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Mechanisms of Chemiluminescent Electron-Transfer Reactions. I. The Role of the Triplet State in Energy-Deficient Systems

D. J. Freed and Larry R. Faulkner*

Contribution from the Coolidge Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138. *Received July 17, 1970*

Abstract: Two separate studies were carried out to elucidate the role of the triplet state in energy-deficient chemiluminescent electron-transfer reactions occurring in *N,N*-dimethylformamide. The first of these was an investigation of the nature of luminescence from a series of reactions involving the radical anions of anthracene, 9,10-diphenylanthracene, rubrene, and fluoranthene as reductants and the radical cations of *N,N*-dimethyl-*p*-phenylenediamine and 10-methylphenothiazine as oxidants. All experiments were conducted with reactants generated at an electrode at controlled potential. The results for systems containing fluoranthene indicate that a critical value of electron-transfer enthalpy exists which must be exceeded for luminescence to occur. The value is near the energy required to excite fluoranthene to its lowest triplet state. A second investigation was a study of the effect of a series of chemically inert triplet quenchers on the reaction between the fluoranthene radical anion and the 10-methylphenothiazine radical cation. *trans*-Stilbene, anthracene, and pyrene were able to quench the normal fluoranthene emission. Moreover, the systems containing anthracene and pyrene emitted light characteristic of the fluorescence of these molecules. This behavior was interpreted as providing *prima facie* evidence for a required triplet intermediate in the energy-deficient chemiluminescent reactions of fluoranthrene. The results are discussed in terms of possible mechanisms for luminescence.

Because electron-transfer reactions are fundamental to all of chemistry, and because the chemiluminescent electron-transfer reactions involving radical ions of aromatic compounds offer a unique opportunity to study the detailed course of one type of electron transfer, a significant effort has been invested recently in mechanistic studies of these systems.[1,2] The simpler systems feature only one emission component, which is spectrally identical with the fluorescence of one of the products of the electron-transfer reaction. In these systems it is clear that the emitting first excited singlet state is populated in some way as an accompaniment to the electron-transfer process. Indeed, most current thinking presumes a direct population of some excited state of a product molecule in this process. Clearly the relative energetics of excitation and electron transfer are important considerations in such an hypothesis. As a consequence, one of the most intriguing aspects of the mechanistic studies has been the problem of "energy-deficient systems," *i.e.*, those for which an emitted photon contains far more energy than is released by a single electron-transfer event.[3,4] Thus, energy considerations for such cases apparently rule out direct production of the emitting state during electron transfer. One must rely on some energy-multiplying step to account for the observed behavior in terms of excited-state generation during the redox process.

Most speculation to date has employed the hypothesis that the redox reactions generate a triplet-state product molecule, which in turn produces the emitting singlet in a following triplet–triplet annihilation. An alternate mechanism, advanced by Zweig, *et al.*, uses the hypothesis that the emitting state is generated directly by multiple electron transfer to or from aggregates of radical ions.[5] This latter view envisions the energy lib-

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(1) A. Zweig, *Advan. Photochem.*, **6**, 425 (1968).

(2) D. M. Hercules, *Accounts Chem. Res.*, **2**, 301 (1969).

(3) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

(4) A. J. Bard and K. S. V. Santhanam, *J. Amer. Chem. Soc.*, **87**, 139 (1965).

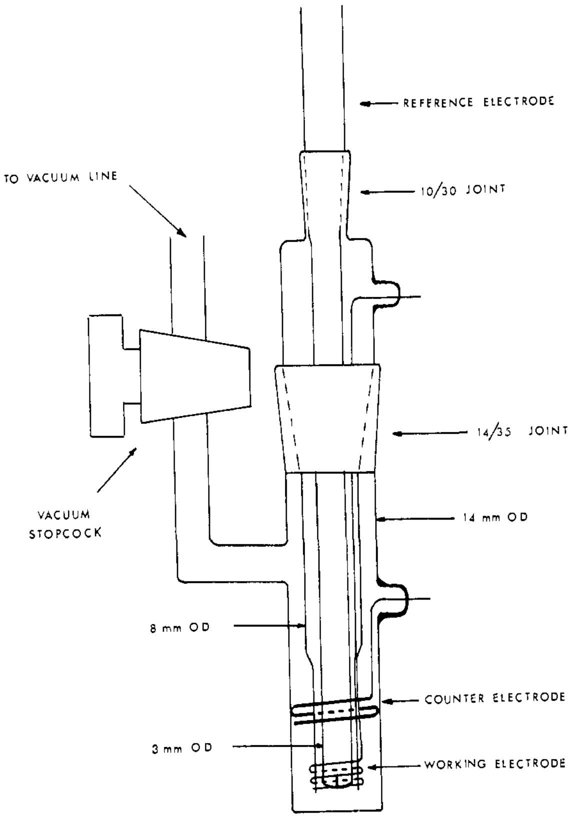

Figure 1. Electrolysis cell used for generation of radical ions.

erated in such a step as being localized on one molecule, a constituent of the former aggregate, which then emits.

Experimental results bearing on these hypotheses have been elusive, and there are few informative reports available. In a study of several energy-deficient reactions using the Wurster's Blue radical cation as an oxidant, Weller and Zachariasse have reported that the emission resulting from chrysene radical anion oxidation contains two components.[3] One of these corresponds to the expected chrysene fluorescence band. The second matches the chrysene phosphorescence spectrum and indicates the presence of the chrysene triplet state. In other work, Chang, Hercules, and Roe have shown that a series of double-potential-step experiments yields behavior which is kinetically consistent with the triplet mechanism if one assumes the radical ions to be effective quenchers of triplet states.[6] Finally, Faulkner and Bard studied magnetic field effects on chemiluminescence and delayed fluorescence.[7] They concluded that these effects can be rationalized in terms of the triplet mechanism, and especially in terms of radical-ion quenching of the triplet intermediates, which they actually found to be an efficient process.

Because it offers the simplest available explanation, and because of these probing experiments, the triplet mechanism is the more widely favored one. Nonetheless, no published report demonstrates that a triplet is a precursor to the emitting singlet. In an effort to fill this void, we have carried out experiments bearing on the problem from two separate approaches. In one study of a group of systems involving only one possible emitter, we sought to determine whether one could observe emission accompanying electron-transfer reactions which are not energetic enough to populate even the emitter triplet state directly. Thus we sought to discover whether a "critical enthalpy" exists for the emission of light, and whether that enthalpy is related to the lowest triplet level of the emitter. In a second study, we investigated the effects of suitable triplet quenchers on the emission from chemiluminescent systems. Because fluoranthene has a high triplet energy compared to its reduction potential, it proved to be an eminently suitable substrate for this work. We believe that the results reported here represent the first hard experimental evidence that a triplet state is a necessary intermediate for chemiluminescence from energy-deficient systems.

Experimental Section

N,N-Dimethylformamide (DMF), bp 152–154°, was purchased from Matheson Coleman and Bell and purified as described previously.[8] This solvent was used in all of the experiments described here. Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) obtained from Southwestern Analytical Chemicals was used directly after drying *in vacuo* at 100° for 48 hr. This salt was the supporting electrolyte in all electrochemical experiments. Blue-violet fluorescence grade anthracene and scintillation grade *trans*-stilbene and fluoranthene were obtained from Eastman Organic Chemicals and were used without further purification. Naphthalene, pyrene, and 10-methylphenothiazine (10-MP) were Eastman reagent grade chemicals and were recrystallized three times from benzene before use. Rubrene and 9,10-diphenylanthracene (9,10-DPA) were purchased from the Aldrich Chemical Co. and were purified by three recrystallizations from absolute ethanol. *N,N*-Dimethyl-*p*-phenylenediamine (WR) was prepared by neutralization of the hydrochloride (Eastman Organic Chemicals) with aqueous KOH and extraction into benzene. Just prior to use it was sublimed *in vacuo*. The helium used (99.995% purity) was produced by Matheson Gas Products and was further purified by passage through a 3 × 40 cm tube of copper wire maintained at 450°.

The electrolysis cell used for generation of the radical ions (Figure 1) was constructed from standard-taper Pyrex joints. It consists basically of three concentric tubes designed to fit in the sample compartment of the spectrophotofluorimeter and is capable of being evacuated to less than 10^{-5} Torr. The working electrode, viewed by the emission monochromator, is a 15-cm length of 28-gauge platinum wire coiled tightly around the bottom edge of the middle tube and is connected externally at the top *via* a graded seal. The lead portion is insulated from the bulk of the solution by Teflon spaghetti. The counter electrode is a 10-cm length of 22-gauge platinum wire coiled around the inside of the outer tube in such a manner as to be concentric with, and about 4 cm above, the working electrode. This arrangement serves to maintain a fairly uniform current density over the working electrode. This electrode, too, is connected through the body by a graded seal. The innermost tube is an aqueous $Ag|AgCl$, saturated KCl reference electrode (−0.038 V *vs.* sce), making electrical contact through an asbestos fiber. An inner saturated KCl–agar plug inhibits diffusion of water into the solution. In order to minimize the effects of uncompensated resistance, the cell was designed so that the tip of the reference electrode is concentric with, and no more than 1 mm from, the working electrode.

Solutions were placed in the assembled cell under a blanket of helium, connected to a vacuum line, and degassed by the freeze–pump–thaw method. This was repeated several times to ensure complete removal of oxygen, with the final pressure never being more than 5×10^{-5} Torr. The reference electrode was then placed in the cell under a positive pressure of helium.

Electrode potentials were controlled by a Wenking Model 61RS potentiostat and the desired potential program was generated by an auxiliary function generator (Hewlett-Packard Model 202A). The working electrode potentials were accurately checked with a

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(5) A. Zweig, A. K. Hoffman, D. L. Maricle, and A. H. Maurer, *J. Amer. Chem. Soc.*, **90**, 261 (1968).

(6) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1969).

(7) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209, 6495, 6497 (1969).

(8) L. R. Faulkner and A. J. Bard, *ibid.*, **90**, 6284 (1968).

Digitec Model 201 digital voltmeter and were continuously monitored with a Tektronix Type 564 storage oscilloscope.

Fluorescence and chemiluminescence spectra were obtained with an Aminco-Bowman spectrophotofluorimeter using an RCA Model 1P21 photomultiplier tube, and the recorded spectra were displayed on a Hewlett-Packard Model 2D X-Y recorder. Fluorescence spectra were obtained on dilute (*ca.* 10^{-5} *M*) solutions of the compounds of interest using right-angle illumination.

Cyclic voltammetry was used to examine pertinent electrochemical properties of the compounds studied. Solutions were 1 m*M* in the desired compound and 0.1 *M* in supporting electrolyte (TBAP), and prepurified nitrogen was used as an oxygen purge. The cyclic voltammetric data were obtained at a platinum disk microelectrode with the aid of a controlled-potential voltammeter based on operational amplifiers (Indiana Instrument Model ORNL-1988A), but modified to permit scan rates to 500 mV/sec and to provide a follower input for the reference electrode.

Electron-Transfer Enthalpy as a Criterion for Chemiluminescence

Our investigation of the relationship between luminescence and the energetics of the electron-transfer reaction took the form of a study of the nature of the chemiluminescence arising from a variety of electron-transfer systems. The reactions studied are listed in Table I. In the tabulation of reactants the symbol (−) following a compound denotes the radical anion derived from that compound, and likewise (+) denotes the radical cation species.

Table I. Reaction Enthalpies and Emission Characteristics

Reactants	$-\Delta H$, eV	Chemiluminescence
Rubrene(−), WR(+)[a]	1.8	Rubrene
Rubrene(−), 10-MP(+)	2.1	Rubrene
9,10-DPA(−), WR(+)	2.3	9,10-DPA
9,10-DPA(−), 10-MP(+)	2.7	9,10-DPA
Fluoranthene(−), WR(+)	2.1	None
Fluoranthene(−), WB(+)[b]	1.9	None
Fluoranthene(−), 10-MP(+)	2.6	Fluoranthene
Anthracene(−), 10-MP(+)	2.7	Anthracene

[a] WR(+) = Wurster's Red radical cation. [b] WB(+) = Wurster's Blue radical cation. This value is taken from A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

The reactions were carried out in the diffusion layer surrounding the working electrode of the cell shown in Figure 1. The reacting radical ions were generated at the working electrode in a series of potential steps alternating between production of the radical anions and production of the radical cations. The frequency of the potential program was 20 Hz and the wave form was a square wave. In every case, the radicals were generated at their cyclic voltammetric peak potentials.

In order to ascertain the correct reduction–oxidation potentials, cyclic voltammograms were obtained for all compounds used and the peak potentials are shown in Table II. All of the hydrocarbons show well-developed forward and reverse peaks with peak separations of about 60 mV, indicating reversible reduction to the stable radical anions. Likewise, the voltammograms of the oxidants used show well-developed peaks, indicating reversible oxidation to the radical cations. All of these radical ions have been shown to be stable in aprotic solvents, by both esr measurements[9] and electrochemical techniques.[10]

Table II. Electrochemical and Spectroscopic Data

Compound, R	E_p $(R/R^+)^i$	$-E_p$ $(R/R^-)^i$	$E(^1R^*)$, eV	$E(^3R^*)$, eV
Naphthalene	NO[a]	2.50	3.9	2.6[b]
trans-Stilbene	NO	2.11	3.8	2.0[c]
Fluoranthene	NO	1.70	3.0	2.3[d]
Anthracene	1.34	1.90	3.3	1.8[b]
9,10-DPA	1.30	1.86	3.0	1.8[e]
Pyrene	1.29	2.10	3.4	2.1[d]
Rubrene	0.98	1.34	2.2	
10-MP	0.90	NR[a]	3.4	2.4[f]
WR	0.45	NR		2.7[g]
WB	0.28	NR		2.7[h]

[a] NO = Not oxidized; NR = not reduced. [b] S. P. McGlynn, M. R. Padhye, and M. Kasha, *J. Chem. Phys.*, **23**, 593 (1955). [c] G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964). [d] E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956). [e] J. S. Brinen and J. G. Koren, *Chem. Phys. Lett.*, **2**, 671 (1968). [f] Estimated from value for phenothiazine; see J. M. Lhoste and J. B. Merceille, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1889 (1968). [g] Estimated from value for Wurster's Blue. See ref *h*. [h] D. W. Skelly and W. H. Hamill, *J. Chem. Phys.*, **43**, 3497 (1965). [i] V *vs.* Ag|AgCl, KCl (satd).

Table II also shows the energy levels for the pertinent excited states of the compounds employed in this study. The energies of the first excited singlet states, $E(^1R^*)$, were obtained in this laboratory from fluorescence data (*cf.* Experimental Section). The lowest triplet energies, $E(^3R^*)$, were obtained from the literature and, wherever possible, phosphorescence data were used.

Under the heading $-\Delta H$, Table I shows the enthalpy for the electron-transfer reaction resulting in ground-state products. These values were calculated according to the equation $-\Delta H = E_p(R/R^+) - E_p(R/R^-) - T\Delta S$, adapted from Weller[3] and from Hoytink.[11] In this equation, the measured peak potentials are used as approximations for the thermodynamic standard potentials. The value of the entropy correction term was chosen to be 0.1 eV.

Comparing the values of ΔH with the energies of the excited states of the compounds involved (Table II) it is clear that none of these electron-transfer reactions is sufficiently energetic to populate any first excited singlet state directly. Yet as Table I indicates, whenever luminescence is observed it is spectrally identical in all respects with the fluorescence emission of the hydrocarbon product of the electron-transfer reaction. The data for the reactions of the familiar radical anions of anthracene, 9,10-DPA, and rubrene with the WR and 10-MP radical cations indicate that the two oxidants show simple behavior in their chemiluminescent reactions. In this regard, the WR and 10-MP radical cations are very similar to the well-studied Wurster's Blue cation.[3] In each of these cases, the energy released in the electron-transfer reaction is more than enough to raise the product hydrocarbon to its lowest triplet state directly. This supports the view that triplets are true intermediates in the emission process, since formation of the emitting singlet state in these reactions is energetically impossible.

The reaction of the anthracene radical anion with the 10-MP radical cation presents an interesting case.

(9) J. B. Billon, G. Cauquis, and J. Combrisson, *J. Chim. Phys. Physicochim. Biol.*, 61, 374 (1964).

(10) M. E. Peover in "Electroanalytical Chemistry," Vol. 2, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1967, Chapter 1, and references contained therein.

(11) G. J. Hoytink, *Discuss. Faraday Soc.*, **45**, 14 (1968).

The triplet mechanism predicts that the energy available from the electron-transfer reaction should be sufficient to raise either anthracene or 10-MP to the lowest triplet state. However, this mechanism also predicts quenching of the 10-MP triplet by anthracene, whose triplet lies some 0.5 eV lower. When the reaction was carried out, only anthracene fluorescence was observed, as expected from these predictions.

Experiments with fluoranthene offered more direct evidence of a possible triplet intermediate in the luminescence scheme. When the fluoranthene radical anion was oxidized by the WR radical cation no light was observed, even by a dark-adapted eye. That radical production occurred was evident; the intensely colored radical ions could clearly be seen, and the current passing at the working electrode indicated an electrode reaction was occurring. In a similar manner, Weller reported that the fluoranthene radical anion, when oxidized by the Wurster's Blue radical cation, gave no emission.[12] A consideration of the reaction enthalpy (Table I) shows that in neither of these cases is enough energy obtained in a single electron-transfer event to raise fluoranthene even to its lowest triplet state. However, when the fluoranthene radical anion was oxidized by the 10-MP radical cation a strong blue emission was seen, which proved to be identical with the fluorescence emission of fluoranthene. This reaction, in contrast to the others, does provide enough energy to produce the triplet state of fluoranthene directly.

The above experiments lend credence to an hypothesis of a triplet-state intermediate in the luminescence process, since in none of the cases observed is there enough energy obtained to produce directly the singlet state which emits. Furthermore, in those cases where no light was seen, the experimental results are wholly consistent with the theory of a single electron-transfer event giving rise to an excited state, rather than the hypothesis of multiple electron transfers from radical-ion aggregates. There seems to be a requirement for a "critical enthalpy" in these reactions, which, if exceeded, leads to formation of the excited singlet state through the intermediacy of a triplet. In those cases where this critical enthalpy is not exceeded in the electron-transfer reaction (fluoranthene and WR or Wurster's Blue), the excess energy is simply dissipated by rotational and vibrational energy transfer to solvent molecules.

Triplet Quenching Experiments

A consideration of the triplet energy levels involved led us to believe that if a triplet intermediate were involved, one should be able to intercept it by the addition of suitable triplet quenchers. Porter and Wilkinson have shown that triplet–triplet energy transfer occurs with an encounter efficiency approaching unity if the acceptor triplet lies as little as 0.2 eV below the donor triplet.[13] In addition to this energy level requirement, it is clear that the quencher must not quench the singlet state nor react chemically with other components of the system. Finally, the quencher should not react at the electrodes in the potential range of interest. The reaction between the fluoranthene radical anion and the 10-MP radical cation proved to be quite suitable for such a study. Even though the fluoranthene molecule has a high triplet energy, it is fairly easily reduced. Chemically inert triplet quenchers were therefore not difficult to find.

One such system employed *trans*-stilbene as the quenching species. When the fluoranthene radical anion was oxidized by the 10-MP radical cation in the presence of *trans*-stilbene, no emission was observed. The orange fluoranthene radical anion and the red 10-MP radical cation could clearly be seen in the solution, however, and the monitored current clearly indicated a reaction occurring at the working electrode.

In order to examine the possibility of side reactions implicating *trans*-stilbene, cyclic voltammograms of fluoranthene reduction and 10-MP oxidation were obtained in its presence. The data showed no change in the reversible reduction or oxidation processes. Since the reduction potential of *trans*-stilbene is some 0.4 V more cathodic than that of fluoranthene, and since its oxidation potential is far more anodic than that of 10-MP, *trans*-stilbene is clearly not involved in the electrode reactions. Moreover, the reversibility of the oxidation and reduction processes militates against the possibility of a homogeneous electron-transfer reaction from fluoranthene anions to *trans*-stilbene.

A further experiment showed that when the 9,10-DPA radical anion was oxidized by the 10-MP radical cation in the presence of *trans*-stilbene, the characteristic 9,10-DPA fluorescence was observed. This observation provides additional support for the view that *trans*-stilbene is inert toward the radical ions.

Thus one must rationalize the absence of light from fluoranthene as the result of triplet–triplet energy transfer between fluoranthene and *trans*-stilbene, which subsequently returns to the ground state *via* radiationless processes.[14] A comparison of the relative energy levels involved (Table II) shows that the fluoranthene triplet lies some 0.3 eV above that of *trans*-stilbene; thus triplet energy transfer from fluoranthene to *trans*-stilbene should be a facile process. However, in the case of 9,10-DPA, whose triplet lies 0.2 eV below that of *trans*-stilbene, quenching of the 9,10-DPA triplet is improbable, and the expected 9,10-DPA fluorescence is observed.

Reasoning that if one could observe a positive result of the triplet energy transfer, more credence would be lent to the idea of a triplet intermediate, we turned to a system involving anthracene as a triplet quencher. When the fluoranthene radical anion was oxidized by the 10-MP radical cation in the presence of anthracene, a strong blue-violet emission was seen. Upon recording its spectrum, we found it to be identical with the fluorescence emission of anthracene (Figure 2). The spectrum is extremely well resolved; although the peak at 385 nm is reduced in intensity due to reabsorption, the vibrational transitions at 400 and 420 nm due to anthracene are unmistakable.

Immediately afterward, the same cell was cleaned thoroughly and a solution containing only anthracene and 10-MP was introduced and degassed as before.

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(12) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(13) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).

(14) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

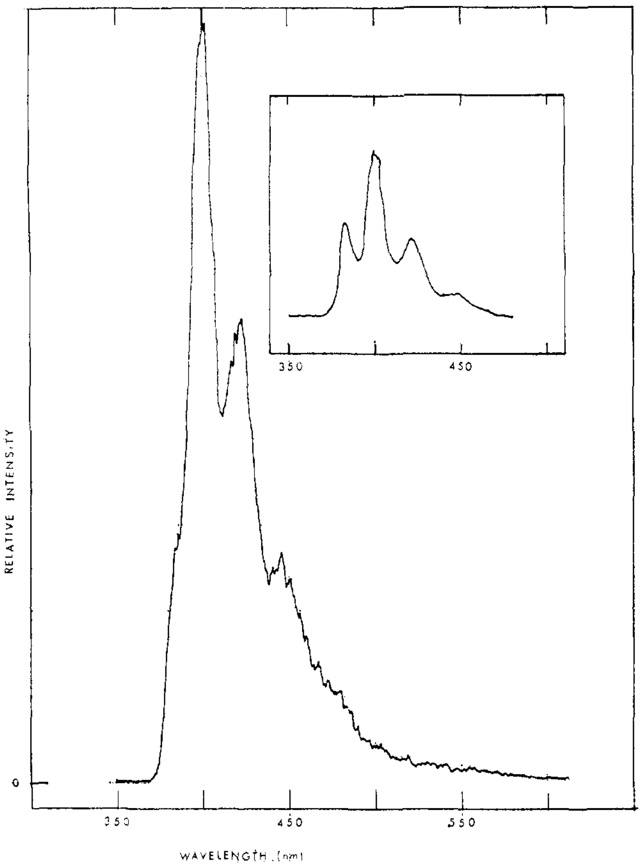

Figure 2. Chemiluminescence spectrum obtained in energy-transfer experiment with fluoranthene and anthracene. Inset shows anthracene fluorescence spectrum (10^{-5} M in DMF).

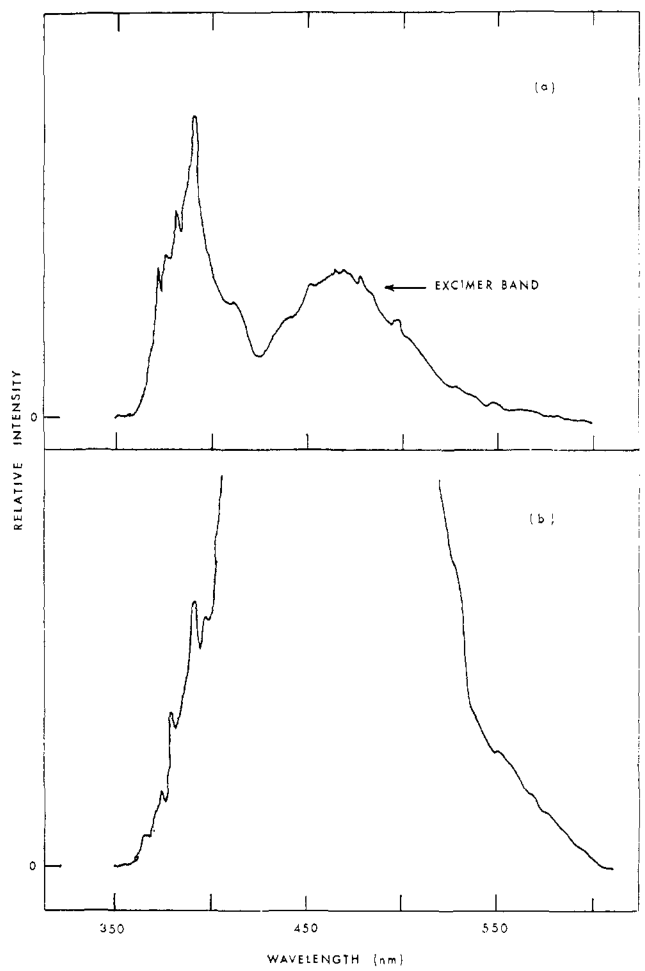

Figure 3. (a) Fluorescence spectrum of pyrene ($10^{-3}M$). Note excimer band in the region 400–600 nm. (b) Chemiluminescence spectrum obtained in energy-transfer experiment with fluoranthene and pyrene.

When the electrode potentials were maintained at the same values as those used for generation of the fluoranthene and 10-MP radical ions, no emission was observed. However, when the reducing potential was shifted to a value 0.2 V more cathodic, the characteristic anthracene emission was seen. Clearly the emission of anthracene fluorescence described above from the solution containing both anthracene and fluoranthene cannot be ascribed to the presence of anthracene radical anions.

In order to preclude the possibility of singlet–singlet energy transfer between fluoranthene and anthracene, a solution 10^{-5} M in both was illuminated at 290 nm, where only fluoranthene absorbs appreciably. Only fluoranthene emission was observed. In any event, one would not expect such a transfer to occur since it is energetically an uphill process.

In a third experiment, the fluoranthene radical anion was oxidized by the 10-MP radical cation in the presence of naphthalene. Only fluoranthene emission was observed.

The final system studied employed pyrene as the triplet quencher. When the fluoranthene radical anion was oxidized by the 10-MP radical cation in the presence of pyrene, intense blue-violet emission was seen. The recorded spectrum (Figure 3) was seen to consist of several components. When compared with the normal pyrene fluorescence spectrum (Figure 3), it is seen that the vibrational structure below 400 nm corresponds exactly to that of pyrene. However, a comparison of the fluoranthene and pyrene fluorescence spectra shows that the radiative excimer band of pyrene overlaps the fluoranthene emission considerably, making further identification difficult.

In a separate experiment, a solution consisting only of pyrene and 10-MP was placed in the same cell and degassed as before. When the potentials were maintained at the same values as used in the experiment described immediately above, no emission was observed. Since the reduction potential of pyrene is some 0.4 V more cathodic than that of fluoranthene, and its oxidation potential is 0.3 V more anodic than that of 10-MP, it is clear that the emission occurring from the pyrene in the previous experiment cannot be ascribed to the reactions of pyrene radical ions.

The fluorescence spectrum of a solution of pyrene and fluoranthene (10^{-3} M in both) showed only the presence of fluoranthene emission when illuminated at 285 nm (where only fluoranthene absorbs appreciably), indicating that sensitized emission from pyrene due to singlet–singlet energy transfer does not occur.

This behavior can be nicely rationalized in terms of the triplet mechanism when one considers the relevant energy levels. Since the fluoranthene triplet lies some 0.5 eV above that of anthracene, the triplet mechanism requires efficient triplet energy transfer from fluoranthene to anthracene. The anthracene triplet thus formed can then react with another anthracene triplet to produce the first excited singlet state of anthracene, which then emits. Since the naphthalene triplet lies 0.3 eV above that of the fluoranthene triplet, quenching by naphthalene is improbable; thus fluoranthene must undergo triplet–triplet annihilation to produce its emitting singlet.

The fluoranthene triplet also lies 0.2 eV above that of pyrene and triplet energy transfer is expected in the same manner as above. Clearly, the presence of pyrene emission bands below 400 nm is most reasonably ascribed to this process. However, the presence of a radiative excimer band overlapping the normal fluorescence band of fluoranthene complicates matters somewhat, especially since higher excited states of this excimer have been proposed[15] which may transfer energy back to the fluoranthene triplet. However, these complications in no way vitiate the conclusions to be drawn, namely that triplets are present as a result of the electron-transfer reactions.

Since the experiments performed rule out the possibility of singlet–singlet energy transfer in the systems examined, we believe we have here the first hard evidence for *required* triplet intermediates in the chemiluminescence from energy-deficient systems; indeed this seems the only rational explanation for the observed behavior.

Conclusion

The results presented above imply two conclusions about the nature of the chemiluminescent processes in energy-deficient systems involving fluoranthene. The data show that a critical electron-transfer enthalpy does exist, which must be exceeded for luminescence to occur. Furthermore, the value of this critical enthalpy is very near the energy required to excite fluoranthene to its lowest triplet state. The second group of experiments has strongly implied that a fluoranthene triplet is required as an intermediate in the process which ultimately results in chemiluminescence. These conclusions for fluoranthene-containing systems, taken together with the obvious inference that similar statements could be made for other energy-deficient systems, constitute a formidable body of evidence to be entered in favor of the triplet mechanism.

The close relationship between the critical enthalpy and the triplet energy of fluoranthene lends significant experimental support to the view that the triplet state of fluoranthene is populated directly in a single electron-transfer event. One must conclude that the ion-aggregate mechanism is an improbable one, at least in the form in which it has been proposed, requiring generation of the emitting species in a multiple electron transfer. At the least, its complexity seems unnecessary.

The fact that the fluoranthene triplet is a required intermediate has the rather important implication that at least some of the emission observed from these systems must arise as a result of triplet–triplet annihilation, which Stevens and Walker have demonstrated to be operative for fluoranthene.[16] This may indeed be the only luminescent pathway. Data currently available demand nothing more complicated.

Acknowledgment. The authors wish to acknowledge gratefully a grant from the Milton Fund of Harvard University which enabled the purchase of the spectrophotofluorimeter used in these studies.

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