The above reaction mixtures were analyzed under temperature-programmed conditions on a dual-column F & M 810 instrument equipped with thermal conductivity detectors. Aluminum columns, 6 or 7 ft by 0.25 in., packed with 20% SE-30 on 60–80 Chromosorb W regular, were used. The percentages of α and β scission products were determined by analysis of the products toluene (octane), *O,O*-diethyl *S*-isopropyl, *tert*-butyl, and benzyl phosphorodithioates (tridecane), and diethyl benzyl phosphonothionate (tridecane). The internal standards used for each analysis are given above in parentheses. Sensitivity calibrations in each case were carefully determined using a series of solutions in *o*-dichlorobenzene in which the weight ratio of compound to standard was varied from 0.5 to 2.0. A series of these standards was run before each set of analyses and with each column. In the reactions of *i*-PrSH with diethyl *tert*-butyl- and benzylphosphonites the peak for product phosphorodithioate was sufficiently well separated from other products to allow reliable quantitative analysis. Essentially identical results ($E_\beta - E_\alpha$) were obtained in the *i*-PrSH/PhCH$_2$(OEt)$_2$ reaction with either toluene or the phosphorodithioate. For the other two reactions, the amount of α scission product was determined by analysis for toluene. In all cases the formation of the appropriate phosphorodithioate was demonstrated by VPC analysis on several different columns of product mixtures doped with authentic phosphorodithioate. Accountability of starting phosphite in terms of α and β cleavage products was usually 90–95% but in some cases was as high as 98% or as low as 88%. In addition 1–3% of the diethyl benzylphosphonate was present among the products along with the apparent thio analogue of a 1–2% impurity present in all preparations of the benzylphosphonite. Thus accountability is in fact very near quantitative.

At each temperature, 3 to 8 samples were run. Quantitative results were then calculated from peak areas obtained by use of a Disc integrator or a Vidar Autolab Model 6300 Digital Integrator. Plots of ln k_α/k_β vs. $1/T$ using all points were subjected to linear regressions analysis. By this means the error in slope at a 95% confidence level and a correlation coefficient were obtained for each plot (Table I).

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Chemiluminescence and Energy Transfer in Systems of Electrogenerated Aromatic Anions and Benzoyl Peroxide

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Abstract: Studies of energy transfer for mixed systems of every binary combination of anthracene, fluoranthene, 9,10-diphenylanthracene (9,10-DPA), rubrene, and coronene, in which anions are generated in the presence of benzoyl peroxide (BPO), are explained in terms of homogeneous generation of triplet molecules which subsequently form cations through quenching interaction with BPO, this step then being followed by mixed electron transfer reactions which lead to a predominant anion and cation (in terms of concentration) which may undergo anion–cation annihilation. For "energy-sufficient" systems this annihilation step can lead to the formation of excited singlet molecules, while, for "energy-deficient" systems, triplet–triplet annihilation is the essential path through which excited singlet molecules are formed. In the mixed system coronene–9,10-DPA, we find that unlike all mixed systems reported in the literature, the luminescence observed is from the species with the higher singlet level (i.e., 9,10-DPA) and is rationalized in line with a mechanism we propose. In the nine other binary mixtures we have examined the emitting species is also in line with the prediction we make from our mechanism. Ecl from unmixed systems of aromatic hydrocarbon as well as heteroaromatics have also been studied. We have found quite generally that one does not have to invoke the direct generation of singlet molecules, as a result of homogeneous electron transfer reaction between an electrogenerated anion and the bulk oxidant (e.g., either BPO or its decomposition product, benzoate radical (Ph-CO$_2\cdot$)), in order to rationalize excited singlet formation.

I. Introduction

In a recent preliminary publication,[2a] hereinafter referred to as part I, we discussed chemiluminescence and its mechanism for systems consisting of electrogenerated aromatic hydrocarbon anions and benzoyl peroxide dissolved in aprotic solvents. Our mechanism differed from that of Siegel and Mark,[2b] who proposed for similar systems of electrogenerated aromatic hydrocarbon anions with either 1,2-dibromo-1,2-diphenylethane (DPEBr$_2$) or 9,10-dichloro-

9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) as the bulk oxidant, that even when anion–cation annihilation lacked the exothermicity to form the excited singlet state directly (i.e., energy-deficient system), the excited singlet state is directly populated through a secondary path involving a strong oxidizing agent generated by a homogeneous electron-transfer reaction in situ involving the bulk oxidant. We felt[2a] that a triplet intermediate was involved in the mechanistic scheme for this type of electrogenerated chemiluminescence (ecl) since its presence would obviate the need for postulating the unlikely homogeneous formation of a strong oxidizing agent and maintain a logical consonancy with energy-deficient anion–cation annihilation processes.[3] Siegel and Mark in their mechanism have ruled out triplet formation as subsequently giving rise to excited singlet molecules since extensive energy transfer studies, for mixed systems, showed luminescence from the lowest excited singlet level, irrespective of the relative energies of the triplet states.

We advance, as reported in part I, that for systems in which benzoyl peroxide is the oxidant precursor, it is not necessary to postulate homogeneous generation of an oxidizing agent strong enough to enable direct population of the excited singlet state. Rather it is reasonable that the oxidant would only need to be sufficiently strong to form the triplet state. The observations and calculations we have made are all compatible with the incorporation of triplet formation as a pathway in the overall mechanism.

Once the triplet state is generated, we postulate that it may either undergo triplet–triplet annihilation to form the excited singlet or a parallel step in which the triplet reacts with the oxidant to form cations which may then undergo anion–cation annihilation, thereby providing a second possible pathway for direct formation of excited singlet molecules. A question arises here, as pointed out by Hercules,[4] as to whether Siegel and Mark's observations, as well as our own,[2a] for mixed systems would not equally as well be explained by the conventional triplet–triplet annihilation scheme followed by singlet energy transfer. More specifically, if by some means triplet molecules are formed, triplet transfer might be expected to be followed, for all systems, by the reactions:

$$ {}^3R_i + {}^3R_i \rightarrow {}^1R_i^* + R_i \tag{1} $$

$$ {}^1R_i^* + R_j \rightarrow {}^1R_j^* + R_i \tag{2} $$

where reaction 1 represents triplet–triplet annihilation for the species with the lower triplet state, and process 2 represents singlet energy transfer (long-range singlet–singlet and exchange transfer which can populate the first excited singlet state of the species R_j with the lower first excited singlet state).[5,6] Since in Siegel and Mark's work and part I emission from the species with the lower first excited singlet level was observed, the above conventional scheme would indeed require a fundamental challenge before a mechanism as we proposed in part I can be granted scientific merit. Such a challenge is provided we believe by the observation of Boto and Bard,[7] that magnetic fields up to 7.5 kG have no effect on 9,10-DPA ecl from a system in which $DPACl_2$ is the bulk oxidant. The absence of a magnetic field effect on such a system, which is quite similar to those in which BPO is the bulk oxidant, strongly suggests that singlet formation must be a direct process and reaction 1 does not play a major role in the kinematics of the emission process.[8-11] Since for 9,10-DPA the anion–cation annihilation is energy sufficient for forming the first excited singlet state,[12] such an annihilation seems an ideal candidate for direct singlet formation in the system 9,10-DPA–$DPACl_2$ as well as for other energy sufficient systems. As mentioned above we have suggested that the cations, required for the annihilation interaction, are created by an electron-exchange reaction between triplet molecules and the bulk oxidant. This latter process would not necessarily be expected to be field dependent, thereby invalidating a priori this approach, since electron-transfer reactions are apparently field independent.[8-11]

We summarize our comments in a mechanism (see also part I) that represents what we believe to be the important elementary reactions (eq 3–18) in a scheme for the production of excited singlet molecules in systems of electrogenerated aromatic anions with benzoyl peroxide (BPO) as the homogeneous oxidizing agent,

Heterogeneous reduction	$R_i + e \rightarrow R_i^-$ $BPO + ne \rightarrow$ products	(3) (4)
Oxidation of anion	$R_i^- + BPO \rightarrow R_i + BPO^-$	(5)
Dissociation	$BPO^- \rightarrow Ph\text{-}CO_2^- + Ph\text{-}CO_2\cdot$	(6)
Triplet formation	$R_i^- + Ph\text{-}CO_2\cdot \rightarrow {}^3R_i^* + Ph\text{-}CO_2^-$	(7)
Triplet transfer	${}^3R_i^* + R_j \rightleftarrows {}^3R_j^* + R_i \quad (i \neq j)$	(8)
Impurity quenching	${}^3R_i^* + Q \rightarrow R_i + Q'$	(9)
Triplet–triplet annihilation (TTA)	${}^3R_i^* + {}^3R_i^* \rightarrow {}^1R_i^* + R_i$	(10)
Triplet quenching to form cation	${}^3R_i^* + BPO \rightarrow R_i^+ + BPO^-$ ${}^3R_i^* + Ph\text{-}CO_2\cdot \rightarrow R_i^+ + Ph\text{-}CO_2^-$	(11) (12)
Mixed electron transfer	$R_i^- + R_j \rightleftarrows R_j^- + R_i \quad (i \neq j)$ $R_i^+ + R_j \rightleftarrows R_j^+ + R_i \quad (i \neq j)$	(13) (14)
Anion–cation annihilation	$R_i^- + R_i^+ \rightarrow {}^1R_i^* ({}^3R_i^*) + R_i$ $R_i^+ + R_j^- \rightarrow {}^1R_{i,j}^* ({}^3R_{i,j}^*) + R_{i,j} \quad (i \neq j)$	(15) (16)
Singlet energy transfer	${}^1R_i^* + R_j \rightleftarrows {}^1R_j^* + R_i$	(17)
Fluorescence	${}^1R_i^* \rightarrow R_i + h\nu$	(18)

where i and j allow for the case of a mixed system. Only key points will be pointed out here concerning this mechanism. For example, it is found that the moderate value 0.8 V vs. SCE for the oxidation potential of the benzoate ion (i.e., $Ph\text{-}CO_2^- \rightarrow Ph\text{-}CO_2\cdot + e$), as discussed in part I, gives an exothermicity for forming ground-state products, greater than the energy required to reach the triplet state of the hydrocarbons studied, indicating that reaction 7 is possible. Reaction 11 is a fundamental step in our mechanism and is in parallel to reaction 8, triplet transfer, and reaction 10, triplet–triplet annihilation, such that reactions 10 and 11 are branch points in the mechanistic scheme. Calculations for the enthalpy changes of reactions 7 and 11 are given in the body of the paper and suggest the thermodynamic feasibility for the processes indicated. The i,j subscript in reaction 16, when subscripting an excited singlet molecule, emphasizes that in an energy sufficient, mixed annihilation process the molecule with the lowest first excited singlet state, from a purely thermodynamic argument, will be the one excited, while i,j in reaction 16, when subscripting a molecule designated as being in a triplet state, suggest that either of the molecules may be formed in their respective triplet state.

Table I. Electrochemical and Spectroscopic Data

			V vs. SCE					
Chemical	E_s, eV[a]	E_t, eV[a]	$E_p(R^+/R)$[b]	$-E(R/R^-)$[b]	$-\Delta H$, eV[c]	E_{ex}, eV[d]	ΔE^*, eV[e]	λ_{max}, nm
Azulene	1.76	1.04	0.91	1.60	2.30	1.26	−0.57	*x*
Rubrene	2.39	1.20	0.82[h]	1.41	2.11	0.91	−0.32	575
Perylene	2.85	1.56	0.85	1.67	2.37	0.81	0.01	473
Anthracene	3.28	1.82	1.20	1.92	2.62	0.80	−0.08	450
Pyrene	3.33	2.08	1.36	2.09	2.79	0.71	0.02	*y*
9,10-Diphenylanthracene	3.0[w]	1.81	1.20[i]	1.84[i]	2.54	0.73	0.11	437
9,10-Dimethylanthracene	3.10	1.80	0.87[j]	1.82[k]	2.52	0.72	0.23	*y*
Thianthrene	2.86[f]	2.60[f]	1.22[l]	2.54[l]	3.24	0.64	0.68	*z*, *aa*
Coronene	2.95	2.37	1.23	2.04	2.74	0.37	0.44	472
Acridine	3.19	1.96		1.62[n]	2.32	0.36		450
Carbazole		3.04[g]	1.16	2.68[o]	3.38	0.34	1.18	*y*
Decacyclene	2.64	2.00		1.49[m,p]	2.19	0.19		514
Fluoranthene	3.0[w]	2.29	1.48	1.74	2.44	0.15	0.11	480
Benzophenone	3.27	3.01		1.72	2.42	−0.59		*aa*
Picene	3.30	2.49	1.33[m,j]				0.46	410
Acenaphthylene	2.9		1.53	1.65[m,p]	2.35			*bb*
Phenylcarbazole			1.21[q]					370
Thioxanthrene	3.62[r]		1.33[q,s]					*aa*
9-Fluorenone				1.3[t]				*aa*
Fluorescein		2.21[u]						*y*
2,2′-Bipyridine			2.19[i]					*y*
9,10-Dichloroanthracene		1.37[v]						432

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Lastly, as Hercules[4] has communicated, whenever excited singlet molecules of one molecular species are near unexcited ground-state molecules of another species, regardless of how formed, long-range singlet-singlet and exchange transfer of singlet energy have to be considered in any discussion of which species might emit fluorescence [reaction 17]. Typically, in long-range singlet-singlet and exchange transfer both species are found to emit[5,6] unless the relative lifetimes of the species and concentrations are such that forward and back transfer, as indicated in reaction 17, lead to essentially one pure emission.[17]

In part I the only binary mixtures studied were anthracene-fluoranthene and rubrene-9,10-DPA. In this paper we test our mechanism further and report on ecl from mixed systems consisting of all binary combinations of anthracene, fluoranthene, coronene, 9,10-DPA, and rubrene. Also a series of aromatic and heteroaromatic molecules have been examined for ecl from solutions containing BPO. On the basis of the spectroscopic and electrochemical data, and the results of the energy transfer studies, we discuss the compatibility of our mechanistic scheme and experimental observations.

II. Experimental Section

All chemicals were used as received from either the Aldrich Chemical or Eastman Organic Chemicals Co. The solvent, *N,N*-dimethylformamide (DMF), was Matheson Coleman and Bell (MCB) spectroquality solvent and was also used as received. Lengthy and arduous purification procedures were omitted for these experiments because the positions and relative intensities of emission features are in line with those found by others when ecl was observed from similar systems under strenuous purification.

Solutions of benzoyl peroxide and hydrocarbon(s) were prepared at concentrations of ca. 1 mM for each compound in DMF with tetraethylammonium perchlorate (TEAP) at 0.1 M, used as supporting electrolyte. Solutions were electrolyzed in a commercial cell (EA-880 of Metrohm Division, Brinkman Instruments) with a rectangular Pt sheet working electrode (0.7 cm × 0.9 cm), a saturated calomel reference electrode (SCE) (which was separated from the main solution by a salt bridge filled with electrolyte solution (tetraethylammonium perchlorate (TEAP) dissolved in DMF) terminated by a sintered glass frit, and with an isolated counter electrode (Pt wire) separated from the solution by a sintered glass frit. The working electrode potential was controlled with a Wenking 68FR 0.5 potentiostat. All solutions were deaerated with a vigorous stream of prepurified grade argon. During the generation of the ecl, the inert gas was continually and vigorously passed through the solution. This rather imprecise hydrodynamic control is believed to limit the concentration gradients produced by electrolysis to a thin Nernst boundary layer at the surface of the electrode; if the bubbling was stopped, the luminescence intensity decreased in line with what is expected from such a stirring effect.[2a]

The electrolysis cell was positioned at the entrance slit of a SPEX 1704 scanning monochromator, while on the exit slit housing a EMI 9558QB photomultiplier tube, cooled to −25 °C, was used for detection of radiation.

The ecl was only generated when the applied potential between the Pt working electrode and the SCE was sufficiently negative to produce the radical anions of the individual hydrocarbons.

III. Results and Discussion

A. Compendium of Chemiluminescences. We have examined a number of aromatic hydrocarbons and heteroaromatics for chemiluminescence in a system in which the anion is generated in the presence of BPO as a homogeneous oxidant with DMF as the solvent and ca. 0.1 M TEAP as the electrolyte. We have found ecl in such systems to be a quite general phenomenon. In Table I the compounds examined are listed with the last column indicating the peak wavelength of the luminescence. The absence of luminescence, where it occurs, can be explained on photochemical grounds.

The electrochemical and spectroscopic data for the mole-

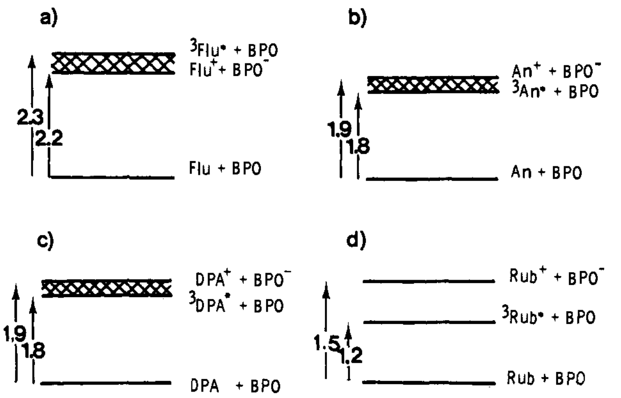

Figure 1. Relative enthalpies of reaction for forming cations from triplet molecules.

cules studied are presented in columns 2 through 5 of Table I and the enthalpies of reaction ($-\Delta H$) for the electron transfer between the indicated species and Ph-CO$_2$· [reaction 7] are given in column 6. The latter quantity is calculated using the relationship,

$$-\Delta H = E_p(\text{Ph-CO}_2\cdot/\text{Ph-CO}_2^-) - E_p(\text{R}/\text{R}^-) - 0.1 \tag{19}$$

where the numerical term of magnitude 0.1 is an entropy correction and the value 0.8 V vs. SCE is used for E_p(Ph-CO$_2$·/Ph-CO$_2^-$) as mentioned earlier. We see that, as a general rule, $-\Delta H$ is greater than E_t, the lowest triplet energy of the emitter species. The excess enthalpy $E_{ex} = -(\Delta H + E_t)$ is given in column 7 and for each species where the calculation is possible, the value E_{ex} is positive with the sole exception of benzophenone. Thus the formation of excited triplets is a perfectly reasonable possibility on thermodynamic and electrochemical grounds.

Grellmann et al.[13] have shown that a negative reaction enthalpy for reaction 11 favors formation of cations. Determination of the enthalpy change for reaction 11 can be made using the triplet energy of R$_i$ and calculating the enthalpy for the reaction,

$$\text{R}_i + \text{BPO} \rightarrow \text{R}_i^+ + \text{BPO}^- \tag{20}$$

with, as pointed out in part I, the value -0.8 V for the reduction potential of BPO/BPO$^-$. Figure 1 is a pictorial representation of the relative enthalpies of forming the cations from R$_i$ and ^{3}R$_i$* for four aromatic hydrocarbons. It can be seen that ΔH for reaction 11 is essentially zero for fluoranthene, anthracene, and 9,10-DPA since an error of a couple-of-tenths of an electron volt is easily rationalized in terms of the reduction potential of BPO (e.g., -0.7 V instead of -0.8 V), inaccuracy in the triplet energy, etc. The important points here are that in all likelihood triplet fluoranthene molecules can form cations through an electron-exchange reaction with BPO, while triplet anthracene and 9,10-DPA probably can, though possibly less efficiently, and last, the large positive enthalpy change for forming rubrene cations from triplet molecules, as shown in Figure 1d, in all likelihood means that the process is very inefficient.

In column 8 of Table I we give the reaction enthalpy ΔE^* for forming cations as a result of electron-transfer reaction between triplet molecules and BPO (reaction 11). This latter quantity, ΔE^*, is calculated using the following relationship

$$\Delta E^* = E_t + E_p(\text{BPO}/\text{BPO}^-) - E_p(\text{R}^+/\text{R}) + 0.1 \tag{21}$$

where E_p(R$^+$/R) is given in column 4 of Table I, E_t is the energy of the triplet state given in column 3, E_p(BPO/BPO$^-$) is the peak reduction potential for BPO + e → BPO$^-$ (~−0.8 V), and the numerical term is the entropy correction.[3,14] In every case except azulene, rubrene, and anthracene, cation formation is favored.

Table II. Fluorescence from Binary Mixed Systems[a]

	R	C	D	F
A	R	C	D	F
F	R	C	D	
D	R	D		
C	R			

[a] A = anthracene, C = coronene, D = 9,10-DPA, F = fluoranthene, R = rubrene.

As pointed out earlier when the enthalpy change for forming ground state products in the anion-cation annihilation process is greater than E_s, the process is said to be energy sufficient. Thus if the values in column 5 of Table I are subtracted from the corresponding values in column 4, with 0.1 subtracted as the entropy correction term, and the resultant is greater than the value given in column 1, the process is said to be energy sufficient. Several emitter species have annihilations which have this nature[12] and we note that of the five hydrocarbons used in our study of mixed binary systems, coronene, fluoranthene, and 9,10-DPA are energy sufficient, while anthracene and rubrene are energy deficient. We expect for unmixed energy-sufficient systems that excited singlet molecules are formed principally through reaction 15, since Bard[7] has shown that triplet-triplet annihilation does not play a predominant role in the evolution of ecl from a typically energy-sufficient system, while we expect that energy-deficient systems proceed through reaction 10, the TTA reaction, or possibly through an energy-sufficient mixed anion-cation annihilation reaction. Cases in which ecl is not observed are explained under the designated greek letter in the last column of the table. The lack of fluorescence in the heterocyclics is rationalized by the preeminence of nonradiative processes in such molecules.[15]

B. Ecl from Binary Mixed Systems. In part I, binary mixed systems of anthracene-fluoranthene and rubrene-9,10-DPA gave ecl from the species with the lower first excited singlet state independent of whether one or both aromatic hydrocarbon anions was electrogenerated. We have expanded such studies to include all binary combinations of anthracene, fluoranthene, 9,10-DPA, rubrene, and coronene with the aim of ascertaining whether our mechanism rationalizes all observed ecl's. Figure 2 shows the individual ecl's from each of these aromatic hydrocarbons, while Table II lists the ecl's for the binary mixtures. All aromatic hydrocarbons were ca. 1 mM in DMF with the supporting electrolyte (TEAP) at ca. 0.1 M and BPO at ca. 1 mM.

Mixtures Involving Rubrene. All mixed systems involving rubrene should have rubrene anions and possibly cations as the predominant ions in solution since rubrene has the lowest oxidation and reduction potentials (see reaction 13 and 14) and/or rubrene triplet molecules since rubrene has the lowest triplet of the five hydrocarbons; any other triplets formed through reaction 7 would transfer their energy to rubrene as shown by reaction 8. The anion-cation annihilation is energy deficient, meaning that for all mixtures, rubrene should undergo TTA, forming the first excited singlet state. Further, since rubrene has the lowest first excited singlet state of the five hydrocarbons, and because equimillimolar solution were used, singlet energy transfer, reaction 17, also favors formation of rubrene singlet molecules. Thus, rubrene should be the emitting species, and as shown in Table II, indeed, this is the case.

Mixtures of Coronene with Anthracene, Fluoranthene, and DPA. In the coronene-anthracene mixture, the emit-

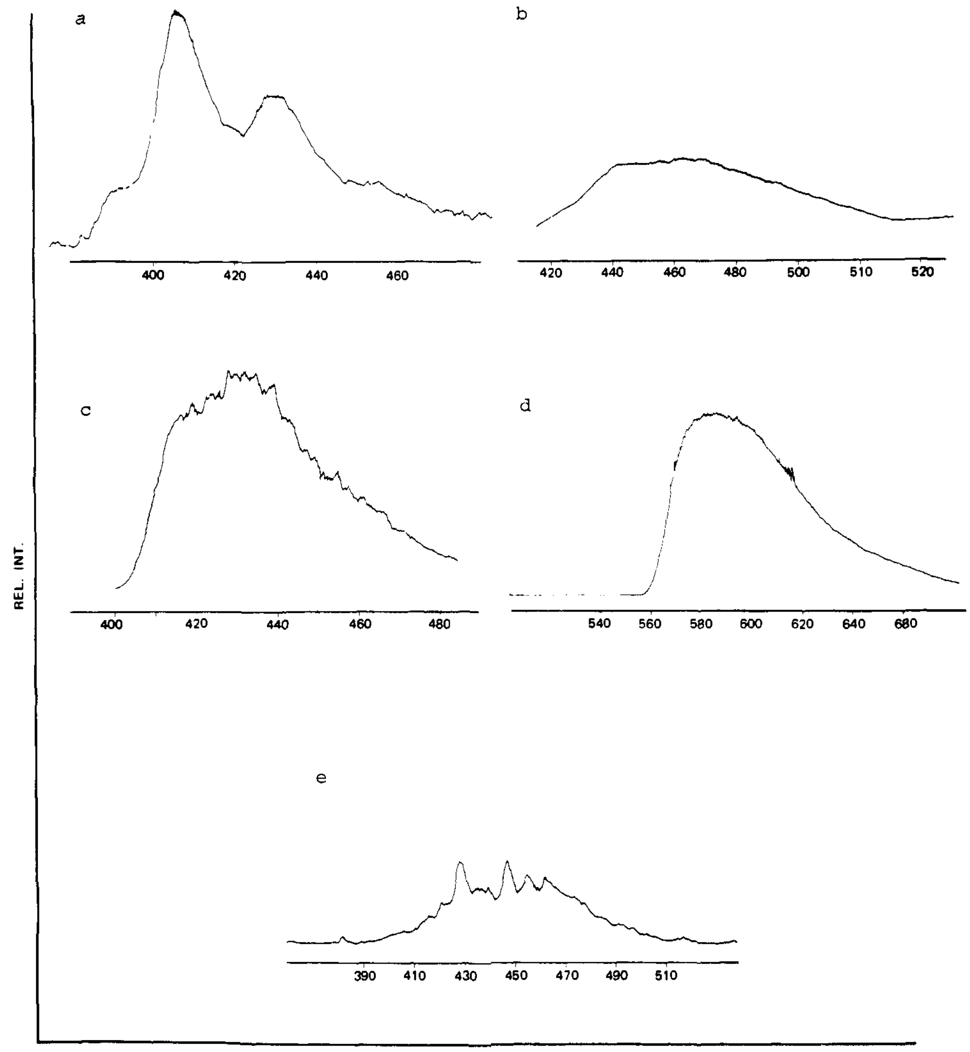

Figure 2. Ecl from electrochemical systems in which anions are generated in the presence of a homogeneous bulk oxidant: (a) anthracene ecl, (b) fluoranthene ecl, (c) 9,10-DPA ecl, (d) rubrene ecl, and (e) coronene ecl.

ting species is found to be coronene. This is rationalized by noting that the ΔE^* values for the two hydrocarbons (Table I, column 8) suggest production, through reaction 11, of cations of coronene and possibly anthracene. However, the oxidation potentials of anthracene (1.20 V vs. SCE) and coronene (1.23 V vs. SCE) are such that slightly more anthracene cations than coronene cations are formed. In addition, the reduction potentials of anthracene of -1.92 V vs. SCE and coronene of -2.0 V vs. SCE lead to anthracene anions as the predominant anionic species. The anthracene anion-cation annihilation is energy deficient; however, the mixed annihilation between the lower concentration of coronene cations and anthracene anions is energy sufficient for the formation of the lowest first excited singlet of coronene. This mixed annihilation excitation step, if fast, can be expected to lead to a bypass of triplet transfer (TT) and subsequent TTA. Since coronene has the lower first excited singlet state, reaction 17 would not militate against first excited singlet molecules of coronene and excited coronene should exist. We believe this is the case and the reason coronene ecl is observed.

In the coronene-fluoranthene mixed system, data in Table I show that reactions 11 and 14 would lead to coronene cations being the predominant cation present in solution, while reaction 13 would lead to fluoranthene as the predominant anionic species. With mixed annihilation being energy sufficient and with coronene having the lower singlet (by 0.09 eV), we would predict it to be the emitting species, since again reaction 17 would play no mediating role, and indeed this is what is observed.

In the coronene-DPA system, we found, that unlike all mixed systems reported in the literature, emission is from the species with the higher singlet level (i.e., 9,10-DPA). This is easily rationalized in terms of our mechanistic scheme since from the oxidation and reduction potentials of coronene (1.23 and -2.04 V vs. SCE, respectively) and DPA (1.19 and -1.84 V vs. SCE, respectively) we predict the predominant anion and cation to be those of the DPA molecule and since the annihilation is energy sufficient, DPA excited singlet molecules should be formed. In general, however, reaction 17 in such a case would lead to some ecl from the species with the lower singlet state. But since coronene has a long fluorescence lifetime,[16] back-transfer[17] would lead to the predominance of 9,10-DPA luminescence. We, in fact, with our sensitive detection system (see for example, ref 18, could not pick out any perturbation in the resultant spectrum that might be attributable to coronene ecl.

Mixtures of DPA with Anthracene and Fluoranthene. In the case of the DPA-anthracene mixture, the data in Table I indicated that DPA cations will be the predominant cationic species and both anthracene and DPA anions will exist in solution, since their reduction potentials are nearly equal. Either energy sufficient DPA anion-cation annihilation or mixed energy sufficient DPA cation-anthracene anion annihilation is feasible. In either case, however, we expect DPA ecl since it has the lower first excited singlet state.

The experimental observation is emission from DPA.

In the DPA-fluoranthene mixture, cation formation via reaction 11 is feasible for both species. The redox potentials are such that DPA cation and fluoranthene anion are the predominant ionic species; however, the mixed annihilation is energy deficient. Thus, it would seem that triplet states are involved, and since DPA has the lower triplet level, TT should occur followed by TTA yielding first excited singlet DPA molecules. Table I shows that the lowest excited singlet states of DPA and fluoranthene are essentially equal, while the fluorescence lifetimes as given by ref 16 are of similar magnitude. Thus here we might expect ecl from fluoranthene to contribute to the overall luminescence; however, the observed ecl appears to be due solely to DPA.

Mixture of Fluoranthene and Anthracene. For the mixed system anthracene-fluoranthene, regardless of which anion is electrogenerated, we see from the reduction potentials listed in Table I that fluoranthene anion would be the predominant anion as a result of the rapid-mixed electron-transfer process described in reaction 13. Further, reaction 14 favors anthracene cation formation, R_j^+, since the oxidation potential of fluoranthene is greater than that of anthracene. It thus seems reasonable to expect, using the above mechanistic scheme, that the predominant anion, which should be the fluoranthene anion, and the predominant cation, which should be the anthracene cation, would undergo a mixed anion-cation annihilation, reaction 16, to form excited fluoranthene singlet molecules, since it has the lower singlet level, which in turn should fluoresce. This, of course, is what is observed.

We conclude this section by restating some of our peripheral conclusions and comments in part I. We stated there that the apparent contradiction between results of Freed and Faulkner[14] and Siegel and Mark[2b] could be explained by way of reaction 11. Freed and Faulkner found that addition of anthracene or pyrene to the fluoranthene system yielded fluorescence characteristic of the added molecules (due to triplet transfer, since both anthracene and pyrene have lower lowest triplet states than fluoranthene, followed by TTA giving the fluorescences), while Siegel and Mark found that anthracene and pyrene catalyze fluoranthene luminescence. We believe that reaction 11 dominates in the Siegel and Mark study since 1,2-dibromo-1,2-diphenylethane ($DPEBr_2$) is at high relative concentration. In addition, the reduction potentials of both anthracene and pyrene are greater than that of fluoranthene, favoring mixed electron-transfer formation of the fluoranthene anion. These two circumstances along with the fact that anion-cation annihilation, both unmixed and mixed, would populate the fluoranthene first excited singlet which is lower than those of anthracene or pyrene (see Table I), and self anion-cation annihilation for fluoranthene is energy sufficient, means ecl from fluoranthene is to be expected. The above is not the case for the Freed and Faulkner study in which 10-methylphenothiazine radical cation and the fluoranthene anion are a mixed, energy-deficient system. Since the 10-methylphenothiazine radical cation was sequentially generated in low concentration, reaction 11 would be slow and there is no short circuit of TTA [reaction 10]. One expects and finds under these circumstances a delayed fluorescence from the species with the lowest triplet state.

IV. Conclusion

Even though these studies are in line with predictions from our mechanistic scheme, they, of course, are by no means conclusive in their inference. Two additional studies which we are undertaking are magnetic field effects on ecl intensity and current vs. time and intensity vs. time dependence for ecl systems. These studies should provide the kind of information which could directly substantiate our mechanistic conclusions.

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