Mechanisms of Chemiluminescent Electron-Transfer Reactions. IV. Absolute Measurements of 9,10-Diphenylanthracene Luminescence in *N,N*-Dimethylformamide

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Abstract: The chemiluminescent reaction between the anion and cation radicals of 9,10-diphenylanthracene (DPA) has been studied by the triple-potential-step method, in which the reactants were electrochemically generated from solutions of DPA in *N,N*-dimethylformamide. Absolute intensity–time measurements and total quantum output data were analyzed by recently published procedures. The results suggest that the emitting DPA singlet arises by direct generation in the redox reaction and that triplet states are unimportant as intermediates. The emission probability of charge transfer can be calculated, with good agreement, from either the total quantum output data or the linearized intensity–time curves. It is observed that the reciprocal emission efficiency is linear with the reciprocal DPA concentration, and it is suggested that this behavior reflects chemical interferences presented to the main reaction by anodically generated impurities. The true emission efficiency for the DPA reaction is probably near the asymptotic limit, which is 2.5×10^{-3}.

The electron-transfer reaction between the anion and cation radicals of 9,10-diphenylanthracene (DPA), which yields a blue luminescence characteristic of emission from DPA's first-excited singlet state, has been frequently studied.[1-7] The reaction has an important place in the development of mechanistic understanding about electrogenerated chemiluminescence (ecl) because it is the only well-documented system that is demonstrably energy sufficient, in that the emitting state is energetically accessible to the redox process.[7] In this particular system, it is therefore possible that luminescence results exclusively from first-excited singlet species produced directly in the charge-transfer reaction (the S route). However the energy sufficiency also implies that the lowest DPA triplet is likewise accessible to charge transfer, so a triplet pathway, featuring the mutual annihilation of triplets generated in the redox step, could well contribute to emission. If so, the singlet and triplet pathways may both be operative (the ST route), or the triplet pathway may be the only means to emission (the T route). Determining which of these alternatives is most likely has been an important goal of research with this system.

Recent efforts by Bard and his coworkers have suggested that the singlet pathway is the dominant contributor to emission. In particular, the lack of a magnetic field enhancement for luminescence from the DPA anion–cation reaction has been cited as evidence that only a negligible fraction of luminescence arises *via* triplet intermediates.[4,7] Moreover, Maloy and Bard have reported emission efficiencies for this reaction (photons emitted per reaction event) that are an order of magnitude greater than those measured for several energy-deficient systems.[5,6] Luminescence from the latter probably comes about by the T route;[7-9] hence it depends upon easily quenched triplet intermediates. Obviously the markedly greater emission efficiencies recorded for DPA are consistent with the intermediacy of less easily quenched singlet states, but the contrasting results can also be explained by large differences in the excited state yield of charge transfer.

Using total quantum output measurements and analyses of intensity–time curves, we have examined the behavior of luminescence from the DPA anion–cation reaction as it was generated *via* the triple-potential-step method from *N,N*-dimethylformamide (DMF) solutions. For several reasons, this particular system seemed a suitable subject for our initial absolute luminescence study to be carried out by transient techniques. First, one can use a variation of Feldberg's method to determine the relative importance of the triplet pathway to emission.[10,11] The results presented below corroborate the previous conclusions in suggesting that ecl arises effectively by the S route. The mechanism for chemiluminescence is therefore less complicated than in any other well-documented case, and this system offers the best opportunity to verify the essential quantitative elements of the treatments of intensity–time curves presented in other papers.[10-12] Finally, from a mechanistic viewpoint it is important to obtain information about the efficiencies of processes leading to ecl; thus it seemed intrinsically worthwhile to carry out such measurements for this prominent system. The comparability of our estimates with those of Maloy and Bard,[5,6] which were obtained by an entirely different steady-state procedure, provides improved confidence in the reliability of these figures and in others obtained by the two methods.

Experimental Section

The DPA used for this work was supplied by the Aldrich Chemical Co. (99%, mp 249–253°). No measurable quantities of im-

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(2) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).
(3) S. A. Cruser and A. J. Bard, *ibid.*, **91**, 267 (1969).
(4) L. R. Faulkner and A. J. Bard, *ibid.*, **91**, 209 (1969).
(5) J. T. Maloy, Ph.D. Thesis, The University of Texas at Austin, 1970.
(6) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).
(7) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *ibid.*, **94**, 691 (1972).
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(9) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).
(10) S. W. Feldberg, *ibid.*, **88**, 390 (1966).
(11) S. W. Feldberg, *J. Phys. Chem.*, **70**, 3928 (1966).
(12) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 3699 (1972).

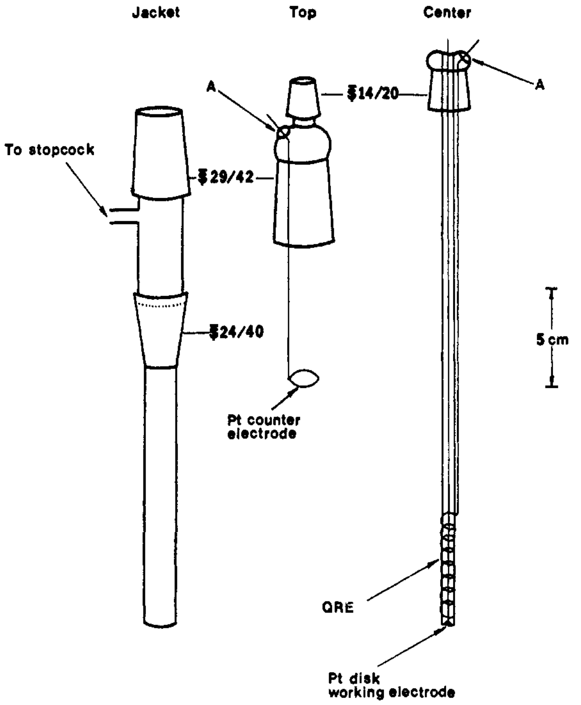

Figure 1. Electrochemical cell used for generation of luminescence. Points A are tungsten-through-glass seals.

purities were detected by either absorption or fluorescence spectroscopy or by cyclic voltammetry, so the substance was used as received.

Southwestern Analytical Chemicals manufactured the tetra-*n*-butylammonium perchlorate (TBAP) used as a supporting electrolyte in all experiments. A stock of this polarographic grade material was dried under vacuum at 90° for 72 hr and was stored over P_2O_5. However, prior to its actual use, the amount needed for the preparation of a given solution was redried under the same conditions overnight.

The DMF solvent was produced by Matheson Coleman and Bell or by Fisher (bp 152–154°). It was purified by an extensive procedure that was initiated by storing the crude solvent over anhydrous $CuSO_4$ for 2-3 days. Using a 120-cm vacuum-jacketed column packed with 7-mm Raschig rings, the decanted DMF was subsequently distilled at a unit reflux ratio under 18 Torr of prepurified N_2. The middle 80% was collected and dried for 24 hr under N_2 atmosphere with activated type 4A molecular sieves. It was then decanted and redistilled under the same conditions used for the first distillation. The middle 80% of this second fractionation was collected in a special storage flask, where it was maintained under an argon atmosphere (Matheson Gas Products, 99.995%). This flask features a spigot through which the DMF can be dispensed by appropriate manipulation of the argon pressure on a vacuum line. At no time was the bulk of the purified solvent exposed to the atmosphere.

Solutions were prepared just prior to the start of an experimental run by dispensing DMF into a volumetric flask into which the recently dried supporting electrolyte and the DPA had been previously weighed. The supporting electrolyte concentration was uniformly 0.105 ± 0.001 *M*, and the weighings of the DPA were accurate and precise to at least 1%. Though the solutions were exposed to the atmosphere during preparation, extreme care was taken to reduce the exposure to a minimum. In particular, magnetic stirring was used to effect dissolution in the tightly stoppered flask so that only about 15 min was required from the addition of DMF to the introduction of the solution into the cell. To forestall photochemical alterations in the materials, the stirring was carried out in the dark, and the DPA and DMF were stored away from light.

Figure 1 depicts schematically the electrochemical cell assembly used for generating luminescence and for most electrochemical measurements. The central element of this assembly supports the highly polished, planar Pt working electrode of about 0.08-cm^2 geometric area and the coil of 28-gauge Pt wire which serves as a quasi-reference electrode (qre). Fisher, Belew, and Kelley have shown that qre's provide stable, but nonreproducible, reference potentials,[13] and for this application the disadvantage of a reference potential that varies from day to day seems more than offset by the qre's simplicity and durability. Perhaps more importantly, the possibility of introducing contaminants into the working solution is greatly reduced in comparison to the usual poised reference, because the qre requires no salt bridge.

The cell top, the middle element of Figure 1, features a circular counter electrode, made from 24-gauge Pt wire, whose vertical location was adjusted to place the loop's plane at the dotted line on the jacket. Thus the counter electrode is outside the integrating sphere used in the photometric apparatus (see below), so any luminescence generated there contributes negligibly to the measured intensities of light produced at the working electrode. The counter electrode's ring configuration induces uniform current densities at the working electrode, and its larger area compared to the latter ensures that background reactions leading to contaminant buildup will be minimized.

The 24/40 joint on the cell-jacket mates with that serving as the entry port to the photometric integrating sphere, thereby providing quite reproducible placement. The sidearm has a 4-mm vacuum stopcock and an 18/9 standard ball joint to permit deaeration and sealing on a vacuum line.

To begin an experimental run, the DPA solution was added to the cell jacket, and the top, capped by a sealed-off 14/20 outer joint, was fitted into place. The solutions were all deaerated, except as otherwise noted, by at least three freeze–pump–thaw cycles, for which the minimum pressure in the third cycle never exceeded 10^{-4} Torr. Fisher, *et al.*, have demonstrated that much of the qre's potential drift results from changing stresses in the electrode metal.[13] The solutions were therefore allowed to warm to room temperature, to minimize thermal stresses, before the center element of the cell was installed. For this operation the cell was filled with high purity Ar, and the actual installation occurred under a positive pressure of Ar.

Electrochemical control over the cell was exercised by the fast-rise potentiostatic circuitry described by Bezman and McKinney,[14] which was constructed from solid-state operational amplifiers according to conventional principles. The triple-step program was furnished to the potential control amplifier by a modified version of the digitally controlled function generator also described previously.[14] The step durations were set each workday with a calibrated oscilloscope.

Electrolysis currents were monitored through a current-to-voltage transducer constructed from an Analog Devices Model 142B operational amplifier. Because this device can be used as either a current follower or an analog integrator, one can conveniently measure the integrals of current transients as well as the transients themselves. Each measurement range was individually calibrated to ±1% precision, and subsequent checks indicated the calibrations to be stable within the same range.

Cyclic voltammograms were recorded on a Moseley Model 7000 AM X-Y recorder, and chronoamperometric and chronocoulometric measurements were displayed on a Tektronix Type 564 storage oscilloscope, whose time base and vertical amplifier had been recently calibrated to ±1% precision with a crystal oscillator and a mercury cell, respectively. Photographic records of oscilloscope traces were rendered more reliable by the ancillary use of the Tektronix Model 100 projected graticule.

The photometric apparatus employed for absolute luminescence measurements and its auxiliary equipment have been elaborated in great detail elsewhere.[15] Briefly, the apparatus comprises an integrating sphere monitored by a quantum-counter detector. The latter involves the use of a 3.0-g/l. rhodamine B solution and an EMI Model 9656R photomultiplier, and it provides quantum flat detector response at wavelengths shorter than 610 nm. Attached to the integrating sphere is a 24/40 ₸ joint, which serves as a convenient entry port and locator for the cell. Although the axis of the joint is in the sphere's vertical bisecting plane, it is at an angle of about 50° to the vertical. By this means, the working electrode is faced away from the detector port, so that no luminescence is viewed directly, a required condition for proper operation of the sphere. The transient photomultiplier anode currents were recorded on the oscilloscope through the current-to-voltage trans-

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(13) D. J. Fisher, W. L. Belew, and M. T. Kelley in "Polarography 1964," Vol. 2, G. J. Hills, Ed., Interscience, New York, N. Y., 1966, p 1043.

(14) R. Bezman and P. S. McKinney, *Anal. Chem.*, **41**, 1560 (1969).

(15) R. Bezman and L. R. Faulkner, *ibid.*, 43, 1749 (1971).

ducer described above, but the total integrated anode current was always obtained using the integrator function of a Keithley Model 610B electrometer. By our published actinometric procedure, the calibration factor for the apparatus was determined to be (6.46 ± 0.19) × 10^{10} photons/(sec μA),[15] and daily checks *via* the built-in secondary standards have never shown a deviation from this value greater than 1%.

Demas and Crosby have pointed out that the problem of luminescence reabsorption by the emitting solution is often exacerbated in integrating spheres because luminescence may pass through the solution many times.[16] However, this effect probably is not applicable to ecl because luminescence is usually produced quite deep in a concentrated solution of the emitter. Thus the effects of reabsorption have ordinarily been completely manifested by the time the luminescence emerges initially. In any case, reabsorption will not diminish DPA's quantum output appreciably because the molecule has a near-unit fluorescence efficiency.[16,17]

To minimize variations due to inhomogeneities in temperature or concentration, each solution was initially equilibrated with a water bath maintained at 25° and was simultaneously stirred magnetically. Though the actual measurements could not be carried out under conditions of controlled temperature, the cell was removed from the water bath only for about 30 sec for each generation sequence, and it was returned immediately afterward to rehomogenize the solution and to maintain the temperature.

Results and Discussion

All the luminescence measurements reported below pertain to single pulses of light resulting from sequential generation of the DPA radical ions at a planar electrode by a triple-potential-step program. Techniques for the extraction of information from chemiluminescence measurements obtained by this method have been discussed extensively in a previous paper.[12] In the program used for this work, the initial potential was always 0.0 V *vs.* the Pt-wire qre, which in these solutions adopted a potential very near 0.0 V *vs.* an aqueous sce. Of course, no significant faradaic processes occurred at this potential before the start of the experiment. At zero time, the generation sequence began with an abrupt change in the working electrode potential from its initial value to a potential in the diffusion-limited region for generation of the first reactant. This forward step could be either anodic or cathodic, and its duration was t_f. In the reversal step, the working electrode potential was changed from the forward step potential to a value in the diffusion-limited region for production of the second reactant. This second step lasted as long as the first, and time into this step, $t - t_f$, is designated t_r. The experiments ended with a third step, which was always back to the initial potential. Of course, most of the luminescence appears in the interval $0 < t_r < t_f$, and useful mechanistic information may be extracted independently from the total quantum output and from the luminescence decay curve. Treatment of the latter involves comparisons with model decay curves obtained by digital simulation and displayed elsewhere.[12] In the simulations, it has been assumed that potential changes are instantaneous; hence valid treatment of experimental data demands first that the real electrode boundary conditions change essentially instantaneously from those of one diffusion-controlled process to those of another whenever a potential shift occurs. Satisfying this demand requires one to pay careful attention to the selection of the cathodic and anodic potential limits of the step program.

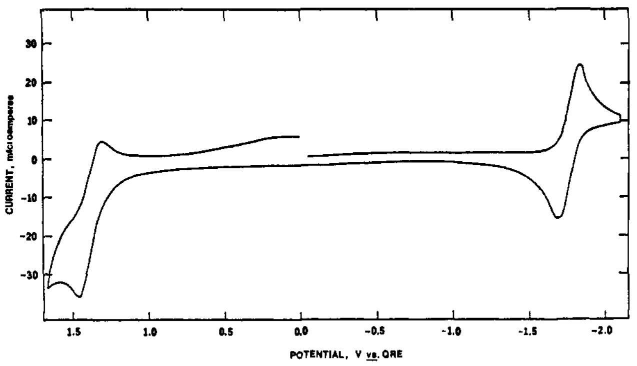

Figure 2. Cyclic voltammogram of a 0.98 mM solution of DPA in DMF–TBAP. The curve was recorded at a scan rate of 0.200 V/sec with the cell of Figure 1.

Electrochemical Measurements. A typical cyclic voltammogram for a DPA solution in DMF is shown in Figure 2 as obtained with the cell of Figure 1. The reduction of DPA to its stable anion occurs without complications, a fact that the reverse-to-forward peak current ratio of 1.00 ± 0.02 (by the method of Nicholson[18]) indicates. The generation of the DPA cation radical occurs at the threshold of background oxidation; hence a reliable estimate of that ion's stability could not be made electrochemically. However, the sizable reversal peak in the voltammogram suggests moderate stability. The broad cathodic hump at 0.2 V results from background oxidation products; if anodic sweeps were reversed before about 1.2 V, the wave was not observed on the following cathodic scan. The identity of the reducible substance (or substances) is not known.

If uncompensated resistance is overlooked, it can exert important, if subtle, effects on the results of triple-step experiments by essentially slowing the rate at which potential changes can be made. However, these departures from the ideal program become significant only if the accompanying changes in boundary conditions are slowed significantly, and one can minimize or eliminate the effect by using comparatively large overpotentials for reagent generation. The technique is illustrated by the results of a series of experiments in which the DPA anion was generated in a 1.00-sec step from an initial potential of 0.0 V *vs.* qre to a potential cathodic of the first cyclic voltammetric reduction peak. It was observed that as the step potential was increased to more cathodic values, the total charge passed in the step increased to a limiting value, which was essentially reached at overpotentials (relative to $E_p(R/R\cdot^-)$) greater than 250 mV. These results indicate that, although uncompensated resistance introduces nonideality into the potential program, the changes in electrode boundary conditions become effectively instantaneous at large overpotentials. Thus the cathodic step of the potential program was chosen, for all the work reported below, to be at least 250 mV more cathodic than $E_p(R/R\cdot^-)$. Figure 2 demonstrates clearly that the presence of the anodic background would not allow a similar optimization procedure for the anodic step, so its potential was set at that of the cyclic-voltammetric current minimum just anodic to $E_p(R/R\cdot^+)$. Though this allowed only a 180-mV over-

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(16) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).

(17) C. A. Parker, "Photoluminescence of Solutions," Elsevier, Amsterdam, 1968, and references contained therein.

(18) R. S. Nicholson, *Anal. Chem.*, **39**, 1406 (1967).

potential, the observation of linear charge *vs.* concentration plots for anodic steps (see below) provides some assurance that serious distortions in the electrode boundary conditions do not arise here.

Even so, we have investigated the expected effects of uncompensated resistance on the luminescence decay curve by digital simulation, and we have discovered that the Feldberg plot is remarkably insensitive to such a distortion. Apparently the necessary data are taken sufficiently late in the pulse that really severe distortions in the potential program are required to seriously disrupt the diffusion pattern. In contrast, the early part of the pulse is fairly sensitive to alterations in the wave form. In effect, the parameter we have previously[12] called θ is altered, and one expects less total emission. These considerations suggest that uncompensated resistance can cause negative errors in ϕ_{ecl} values derived from total quantum output. Our results may actually manifest this behavior in the data for the more concentrated solutions, which show ϕ_{ecl} from total output uniformly lower than ϕ_{ecl} derived from Feldberg analyses (see below). Nevertheless, the differences are hardly greater than the measurement precision, and we feel that the theoretical considerations and the experimental data both suggest that uncompensated resistance exerts no important effects on the present measurements.

The total charge, Q, passed in generating the DPA anion radical in chronocoulometric experiments like those outlined above showed a linear relationship with DPA concentration, as described by the following equations.

$$t_f = 1.00 \text{ sec}$$

$$Q = (7.41 \pm 0.34) + (25.7 \pm 0.5)[\text{DPA, m}M] \quad (\text{in } \mu\text{C})$$

$$t_f = 2.00 \text{ sec}$$

$$Q = (11.5 \pm 0.2) + (36.1 \pm 0.2)[\text{DPA, m}M] \quad (\text{in } \mu\text{C})$$

Uncertainties are expressed here as standard deviations. A comparison of the slopes of these two lines corroborates the conclusion that DPA reduction is a simple process. From the integrated Cottrell equation, one can identify these slopes as $2FAD^{1/2}t_f^{1/2}\pi^{-1/2}$, where D is the diffusion coefficient of DPA and the other variables have their usual electrochemical meanings and dimensions.[12,19] This consideration indicates that the ratio of the second slope to the first should equal $\sqrt{2}$, and the measured ratio of 1.41 ± 0.03 is certainly in good accord. The intercepts of these plots are too large to be ascribed entirely to double-layer charging; hence there is a secondary faradaic process involved. The fact that individual Q *vs.* $t_f^{1/2}$ plots show intercepts of about 3 μC suggests that the secondary process concerns diffusing, rather than adsorbed, substances.

The total charge data for the analogous experiments involving the generation of DPA cation were also linear with DPA concentration and followed the relationships

$$t_f = 1.00 \text{ sec}$$

$$-Q = (18.5 \pm 1.0) + (31.1 \pm 1.3)[\text{DPA, m}M] \quad (\text{in } \mu\text{C})$$

$$t_f = 2.00 \text{ sec}$$

$$-Q = (17.8 \pm 4.3) + (56.6 \pm 6.7)[\text{DPA, m}M] \quad (\text{in } \mu\text{C})$$

In the absence of kinetic steps following the generation of DPA cation, one expects the slopes of these lines to exactly equal their counterparts for reduction. The fact that they are much greater and the fact that the ratio of the second oxidation slope to the first (1.82 ± 0.29) is substantially larger than $\sqrt{2}$ indicate that the DPA cation undergoes a following chemical reaction leading to an additional faradaic process. Of course, such behavior is common among aromatic hydrocarbons, and it has been subjected to repeated investigation.[20-23]

The simplest mechanism that can account for the observed effects is the basic first-order ece process.

$$\text{DPA} \longrightarrow \text{DPA}\cdot^{+} + \text{e} \tag{a}$$

$$\text{DPA}\cdot^{+} \xrightarrow{k} \text{X} \tag{b}$$

$$\text{X} \longrightarrow \text{Y} + \text{e} \tag{c}$$

Of the two faradaic processes, a and c, the latter is assumed to occur more easily. The value of the pseudo-first-order rate constant, k, for the homogeneous decay reaction, b, can be extracted from the luminescence measurements, and it is suggested below that k averages about 0.67 sec^{-1}. Using this value and conventional calculation methods,[24] digital simulation of this ece mechanism predicts that the slopes of charge *vs.* concentration plots should be greater than those observed without kinetic complications by factors of 1.20 and 1.33 for t_f values of 1.00 and 2.00 sec, respectively. A valid comparison to this prediction can be made by using the ratios of the charge–concentration slopes for oxidation to the corresponding figures for reduction. From the data given above, one obtains 1.21 ± 0.07 and 1.57 ± 0.20, respectively, for the 1.00- and 2.00-sec experiments; hence there is but fair agreement with the simulated behavior. Better agreement could perhaps be achieved within the framework of the mechanism recently presented by Marcoux,[23] wherein it was postulated that DPA$\cdot^{+}$ undergoes disproportionation and that the resulting dication decays irreversibly to electroinactive products. Indeed, Marcoux's experiments in acetonitrile have suggested this to be a more viable route for DPA$\cdot^{+}$ decay in the presence of pyridine. Some support for the hypothesis may also be found in our observation, reported below, that k increases with DPA concentration, a fact that suggests the decay kinetics to be of higher order in species derived from DPA. However, our data are neither extensive nor precise enough to contribute significantly to the resolution of this interesting electrochemical question, and we wish only to indicate the complications associated with DPA oxidation in DMF and to show that the pseudo-first-order rate constants obtained from the luminescence measurements are very near the value needed to rationalize the electrochemical behavior. In any case, an adequate accounting of the effects of ion decay on the luminescence curve does not usually

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(19) F. C. Anson, *Anal. Chem.*, **38**, 54 (1966).

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

(21) R. N. Adams, "Electrochemistry at Solid Electrodes," Marcel Dekker, New York, N. Y., 1969, and references contained therein.

(22) G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, **91**, 4584 (1969).

(23) L. Marcoux, *ibid.*, **93**, 537 (1971).

(24) S. W. Feldberg in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969.

require detailed knowledge of the decay mechanism. One generally needs only to know an average lifetime (which is expressible as the reciprocal of the pseudo-first-order decay constant), provided the lifetime is not short compared to the time domain of the experiment.

As we have noted in a prior publication,[12] the quantity $2 \cdot FAD^{1/2}t_f^{1/2}\pi^{-1/2}$ which is needed for the analysis of luminescence data is conveniently obtained from the slopes of the charge–concentration plots. In view of the complications accompanying DPA oxidation, slopes obtained only from the reduction experiments have been used in the calculations reported below.

Luminescence Measurements. The characteristics of the DPA ecl emission were found to depend strongly upon the order in which the reacting ions were generated, a fact illustrated in Figure 3. Though experiments featuring anodic forward steps display the expected exponential luminescence decay, the opposite generation sequence yields complex departures from the norm. This behavior, which we have observed only in the case of DPA, probably results from interferences by impurities generated in the complex anodic electrolysis. Because the effect persists even when the anodic step potential is set for the foot of the DPA wave, a case could be made that DPA's cation is a necessary precursor. However, the oxidation of DPA is quite close to the background limit, and it is difficult to assess the importance of species derived from other components of the system. Certainly the cyclic voltammogram of Figure 2 shows that significant amounts of reducible substances are produced concurrently with the DPA cation, and the explanation for the anomaly may reside in the different diffusion-kinetic patterns experienced by these substances with the two separate step sequences. When a cathodic forward step is used, luminescence is always produced during a time period in which foreign substances are continuously generated. They face only one concentration gradient, which is toward the reaction zone; hence their presence there may be quite substantial. However, in experiments for which the forward step is anodic, electrolytic reduction of the impurities occurs simultaneously with ecl emission. Moreover, the species face concentration gradients in two directions. These facts suggest a decreased presence of the foreign materials in the reaction zone compared to the former case, and one expects even greater contrasts if the impurities have comparatively large diffusion coefficients. This latter possibility could be quite real if, as Mann suggested,[25] the important species are derived from DMF and are able to undergo transport by exchange processes.

It is perhaps pertinent to note here that this same intensity–time behavior can be induced in rubrene–DMF systems by the addition of water. Ordinarily, the ecl produced from the rubrene anion–cation reaction by the triple-step method decays by the usual exponential form.[26] When the water concentration is increased by 200 mM, the light pulses accompanying sequences begun by cathodic steps are greatly altered in shape and amplitude and closely resemble those observed with DPA. In marked contrast, the opposite sequence generates pulses that are changed but little.

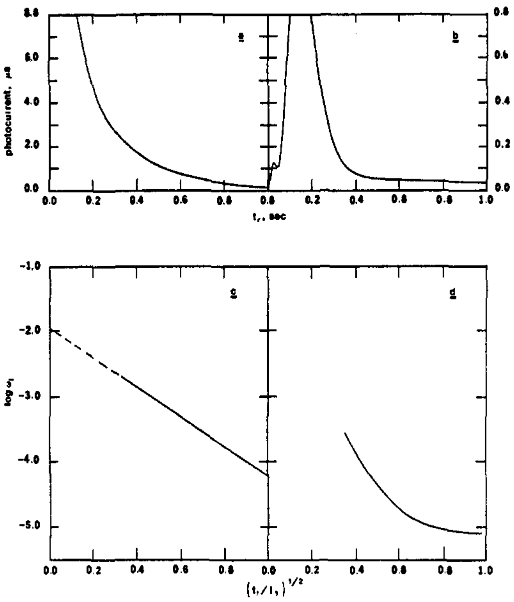

Figure 3. Contrasting ecl behavior with generation sequence: a and b depict typical light decay curves, and c and d are their corresponding Feldberg plots. Curves a and c were obtained from a 1.84 mM solution of DPA using an anodic forward step. The others were generated from a 2.20 mM solution *via* the alternate sequence. Note the large difference in scale between a and b.

The mechanism by which the anomaly arises is not known. It is possible that the foreign species decrease ion stabilities, that they act as effective quenchers, or that they undergo competitive electron-transfer processes. The anomalous intensity–time curves (as in Figure 3) do show long-lived luminescence components which could result from a chemiluminescent, competitive charge-transfer reaction, and additional support for the importance of extraneous redox chemistry may be found in the discussion below. The roots of the extraordinary behavior are obviously complex, and we have not deemed their unraveling to be worthwhile. In any event, the experiments involving anodic forward steps behave quite explicably, so the remaining discussion deals exclusively with such work.

The first four columns of Table I display the primary experimental measurements for a series of trials at t_f =

Table I. Characteristics of DPA Luminescence in DMF[a]

[DPA], mM	Feldberg plot[b]		$\phi_{\text{coul}} \times 10^4$	k, sec^{-1}	$\phi_{\text{ecl}} \times 10^4$	
	Slope	Intercept			From ϕ_{coul}	From intercept
0.27	−1.84		3.16	0.42	4.58	
0.36	−1.95	−2.54	2.83	0.54	4.70	5.02
0.45	−2.07	−2.39	4.10	0.67	7.69	6.84
0.51	−1.99	−2.32	4.26	0.59	7.50	7.97
0.62	−1.93		4.74	0.52	7.77	
0.69	−2.00		5.04	0.60	8.87	
0.70	−2.03		5.01	0.63	9.02	
0.81	−2.00	−2.26	5.65	0.60	9.94	9.41
0.88	−2.01	−2.18	6.38	0.61	11.1	11.2
0.92	−2.04	−2.33	5.68	0.64	10.3	11.5
1.04	−2.19	−2.08	5.85	0.81	12.4	12.6
1.17	−2.22	−2.05	5.78	0.84	13.2	13.2
1.56	−2.15	−2.09	5.48	0.77	11.3	12.8
1.84	−2.25	−1.96	5.95	0.87	13.3	16.5
2.20	−2.28	−1.98	5.75	0.91	13.3	15.0
2.42	−2.20	−1.99	6.44	0.82	13.8	15.2

[a] t_f = 1.00 sec. [b] Plot of log ω_i *vs.* $(t_r/t_f)^{1/2}$. See ref 12.

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(25) C. K. Mann in ref 24, Chapter 2, and references contained therein.

(26) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 6324 (1972).

1.00 sec. The Feldberg plots, whose descriptive parameters are summarized in the second and third columns, are dimensionless intensity–time curves that have been linearized according to the previously described convention.[12] The values of the slopes and intercepts were obtained *via* a least-squares procedure, and they are considered to be precise to ±2%. Coulombic efficiencies, ϕ_{coul}, which represent the emission probabilities per reactant ion produced in the forward steps, are defined by

$$\phi_{\text{coul}} = (F/Q_f)\int_{t_f}^{\infty} I\,dt$$

The integral denotes the total quantum output of a pulse, and F and Q_f are, respectively, the Faraday and the total charge attributable to reactant generation in the forward step. In Table I the final three columns are quantities extracted from the primary data in accord with the interpretation given below.

Several prior studies supporting the S route as the operative ecl mechanism for DPA have already been cited above, and we believe the present results generally substantiate that viewpoint. Though a first glance at the Feldberg slopes given in Table I may suggest the participation of a triplet pathway, a closer examination reveals that the deviations from the S-route norm (−1.48) are wholly attributable to the effects of ion decay. Working curves have been published by which one can extract the first-order rate constant for ion decay, as the product kt_f, from the Feldberg slopes of S-route systems.[12] If the cation decomposition accounts entirely for the increased slope magnitudes, then experiments executed for a given system at several step times, t_f, ought to be accompanied by a systematic variation in the slope such that a common value of k can be derived. In several tests of this type involving DPA concentrations from 0.4 to 1.2 mM, this expectation was fulfilled within the measurement precision. As a typical example, the data obtained for a 0.51 mM solution yielded the following.

t_f, sec	Feldberg slope	k, sec^{-1}
0.50	−1.74	0.58
1.00	−2.00	0.60
2.00	−2.19	0.45

The theoretical treatment of this transient method indicates that such a result would be fortuitous indeed if the large slope magnitudes were caused by triplet quenching.[12] Moreover, repeated runs with a given system composition yielded highly reproducible Feldberg slopes, an observation at variance with our general experience with cases for which a triplet lifetime controls the slope.[26] These observations, taken together with previous evidence, provide a reasonably firm basis to justify our interpretation of the results of Table I within the S-route framework. The excellent quantitative coherence of the interpretation (see below) is additional important evidence that the singlet pathway is the only significant means to emission in the DPA system.

At a given concentration, the performance of an S-route ecl system is specified by the single parameter, ϕ_{ecl}, which is the emission probability per reaction event. When both ions are stable, these emission efficiencies can be determined independently from either total quantum output or intensity–time data.[12] Although the DPA–DMF system does essentially involve singlet intermediates exclusively, the cation radical's instability implies a need for its apparent decay rate constant, k, so that the reaction's effects on ϕ_{ecl} can be rendered quantitatively accountable. However, we have already noted that k is conveniently extractable from the slopes of the Feldberg plots. Thus the redundant calculation of ϕ_{ecl} by two methods affords an opportunity to verify the theoretical relationships between ϕ_{ecl} and the intensity–time behavior and also those describing the effects of reactant decay on single-pulse experiments.

Table I displays in its last three columns the values of k, as derived from the Feldberg slopes, and ϕ_{ecl}, as calculated separately from ϕ_{coul} and the Feldberg intercepts. The procedures and working curves used to determine these parameters have been reported in detail elsewhere.[12] A comparison of the final two columns shows quite good agreement between the emission efficiencies calculated by the two methods; hence the validity of the mechanistic interpretation and the reliability of the theoretical relationships are strongly implied.

It is interesting to note that the pseudo-first-order rate constants measured here are considerably smaller than the values of 142 and 4.1 sec^{-1} reported earlier for the DPA cation decay in DMF.[3,5,27] Maloy, Prater, and Bard have noted that the greatly increased ion stability reflected by the latter result is due to improvements in the solvent purification procedure.[5,27] The further reduction in the ion decay rate observed in this work may result from the special precautions taken with the supporting electrolyte. In any event, the disparities in the three rate constants certainly suggest the system to be highly sensitive toward the procedures used for handling materials.

Perhaps the most striking aspect of the luminescence measurements is that ϕ_{ecl} increases with concentration and approaches an asymptotic limit at high [DPA]. The increase with concentration probably reflects a gradual overcoming by the system of chemical effects resulting from the troublesome anodically produced impurities. One can readily see that ϕ_{ecl} is the product of DPA's fluorescence efficiency, ϕ_f, and the singlet yield of charge transfer, ϕ_s; thus it is conceivable that changes in either quantity or both cause the rise in ϕ_{ecl} with DPA concentration. However, in considerations of the effects of impurity quenching, we have been unable to derive functional form for the variation of ϕ_f that is compatible with experimental observation. Furthermore, it is unlikely that impurities reach concentrations even close to those needed to affect DPA fluorescence appreciably (5–10 mM). One can therefore assume that ϕ_f is relatively constant through all this work and that apparent changes in ϕ_s produce the variation in ϕ_{ecl}.

The simplest rationale for this behavior involves the assumption that the anodic step of each experiment produces a constant quantity of a foreign substance which is reactive toward the DPA anion. Under these circumstances, the nature of the data analysis is such that an apparent ϕ_{ecl} will be measured according to

$$\phi_{\text{ecl}} = N_1\phi^0_{\text{ecl}}/(N_1 + N_2)$$

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(27) J. T. Maloy, K. B. Prater, and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5959 (1971).

Here, ϕ^0_{ecl} is the true emission efficiency of the DPA anion–cation reaction, N_1 is its overall rate, and N_2 is the overall rate of the nonluminescent side reaction. If N_1 and N_2 are apportioned according to the relative concentrations of DPA cation and the competing species (hence to those of their parents), then

$$\phi_{ecl} = [\mathrm{DPA}]\phi^0_{ecl}/([\mathrm{DPA}] + \gamma)$$

One may view γ as the effective concentration of the precursor to the competing species, but it really is little more than an adjustable parameter if the foreign material is not generated in a diffusion-limited electrode process. This treatment predicts the linear form

$$\phi_{ecl}^{-1} = \phi^0{}_{ecl}^{-1} + (\gamma/\phi^0_{ecl})[\mathrm{DPA}]^{-1}$$

and one can see from Figure 4 that our results actually do obey such a relationship. Thus we feel that the upper limiting value of ϕ_{ecl}, which from Figure 4 is about 2.5×10^{-3}, is the true measure of the emission efficiency of the DPA cation–anion reaction.

Our observation here of a concentration dependence for ϕ_{ecl} renders a comparison with the results of Maloy and Bard somewhat ambiguous. Working with 1.0 m*M* solutions of DPA, they measured a maximum value of ϕ_{ecl} of 8.5×10^{-4} under conditions involving anion generation at the disk.[5,6] Our result for the same concentration is near 11.9×10^{-4}. When one considers the gross differences between the two measurement techniques and the quantity's apparent sensitivity to methods of handling materials, one must consider the agreement satisfactory.

Since the fluorescence efficiency of DPA is nearly unity, the conclusion that ϕ_{ecl} is about 2.5×10^{-3} implies that ϕ_s is about the same magnitude. Obviously this singlet yield is quite low, but we hasten to point out that the total excited state yield may actually be fairly high. In subsequent papers we will show that triplet yields in some systems can approach unity and that the low emission efficiencies typically accompanying the T route result from losses in triplet–triplet annihilation and by triplet quenching. The ϕ_{ecl} values we have observed in T-route systems suggest strongly that a T-route component in DPA could produce only about 10% of the observed emission. It is doubtful that one could distinguish such an ST mixture from the purely S-route case; hence DPA behaves experimentally as an S-route system even though it may in fact have T-route component.

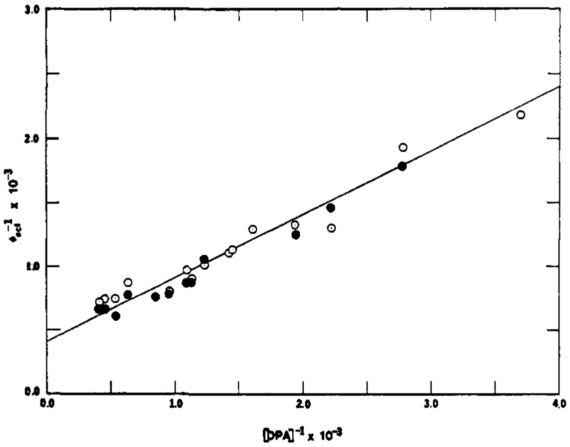

Figure 4. Concentration dependence of ϕ_{ecl}. Open circles show values derived from ϕ_{coul}, and filled circles represent data obtained from Feldberg intercepts.

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