

Table VII. Definition of the Vector d and of the Integrals $I(d)$ and S for the Various Cases Encountered in the Evaluation of the Integrals $I_{\sigma^{*j*}}(i)$.

Integral	d	$I(d)$	S
$\langle \phi_i h_i \phi_i \rangle$ $i \neq 1$	Joins atoms 1 and i	$I_0(d)$	1
$\langle \phi_i h_i \phi_i \rangle$	Joins atoms 1 and i	$I_1(d)$	1
$\langle \phi_i h_i \phi_j \rangle$ $i, j \neq 1$	Joins atom 1 to the center of the transition density $\phi_i \phi_j$ (midway point between i and j)	$I_0(d)$	$I_2(d')$, d' being the distance between atoms i and j

basic integrals I_i ($i = 0, 1, 2$) have been tabulated for various distances d and are independent of the particular benzene problem.^{16b}

Table VIII. Integrals I_1^R and I_2^U for the Nine Transition Densities $\rho(i)$ (Values are Given in eV/Å)

	T_1	T_2	T_3
I_1^R	-1.3681	0.7867	0.4912
I_2^U	2.8290	3.5924	0.1171
	S_1	S_2	S_3
I_1^R	0.1396	1.6629	0.3640
I_2^U	3.8926	2.5394	0.1033
	V_1	V_2	V_3
I_1^R	-0.9490	0	0.1060
I_2^U	0	0.7908	0

The integrals $I_{\sigma^{*j*}}(i)$ for the nine transition densities $\rho(i)$ are summarized in Table VIII.

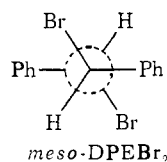
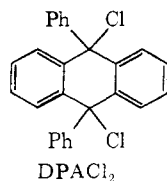
Mechanism of the Chemiluminescent Reaction of Certain Alkyl Halides with Electrogenerated Aromatic Hydrocarbon Radical Anions^{1,2}

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Abstract: The electroreduction of a variety of polycyclic, aromatic hydrocarbons (R) in the presence of either 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) or 1,2-dibromo-1,2-diphenylethane (DPEBr₂) was found to result in intense luminescence. In each instance the spectrum of this electrochemiluminescence (ecl) was virtually identical with the singlet emission spectrum of the aromatic hydrocarbon. In general, the efficiency of this luminescence was found to be greater than that of the normal radical anion-radical cation ecl of the same hydrocarbon. It was also found that when two or more aromatic hydrocarbons were present in the same solution only the emission spectrum of the lower singlet energy species could be observed regardless of which aromatic radical anion was being generated at the electrode. Experiments with mixed systems containing fluoranthene, which did not exhibit ecl by itself with DPEBr₂, and several aromatic hydrocarbons which have lower triplet energies than fluoranthene, resulted in only fluoranthene singlet emission. These experiments indicated the excited singlet is generated directly upon electron transfer from R^{•-} rather than through a triplet-triplet annihilation reaction. The following general mechanism was found consistent with the observed experimental results: R + e ⇌ R^{•-} (1), R^{•-} + AX₂ ⇌ R + AX₂^{•-} (2), AX₂^{•-} → AX[•] + X⁻ (3), R^{•-} + AX[•] ⇌ ¹R* + AX⁻ (4), R + AX[•] ⇌ R^{•+} + AX⁻ (5), AX⁻ → A + X⁻ (6), R^{•-} + R^{•+} → ¹R* + R (7), ¹R* → R + hν (8). (AX₂ represents the alkyl halide.) The efficiency of the DPACl₂ systems and the behavior of the fluoranthene mixed systems indicate that the excited singlet can arise by both reaction 4 and reactions 5 plus 7.

Recently, preliminary observations concerning the electrochemiluminescence, ecl, obtained upon the reaction of electrogenerated aromatic hydrocarbon radical anions, R^{•-}, of a variety of aromatic hydrocarbons (in various nonaqueous solvents) with either 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene (DPACl₂) or 1,2-dibromo-1,2-diphenylethane (DPEBr₂)



have been reported.² For the DPACl₂ system it was found that the intensity of the observed emission of the aromatic hydrocarbon, DPA, was unexpectedly about two orders of magnitude greater than that observed for the more commonly reported ecl obtained upon the annihilation of the electrogenerated radical anions and radical cations of 9,10-diphenylanthracene (DPA).³ Also, it was reported that for solutions con-

(3) (a) The intensity of the 9,10-diphenylanthracene (DPA) singlet emission obtained for the reaction of DPACl₂ with electrogenerated DPA^{•-} was compared with DPA^{•-}/DPA^{•+} annihilation ecl using the same solvent-supporting electrolyte system. Square wave voltages (-0.1 to -2.0 V for the DPACl₂ case, +1.4 to -2.0 V for the DPA case) of the same frequency were employed and integrated light intensities during negative pulses were compared. (b) For detailed discussion of radical cation-radical anion annihilation ecl, see A. J. Bard, K. S. V. Santhanam, S. A. Cruser, and L. R. Faulkner in "Fluorescence," G. G. Guibault, Ed., Marcel Dekker, New York, N. Y., 1967, pp 627-651; D. M. Hercules in "Physical Methods of Organic Chemistry," 4th ed., Part II, A. Weissberger and B. Rossiter, Ed., Academic Press, New York, N. Y., 1971; A. Zweig, *Advan. Photochem.*, 6, 425 (1968).

(1) This research was supported by a grant from the National Science Foundation, No. GP-27216.

(2) A preliminary communication concerning this phenomenon has been published: T. M. Siegel and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, 93, 6281 (1971).

taining two or more aromatic hydrocarbons in approximately equal concentrations, the observed emission always corresponded to the fluorescence of the most easily reduced (and lowest singlet energy) hydrocarbon of the mixture.⁴ This was true regardless of whether radical anions of only one aromatic component or both were being generated at the electrode. This apparent efficient energy trapping phenomenon could not be explained on the basis of collisional exchange of excited singlet energy. Long-range resonant transfer (Förster's transfer)⁵ of singlet energy was also ruled out by choosing mixed aromatic systems which had virtually no adsorption-emission overlap of the two species and gave no evidence of photochemically induced Förster's transfer.

As the lifetimes of the triplet excited states of these aromatic hydrocarbons are long enough to allow efficient energy trapping by collisionally controlled energy transfer,⁶ the observed energy trapping suggested that the homogeneous reaction of electrogenerated $R\cdot^-$ with the alkyl halides involved the generation of the excited triplet state of the aromatic, followed by triplet-triplet annihilation, TTA, to produce the singlet.^{6,7} Such a TTA scheme has previously been suggested by other workers^{8b,8} to account for the singlet emission observed during ecl reactions in which the energy from the radical ion annihilation process is insufficient to promote R directly to the excited singlet state.

Recent studies have been carried out by several investigators which demonstrated the existence of the excited triplet species taking part in the reaction mechanism of these so-called "energy-deficient" ecl reactions. Faulkner and Bard⁹ have demonstrated a pronounced effect of a magnetic field on the emission intensity of the "energy-deficient" systems. This effect is not present when sufficient energy is available to populate the singlet state directly upon electron transfer. Weller and Zachariasse¹⁰ have shown, for a series of energy-deficient annihilation reactions, that it is necessary for the triplet energy of the aromatic hydrocarbon to be at least equal to one-half its singlet energy in order for the reaction to result in light emission. Freed and Faulkner,¹¹ in addition to confirming Weller's results for several different reaction systems, have also obtained other evidence of the role of the triplet state in energy-deficient ecl. In studies of the reaction of the electrogenerated fluoranthene radical anion and the 10-methylphenothiazine (10-MP) radical cation, which is an energy-deficient system resulting in fluoranthene

singlet emission, it was found that the addition of an aromatic hydrocarbon with a triplet energy level lower than that of fluoranthene resulted in emission only of the singlet of the added hydrocarbon. Such a result is an electrochemical analog of photochemically generated sensitized delayed fluorescence.^{7a}

Thus, a detailed study of the radical anion-alkyl halide ecl reaction mechanism was undertaken, using an approach similar to that of Freed and Faulkner,¹¹ to distinguish between direct singlet formation or TTA. It was found that the experimental results, as reported below, were essentially the opposite of those of Freed and Faulkner.¹¹ On the basis of these experiments a triplet mechanism (or any resemblance to an energy-deficient ecl mechanism) must be ruled out in this case. The observed results are consistent with a mechanism involving the direct population of the excited singlet energy state of the aromatic hydrocarbon. Thus, a strong oxidizing species must be formed during or as a result of the reaction of $R\cdot^-$ with the alkyl halide. Although no direct observation of an aromatic radical cation or other strong oxidant has been obtained and the generation of such a strong oxidizing agent in a solution undergoing electroreduction is contradictory at first thought, no other reactant and/or reaction sequence can provide the necessary energy to produce the singlet directly nor can explain the "anomalous" energy transfer or trapping process observed, as described and discussed below.

Experimental Section

The DPA, rubrene, coronene, perylene, azulene, pyrene, acenaphthalene, and fluoranthene were obtained from the Aldrich Chemical Co. The 1,2-benzanthracene was obtained from K & K Laboratories and the anthracene, chrysene, and *trans*-stilbene from Eastman Chemical Co. Acenaphthylene was purified by standard procedures. The DPA, rubrene, coronene, perylene, and azulene and the chrysene and *trans*-stilbene, which were scintillation grade, were used without further purification. The pyrene, 1,2-benzanthracene, and anthracene were recrystallized twice from hexane. The fluoranthene was recrystallized twice from hexane and once from ethanol. The DPEBr₂ was prepared according to the procedure of Fieser¹² and recrystallized from methylene chloride. The DPACl₂ was prepared by two separate procedures, those of Bergmann¹³ and Chandross and Sonntag,¹⁴ and identical results were observed using either preparation. The melting points of all compounds employed were essentially the same as those reported in the literature. All chemicals were stored prior to use in a desiccator in the absence of light.

Tetra-*n*-butylammonium perchlorate (TBAP), used as supporting electrolyte in all experiments at a concentration of 0.1 *M*, was obtained from Southwestern Analytical Chemicals. The TBAP was always recrystallized from acetone, dried in a vacuum oven at 75° for a minimum of 4 hr, and stored in a desiccator in the absence of light prior to use.

The *N,N*-dimethylformamide (DMF) was Matheson, Coleman and Bell (MCB) spectroquality solvent. It was purified by storing over anhydrous CuSO₄ for at least 1 week and then distilled on a vacuum line at 10⁻³ Torr. The distilled DMF was then stored under vacuum over 4A molecular sieves and then vacuum distilled as needed. Prior to use the DMF was also subject to several freeze-pump-thaw cycles to remove any remaining dissolved amines. MCB spectroquality dimethyl sulfoxide (DMSO) and acetonitrile (AN) were used directly from the bottle after sitting over 4A molecular sieves for at least 3 days. Tetrahydrofuran (THF) was stored 2 days over KOH, refluxed at least 1 hr with LiAlH₄ under a dry nitrogen atmosphere, and then distilled under

(4) Only when the more difficultly reduced aromatic hydrocarbon was in large excess (10:1 or greater) was mixed fluorescence observed at the reduction potential of this hydrocarbon.²

(5) (a) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964); (b) T. Förster, *Discuss. Faraday Soc.*, No. 27, 7 (1959); (c) E. L. Wehry in "Fluorescence," G. G. Guibault, Ed., Marcel Dekker, New York, N. Y., 1967, pp 114-115; (d) S. A. Cruser and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 267 (1969).

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

(7) (a) C. A. Parker and C. G. Hatchard, *ibid.*, **269**, 574 (1962); (b) C. A. Parker, *Advan. Photochem.*, **2**, 305 (1964).

(8) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **87**, 139 (1965); J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1968); D. L. Maricle, A. Zweig, A. H. Maurer, and J. S. Brinen, *ibid.*, **13**, 1209 (1968).

(9) (a) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209 (1969); (b) *ibid.*, **91**, 6495 (1969); (c) *ibid.*, **91**, 6497 (1969); (d) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *ibid.*, **94**, 691 (1972).

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

(11) (a) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971); (b) R. Bezman and L. R. Faulkner, private communication.

(12) L. S. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1965, p 222.

(13) E. Bergmann and O. B. Bergman, *J. Amer. Chem. Soc.*, **59**, 1439 (1937).

(14) E. A. Chandross and F. I. Sonntag, *ibid.*, **88**, 1089 (1966).

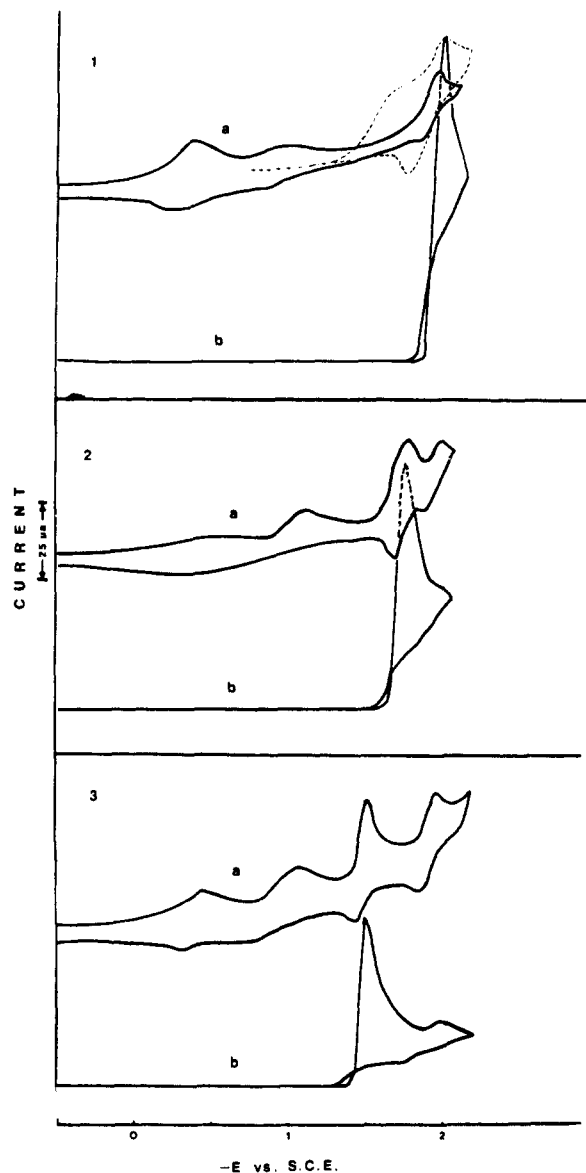


Figure 1. Electrochemical (a) and electrochemiluminescence (b) behavior of DPACl_2 in DMF (0.1 M TBAP supporting electrolyte, sweep rate = 0.5 V per sec): (1) $\sim 0.2 \times 10^{-3}$ M DPACl_2 only (---, THF solvent), (2) $\sim 0.2 \times 10^{-3}$ M DPACl_2 - 0.3×10^{-3} M perylene, and (3) $\sim 0.2 \times 10^{-3}$ M DPACl_2 - 0.3×10^{-3} M rubrene.

nitrogen. Only the middle 70–80% fraction was employed in experiments.

Nitrogen for degassing solutions was purchased from Air Products and Chemicals Corporation and was at least 99.995% pure. The nitrogen stream was passed through a solvent saturator. The DMF saturator also contained anhydrous CuSO_4 .

The reference electrode consisted of a silver wire in an AgNO_3 saturated solution of the solvent in use. This reference solution was then isolated from the cell solution by a salt bridge filled with TBAP saturated solvent. Porous ("thirsty") glass cane was used as frits between the cell solution and the salt bridge and the salt bridge and reference compartments. The frits and the various electrode compartments were held together by heat shrinkable Teflon tubing. The overall dimensions of the reference electrode was about $1/8$ in. in diameter by 4–5 in. in length. Reference electrodes constructed in this manner were found to be stable for several months with only about a 10-mV drift before decomposition limited mass transport through the frit to the point where the electrode could no longer be used.

The cell, potentiostat, and light measuring systems are essentially the same as previously described.¹⁵

(15) M. D. Malbin and H. B. Mark, Jr., *J. Phys. Chem.*, **73**, 2992 (1969).

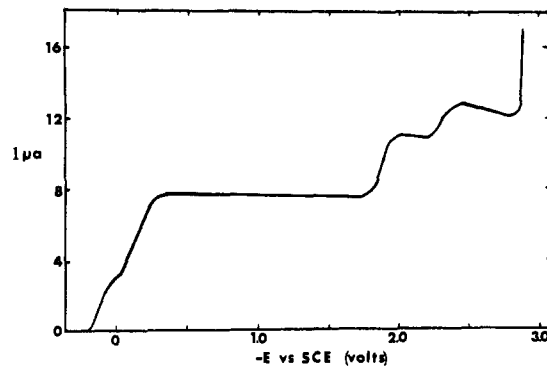


Figure 2. Polarogram in AN (0.1 M TBAP supporting electrolyte) of 0.2×10^{-3} M DPACl_2 .

The reproducibility of the light intensities measured in the ecl experiments was about $\pm 50\%$ for successive samples owing chiefly to the lack of reproducibility of electrode position in the cell. All experiments were run at room temperature, which varied no more than 3° , and no attempt was made to thermostat the cell. Because of the lack of exact control over these experimental parameters no quantitative values of ecl intensities are reported and only relative intensities are noted where there is an obvious difference.

Results and Discussion

A variety of polycyclic, aromatic hydrocarbons were reduced at a stationary platinum electrode in DMF in the presence of either DPACl_2 or DPEBr_2 and the accompanying luminescence, as noted by the response of a photomultiplier tube, was recorded simultaneously with the current voltage curves on an X-Y, Y' recorder. During subsequent reductions, the spectrum of the resultant emission was recorded using a scanning monochromator.¹⁶

Ecl with DPACl_2 . The solid line of Figure 1, curve 1a, represents the cyclic voltammogram of DPACl_2 in DMF. The first two waves, at -0.4 and -0.9 V, correspond to the DPACl_2 decomposition product wave (H^+)² and the DPACl_2 reduction wave, respectively. It can be seen that the luminescence, curve 1b, is concomitant only with a third wave at -1.9 V. The spectrum of this ecl is virtually the same as the DPA fluorescence spectrum in this solvent system. The third reduction wave observed is that of the DPA which was a product of the DPACl_2 reduction itself.¹⁷



The polarogram of the system is shown in Figure 2. The first wave at -0.2 V at the mercury electrode is that of the DPACl_2 reduction ($n_{\text{app}} = 2$) and the subsequent waves at -1.9 and -2.3 V are the first and second one-electron reduction waves of the product DPA. The dashed line of Figure 1 (curve 1a) represents the cyclic voltammogram of DPACl_2 in THF. A very strong solvent effect on the kinetics of the DPACl_2 reduction is evident here as there is a large negative shift of the DPACl_2 reduction wave. There is no significant decomposition of DPACl_2 in the THF and,

(16) When the luminescence was sufficiently intense the spectrum was recorded under steady-state reduction conditions, where the electrode was potentiostated at the aromatic reduction wave. For low level emission systems it was necessary to step the potential at the electrode from rest potential to the limiting portion of the aromatic reduction wave at constant intervals and record the spectrum as the high intensity spikes.

(17) O. R. Brown and J. A. Harrison, *J. Electroanal. Chem.*, **21**, 387 (1969).

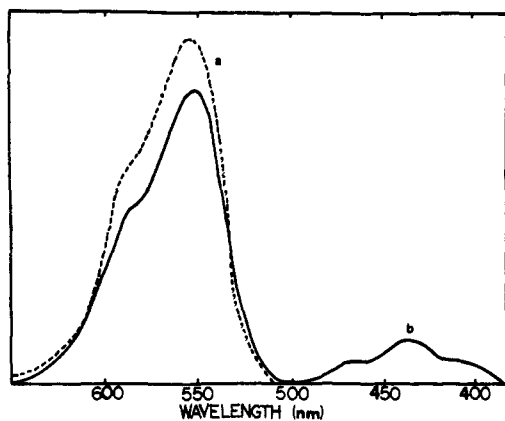
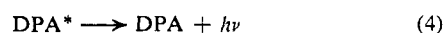
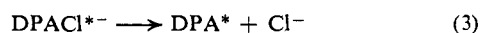


Figure 3. Electrochemiluminescence spectra of $0.5 \times 10^{-3} M$ DPACl₂ and $0.5 \times 10^{-4} M$ rubrene in DMF (0.1 M TBAP) supporting electrolyte. (a) $E = -1.45 V$ vs. sce and (b) $E = -1.85 V$ vs. sce.

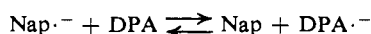
hence, no H⁺ wave. In addition, the relative ecl intensity is much lower in THF indicating that the solvent also plays an important role in the rate of the ecl mechanism.

As no ecl is observed during the direct electrochemical reduction wave of DPACl₂ (or DPEBr₂) regardless of electrode material, it is felt that the ecl observed at the anion radical wave results from a homogeneous redox reaction between R^{•-} diffusing from the electrode surface and unreacted DPACl₂ diffusing toward the electrode from the bulk solution. It further suggests that the reaction path by which DPA is produced on the reduction of DPACl₂ is distinctly different in the heterogeneous reduction and in the homogeneous reduction by the electrogenerated R^{•-}.

Chandross and Sonntag¹⁴ and Rauhut¹⁸ had previously reported that when DPACl₂ is allowed to react with the sodium or potassium salt of DPA or naphthalene in ether, chemiluminescence, cl, is observed which is identical with DPA fluorescence. When the DPA salt is used, DPA is the only organic product of the reaction identified. Chandross and Sonntag proposed the following mechanism for the cl process.



It is not possible to determine if the DPA luminescence observed during reduction by naphthalenide is due to direct electron transfer from the naphthalenide to one of the halo species or if there is a prior electron transfer to DPA.¹⁴



This electron transfer to DPA would be kinetically very fast and, because of the great difference in reduction potentials, the equilibrium would be far to the right.

In an effort to examine the validity of the above mechanism, experiments were carried out with either the rubrene or perylene electrogenerated radical anions as the reducing agent. Both of these hydrocarbons are more easily reduced than DPA.

(18) M. M. Rauhut, American Cyanamid Co., U. S. Patent 3,391,068 (July 2, 1968).

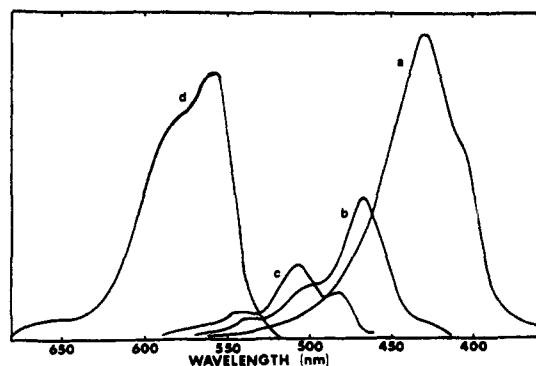


Figure 4. Electrochemiluminescence spectra in THF (0.1 M TBAP supporting electrolyte). Curves a-d are all in the same solution, $E = -1.9 V$ vs. sce. Hydrocarbons were added to the initial DPACl₂ solution singly. Spectra were taken before the next addition: (a) $1.0 \times 10^{-3} M$ DPACl₂, (b) $1.1 \times 10^{-3} M$ perylene, (c) $1.1 \times 10^{-3} M$ tetracene, and (d) $0.5 \times 10^{-3} M$ rubrene.

Figure 1, curves 2a and 3a, represent the cyclic voltammograms, and curves 2b and 3b represent the accompanying ecl for the systems perylene-DPACl₂ and rubrene-DPACl₂ (in equimolar concentrations), respectively, in DMF. In both these systems, the emission, which has intensity maxima accompanying both aromatic reduction waves (those of the added hydrocarbon and the reduction product, DPA), is only that of the added hydrocarbon (either rubrene or perylene) and no DPA emission is observed. It is not until DPACl₂ (and thereby DPA) is in great excess (10:1 or more) that any mixed emission, containing DPA fluorescence is observed (Figure 3). Furthermore, this mixed emission is observed only at the DPA reduction wave. It is evident from these experiments that the Chandross and Sonntag mechanism, leading to direct singlet excitation *via* reaction 3, cannot be correct. If the DPA excited singlet state were to arise from reaction 3, or a combination of reactions 2 and 3, only DPA emission would be expected as there is no evidence of an efficient singlet energy transfer mechanism, either collisional or long range, in operation for these systems.¹⁹ It would still be possible, however, to proceed through a similar mechanism if the initial DPA excited state generated was the triplet. The relatively long life of the triplet state could result in efficient energy transfer on a collisional basis between DPA and perylene or DPA and rubrene. This energy transfer would then be followed by TTA between the lower energy triplet traps resulting in an energy accumulation on one molecule and the promotion of an electron in that molecule to the excited singlet state.

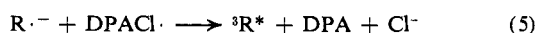
There is the other possibility, however, that the reaction of any R^{•-} with DPACl[•] (step 2) results in direct population of the R (perylene or rubrene here) singlet (or triplet) excited state.

Figure 4 illustrates the efficiency of the energy trapping for a variety of hydrocarbons. Initially, the solution contained only DPACl₂ and, upon reduction at the DPA wave, only DPA fluorescence was obtained (curve a). The other spectra (curves b to d) were taken after sequential addition to the same solution of other

(19) We have not observed any experimental evidence for singlet energy transfer during normal fluorescence excitation. In addition, Cruser and Bard^{2d} did not observe such an effect during mixed ion annihilation ecl reactions.

hydrocarbons with sequentially lower singlet energies and reduction potentials. The electrode was still potentiostated at the DPA reduction wave. It can be seen that there is a complete absence of any higher energy singlet emission in each case. Thus, even in the case where all four radical anions are being generated and reacting with DPACl₂, only rubrene light is observed (curve d). There is also a marked difference in intensities between the various species which cannot be readily explained. It should perhaps be noted that the rubrene emission is more intense than that of DPA. This is significant in light of recent evidence by Bezman and Faulkner^{11b} and under normal ion annihilation ecl conditions DPA is a more efficient system. This will be discussed in more detail later.

It is important to note that Matsui, *et al.*,²⁰ have suggested that the reduction potential of the diphenylmethyl radical in DMF, at a dropping mercury electrode, is 0.67 V positive of the diphenylmethyl chloride reduction potential. The diphenylmethyl chloride system can be considered similar to the DPACl₂ system. If so, the $\Delta E_{1/2}$ between the transfer of a first electron to DPACl₂ and the second electron to the radical, DPACl·, might be of a similar magnitude, and there would be sufficient energy from the radical reduction by R·⁻ to populate the aromatic triplet state of most of the species studied.



This could then be followed by the normal TTA mechanism.

Ecl with DPEBr₂. A more systematic and a broader series of experiments was conducted with DPEBr₂ in an effort to distinguish whether direct singlet or a TTA mechanism produced the observed ecl. Table I lists those aromatics which were reduced in the presence of DPEBr₂ and the relative intensities of the observed emissions.²¹ Again, in every instance the emission observed corresponded to the excited singlet emission of the aromatic hydrocarbon. The oxidation and reduction potentials and the singlet and triplet energies, E^s and E^t , respectively, of these compounds are also listed in Table I. In several cases there is no singlet emission. This cannot be explained on the basis of singlet or triplet energy considerations alone. However, it is possible to account for the behavior of most of these systems by their electrochemical or photochemical properties. It is likely that the chrysenic radical anion, with its high reduction potential which is near solvent background, is chemically unstable, and in addition, it could homogeneously transfer an electron to *trans*-stilbene, which is the DPEBr₂ reduction product. Acenaphthylene is known to dimerize in both the singlet and triplet excited states²³ while the *trans*-stilbene triplet²⁴ and the azulene triplet

(20) Y. Matsui, T. Soga, and Y. Date, *Bull. Chem. Soc. Jap.*, **44**, 513 (1971).

(21) While the emission intensities for the reactions of aromatic radical anions with DPACl₂ are always greater than those for the DPEBr₂ reactions by about a factor of 10, systematic comparisons of relative intensities of the ecl were not made owing to the difficulties encountered because of the DPACl₂ chemical instability.^{13,22}

(22) C. K. Ingold and P. G. Marshall, *J. Chem. Soc.*, 3080 (1926); C. Dufraisse, A. Etienne, and J. Salmon, *Bull. Soc. Chim. Belg.*, **62**, 21 (1953).

(23) E. H. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970).

(24) 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, *ibid.*, **86**, 3197 (1964).

Table I. Electrochemical and Spectroscopic Data

	Red, $-E_{1/2}^a$	Ox, $E_{1/2}^a$	E^s	E^t	Ecl ^k
Chrysenic	2.25	1.35	2.5 ^h	3.4 ^e	NO
<i>trans</i> -Stilbene	2.19	1.51 ^d	2.0 ^f	3.8 ^f	NO
Pyrene	2.09	1.16	2.1 ^h	3.3 ^e	W
Coronene	2.04	1.23	2.4 ^h	2.9	W
1,2-Benzanthracene	2.00	1.18	2.1 ^h	3.2 ^e	W
Anthracene	1.94	1.20	1.8 ^h	3.3 ^e	W
Fluoranthene	1.74	1.45	2.3 ^h	3.0 ^f	NO
DPA	1.84	1.19 ⁱ	1.8 ^f	3.0 ^f	S
Perylene	1.67	0.85	1.6 ^h	2.8 ^e	M
Acenaphthylene	1.65 ^j	1.21		2.9	NO
Azulene	1.10 ^b	0.71	1.4 ^g	1.8	NO
				3.5 ^g	
Tetracene	1.58	0.77	1.3 ^h	2.6 ^e	W
Rubrene	1.41	0.82 ^c	1.2 ⁱ	2.3 ⁱ	S

^a C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970. Except as otherwise noted all potentials in volts *vs. sce*, reductions in *N,N*-dimethylformamide and oxidations in acetonitrile. ^b Hg pool reference. ^c Methylene chloride. ^d Acetic acid. ^e Reference 10. ^f Reference 11. ^g Reference 25. ^h I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971. ⁱ E. A. Chandross and R. E. Visco, *J. Phys. Chem.*, **72**, 378 (1968). ^j G. J. Hoytink, *Recl. Trav. Chim. Pays-Bas*, **74**, 1525 (1955); 96% aqueous dioxane. ^k NO = not observed; W = weak; M = medium; S = strong. ^l R. E. Visco and E. A. Chandross, *J. Amer. Chem. Soc.*, **86**, 5350 (1964). ^m There is considerable variation in the literature concerning the oxidation potential of anthracene [from 1.09 V (see footnote a) to 1.4 V]: M. Peover and R. White, *J. Electroanal. Chem.*, **13**, 93 (1967). We have used +1.2 V in this paper as it is our measured value in DMF and is also the approximate average of the literature values.

and first excited singlet²⁵ decay to their ground states by rapid, nonradiative processes. It would appear reasonable to rule out direct generation of the *trans*-stilbene singlet just on the basis of the high energy involved. The absence of fluoranthene singlet emission cannot be explained readily by either its own chemical and/or photochemical behavior and it would appear that the explanation lies in the ecl mechanism itself.

It is readily apparent that the observation of any singlet emission in these systems rules out the population of an excited triplet state of the *trans*-stilbene product following the electron transfer. The rapid nonradiative decay of the *trans*-stilbene excited triplet states precludes any significant triplet energy transfer mechanism, and there is no efficient singlet energy transfer mechanism that could be operative with all of the aromatic hydrocarbons which exhibit ecl. This further indicates that the Chandross and Sonntag mechanism must be incorrect.

The electrochemical reduction characteristics of DPEBr₂ are similar to those of DPACl₂. The polarogram in DMF, shows a wave at -0.2 V *vs. sce*, with an n_{app} value of 2, corresponding to the DPEBr₂ reduction to *trans*-stilbene



followed by the one-electron reduction wave of stilbene at -2.1 V. In the cyclic voltammogram, at a stationary platinum electrode (Figure 5), the DPEBr₂ reduction wave arises at about -1.1 V followed by the one-electron reduction wave of stilbene to the radical anion.

(25) P. M. Renzepis, *Science*, **169**, 239 (1970).

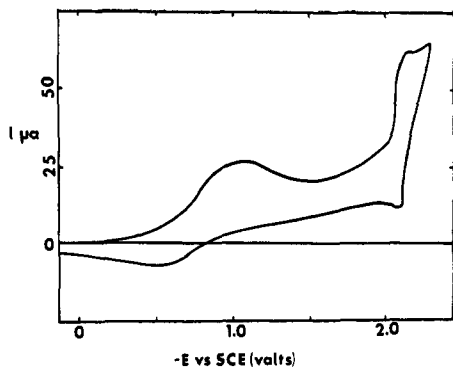


Figure 5. Cyclic voltammogram of $0.5 \times 10^{-3} M$ DPEBr₂ in DMF (0.1 M TBAP supporting electrolyte, sweep rate = 0.5 V/sec).

(It is also possible to observe the second stilbene reduction wave in DMF.)

From Table I, it can be seen that the use of DPEBr₂ increases the number of aromatic hydrocarbons that reduce more easily than the halide reduction product. *trans*-Stilbene also has a higher singlet and triplet energy than DPA. In addition, as the emission from the *trans*-stilbene excited singlet state is of very high energy, there can be no spectral measurement interference. However, the lower ecl intensities of the DPEBr₂ systems, in comparison with the DPACl₂ systems, made it impossible to use THF as a solvent because of the overall lower efficiency or rate of the ecl mechanism which is operative in nonpolar solvents. (It was observed that the relative intensities always decreased as the polarity of the solvent used decreased.)

In order to determine if the same efficient energy trapping, as observed in the DPACl₂ systems, is also operative in the DPEBr₂ systems and, therefore, whether the same ecl mechanism is operative for the two systems, we studied a number of mixtures of aromatic hydrocarbons with DPEBr₂. These mixtures were analogous to the DPACl₂ systems in which the DPACl₂ reduction product, DPA, was present with another aromatic hydrocarbon. In each case there were two aromatic hydrocarbons present in equimolar concentrations with the DPEBr₂ and the electrode was either cycled or stepped to the reduction wave of one of the hydrocarbons. In these mixed DPEBr₂ systems, once again, as with DPACl₂, only emission from the species with the lowest available excited singlet state is observed, although individually each aromatic hydrocarbon displayed its own characteristic fluorescence spectrum. When the concentration of the DPEBr₂ was significantly greater than that of the two aromatic species, it was then possible in some cases to observe mixed emission in which the two components were proportional in relative intensity to the concentrations of the two emitting species (Figure 6).

If one were to assume here that a triplet mechanism were in operation, it might then be possible to explain the lack of fluoranthene emission with DPEBr₂ by triplet quenching due to the presence of *trans*-stilbene. It has previously been observed by Freed and Faulkner¹¹ that *trans*-stilbene is an efficient quencher of the fluoranthene triplet states under ecl conditions, as would be expected considering their respective triplet energies. However, the absence of coronene emission quenching by the *trans*-stilbene under similar conditions is very

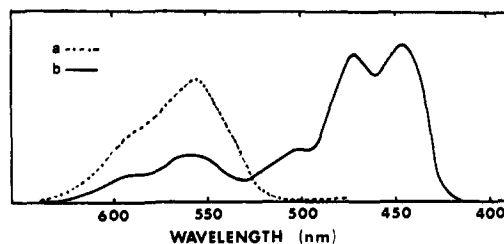
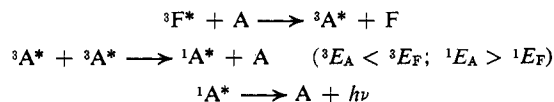


Figure 6. Electrochemiluminescence spectra of $0.1 \times 10^{-3} M$ perylene and $0.2 \times 10^{-4} M$ rubrene with $0.7 \times 10^{-3} M$ DPEBr₂ in DMF (0.1 M TBAP supporting electrolyte). (a) $E = -1.45 V$ vs. sce and (b) $E = -1.70 V$ vs. sce.

difficult to explain by such a mechanism as coronene has an even higher energy triplet state than fluoranthene. Another possible explanation, which is still consistent with a triplet mechanism, is that there is not enough energy available from reaction 5 to promote fluoranthene to its excited triplet state.

However, a contradictory result with respect to a triplet mechanism was obtained when a mixture of fluoranthene, anthracene, and DPEBr₂ in DMF (in equimolar concentrations) was electrolyzed. Both potential sweep and potential step wave forms were employed and surprisingly ecl emission was observed at both the fluoranthene and anthracene waves, which was that of the fluoranthene singlet only. This behavior cannot be explained on the basis of triplet energy transfer and is contrary to previous observations by Freed and Faulkner¹¹ in studying energy-deficient ion annihilation ecl from similar systems. They considered that the fluoranthene triplet excited state was initially populated following an ion annihilation reaction between the fluoranthene anion radical and the 10-methylphenothiazine cation radical. TTA then resulted to yield fluoranthene singlet emission (not enough energy was considered to be available from the ion annihilation to reach the singlet state). They demonstrated the presence of the triplet intermediate by the addition of anthracene which resulted in quantitative energy transfer to anthracene, and consequently, only anthracene singlet emission was observed. This phenomenon, similar to sensitized delayed fluorescence, follows the mechanism



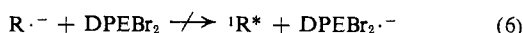
Freed and Faulkner¹¹ observed a similar energy transfer mechanism when pyrene was present rather than anthracene. We found that with the addition of either pyrene or 1,2-benzanthracene to a solution of fluoranthene and DPEBr₂, the results upon reduction of the fluoranthene were the same as when we used anthracene. Only fluoranthene singlet emission was observed. Added *trans*-stilbene, which Freed and Faulkner found to compete²⁶ with anthracene as a fluoranthene triplet energy trap when both were present or to quench¹¹ fluoranthene emission when no anthracene was present, has no observable effect as a neutral molecule in our system. However, upon reduction to the stilbene radical anion, a marked increase in fluoranthene singlet emission intensity was obtained.²⁷

(26) D. J. Freed and L. R. Faulkner, private communication.

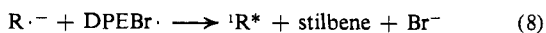
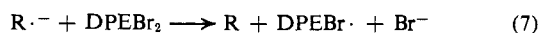
Furthermore, it is hard to understand how the presence of the neutral anthracene or other difficultly reduced hydrocarbons "catalyzes" the fluoranthene emission. No significant electron transfer to anthracene, etc., is possible due to the large potential differences. No spectroscopic evidence for any chemical interactions of the anthracene with the DPEBr₂, fluoranthene, F^{·-}, etc., could be found either.

The complete lack of any predictable excited triplet state energy transfer and/or quenching necessitates that we postulate the direct population of the excited singlet state of the aromatic hydrocarbons during these aromatic radical anion-alkyl halide eel reactions.

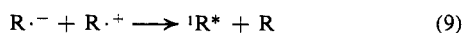
It can be estimated from the heterogeneous two-electron reduction potentials of the alkyl halides, $E_{1/2} = -0.2$ V,²⁸ that there would be insufficient energy from the first homogeneous electron transfer to give direct rise to any aromatic singlet.



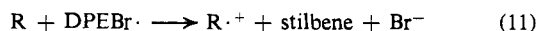
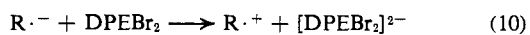
Thus the energy must arise from a very highly exothermic electron transfer to the monohalo radical (DPEBr[·]) which is more easily reduced than the parent.²⁰



In order that there be enough energy from the electron transfer (reaction 8) to result in an excited singlet state, it is necessary that the reduction potential of the radical be at least as positive as the oxidation potential of the aromatic hydrocarbon itself. This is necessary because the energy in the normal ion annihilation reactions



is, in most instances of eel, near the minimum energy necessary to promote an electron to an excited singlet state.^{3h, 8, 9d} Thus, reactions of the type



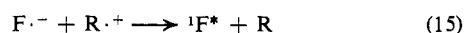
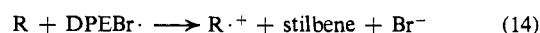
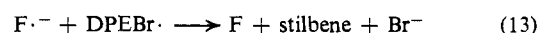
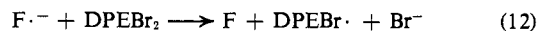
would have to be thermodynamically possible, so that the aromatic hydrocarbon excited singlet could arise *via* the normal eel annihilation reaction 9. Kinetically it is probable that the reduction of the halide proceeds *via* two one-electron steps and that reaction 10 does not occur. Further evidence of this is given by the solvent effect of the eel mechanism which could indicate that a slow step involving loss of halide occurs prior to the electron transfer step which results in the excited state. However, we do not have sufficient qualitative and quantitative data on the effects of solvent nature on intensities and kinetics to draw any definite conclusions concerning the rate determining step.

If one considers that reaction 11 is one that can give rise to a radical cation, an explanation as to why no fluoranthene emission is observed can be arrived at by considering the oxidation potentials listed in Table I

(27) This is to be expected as the reaction of the stilbene radical anion with DPEBr₂ ($S^{\cdot-} + DPEBr_2 \rightarrow S + DPEBr^{\cdot} + Br^-$) or with the more easily reduced hydrocarbon $S^{\cdot-} + R \rightarrow R^{\cdot-} + S$ would tend to increase the concentration of the species involved in the luminescence, reactions 7-15.

(28) The actual $E_{1/2}$ of the first electron transfer would be thermodynamically negative of that observed polarographically. The overall observed positive shift is due to the eel mechanism of the two-electron reduction.

and assuming that the DPEBr[·] reduction potential is about +1.2 V as a maximum (see Table I, footnote *m*) (less positive with respect to the oxidation potential of fluoranthene). Thus, no fluoranthene cation radical, which is formed at +1.45 V, would be present. If another aromatic hydrocarbon, R, such as anthracene, which is more easily oxidized than fluoranthene is present (see Table I), the DPEBr[·] is a sufficiently strong oxidizing agent to form R^{·+} (reaction 11). Once R^{·+} is formed, an ion annihilation reaction with F^{·-} can take place which is energetically sufficient to form ¹F*. This reaction sequence is given below.



Although this reaction sequence explains how R can "catalyze" fluoranthene emission, there is one questionable step. Reaction 13 obviously must also be energetic enough to populate the fluoranthene singlet. It is, therefore, necessary to postulate that some quenching mechanism be in operation during this step to prevent the formation of ¹F*. There are several possible mechanisms which can be suggested such as external heavy atom quenching by Br⁻ or DPEBr[·],^{29, 30} radical addition of DPEBr[·] to F^{·-},³¹ or perhaps a slow electron transfer from F^{·-} to DPEBr[·]. However, no experimental evidence has been found to demonstrate any of these mechanisms. Reaction 15 would result in an accumulation of the electron transfer energy predominantly with the molecule that has the lower available excited singlet energy level. In the three cases reported in this study the emitting species would be fluoranthene.^{32a} In order to test this possible mechanism cyclic voltammetric experiments in DMF, at scan rates up to 64 V/sec, were conducted in which the fluoranthene radical anion and the anthracene radical cation were alternately generated. These experiments yielded an emission which resembled fluoranthene^{32b} emission and was similar to that observed during the DPEBr₂ experiments. No anthracene emission was evident.

(29) N. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, pp 50, 57.

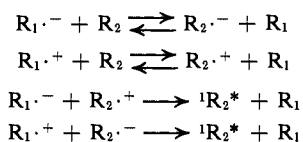
(30) The addition of up to 10 mM tetra-*n*-butylammonium bromide (TBAB) to a fluoranthene, anthracene, DPEBr₂ solution did not have a significant effect on the overall eel intensity. If there is a heavy atom effect in operation perhaps it is due to a species which is directly involved with the fluoranthene singlet in the solvent cage during the electron transfer.

(31) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

(32) (a) One side reaction that might be expected to limit the efficiency of the overall eel mechanism is the reaction $R^{\cdot+} + X^- \rightarrow R + X$. Such a reaction would be thermodynamically favorable and a similar reaction would be expected to occur between DPA^{·-} and Cl⁻. These species are actually present in the "efficient" DPACl₂ systems. Thus, this possible alternate path of decay of R^{·+} which would be expected to decrease eel efficiency does not appear to be significant. Experimentally, no effect on the eel was noted when tetra-*n*-butylammonium bromide was added in a concentration as high as 10 mM. Perhaps the activation energy of the Br⁻ or Cl⁻ oxidation is sufficiently high to permit the luminescence producing reactions to proceed without significant competition. (b) It should be pointed out that the identification of this emission as fluoranthene fluorescence would be very questionable. Anthranol, which is a product of the rapid reaction of the anthracene radical cation with solvent impurities [presumably water, T. C. Warner, J. Chang, and D. M. Hercules, *J. Amer. Chem. Soc.*, **92**, 763 (1970)], exhibits an emission similar to fluoranthene. Thus, if the anthracene radical cation is produced during this eel reaction as suggested, it is possible that the observed emission is that of anthranol and fluoranthene.

Similarly Fleet, *et al.*,³³ studied mixed systems containing either DPA and rubrene or DPA and rubicene under conditions where the radical cations of both species were electrogenerated but only the radical anion of the more easily reduced species (rubrene or rubicene) is produced. They noted mixed emission which also indicates mixed ion annihilation processes can occur.

The virtually complete absence of any higher energy emission in the mixed systems in the case where the radical anions of both species are being generated at the electrode and both species are present in equimolar concentrations, is not difficult to explain on the basis of simple electron transfer reactions. One can write the several mixed electron transfer reactions possible



where R_1 has the higher oxidation and reduction potential and also the higher singlet energy. The relative significance of each of these reactions is impossible to determine but one can conjecture that in the luminescence reaction zone the ions of the species with the lower excited singlet energy predominate by simple thermodynamic considerations and considering that these electron exchange reactions are close to diffusion controlled. When the halide species is present in excess in a mixed system (Figure 6), it is likely that the electron transfer reactions with the halide species (reactions 7 and 8) compete favorably with electron transfer to the more easily reduced aromatic hydrocarbon. This leads to luminescence intensities which correlate more with the bulk concentrations of the species involved. One might expect that in a system where R_1 and R_2 have excited singlet states very close in energy it would be possible to observe a mixture of their singlet emissions. This does appear to be true when both fluoranthene and DPA are reduced in the presence of $DPEBr_2$ although with the spectral resolution of the apparatus used here we cannot be absolutely sure of the spectral analyses.

It is impossible to experimentally demonstrate that the mechanism for the $DPEBr_2$ system is valid also for the $DPACl_2$ systems due to the presence of DPA as the reduction product. Unlike the $DPEBr_2$ system, the reduction of fluoranthene in the presence of $DPACl_2$ does result in fluoranthene singlet emission. This could be explained if the $DPACl \cdot$ species is more easily reduced compared to $DPEBr \cdot$ or by the simple presence of DPA which results in the formation of the DPA radical cation *via* the above mechanism given by reactions 12–15. The observation of perylene or rubrene emission, when those compounds are reduced in the presence of $DPACl_2$, can be explained by reactions similar to those postulated for $DPEBr_2$ systems (reactions 7, 10, 11, and 9). The observation of an approximate two order of magnitude greater luminescence intensity for the electroreduction of DPA (from $DPACl_2$ reduction) in the presence of $DPACl_2$ over that of normal DPA ion annihilation ecl^{3a} might appear unreasonable considering that the proposed mechanism involving the formation of $DPA \cdot^+$ discussed here is a more complex route to the same ion annihilation reaction. Furthermore,

(33) B. Fleet, P. N. Keliher, G. F. Kirkbright, and C. J. Pickford, *Spectrosc. Lett.*, **2**, 133 (1969).

Bezman and Faulkner³⁴ and Maloy and Bard³⁵ have determined that the absolute efficiency of generation of excited singlet states from the DPA radical anion–radical cation annihilation system in DMF is no more than 0.25%. This seems to indicate that at least in the $DPACl_2$ systems a reaction more efficient than radical ion annihilation must account for most of the observed ecl. It is possible in the $DPACl_2$ case that the reaction of the $DPACl \cdot$ and $DPA \cdot^-$ does result in ${}^1DPA^*$, reaction 8, and the quenching reactions discussed above for the $DPEBr_2$ –fluoranthene case do not occur to a significant extent. This would also explain the very high intensity emission from the rubrene– $DPACl_2$ system. Bezman and Faulkner³⁴ have found that rubrene radical ion annihilation reaction proceeds by a triplet–triplet annihilation mechanism rather than by direct singlet formation. For this reason they have found that rubrene ecl is less efficient than DPA ecl. At present we do not understand why the efficiency of the quenching of the excited singlet would differ in the $DPEBr_2$ and $DPACl_2$ systems. One could suggest that completely different mechanisms are operative in the two systems. However, there are too many similarities in both the observed phenomena and in the chemical nature of $DPEBr_2$ and $DPACl_2$ to make this an attractive argument. We plan to redesign our electrochemical and spectral measurement apparatus in order to obtain quantitative spectral and kinetic data on these reactions. This will allow us to carry out simulation studies³⁶ which will give more specific understanding of the actual mechanism in each case and allow us to determine if a radical–anion radical process, reaction 8, or an ion annihilation process, reaction 9, is the predominant path by which the excited singlet state of R is obtained. It will be necessary to examine other alkyl halide–radical anion systems such as the *n*-propyl bromide–naphthalide system in order to determine if such a mechanism is general for all types of alkyl halide systems that have been observed to luminesce on chemical reduction.^{18, 37}

Conclusion

The high ecl efficiency and the lack of any evidence of triplet energy transfer in these aromatic radical anion–alkyl halide systems indicate that the hydrocarbon excited singlet state results directly upon electron transfer from a radical anion to some strongly oxidizing species which arises during the homogeneous alkyl halide reduction by $R \cdot^-$. The energy requirements of the ecl suggests that this oxidant is as strong an oxidant as the cation radical of most aromatic hydrocarbons. The observation that fluoranthene emission occurs only in the presence of a “spectator” hydrocarbon which itself is “electroinert” suggests that the radical cation of the spectator hydrocarbon is formed during the net reduction process and is involved in the ecl mechanism in at least some of the systems investigated.

Acknowledgment. We thank Professors A. J. Bard, L. R. Faulkner, and Sherlock Swan, Jr., for very helpful discussions and comments on the research and this manuscript.

(34) R. Bezman and L. R. Faulkner, submitted for publication.

(35) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).

(36) S. W. Feldberg, *ibid.*, **88**, 390 (1966); *J. Phys. Chem.*, **70**, 3928 (1966).

(37) J. W. Haas, Jr., and J. E. Baird, *Nature (London)*, **214**, 1006 (1966).