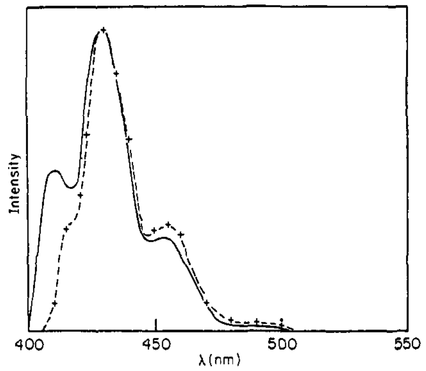


Figure 4. Comparison of fluorescence and ecl spectra of DMA in acetonitrile (anion to cation pulse): ——, fluorescence (*ca.* 10^{-3} *M*, 365 nm excitation); +--- +, ecl (*ca.* 10^{-3} *M*).

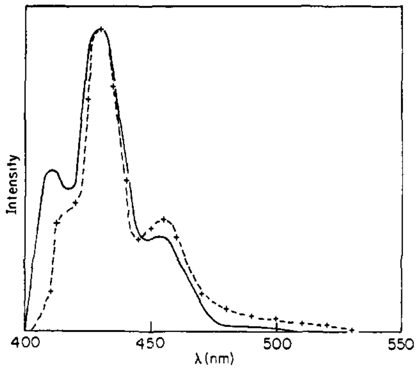


Figure 5. Comparison of fluorescence and ecl spectra of DMA in acetonitrile (cation to anion pulse): ——, fluorescence (*ca.* 10^{-3} *M*, 365 nm excitation); +---- +, ecl (*ca.* 10^{-3} *M*).

to the anthracene solution (10^{-3} *M*), the ecl intensity increased, but the amount of the longer wavelength component was not as great as in the anthracene annihilation reaction, as can be seen from Figure 3. Ecl with benzonitrile added was generated by switching from the benzonitrile reduction potential to anthracene cation formation. Thus, the reactants are the benzonitrile anion radical and the anthracene cation radical.

DMA. The ecl spectra of DMA in acetonitrile were obtained by single pulse excitation using a potential step with limits 60 mV past the peak potential of ion radical formation. Larger ranges decreased the ecl intensity due to formation of diions.

Ecl spectra taken by single pulse excitation are shown in Figures 4 and 5. For both cycles, the ecl contains mostly DMA monomer fluorescence plus a small amount of a long wavelength component. The amount of the long wavelength component appears to be greater on the + to − potential step. Ecl spectra in dimethylformamide are quite similar to those in acetonitrile; however, the ecl intensity in DMF is considerably decreased relative to acetonitrile.

Discussion

Anthracene. Assignment of the long wavelength component of anthracene ecl, shown in Figure 3, to an excimer is not consistent with known anthracene excited state behavior. Recent work indicates that the anthracene excimer configuration is stable only at low temperatures in solid matrices, when prepared by photolytic dissociation of dianthracene.[16] Any excimer formed in solution at room temperature by photoexcitation reverts exclusively to the ground state dimer, dianthracene, and anthracene excimer emission in solutions is not observed.[17]

If direct excimer formation occurred during anthracene ecl one would expect to find large amounts of dianthracene, providing that the ratio of excimer:dianthracene formation is similar for ecl and photoexcitation. Evidence for dianthracene formation was not found.

Formation of anthracene excited states, capable of emitting in solution, is more likely on the − to + cycle because of the difference in relative stabilities of the anthracene ion radicals. After generating the anion radical and switching to the potential of cation formation, the following cation reactions are possible.

$$A\cdot^{+} + A\cdot^{-} \xrightarrow{k_a} \text{ecl} \qquad (2)$$

$$A\cdot^{+} + H_2O \xrightarrow{k_h} \text{decomposition products} \qquad (3)$$

$$A\cdot^{+} + S \xrightarrow{k_s} \text{decomposition products} \qquad (4)$$

Reaction 2 is probably diffusion controlled, but the concentration of water (*ca.* 30 mmol/l.) and solvent (S) enable (3) and (4) to compete successfully with (2). For hydrocarbons with more stable cations (9,10-dimethylanthracene, perylene) reactions 3 and 4 become less important, and consequently ecl from these hydrocarbons is orders of magnitude greater than for anthracene.

Reactions 3 and 4, especially 3, have been shown to produce species which emit in the region of the long wavelength component of anthracene ecl. From the decomposition mechanism and the spectra in Figures 1 and 3 the most likely emitter is 9-anthranol. The absorption spectrum of 9-anthranol and the fluorescence spectrum of anthracene show a high degree of overlap. Since the fluorescence quantum yield of 9-anthranol is reasonably high and its extinction coefficient large, conditions for energy transfer, either trivial or nontrivial, are met. An anthracene singlet formed initially by reaction 2 can transfer its energy to an anthranol molecule to produce the long wavelength ecl. Bard, *et al.*, have demonstrated energy transfer between anthracene and 9-anthranol.[5] Other possible acceptors are 9,10-dihydroxyanthracene[1a] and 9-acetamidoanthracene.

Another possible mechanism for producing excited states of cation decomposition products involves a mixed annihilation reaction, for example, production of singlet excited 9-anthranol (A–OH).

$$(\text{A-OH}) \longrightarrow (\text{A-OH})\cdot^{+} + e^{-}$$

$$(\text{A-OH})\cdot^{+} + A\cdot^{-} \longrightarrow (\text{A-OH})^{*} + A \longrightarrow \text{A-OH} + h\nu$$

The cation radical of 9-anthranol, as for anthracene and other 9-substituted anthracenes, would be unstable. However, on − to + excitation, conditions are more favorable for the 9-anthranol cation radical reaction with the anthracene anion radical before the former decomposes. Such mixed annihilation reactions can also be envisioned for other cation decomposition products. The rapid decomposition of the anthracene cation could yield a substantial amount of product cation radicals capable of reacting with $A\cdot^{-}$.

---

(16) E. A. Chandross, J. Ferguson, and E. G. McRae, *J. Chem. Phys.*, **45**, 3546 (1966).

(17) R. L. Barnes, J. B. Birks, *Proc. Roy. Soc., Ser. A*, **291**, 570 (1966).

Therefore, ecl components at longer wavelengths than monomer fluorescence can be reasonably accounted for by known excited-state behavior in solution. Postulation of a unique charge-transfer excimer in ecl is not needed or substantiated.

The spectrum of Figure 3 obtained with added benzontrile is from the mixed annihilation reaction between the anthracene cation and the benzonitrile anion.

$$A\cdot^{+} + B\cdot^{-} \xrightarrow{k_m} \text{ecl}$$

Concentrations of benzonitrile are about 50 times that of anthracene. Assuming $k_m = k_a$ the rate of the mixed annihilation reaction ($k_m[B\cdot^{-}]$) will be greater than the rate of the normal annihilation reaction ($k_a[A\cdot^{-}]$). This enables $B\cdot^{-}$ to compete more successfully for $A\cdot^{+}$ than water and solvent. Consequently, excited anthracene singlets are formed more efficiently by the mixed annihilation reaction. Mixed annihilation ecl is more intense than normal anthracene ecl, but contains a smaller amount of long wavelength component. Some of the intensity difference between the mixed and normal annihilation reactions might be explained by more efficient excited singlet-state production by the mixed reaction. Hoytink suggests that the energy difference between anthracene oxidation and reduction ($-\Delta H$ = 3.1 eV) may not be sufficient to produce excited singlet states (ΔE_s = 3.3 eV) directly.[4] It is possible that triplet–triplet annihilation, a less efficient process than direct excited singlet formation, may account for much of the anthracene ecl. Uncertainties in the estimation of the annihilation reaction entropy and in $E_{1/2}$ for the irreversible anthracene oxidation make it impossible to rule out any direct excited singlet formation. The energy from the mixed annihilation reaction is more than sufficient to produce an excited singlet state directly, since the reduction potential of benzonitrile is *ca.* 0.4 V more negative than anthracene reduction. Therefore, one would expect more efficient excited singlet-state production for the mixed annihilation reaction and greater ecl intensity.

9,10-Dimethylanthracene. The ecl spectra of DMA in acetonitrile shown in Figures 4 and 5 indicate that the DMA excited singlet state is responsible for most of the emission. Components at longer wavelengths than DMA fluorescence are overemphasized by the image intensifier. Instrument response at the maximum of DMA fluorescence (430 nm) is about half that where the longer wavelength component is observed (490–510 nm).

The ecl of DMA in DMF, though reduced in intensity relative to acetonitrile, is spectrally similar to the acetonitrile spectra despite the obvious difference in DMA cation stability in these two solvents. This lack of decomposition product participation relative to the anthracene ecl process is consistent with the type of DMA cation decomposition product expected. Saturation of the middle ring of DMA produces species not capable of acting as energy acceptors of DMA fluorescence or engaging in mixed annihilation reactions with DMA to produce long wavelength emission.

Even if all of the long wavelength component in Figures 4 and 5 is attributed to the direct formation of an excimer in the annihilation reaction, this process is not as significant as has been suggested,[3] and is consistent with Hoytink's predictions.[4] However, the direct formation of excimers cannot be completely ruled out on the basis of our studies. Unlike anthracene, DMA does form a radiative excimer in solution, and consequently it is not necessary to involve the formation of charge-transfer excimers exclusive to the ecl mechanism. It is possible that a small percentage of the electron transfer encounters occur over a small enough intermolecular distance that interaction between the resulting singlet and ground state molecules will be sufficient to produce an excimer.

Two other mechanisms of excimer formation could also occur. The first, involving cation dimers, is consistent with the slightly greater long wavelength ecl on the + to − pluse. Current–voltage curves do not indicate that significant dimerization occurs, but the intensity of the long wavelength ecl is so low that excimer formation *via* a cation dimer–anion radical reaction cannot be completely ruled out.

The second mechanism involves formation *via* triplet–triplet annihilation (tta). Evidence for tta in the production of ecl has been previously presented.[18] For DMA, the ratio of excimers to singlet excited monomers formed in tta is 0.19.[19] If tta is significant in the ecl of DMA, the long wavelength component of the ecl will be a result of excimers formed by this mechanism rather than direct excimer formation.

Parker and Short's published ecl spectra for DMA in dimethylformamide show considerably more long wavelength component than the spectra in Figures 4 and 5.[3] Their spectra were taken at ten times the DMA concentration used for the present spectra. The increased rates of cation dimer formation and of tta at the higher concentration might account for some of the discrepancy. For reasons given in the Experimental Section, the image intensifier spectra should give a "truer" ecl spectrum than a scanning technique used by Parker and Short. In addition, they did not use controlled potential excitation. Therefore, the ecl spectra in Figures 4 and 5 are thought to be a more accurate measure of the amount of possible direct excimer component in DMA ecl.

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

---

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

(19) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 744 (1967).