Electrogenerated Chemiluminescence. I. Mechanism of Anthracene Chemiluminescence in N,N-Dimethylformamide Solution

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Abstract: The electrogenerated chemiluminescence (ECL) of anthracene is characterized by emission at the frequency of anthracene fluorescence and also at longer wavelengths. One longer wavelength component is shown to be caused by emission from anthranol produced by decomposition of the cation radical of anthracene and probably excited by energy transfer from excited anthracene. Another component, arising from ECL of anthranol itself, is also observed.

Previous reports of electrogenerated chemiluminescence (ECL) from anthracene solutions in N,N-dimethylformamide (DMF) have noted that the emission spectrum comprises two or more components. The spectral distribution of the component shortest in wavelength is similar to that of anthracene fluorescence, but the others are broad, structureless, and located toward the red with respect to the first component.[2,3]

This general behavior is common among several polycyclic hydrocarbons and their derivatives. Presently four alternatives are available to explain the long-wavelength emission from these systems. Chandross, Longworth, and Visco[2] have proposed the formation of an anthracene excited state dimer (excimer), which radiates to produce the low energy emission. A similar explanation is the formation of an anthracene excited state complex with some other species (exciplex). Both the excimer and the exciplex dissociate into component ground state molecules upon deactivation. Zweig, Maricle, Brinen, and Maurer have suggested that solution phosphorescence may be responsible for the long-wavelength emission in some of these systems.[4] Finally, we[3] have previously pointed out the possibility of emission from an excited state of a product formed during the reaction of the electrogenerated radical ions with their environment.

Anthracene has been chosen for study because it is representative of the class of hydrocarbons exhibiting this behavior and because it is available and easily purified. We have performed a number of experiments designed to aid in identifying the emitting species in the anthracene–DMF system, and to help illuminate the means of exciting the species in solution which do emit.

Experimental Section

The anthracene used in all experiments was produced by Matheson Coleman and Bell (mp 215–217°). It was purified by triple recrystallization from Baker Spectroquality benzene and Baker Reagent Grade methanol according to a modification of a procedure available in the literature.[5] A portion of the triply recrystallized material was also resublimed twice *in vacuo*. No differences in behavior were found between the material which had been doubly resublimed after recrystallization and that which had merely been recrystallized thrice. For this reason, most subsequent experiments used only the triply recrystallized anthracene.

Fluorescence analysis of cyclohexane solutions of the purified anthracene showed no luminescence bands other than those directly attributable to anthracene.[6] Maxima in fluorescence intensity were found at 378, 397, 420, 447, and *ca.* 475 mμ. In particular tetracene was shown by absorption spectroscopy and by fluorescence measurements to be present in amounts less than 0.1%, since none was detectable by these methods.

The solvent used in every case was N,N-dimethylformamide which was also supplied by Matheson Coleman and Bell (bp 152–154°). The solvent was further purified by two methods. Method A involved storing the solvent over anhydrous cupric sulfate for several days to complex water and dimethylamine. The solvent was then decanted and distilled at a reflux ratio of 5 from a glass bead packed column 100 cm high under a nitrogen pressure of 20 mm. The middle fraction was retained for use. Method B also involved storage over anhydrous cupric sulfate for a period of several days. The distillation which followed was under the same conditions as above except that the reflux ratio was unity. Following this distillation, the solvent was stored over Linde Type 4A Molecular Sieves for a period of 48 hr. Then the material was decanted and redistilled using a reflux ratio of 1. Once again, only the middle fraction was taken. The solvent was stored under an inert helium atmosphere. Neither solvent batch showed fluorescence bands, even under the most sensitive conditions.

The supporting electrolyte used in all experiments was tetra-*n*-butylammonium perchlorate (TBAP), Polarographic grade, supplied by Southwestern Analytical Chemicals, Austin, Texas. The TBAP was used without further purification, but was dried in a vacuum oven for 48 hr at a temperature of 100° and then stored in a desiccator over magnesium perchlorate. The TBAP contained no fluorescent impurities.

The electrolysis cell used for ECL emission measurements consisted of two platinum helices inserted through graded seals into the Pyrex wall of a 14/35 standard taper joint, as shown in Figure 1. An adapter was provided so that the cell could be evacuated easily. The electrodes were 2–5 mm apart. It was generally found that greatest emission intensities were incident upon the monochromator entrance slits when the slits and the two electrodes were arranged colinearly. This arrangement was used uniformly in the experiments.

Immediately after loading the cell, it was degassed on a vacuum line similar to that described previously[7] using two freeze–pump–thaw cycles. Minimum pressure over the frozen solution on the second cycle was at most 10^{-4} torr in every case. The voltage applied to the cell was simply the 60-cycle sinusoidally alternating line voltage which was reduced from 110 V root mean square to any

(1) (a) National Science Foundation Predoctoral Fellow; (b) to whom correspondence and requests for reprints should be directed.

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

(3) A. J. Bard, K. S. V. Santhanam, S. A. Cruser, and L. R. Faulkner in "Fluorescence," G. G. Guilbault, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 14.

(4) A. Zweig, D. L. Maricle, J. S. Brinen, and A. H. Maurer, *J. Am. Chem. Soc.*, 89, 473 (1967).

(5) T. Takeuchi and M. Furusawa, *Kogyo Kagaku Zasshi*, 68, 474 (1965); *Chem. Abstr.*, 63, 4060e (1965).

(6) I. Berlman, "Handbook of Fluorescence Spectra of Organic Molecules," Academic Press, New York, N. Y., 1965.

(7) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, 88, 2669 (1966).

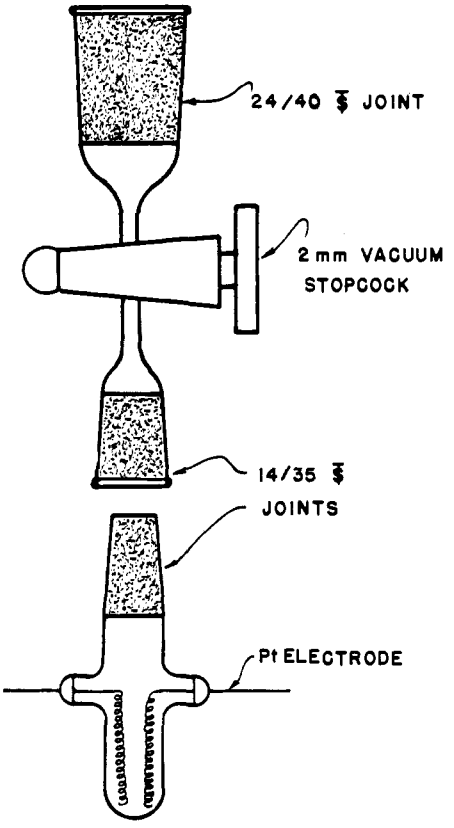


Figure 1. Cell used for ac electrolysis.

value desired between 0 and 7.8 V root mean square through a variable transformer.

Controlled potential oxidation and cyclic voltammetric experiments were performed in a special cell which allowed a three-electrode configuration to be employed, and which permitted fluorescence measurements directly in the spectrophotofluorometer without further transfer of solution. This cell was designed so that it could be evacuated, degassed *via* the freeze–pump–thaw method, and refilled with helium. The helium was continuously passed over the top of the solution during the course of the experiment in order to prevent reentry of atmospheric oxygen.

Fluorescence and emission measurements were all made on an Aminco–Bowman spectrophotofluorometer using a 1P21 photomultiplier tube. The band width for ECL emission measurements was generally about 24 mμ, whereas that for fluorescence emission was 12 mμ. The band width of exciting light in fluorescence measurements was about 12 mμ. These values were obtained using the criterion given by Chen.[8] Recorded spectra were taken on a Moseley 7005A X–Y recorder. A Cary 14 recording spectrophotometer was used for absorption measurements.

The energy-transfer experiments which we performed used the anthracene as purified and the DMF described above. Supporting electrolyte was not added to the solutions. The anthrone used in the experiments was produced by Aldrich Chemical Corp. (mp 152–154°) and was used without further purification. Stock solutions used in energy-transfer experiments were stored under helium during the course of the experiments in order to minimize air oxidation of anthranol.[9] The fluorescence measurements were, however, taken in open quartz cuvettes using right-angle viewing.

Results

ECL Emission. The spectral distribution of ECL emission depends to a high degree upon the applied voltage and upon the method of purification of the solvent. No emission at all is observed until the applied voltage reaches 2.8 V peak to peak. As one increases the applied voltage from this value, the emission

(8) R. F. Chen, *Anal. Biochem.*, **20**, 339 (1967).
(9) H. Bäckstrom and H. Beatty, *J. Phys. Chem.*, **35**, 2549 (1931).

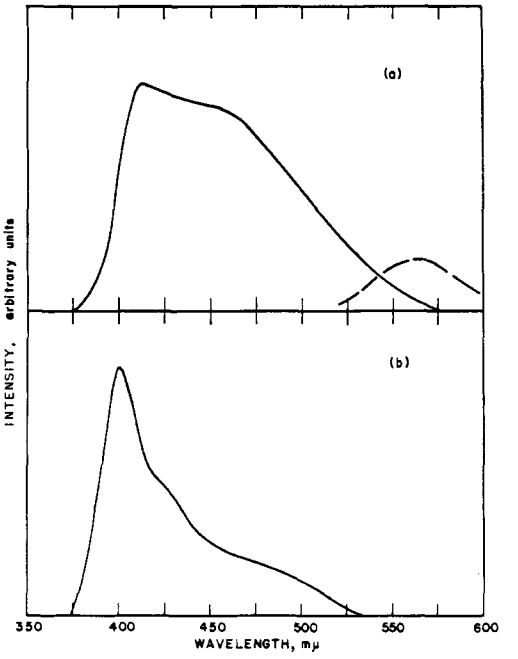


Figure 2. ECL emission spectra from 1 m*M* anthracene solutions: (a) DMF purified by method A; (b) DMF purified by method B. TBAP concentration is 0.1 *M*.

intensity steadily rises, but the spectral distribution remains that shown in Figure 2a (solid line) until the applied voltage reaches about 5.0 V peak to peak. At this point, a new component appears corresponding to the dashed line in Figure 2a, so the resulting spectrum of emission appears as a linear combination of the two curves in Figure 2a. As the applied voltage is increased still further, the component of emission located around 565 mμ becomes more important, but the intensities of of the other bands do not change significantly. At about 6 V applied, however, the emission from the shorter wavelength bands drops off drastically with further increases in the applied voltage, while the intensity of the 565-mμ band becomes steadily greater.

The relative intensities of the ECL emission bands do change with solvent, however. In Figure 2a, the solid line represents the emission spectrum which one observes from a 1 m*M* solution of anthracene in DMF which was purified by method A. In Figure 2b the emission spectrum observed with 1 m*M* solutions of anthracene in DMF which was purified by method B is shown. Both solutions were electrolyzed at 4.8 V peak to peak. Note the marked decrease in the importance of the long-wavelength components for the latter case.

Fluorescence Spectra. The fluorescence of the 1.0 m*M* solutions before electrolysis is shown in Figure 3a. Only bands attributable to anthracene are found. Maxima are observed in 1 m*M* solutions in DMF at 387, 406, 427, and 453 mμ. These values were obtained using a group of slits giving a band width of 12 mμ for both the excitation beam and the emission beam. For comparison with ECL emission spectra, the anthracene fluorescence spectrum shown in Figure 3a employed slits giving an emission beam band width of 24 mμ, the same as those used for ECL spectra. Solution reabsorption reduces the importance of the 387-mμ peak in 1 m*M* solutions, and the wider slits are not

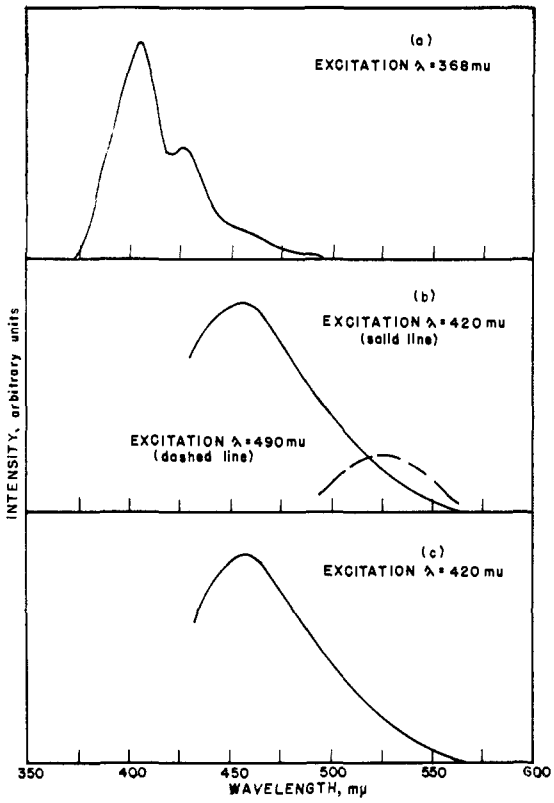


Figure 3. Fluorescence emission spectra: (a) preelectrolysis fluorescence of anthracene; (b) new bands appearing during electrolysis; (c) fluorescence spectrum of anthranol in DMF.

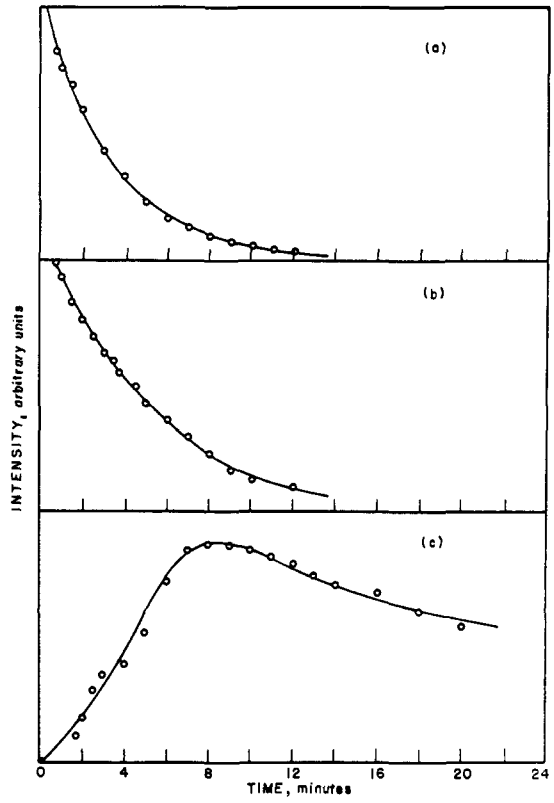


Figure 4. Time dependence of spectral components in 10 m*M* anthracene solutions: (a) ECL emission at 412 mμ; (b) ECL emission at 470 mμ; (c) fluorescence emission at 470 mμ, excited by 420-mμ radiation.

sufficient to resolve it; hence it is not seen in Figure 3a. The fluorescence maxima in DMF are red shifted from those observed in cyclohexane, as expected from the increase in solvent polarity.

During the course of electrolysis, new fluorescence bands appear. If the electrolysis is carried out using applied voltages less than about 6 V peak to peak, the component shown in Figure 3b (solid line) appears. This component is not due to anthracene fluorescence, since anthracene fluorescence is not appreciably excited by the 420-mμ radiation used to excite this species. If the electrolysis is performed at applied voltages greater than about 6 V peak to peak, one observes two new fluorescence bands. One band has the same characteristics as the new one observed at lower applied voltages. The second has the spectral distribution shown by the dashed line in Figure 3b, if one excites the solution at 490 mμ. If excitation at 420 mμ is used, one sees a linear combination of the components shown in Figure 3b, but the component having a fluorescence maximum around 460 mμ greatly predominates. The fact that the combined spectrum has different excitation spectra for the two different components further indicates the presence of two distinct fluorescent species.

Time Dependence of Spectra. The ECL emission spectrum does, additionally, change with time of electrolysis, as shown in Figure 4. The emission intensities of both the 412-mμ (Figure 4a) and 470-mμ (Figure 4b) components decrease from a point near $t = 0$. In fact, one observes little change in the spectral distribution of emission at applied voltages less than 5 V peak to peak with time. The major effect observed is a steady decrease in the intensity at all wavelengths. Depending upon the solvent, one will occasionally observe a rise in intensity of the long-wavelength component in relation to the emission at 412 mμ. This generally implies a slower decay rate for emission at 470 mμ than for emission at 412 mμ.

Above about 5.0 V applied, however, the behavior is different from that observed at lower applied voltages. In this case, the intensity of the extreme long-wavelength (565-mμ) band increases as the electrolysis proceeds. At electrolysis times longer than about 20 min, one observes emission only from this very long-wavelength band. This band persists at a low level for electrolysis times exceeding 90 min.

The fluorescence emission at 470 mμ, excited by 420-mμ radiation, also varies with electrolysis time (Figure 4c). The fluorescence intensity rises to a maximum, then declines slowly at longer electrolysis times. The intensity at the maximum is highly dependent upon the solvent used. Solutions having an anthracene concentration of 10 m*M* produced a maximum fluorescence intensity 30 times greater in solutions employing DMF purified by method A than those in DMF purified by method B.

The very long-wavelength component of fluorescence which appeared during electrolysis of solutions at the higher applied voltages was so weak that one could obtain little further information regarding its nature. However, the new species fluorescing in the region of 460 mμ was present in large enough quantities for other experiments, provided the electrolysis was halted near the time at which the fluorescence intensity reaches a maximum for this component.

Several of the characteristics of the species responsible for the fluorescence band were easily obtainable from simple chemical properties. The intensity of fluorescence at 460 mμ, excited at 420 mμ, was diminished fairly rapidly upon simple exposure of the solution to the atmosphere. This was not merely a quenching effect, since the fluorescence intensity did not rise significantly when the solution and cell were degassed again after a period of exposure. Roughly, the intensity declined to half its original value in 1 hr. Second, the species exhibits a reversible acid–base reaction. When a small amount of 0.1 *M* alcoholic KOH was added to the electrolyzed solution, the fluorescence at 460 mμ was completely quenched. The fluorescence reappeared, however, upon addition of an equivalent amount of alcoholic HCl. Furthermore, the basic solution absorbs in a broad band having an absorption maximum at 490 mμ. The neutral and acidified solutions do not show this absorption.

The concentration of anthracene remaining after 15 min of electrolysis of a 10 m*M* solution was shown by absorption spectroscopy to be about 10^{-4} *M*. The absorption of this anthracene prevented any meaningful interpretation of the absorption spectrum of the new species appearing in the electrolyzed solution.

Discussion

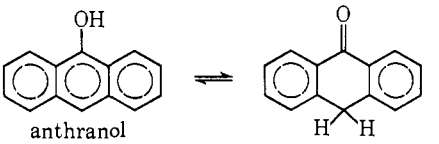
If one assumes that the properties of a molecular state are independent of the mode of excitation, then one cannot ascribe the ECL emission spectrum found with anthracene in DMF solution entirely to emission from the first excited singlet of anthracene. Since there is widespread support for this assumption in the ECL emission spectra of those molecules which we have previously designated as exhibiting type I behavior,[3] one must seek additional emitting species in the solution to explain the presence of the long-wavelength emission bands. The short-wavelength component of the emission spectrum resembles the anthracene fluorescence spectrum, and is probably due to emission from the first excited singlet of anthracene. This comparison is particularly striking in the emission spectrum shown in Figure 2b.

Direct emission from the lowest triplet level to the ground state can be ruled out on spectral grounds alone as a possible process responsible for 460-mμ emission. The 0–0 emission maximum for anthracene phosphorescence in a rigid EPA glass is in the region of 670 mμ.[10] This band probably would not be shifted some 200 mμ to the blue by a simple change in environmental conditions.

An explanation based on the formation of an anthracene excimer also has difficulties. There is experimental evidence to support such a species,[11–14] but it has not been observed to radiate significantly in liquid solution except at the relatively low temperature of −75°.[14] If excimer emission were the origin of light emission at 460 mμ, then one might infer that the excimers are formed in very high yield, or that there exists another type of dimeric species which radiates efficiently. Chandross, Longworth, and Visco[2] have indeed suggested that there does exist a new dimer formed from the annihilation reaction according to the scheme $A\cdot^+ + A\cdot^- \rightarrow A_2^* \rightarrow 2A + h\nu$, where $A\cdot^+$ and $A\cdot^-$ represent the radical cations and radical anions of anthracene generated at the electrode surface. However, this hypothesis further suffers from the inability to explain the dependence of the importance of long-wavelength emission upon the degree of DMF purification.

Exciplex emission also encounters the difficulty that no emission from anthracene exciplexes is observed in solutions which are composed of the species present in our experiments. If a radiative anthracene exciplex is responsible for the long-wavelength emission band, the complex probably would involve either a product molecule of one of the chemical reactions following anthracene oxidation or reduction, or possibly one of the species produced by the electrode reaction.

The experimental evidence is best explained by the formation of a new species which fluoresces in the region in which long-wavelength ECL emission occurs. The spectral matching of emission bands for ECL and fluorescence is a very persuasive argument in favor of this identification. This explanation obtains further support from the simultaneous decrease in peak fluorescence intensity at 460 mμ in the electrolyzed solution and the reduced importance of long-wavelength ECL emission upon changing the solvent purification scheme. If one does suppose that the new fluorescent species is the one responsible for the emission in the 460-mμ region, then questions arise concerning the identity of the product, the origin of the product, and the mode of product excitation. The experimental data suggest that the product shows acidic properties in undergoing a reversible acid–base reaction, that the product species shows marked air sensitivity, and that the basic solution of the product in DMF shows an absorption at 490 mμ, whereas the acidic and neutral solutions do not. In addition, of course, the new product shows a broad, structureless fluorescence spectrum with a maximum at about 460 mμ. One candidate is anthranol, which is the enol form of anthrone. Although



anthranol ⇌ anthrone

solid anthrone itself is nonfluorescent and is air stable, in DMF solution the keto–enol equilibrium is established immediately upon solution, and one observes a very bright, blue fluorescence. The fluorescence spectrum is shown in Figure 3c. It is broad, structureless, and shows a maximum at 457 mμ. The fluorescence intensity declines rapidly if the solution is left exposed to the air. Addition of base quenches the fluorescence, and readdition of an equivalent amount of acid causes its reappearance. The basic solution shows a broad absorption having a maximum at 490 mμ, but the acidic and neutral solutions do not show this absorption.

In order to substantiate the identification further, the electrolyzed solution was analyzed with an F & M gas chromatograph using flame ionization detection with a silicone rubber SE30 column. The electrolyzed solution showed a peak having an retention time iden-

(10) M. R. Padhye, S. P. McGlynn, and M. Kasha, *J. Chem. Phys.*, **32**, 357 (1960).
(11) R. Williams, *ibid.*, **28**, 577 (1958).
(12) A. Dammers de Klerk, *Mol. Phys.*, **1**, 141 (1958).
(13) B. Stevens and P. J. McCartin, *ibid.*, **3**, 425 (1960).
(14) C. A. Parker and T. A. Joyce, *Chem. Commun.*, 744 (1967).

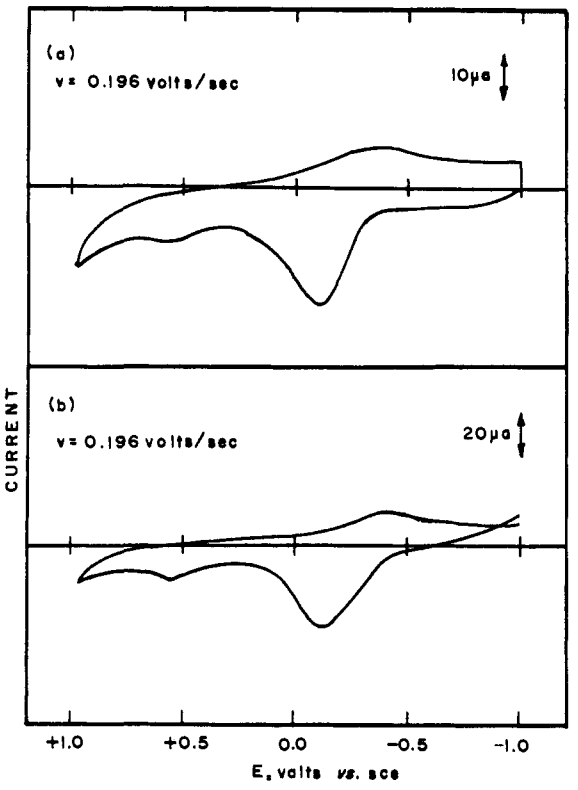


Figure 5. ECL emission spectrum of a solution 1.2 mM in anthrone plus anthranol.

tical with that observed with a test solution composed of DMF, TBAP, and anthrone–anthranol.

Since such an electrolysis product would be derived from anthracene, it would likely arise from reaction of one of the anthracene radical ions with the environment. Anthracene radical anion is relatively stable in DMF solution;[7] hence it is not likely to be involved in a fast reaction producing a fluorescent species. Instead it is much more probable that the very unstable anthracene radical cation is responsible. Indeed, it was found that controlled potential oxidation of a 10 mM anthracene solution at +1.25 V *vs.* sce yielded a new fluorescence band having a maximum at 457 mμ when excited at 420 mμ, identical with the fluorescence maximum of anthranol. This result prompted an attempt to verify the presence of an anthranol still further by electrochemical means. A cyclic voltammetric curve for oxidation at a platinum disk electrode for an anthrone–anthranol solution in DMF is shown in Figure 5a. There are two oxidation peaks, one located at −0.10 V *vs.* sce and the other at +0.54 V *vs.* sce. Both oxidations show a considerable degree of chemical irreversibility on the reverse scan. The reduction wave corresponding to the −0.10-V oxidation peak can be seen in Figure 5a, but that corresponding to the +0.54-V peak cannot be observed unless faster scan rates are employed.

If one did indeed produce anthranol while oxidizing anthracene at +1.30 V *vs.* sce, some of the anthranol which was produced would be oxidized still further at the working electrode, so long as that electrode remained more positive than about −0.20 V. This has the undesirable effect of depleting the anthranol concentration in the vicinity of the electrode, making anthranol more difficult to detect by a potential sweep experiment. To reduce this effect to a minimum, the experiment which was performed to detect anthranol produced during anthracene oxidation by a cyclic potential sweep involved preceeding the sweep by a double potential step. Using a 10 mM anthracene solution in DMF, the working electrode was stepped to +1.30 V *vs.* sce for 15 sec in order to oxidize anthracene and produce the new species, then the potential was stepped to −1.00 V *vs.* sce, and 5 sec later a cyclic voltammetric scan was begun toward the anodic potentials. This scan is shown in Figure 5b. One clearly sees two oxidation peaks with the corresponding reduction peak for the first oxidation observed on reversal of the potential scan. The cyclic voltammogram in Figure 5b is virtually superimposable on that shown in Figure 5a, lending persuasive support to the identification of anthranol as an anthracene oxidation product.

In view of this spectroscopic, chemical, chromatographic, and electrochemical evidence, it is likely that the fluorescent product is anthranol existing in tautomeric equilibrium with anthrone. This conclusion is further supported by the work of Majeski, Stuart, and Ohnesorge,[15] who found evidence for anthranol formation in the controlled potential oxidation of anthracene in acetonitrile. Fluorescence analysis indicates that the sum of the anthrone and anthranol concentrations reaches only about 10^{-4} M in the solutions exhibiting even the highest fluorescence intensities during electrolysis. This indicates a yield of anthranol plus anthrone on the order of 1–10% during the exhaustive electrolysis of 1 mM anthracene solutions.

Possibly the anthranol is formed by reaction of the radical cation of anthracene with traces of water in the solvent. Since the maximum fluorescence intensity from the new species during the elctrolysis is 30 times greater in the solvent purified by method I, when compared to the intensity observed in the more extensively purified solvent of method II, one would expect that some trace component in the system is important for producing anthranol. Water would certainly be suspect, and, since both DMF and TBAP are hygroscopic, it is virtually impossible to exclude it entirely from the system.

In order to check the effect of deliberately added water, we performed several experiments on 10 and 1 mM anthracene solutions, adding water in concentrations from 10 to 300 mM to the solutions. There was a general reduction in total light output with increasing water concentration, and emission was virtually quenched by the time 300 mM water had been added. Effects of water on the intensity of fluorescence emission at 460 mμ excited by 420-mμ radiation were complex. The maximum fluorescence intensity during electrolysis increased sharply with added water, reaching a maximum between 17 and 33 mM, then declining at greater added water concentrations. Qualitatively similar results were observed regarding the relative importance of long-wavelength emission in ECL. These observations may indicate competitive reactions between anthracene and water such as have been observed previously,[15] but this possibility was not explored further.

(15) E. J. Majeski, J. D. Stuart, and W. E. Ohnesorge, *J. Am. Chem. Soc.*, **90**, 633 (1968).

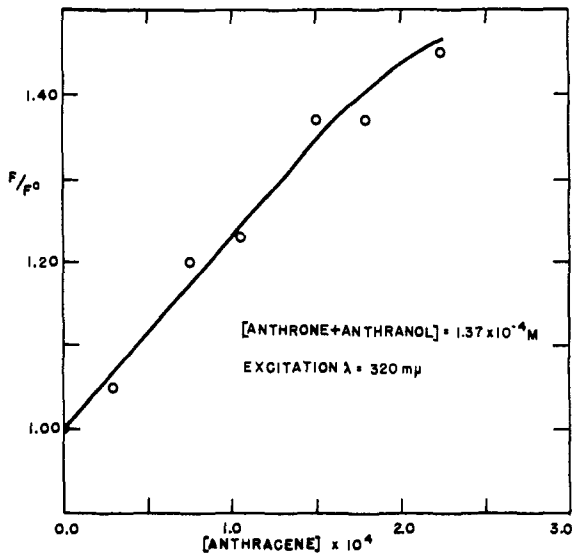


Figure 6. Cyclic voltammetric curves: (a) scan for 2 m*M* anthrone plus anthranol at a platinum disk electrode in DMF and 0.1 *M* TBAP; (b) scan for 10 m*M* anthracene in DMF and 0.1 *M* TBAP at a platinum electrode following a double potential step.

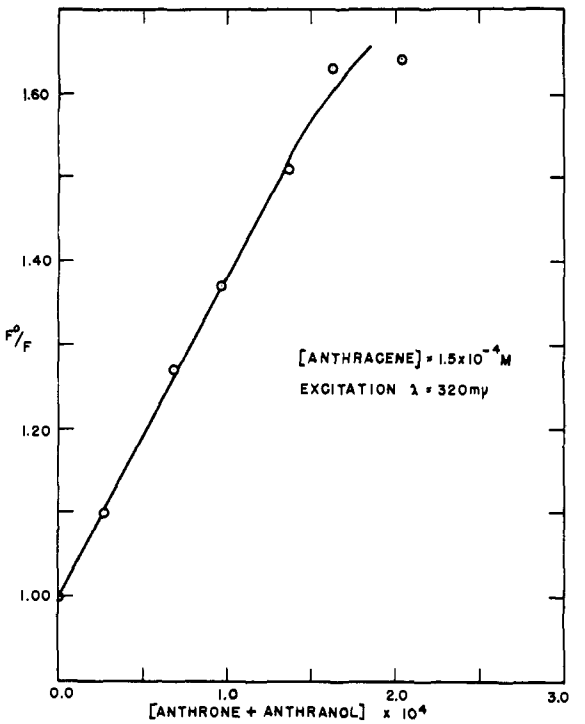


Figure 7. Sensitization of anthranol fluorescence at 457 mμ by anthracene.

Mode of Excitation. The intensity–time curves for ECL emission at 470 mμ and for fluorescence at 470 mμ excited by 420-mμ radiation are very instructive in determining the mode of excitation of the product. The ECL emission curve shows that the intensity decreases rapidly with time; however, fluorescence intensity rises to a maximum, then falls very slowly. If the new species were excited *via* an electrode reaction and a series of homogeneous chemical reactions which depend only on some function of the new product concentration, then one would expect an intensity–time relationship for ECL emission at 470 mμ which shows a rise in intensity with increasing time as product becomes more available. The fact that the intensity–time curve for ECL emission intensity falls with time indicates that the new species is not excited by this kind of mechanism to emit in that region. This curve, in fact, suggests strongly that the anthracene concentration may be a very great factor in governing emission in the region of 460 mμ.

One can conceive of several mechanisms to explain these data. One obvious path is simply the excitation of anthranol upon formation from the anthracene radical cation. A second possibility is a mechanism which involves a homogeneous reaction between products of the electrode reactions of anthranol and anthracene, and a final alternative is simple electronic energy transfer from singlet-excited anthracene.

The second mechanism can be defined a little more closely by examining the electrochemistry of anthranol solutions in DMF. Cyclic voltammetry shows an oxidation wave at −0.10 V *vs.* sce which is chemically irreversible, although some product is detectable on the reverse scan at higher scan rates. No anthranol reduction wave is seen in this system. The only electrode product annihilation reaction which is possible for this system, and which might result in an excited anthranol species, is the reaction between anthracene anion and the oxidation product of anthranol shown as $A\cdot^- + X \rightarrow AnOH^* + Y$, where $A\cdot^-$ is anthracene radical anion, X is the oxidation product of anthranol, and AnOH* is excited singlet anthranol. Since anthracene is reduced at −2.00 V in this system, the annihilation reaction above liberates at most 1.9 eV. However, since the anthranol singlet is at about 2.7 eV, the above reaction is impossible without invoking some energy-doubling scheme like triplet–triplet annihilation to account for excitation of the anthranol to its first singlet. These considerations, in themselves, are not sufficient to rule out such a mechanism, since such "energy-deficient" reactions have been observed in other systems.[16]

To examine the third mechanism for exciting anthranol, outlined above, we have performed some experiments designed to test the effectiveness of energy transfer from anthracene to anthranol using the spectrophotofluorometric method.[17] The results are shown in Figures 6 and 7. In Figure 6 the sensitization of anthranol fluorescence is shown by plotting F/F^0 *vs.* anthracene concentration, where F^0 is the relative fluorescence intensity with added species absent, and F is the fluorescence intensity in the presence of a given additive concentration. The plot was made by using a constant anthrone plus anthranol concentration. In Figure 7 the reduction of anthracene fluorescence at 404 mμ in the presence of anthranol is shown. Here, F^0/F is plotted *vs.* anthranol plus anthrone concentration. According to theory, one expects linear plots in both cases, if energy transfer takes place, provided the absorbance remains below 0.043 at the excitation and emission wavelengths.[17] These plots are linear at lower concentrations. The slight curvature at higher concentrations is possibly due to high absorbance effects.

(16) (a) K. S. V. Santhanam and A. J. Bard, *J. Am. Chem. Soc.*, 87, 139 (1965); (b) A. Weller and K. Zachariasse, *J. Chem. Phys.*, 46, 4984 (1967).

(17) (a) F. Wilkinson and J. T. Dubois, *ibid.*, 39, 377 (1963); (b) F. Wilkinson in "Fluorescence," G. G. Guilbault, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, Chapter 1, and references contained therein.

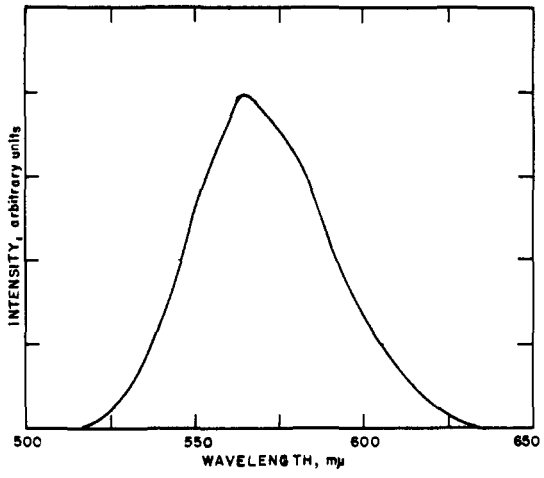


Figure 8. Quenching of anthracene fluorescence at 404 mμ by anthranol.

From these experiments, it is clear that energy transfer does occur from anthracene to anthranol in DMF solution. Whether the nature of the transfer is radiative or nonradiative is not so obvious, because of the large overlap of anthracene emission and anthranol absorption spectra. Certainly one may say that at higher concentrations radiative transfer is important. Probably, a nonradiative transfer mechanism is the important one at lower concentrations. The mechanism of the transfer is not so important here as the fact that energy transfer does take place at the concentrations typically involved in electrolysis. Regardless of the contributions of other mechanisms, if any, to the light emission in the region of 460 mμ, these results show conclusively that energy transfer from anthracene to anthranol is an effective mechanism in DMF solution, and will be responsible for at least a fraction of the emission observed at 460 mμ.

In addition to being involved in the mechanism responsible for emission at 460 mμ, anthranol is probably also implicated in the mechanism producing light in the region of 565 mμ. We have noted previously that the emission and fluorescence intensity–time curves imply no direct excitation of anthranol *via* an electrode reaction of its own. An investigation of the ECL of 1 m*M* anthrone plus anthranol solutions bore this out. Indeed, anthranol did not display ECL emission in the region of 460 mμ. Instead, the emission which was observed is shown in Figure 8. The maximum is at 565 mμ. This emission rapidly reaches a steady state and persists for very long times. The emission intensity rises steadily with increasing applied voltage after the threshold of about 4.5 V peak to peak.

One will note that all of these emission characteristics are present in the ECL emission band which is located at 565 mμ in the anthracene solutions. Although no positive connection has been made, it seems quite probable that the anthranol produced in the electrolysis of anthracene is the cause of this emission band.

The identity of the species emitting at 565 mμ in the anthranol solution is unknown. Certainly it is not singlet anthranol. Even if anthranol is involved in ECL at 565 mμ in anthracene solutions, it is further doubtful that it is the species fluorescing in the region of 520 mμ, but this fluorescence band is so weak that conclusions drawn from its presence are tenuous at best.

The conclusion that excimer emission is not involved in the ECL of anthracene does not rule out its presence in other cases. Indeed Parker and Short[18] have recently provided persuasive evidence for the formation of excimers during ECL of 9,10-dimethylanthracene. We have repeated these experiments and have found no new fluorescence peaks in the solution following exhaustive electrolysis.

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