Mechanisms of Chemiluminescent Electron-Transfer Reactions. VI. Absolute Measurements of Luminescence from the Fluoranthene–10-Methylphenothiazine System in *N*,*N*-Dimethylformamide

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Abstract: Absolute measurements of light pulses generated by the triple-potential-step method have been employed to study the chemiluminescent electron-transfer reaction between the fluoranthene anion radical and the cation radical of 10-methylphenothiazine (10-MP). All work was carried out with *N*,*N*-dimethylformamide solutions. The scheme for analyzing data acquired by this transient method has been extended to cover "mixed" redox processes, in which the two reactants are derived from different precursors. The results are consistent with the intermediacy of the triplet fluoranthene species, and they show the emission efficiency, ϕ_{ecl}, to average about 8×10^{-5}. The efficiency parameter α, which partially determines the luminescence decay curve, decreases with increasing bulk concentrations of the parent substances. None of these observations depends upon the order of reactant generation. The decline in α with concentration probably reflects a decline in the apparent triplet yield of charge transfer. The inverse of α was found to be approximately linear with concentration, and the observation has been shown to be consistent with the presence of the equilibrium: $10\text{-MP}\cdot^{+} + 10\text{-MP} \rightleftharpoons (10\text{-MP})_2\cdot^{+}$. In this interpretation, one finds an equilibrium constant approximating 10^4 l./mol, and the true triplet yield of the 10-MP cation–fluoranthene anion reaction is estimated at 30%.

Recent months have seen considerable interest in the chemiluminescent electron-transfer reaction between the fluoranthene anion radical and the cation radical of 10-methylphenothiazine (10-MP).[1-3] Though the luminescence from this reaction apparently arises from fluoranthene's first-excited singlet state, the system is termed energy deficient because the charge transfer is insufficiently energetic to generate that state directly. Of course, many such systems have been noted in studies of electrogenerated chemiluminescence (ecl), and they have been most often rationalized by the T route, for which the required intermediacy of the emitter triplet state is a fundamental postulate. Generally it is supposed that the intermediates are directly produced in the redox step and that triplet–triplet annihilation accounts for the presence of the emitting singlet. Evidence that this pathway is actually operative has been particularly difficult to obtain, and work with the fluoranthene–10-MP system has provided perhaps the firmest indication of its reality. In particular, Freed and Faulkner demonstrated that for the oxidation of fluoranthene anion there is a critical enthalpy very near the energy of the fluoranthene triplet, which must be exceeded for luminescence to occur.[1] More significantly, they showed in a series of triplet interception experiments that the fluoranthene triplet is a required intermediate for emission from the fluoranthene–10-MP system. In later work, Bard and his coworkers reported that luminescence from this reaction is enhanced by a magnetic field, and they have noted the consistency of their observations with the T route.[3] Certainly this evidence combines neatly with that of Weller and his coworkers to support the idea that the mechanism is general for energy-deficient processes,[4-6] but in a more restricted view it renders the operation of the T route quite likely for the particular system at hand.

Because the mechanism for this reaction is relatively well characterized, we have found it attractive for study by our newly developed transient methods for the acquisition and analysis of absolute liminescence data.[7] These methods offered an independent means by which the T-route hypothesis could be checked, and, in the face of its support, the system seemed an ideal application for our techniques for obtaining fundamental mechanistic information from T-route processes. Moreover, the fluoranthene–10-MP system features the only markedly energy-deficient charge-transfer reaction for which a triplet yield has been reported. Using a method which involved the sensitized photoisomerization of *trans*-stilbene, Freed and Faulkner measured a value of about 0.007.[2] Thus a study of this system had the added advantage that the triplet yields obtained from absolute luminescence measurements could be compared to those determined by a wholly different means. Finally, there was the inherent mechanistic interest in the efficiencies of excited state formation and emission. Reliable information of this sort is presently quite scarce, yet it obviously is immensely valuable to an understanding of the factors governing those efficiencies.

The results reported below for our work with *N*,*N*-dimethylformamide (DMF) solutions support the T route as the mechanism leading to emission and show satisfactory agreement with the earlier estimate of the triplet yield. Perhaps most interesting, however, is the observation that the inverse triplet yield is apparently linear with 10-MP concentration. This functional de-

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(1) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).
(2) D. J. Freed and L. R. Faulkner, *ibid.*, **93**, 3565 (1971).
(3) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *ibid.*, **94**, 691 (1972).
(4) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).
(5) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
(6) A. Weller and K. Zachariasse, *Chem. Phys. Lett.*, **10**, 197 (1971).
(7) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 3699 (1972).

pendence is quite suggestive that a dimer cation of 10-MP is an important element of the system's chemistry.

Experimental Section

The fluoranthene used in this work was Scintillation Grade material supplied by Eastman Organic Chemicals and was used without further purification. Eastman also produced the 10-MP (mp 99–100°), but it was recrystallized three times from ethanol before use. The sources, purification procedures, and special handling precautions pertaining to the DMF solvent and tetra-*n*-butylammonium perchlorate (TBAP) supporting electrolyte have been recently elaborated.[8] In all experiments the TBAP concentration was 0.105 ± 0.001 *M*.

The procedures used for the preparation of solutions and for the measurement of electrochemical and luminescence parameters have been discussed in detail elsewhere;[8] hence they will not be recounted here. All such measurements were conducted at 25°. Details concerning the electrochemical and photometric apparatus employed in this work have also been reported in prior publications.[9,10]

Results

All the luminescence measurements reported below were obtained from single pulses of light resulting from sequential reactant generation at a planar electrode by a triple-potential-step program. The nature of this experimental method and the techniques for data analysis have been elaborated quite extensively elsewhere.[7] Extending our usual practice, the duration of each generating step has been designated t_f, and time measured into the second step is t_r. The initial and final potentials were chosen to be 0.0 V *vs.* a Pt-wire quasi-reference electrode (qre), which adopted a potential in these solutions near 0.0 V *vs.* the aqueous sce.

Electrochemical Measurements. A cyclic-voltammetric curve of a solution containing both fluoranthene and 10-MP shows peak potentials for reduction of the former to its anion radical and oxidation of the latter to its cation radical to occur at −1.70 and +0.77 V, respectively, *vs.* qre. Neither the reduction of 10-MP nor the oxidation of fluoranthene occurs in DMF–TBAP within the background limits. Calculations by the method of Nichlolson[11] from careful voltammetric measurements indicated that the reverse-to-forward peak current ratio for the reduction of fluoranthene was 1.00 ± 0.02. The same quantity for 10-MP oxidation was found to be 0.96 ± 0.02. These data plainly show the fluoranthene anion radical to be stable on the time scale of the 0.200 V/sec scan rate, but they hint at a slight instability of the 10-MP cation.

The uncompensated resistance of the cell rendered voltammetric measurement of the ion's decay rate somewhat difficult, so a chronopotentiometric method was employed. The controlled-potential voltammeter was programmed as a constant current source for this purpose, and the working electrode–qre potential difference was displayed on the storage oscilloscope. A constant anodic current of a magnitude less than that of the cyclic-voltammetric peak current for 10-MP oxidation was impressed on the working electrode. At arbitrary times less than the forward transition time, the current was reversed and the reverse transition was observed. The results, which were obtained for generation times of 0.5–30 sec, were analyzed by the method of Testa and Reinmuth[12] and showed the apparent first-order rate constant for cation decay to be 0.07 ± 0.02 sec^{-1}. Even though the decomposition is probably more complex than a simple first-order decay, the rate is small enough that the apparent first-order decay constant will provide a good estimate of the average cation lifetime. The 14-sec lifetime estimated here is sufficiently long that one can consider the 10-MP cation to be a stable reactant without introducing appreciable error into the analysis of the luminescence data.[7]

In previous publications, we have noted the importance of using large overpotentials for the generation of the reactant ions in the step experiments.[8,13] As a means for defeating the effects of uncompensated resistance, a generating potential at least 250 mV more extreme than the cyclic-voltammetric peak potential for the process of interest has been recommended. Cyclic voltammetric data show the peak potential for fluoranthene reduction to be at least 300 mV anodic of the next reduction process, so the customary 250-mV overpotential could be utilized for cathodic generating steps without difficulty. However, the peak potential for 10-MP oxidation precedes the anodic background limit by only about 220 mV. For anodic generating steps, then, the potential was selected by the optimization procedure used previously in studies of rubrene.[13]

In a series of chronocoulometric experiments featuring 0.0-V initial potentials and 1.00-sec steps at potentials chosen as outlined above, the total charge, Q, passed in steps of either polarity was found to be quite linear with the concentration of electroactive substance. Specifically, the data yielded the following least-squares relationships.

Generation of fluoranthene anion

$$Q = (12.6 \pm 0.3) + (33.6 \pm 0.5)[\text{fluoranthene, m}M]$$

Generation of 10-MP cation

$$-Q = (8.7 \pm 0.3) + (34.7 \pm 0.5)[\text{10-MP, m}M]$$

The values of Q are expressed here in microcoulombs, and the uncertainties are standard deviations. The slopes of these lines are theoretically proportional to the square roots of the diffusion coefficients for the respective parent species,[7,14] and their near equality shows the two coefficients to be almost equal. These data were obtained with a working electrode 1.22 times larger in area than that employed for the earlier work with rubrene,[13] and a comparison of the results of the two studies suggests the diffusion coefficients for fluoranthene and 10-MP to be about 2.5 times larger than that for rubrene. The slopes of these charge–concentration plots are quite useful for reducing the luminescence data,[7] and in all the calculations reported below we have employed the slope of the former line to treat data featuring cathodic forward steps. Conversely, the latter slope was used with the alternate generation sequence.

Luminescence Measurements. The primary luminescence data, obtained from experiments involving each of the two possible generation sequences, are summarized in the first five columns of Table I. The last

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(8) R. Bezman and L. R. Faulkner, *J. Amer. Chem. Soc.*, **94**, 6317 (1972).

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

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

(11) R. S. Nicholson, *ibid.*, **39**, 1406 (1967).

(12) A. C. Testa and W. H. Reinmuth, *ibid.*, **32**, 1512 (1960).

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

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

Table I. Characteristics of Ecl from Fluoranthene–10-MP Solutions in DMF[a]

Concn, m*M*		Feldberg plot[b]					
Fluoranthene	10-MP	Slope	Intercept	$\phi_{\text{coul}} \times 10^5$	$\phi_{\text{ecl}} \times 10^5$	$\alpha \times 10^{+4}$	β
			(a) Cathodic Forward Step				
0.160	0.170	−2.95	−2.97	7.00	7.68	15.1	3.80×10^{-1}
0.184	0.222	−2.88	−2.67	12.4	13.4	35.4	1.20×10^{-1}
0.445	0.439	−2.46	−2.79	7.04	7.79	6.60	1.90×10^{-4}
0.630	0.660	−2.42	−2.81	6.76	7.43	6.30	1.38×10^{-4}
0.621	0.671	−2.33	−2.77	8.37	9.17	6.90	1.07×10^{-4}
0.847	0.820	−2.32	−2.82	7.13	7.90	6.15	9.50×10^{-5}
0.965	0.885	−2.26	−2.89	6.21	6.93	5.25	6.45×10^{-5}
0.885	0.950	−2.20	−2.83	7.99	8.76	6.01	5.88×10^{-5}
1.45	1.44	−2.09	−3.00	5.61	6.21	4.06	2.82×10^{-5}
			(b) Anodic Forward Step				
0.184	0.222	−2.78	−2.67	9.9	11.2	18.2	1.17×10^{-2}
0.445	0.439	−2.67	−2.85	5.54	6.12	8.70	1.38×10^{-3}
0.442	0.400	−2.68	−2.69	7.54	8.23	13.1	1.98×10^{-3}
0.630	0.660	−2.44	−2.89	5.69	6.32	5.25	1.45×10^{-5}
0.621	0.671	−2.30	−2.82	7.65	8.52	6.16	8.50×10^{-5}
0.965	0.885	−2.30	−2.94	5.60	6.12	4.66	6.45×10^{-5}
0.885	0.950	−2.38	−2.89	6.47	7.20	5.25	10.0×10^{-5}
1.45	1.44	−2.10	−2.98	6.38	7.04	4.26	2.96×10^{-5}

[a] t_f = 1.00 sec. [b] Plot of log ω_i *vs.* $(t_r/t_f)^{1/2}$. See ref 7.

three columns display the values of more fundamental parameters which are derived from the primary results as discussed below. The slopes and intercepts of Feldberg plots of the intensity–time decay curves are shown in the third and fourth columns; these were derived by a least-squares procedure and they are considered to be precise to ±2%. The table's fifth column lists the coulombic efficiency, ϕ_{coul}, for each experiment. This quantity is the ratio of the total number of emitted photons to the total number of reactant ions generated in the forward step, and it is evaluated according to the relation

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

In this equation, the integral represents an experiment's total quantum output, F is the Faraday, and Q_f is the total charge attributable to reactant generation in the forward step.

Discussion

We have already noted above the existence of substantial evidence that luminescence from the present system arises *via* the T route. Certainly the slopes observed in this work for the linearized intensity–time curves corroborate this interpretation. Of the processes that are ordinarily considered important in ecl systems, only the participation of a triplet pathway to luminescence or the involvement of an unstable reactant generated in the forward step can produce slopes much more negative than −1.48.[7,15,16] Since the latter possibility is ruled out by the electrochemical evidence, the former is suggested. In this regard, it is interesting to note that slope magnitudes are observed almost to the upper limit of 2.96 that is expected for the T route.[7,16] In the face of the prior and present evidence, we have therefore interpreted our results according to that mechanism's predictions.

Because the reaction of interest here involves ions derived from different precursors, the analysis of experimental results is slightly more complicated than for the simpler case in which both reactants have the same parent. To treat such a "mixed" ecl system, the following T-route reaction scheme can be considered.

$$\mathrm{R}\cdot^- + \mathrm{R}'\cdot^+ \longrightarrow \mathrm{R} + \mathrm{R}' \qquad \text{(a)}$$

$$\mathrm{R}\cdot^- + \mathrm{R}'\cdot^+ \longrightarrow {}^3\mathrm{R}^* + \mathrm{R}' \qquad \text{(b)}$$

$${}^3\mathrm{R}^* + {}^3\mathrm{R}^* \xrightarrow{k_s} {}^1\mathrm{R}^* + \mathrm{R} \qquad \text{(c)}$$

$${}^3\mathrm{R}^* + {}^3\mathrm{R}^* \xrightarrow{k_t} {}^3\mathrm{R}^* + \mathrm{R} \qquad \text{(d)}$$

$${}^3\mathrm{R}^* + {}^3\mathrm{R}^* \xrightarrow{k_g} 2\mathrm{R} \qquad \text{(e)}$$

$${}^3\mathrm{R}^* \, (+\mathrm{Q}) \xrightarrow{1/\tau} \mathrm{R} \, (+\mathrm{Q}) \qquad \text{(f)}$$

$${}^1\mathrm{R}^* \, (+\mathrm{Q}) \longrightarrow \mathrm{R} \, (+\mathrm{Q}) \qquad \text{(g)}$$

$${}^1\mathrm{R}^* \longrightarrow \mathrm{R} + h\nu_f \qquad \text{(h)}$$

In this mechanism, R and R′ are ground-state molecules of the substances from which the radical ions $\mathrm{R}\cdot^-$ and $\mathrm{R}'\cdot^+$ are derived. Excitation is denoted by an asterisk, and the multiplicity of the excited state is represented by a superscripted numeral. The substance Q corresponds generically to any quencher, and $1/\tau$ is considered to be the sum of the pseudo-first-order rate constants for all processes of the type f. Singlet emission, process h, competes with the other singlet-deactivating reaction, g, with a fluorescence efficiency ϕ_f. The two redox reactions, a and b, are assumed to proceed at a combined rate that is diffusion controlled.

For simplicity, this scheme has been written to show only the case featuring excitation of R. Of course the cation precursor is the emitter in many other systems, and, for this alternative possibility, one can easily write the corresponding mechanism, which is symmetrical to the one above. It should be emphasized that the treatment given below applies without reservation to either case as long as only one precursor emits.

The complications pertaining to this mechanism are derived from the presence of two electroactive ion parents in place of the one parent considered in the earlier treatment.[7] There are three different points at which contrasts between the two situations arise.

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(15) S. W. Feldberg, *J. Amer. Chem. Soc.*, **88**, 390 (1966).
(16) S. W. Feldberg, *J. Phys. Chem.*, 70, 3928 (1966).

First, one of the parent substances in the mixed mechanism will be electroinactive at each generating potential. Thus the second step will merely eliminate at the electrode some of the reactant generated in the forward step, rather than convert it to the second reactant. In addition, the presence of two ion precursors implies that there are independent values for their concentrations and their diffusion coefficients. All three of the factors bear upon the concentration profiles; hence they influence the charge-transfer reaction rate. Moreover, many dimensionless parameters defined in the earlier treatments contain the diffusion coefficient, D, and the bulk concentration, C, for the single ion parent considered there. Obviously these definitions become somewhat ambiguous for the present case; hence some redefinition of parameters is in order.

The most advantageous way to define these parameters is suggested by the means by which some are actually calculated from experimental data. Taking ω_i, the dimensionless emission rate parameter, as an example, one finds this quantity defined previously as $It_f^{1/2}/ACD^{1/2}$, where I is the total emission rate and A is the area of the generating electrode. It has been pointed out that $AD^{1/2}$ is most easily obtained from chronocoulometric data *via* the integrated Cottrell equation.[7] To preserve this convenience, it is recommended here that wherever D and C appear in definitions of dimensionless parameters, they represent the diffusion coefficient and the bulk concentration, respectively, of the substance undergoing electrolysis in the forward step. This convention has been utilized uniformly in the theoretical and experimental work leading to the discussion below.

Once these parameters have been carefully defined, the treatment of the mixed annihilation outlined above proceeds exactly as in the previous case, and one obtains the same final result.

$$\omega_i = \beta[1 - (1 + \alpha\omega_n/\beta)^{1/2}] + 0.5\alpha\omega_n \qquad (1)$$

Here ω_n is the dimensionless redox reaction rate parameter defined by $Nt_f^{1/2}/ACD^{1/2}$, where N is the total reaction rate (moles per second). The efficiency parameter α is defined according to $\phi_t\phi_{tt}\phi_f/(1 - g)$, where ϕ_t is the triplet yield of charge transfer and ϕ_f is the emitter's fluorescence efficiency. The efficiency of the excited singlet channel in triplet fusion is ϕ_{tt}, defined kinetically as k_s/k_a, where $k_a = k_s + k_t + k_g$. The quantity g is simply $k_t/2k_a$. The efficacy of triplet quenching relative to fusion is reflected in β, which is $\phi_f\phi_{tt}f(t)t_f/8k_a(1 - g)^2\tau^2C$, where $f(t)$ is a dimensionless width of the reaction zone.[7] If one can obtain the time dependence of ω_n, then one can derive from eq 1 the expected behavior of ω_i with time.

It is widely recognized that the dimensionless reaction rate can be linearized with respect to time by a relation of the type

$$\log \omega_n = a_n + b_n(t_r/t_f)^{1/2} \qquad (2)$$

This linear form is valid for $0.2 < (t_r/t_f)^{1/2} < 1.0$, and a_n and b_n are easily obtained from digital simulations. In the case for which both ions are derived from the same parent, a_n and b_n have values of 0.724 and -1.483, respectively,[7] but for the mixed annihilation, ω_n (hence a_n and b_n) depends upon the relative concentrations and diffusion coefficients of the two ion precursors. If these quantities are known for the experiment of interest, a_n and b_n can be accurately obtained from a simulation. Thus the relation between ω_n and $(t_r/t_f)^{1/2}$ becomes known, and the corresponding relationship for ω_i can be calculated for various values of α and β. Working curves can then be constructed relating α and β to the slopes, b_i, and intercepts, a_i, of the linear plots of log ω_i *vs.* $(t_r/t_f)^{1/2}$. In the established manner, one can therefore extract α and β, *via* these curves, from the Feldberg plots.

To be rigorous, one obviously requires a new set of working curves for each set of pertinent a_n and b_n values. Since the construction of each set is tedious and time-consuming, it seemed worthwhile to investigate the range of concentration relationships between the parent substances over which one could use a single set of working curves without introducing errors greater than those inherent in the experimental method. We have, therefore, modeled the triple-step experiment in a series of simulations for which the relative parent concentrations were varied. In accord with the electrochemical data, it was assumed in each simulation that the diffusion coefficients for all the participating substances were equal. The simulations, which involved 1000 iterations per step, were executed on an IBM 360/65 computer using standard techniques.[7,17] It was found that a_n and b_n obey the linear relations

$$a_n = 0.507 + 0.216R \qquad (3)$$

$$b_n = -1.136 - 0.348R \qquad (4)$$

where R is the ratio of the bulk concentration of the ion precursor electrolyzed first to that of the precursor electrolyzed in the second step. The equations given above are valid over the interval $0.90 \leq R \leq 1.10$, and they show that $\pm 10\%$ variations in R from unity produce only 3% variations in a_n and b_n. Thus one seems entirely justified in using a single set of working curves to extract α and β provided one uses precursor concentrations that are equal within 10%. Moreover, the a_n and b_n values of 0.723 and -1.484, respectively, for $R = 1.00$ are virtually equal to those calculated in the earlier treatment for a single precursor. Thus the results given in the last two columns of Table I were obtained from the Feldberg plots *via* the working curves published previously.[7]

It is probably worth noting here that a serious problem can arise with this treatment whenever the triplet states of both ion precursors are accessible to charge transfer. In such an instance, light may arise from both species as a consequence of parallel triplet–triplet annihilation steps. If so, the kinetic analysis discussed above would clearly need expansion to be properly descriptive. However, in most cases where dual excitation might occur, one triplet will be at a lower energy; hence one expects efficient conversion of the higher triplet to the lower one by energy transfer. The net result is that only one kind of triplet emerges from charge transfer, and only one emission is observed, but ϕ_t reflected by α's magnitude will be the sum of the two triplet yields for the individual excitations.

This is mentioned here because it is possible that the 10-MP triplet is populated in the oxidation of fluor-

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(17) S. W. Feldberg in "Electroanalytical Chemistry," Vol. 3, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 4, and references contained therein.

anthene anion by the 10-MP cation.[1,2] This complication has been discussed in detail in other reports concerning the reaction, and it has been suggested that either the excitation does not occur or that 10-MP triplets are efficiently converted to fluoranthene triplets by energy transfer.[2]

When one turns to the total quantum output measurements, one quickly recognizes that the additional complications pertaining to the mixed T route will modify the interpretation procedure just as they did for the decay curve analysis. However, interpretation is much simpler in this case. One extracts the value of ϕ_{ecl}, which is the emission probability per charge-transfer event, from the measured value of ϕ_{coul}, which is the emission probability per reactant produced in the forward step, simply by multiplying the latter by θ. The value of θ is determined by digital simulation,[7] and the calculations described above have also yielded

$$\theta = 1.230 - 0.125R \qquad (5)$$

for the concentration ratio, R, in the interval $0.90 < R < 1.10$. The emission efficiencies shown in the sixth column of Table I were calculated from the coulombic efficiencies by θ values obtained from this relation.

Perhaps the most noteworthy feature of the interpreted results presented in Table I is that α is a function of concentration. Its decline with increasing concentration is suggestive of a functional relationship of the Stern–Volmer form, and Figure 1 indeed demonstrates the approximate linearity between α^{-1} and [10-MP]. Of course, this linearity suggests, in turn, that a quenching process may be responsible for the variation in α. However, the results cannot be explained by invoking concentration quenching of triplets, for this quenching mode would affect only τ and would therefore appear only in β. In contrast, a quenching of fluoranthene's first-excited singlet state by either 10-MP or fluoranthene itself would give rise to the observed effect by causing a decline in ϕ_f with concentration. Nevertheless, fluoranthene does not self-quench, and its fluorescence lifetime is much too short for diffusional quenching by 10-MP to present a half-quenching concentration near 0.4 mM.[18] Since there is essentially no overlap between fluoranthene's emission spectrum and 10-MP's absorptions, resonance energy transfer and quenching by the "trivial" mechanism can be ruled out. In addition, fluorescence yield measurements on a solution which was 1 mM in both materials showed conclusively that no significant quenching of the fluoranthene singlet by the 10-MP occurred. In considering the remaining components of α, one can apparently also rule out ϕ_{tt} and $(1 - g)$ as factors varying with concentration. These quantities are fundamentally descriptive of the triplet fusion process, and one cannot easily conceive a concentration effect on the basic nature of the reaction. Thus one is led to the intriguing conclusion that the triplet yield itself apparently changes with concentration.

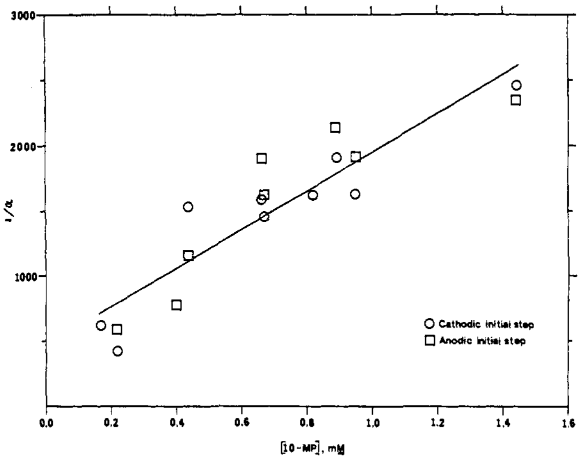

Figure 1. The relation between $1/\alpha$ and 10-MP concentration.

Although it is difficult to imagine such a systematic change in the nature of a single charge-transfer process, one can rationalize the observation with comparative ease by recognizing the possibility that there are two important charge-transfer reactions whose relative frequencies change with concentration. The particular case we consider here involves an equilibrium between the cation radical used in the system, $R'\cdot^+$, and its corresponding "dimer cation," $R'_2\cdot^+$

$$R'\cdot^+ + R' \rightleftharpoons R'_2\cdot^+ \qquad (i)$$

If such an equilibrium is operative, there obviously will be two distinct redox reactions

$$R'\cdot^+ + R\cdot^- \longrightarrow R' + R \qquad (j)$$

$$R'_2\cdot^+ + R\cdot^- \longrightarrow 2R' + R \qquad (k)$$

which may have different triplet yields.

Dimer cations have been postulated previously as precursors to excimer emission in ecl,[19] and they have actually been observed with a number of aromatic systems.[20-22] Still other pertinent studies have shown the facile formation of the "cation dimers," $(R'\cdot^+)_2$, from several ion radicals, including that of phenothiazine.[23] Though the latter association is seen only when no appreciable concentrations of parent substances exist, the nature of bonding in $(R'\cdot^+)_2$ and $R'_2\cdot^+$ is supposedly similar, so the observation of phenothiazine's cation dimer is perhaps indicative that the dimer cation also exists. Esr evidence indicates that the dimer cations have sandwich-like structures with the conjugated systems centered over one another.[20,21] For one species, the naphthalene dimer cation, the interplanar spacing has been estimated at 3–3.5 Å.[22] Experimentation with scale models of 10-MP showed that with a 3-Å spacing, the formation of a sandwich dimer could occur without important steric hindrances. Since the equilibrium constants for the aggregations have generally been calculated to be quite large,[19] production of the dimer during ecl generation seems quite feasible.

If the process were important in this instance, the values of ϕ_t reflected by α would be average values determined by the relation

$$\phi_t = (N_1\phi_1 + N_2\phi_2)/(N_1 + N_2) \qquad (6)$$

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(18) I. B. Berlman, H. O, Wirth, and O. J. Steingraber, *J. Amer. Chem. Soc.*, **90**, 566 (1968).

(19) B. Badger and B. Brocklehurst, *Nature (London)*, 219, 263 (1968).

(20) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965).

(21) O. W. Howarth and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **88**, 4514 (1966).

(22) B. Badger, B. Brocklehurst, and R. D. Russell, *Chem. Phys. Lett.*, **1**, 122 (1967).

(23) K. Kimura, T. Yamazaki, and S. Katsumata, *J. Phys. Chem.*, **75**, 1768 (1971).

The quantities N_1 and N_2 represent the overall rates of charge transfer for reactions j and k, respectively, and ϕ_1 and ϕ_2 are their triplet yields. However, N_1 and N_2 are probably proportional to the relative rates at which $R'\cdot^+$ and $R'_2\cdot^+$ diffuse into the reaction zone. If so, they are proportional to the products $D_1[R'\cdot^-]$ and $D_2[R'_2\cdot^+]$, in which the D's are diffusion coefficients and the concentrations are those of the region adjacent to the reaction zone. Thus one can replace eq 6 with

$$\phi_t = ([R'\cdot^+]D_1\phi_1 + [R'_2\cdot^+]D_2\phi_2)/([R'\cdot^-]D_1 + [R'_2\cdot^+]D_2) \quad (7)$$

If the two concentrations can be related by the equilibrium constant, K, for process i, then

$$1/\phi_t = (1 + K(D_2/D_1)[R'])/(\phi_1 + \phi_2 K(D_2/D_1)[R']) \quad (8)$$

Strictly, $[R']$ refers to the value adjacent to the reaction zone, but simulated concentration profiles show it to be practically indistinguishable from the bulk concentration C'.

There are at least three reasons for believing ϕ_2 to be much smaller than ϕ_1. On the basis of spectroscopic evidence, Badger and Brocklehurst have suggested that the stabilization associated with the formation of a dimer cation is typically 10–15 kcal/mol.[19] If so, the energy available from process k would be less than that obtainable from j by about the same amount. Thus it is likely that k is not even sufficiently energetic to populate the lowest available triplet state,[1,3] and so ϕ_2 is therefore zero. A complementary rationale for a low value of ϕ_2 can be built upon a consideration of the dimer's poorly defined, flexible structure, which features charge delocalization over a very large molecular volume. The structural flexibility may imply the existence of a large number of mechanical modes capable of dissipating the redox energies quite competitively with electronic excitation. This competitive dissipation may also be abetted by the dimer's low charge density. The hypotheses of Chandross and Sonntag[24] and of Hoytink[25] indicate that this property may produce a longer average duration for the charge-transfer event, which may, in turn, result in a decreased excitation probability. Certainly the sum of these considerations renders it likely that $\phi_1 \gg \phi_2$, even if ϕ_2 is not zero.

If one does indeed assume $\phi_1 \gg KC'(D_2/D_1)\phi_2$, then eq 8 reduces to the linear form

$$1/\phi_t = 1/\phi_1 + (KD_2/\phi_1 D_1)C' \quad (9)$$

Since $1/\alpha$ is proportional to $1/\phi_t$, this result is that which is actually observed from Figure 1, and the hypothesis of dimer cation participation is plainly consistent with the experimental results.

From the slope and intercept of the experimental plot, $\phi_1\phi_f\phi_{tt}/(1 - g)$ and KD_2/D_1 are estimated at $2.1 \pm 0.6 \times 10^{-3}$ and 3.1×10^3 l./mol, respectively. A consideration of molecular size indicates that D_2/D_1 should be 0.3–0.7, so K is probably about 6×10^3 l./mol. It is perhaps worth noting that this value is intermediate for the range of constants quoted by Badger and Brocklehurst for known dimerizations.[19]

An estimate of the true triplet yield of the fluoranthene anion–10-MP cation reaction could be made from $\phi_1\phi_{tt}\phi_f/(1 - g)$ if reliable data pertaining to ϕ_{tt}, ϕ_f, and g were available. A previous discussion of this point[7] has suggested that Parker's p_c values[26] for a triplet fusion process should approximate ϕ_{tt} and that the statistical figure of 0.38 could be used for g. Since Parker and his coworkers have reported $p_c = 0.02$ and $\phi_f = 0.21$ for fluoranthene,[26–28] one can estimate ϕ_1 at 0.3. Even though this estimate cannot be made with great precision, it does suggest that the efficiency of excitation in charge transfer is fairly high.

In evaluating the reliability of this quantitative information, it is important to recognize that its extraction depends upon one's knowledge of the overall charge-transfer rate and the cumulative number of reaction events. The data given above have involved the use of θ values and ω_n relationships which were derived for model systems not containing dimer cation participants. In extreme cases, of course, the presence of the association equilibrium will significantly perturb the concentration profiles near the electrode; hence it will affect θ and ω_n. By including equilibrium i in a series of digital simulations, we have investigated the interference presented by this effect. In each of the simulations, the dimer cation's diffusion coefficient was assumed to be 0.4 that of the monomer. This study showed the association to exert no significant effect on the charge-transfer rate for values of KC' less than 1000; hence its influence is properly disregarded in this work, wherein KC' probably never exceeds 10.

Although dimer cation formation has been directly observed only in systems containing one aromatic substance, it certainly seems possible that a cation radical could associate with any available aromatic species. Thus one must entertain the possibility that an aggregate ion involving a 10-MP cation and a fluoranthene molecule exists in the system at hand. If such a species were important, the analysis given above would be considerably more complex, because there is no assurance that the equilibrium constants for the two associations would be equal. However, the α data of Table I do not exhibit a dependence on generation sequence for the solutions containing significantly different fluoranthene and 10-MP concentrations. Since that kind of departure might be expected for dimerization of disparate K values involving both neutral aromatics, it is reasonable to assume that only $(10\text{-MP})_2^+$ is formed or else that both associations have nearly equal equilibrium constants.

There are several other features of these data deserving note, including three interesting, and perhaps interrelated, contrasts to the results obtained earlier with rubrene-containing systems.[13] The first of these is that the fractional participation of triplet intermediates in triplet–triplet annihilation is lower than in the latter case. That fraction is given by $2\phi_{ecl}/(1 - g)\alpha$, so these data suggest that 10–50% of the triplets engage in fusion. The equivalent figures for the rubrene systems range from 50 to 100%, and the comparison suggests that quenching of triplets may play a greater role in the present case. Certainly the fluoranthene triplet (at 53 kcal)[29] should be much more susceptible to en-

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ergy-transfer quenching than the low-lying rubrene triplet.

A second marked difference in this system's behavior, as compared to that of rubrene in benzonitrile, is that none of the luminescence parameters shows a dependence on the ion generation sequence. The dependence seen in the previous case was thought to result from ineffectual quenching of the rubrene triplet by its ion radicals, and it was further supposed that control of τ's magnitude was partially defaulted to anodically generated foreign substances. In the present case, the anodic potential excursions were less extreme than in the rubrene work; hence the lack of an effect of generation order may merely reflect the inconsequential production of foreign substances. In an alternative view, it may be that τ is totally governed by well-controlled substances, such as the ion radicals.

Triplet quenching by the ions may also bear importantly on the third important contrast these results show with the rubrene work: the concentration dependence of β. The ω_i *vs.* $(t_r/t_f)^{1/2}$ plots were, in all cases, highly linear; hence the existence of a time-independent $f(t)/\tau^2$ ratio is implied. At the higher concentrations, β decreases slowly with increasing concentration, but since the parameter's definition includes an inverse concentration term, this behavior seems entirely reasonable. At the lower concentrations, however, β quickly assumes very large values. At present it is not possible to thoroughly rationalize this phenomenon, but it should be noted that at low-substrate concentrations it is likely that the "walls" radical ions, which bound the reaction zone, will be less formidable than at higher concentrations. If so, as the concentrations of the aromatics are decreased, the control of τ may well shift from highly reproducible effects such as those associated with radical ions, to more obscure and variable ones, such as quenching by the solvent or trace impurities.

In addition to the foregoing contrasts, the results given here offer some noteworthy parallels with previous reports. Specifically, an extrapolation of α to higher concentrations indicates apparent triplet yields in accord with those measured earlier by sensitized isomerization of stilbene. Freed and Faulkner recorded a value of $7 \pm 2 \times 10^{-3}$ for the yield at [10-MP] = 2×10^{-2} *M*, compared to the value of 4×10^{-3} obtained from the current data by extrapolation. Considering the imprecision attendant to the extraction of ϕ_t from α and to the extrapolation, one can regard this agreement as encouraging support for the interpretation presented here.

It is further interesting to note that the triplet yields of fluoranthene–10-MP systems are comparable to those reported for the rubrene anion–cation reaction.[13] Moreover, it remains mildly surprising that the fractional participation of triplets in annihilation is so high, even though it is comparatively lower in this case. Thus one can reiterate the earlier conclusion that the low values of ϕ_{ecl} result primarily from inefficiencies in the annihilation process itself, rather than from low excitation yields.

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Mechanism of Ozonolysis. Microwave Spectrum, Structure, and Dipole Moment of Ethylene Ozonide

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Abstract: The structure of ethylene ozonide, $H_2\overline{COOCH_2O}$, has been determined from the microwave spectra of seven isotopic species. The half-chair conformation with C_2 symmetry has been established and there is no evidence for free or hindered pseudorotation. The parameters determined for the ring atoms are as follows: $r(\mathrm{C{-}O_e}) = 1.436 \pm 0.006$ Å, $r(\mathrm{C{-}O_p}) = 1.395 \pm 0.006$ Å, $r(\mathrm{O_p{-}O_p}) = 1.470 \pm 0.015$ Å, $\angle\mathrm{COC} = 102.83 \pm 0.44°$, $\angle\mathrm{COO} = 99.23 \pm 0.38°$, $\angle\mathrm{OCO} = 106.25 \pm 0.64°$, and the dihedral angles $\tau(\mathrm{C_1O_eC_2O_p}) = -16.60 \pm 0.40°$, $\tau(\mathrm{C_1O_pO_pC_2}) = -50.24 \pm 1.26°$, and $\tau(\mathrm{O_eCO_pO_p}) = 41.27 \pm 0.96°$. The dipole moment is $1.09 \pm .01$ D. Three excited vibrational states of the normal isotopic species arising from the asymmetric ring-bending vibration have been assigned. The ozonolysis of $HDC{=}CH_2$ yielded six isotopic species of ethylene ozonide including two singly deuterated ozonides, three doubly deuterated ozonides, and the undeuterated ozonide. This result was analyzed in view of several proposals for the mechanism of ozonolysis.

The mechanism of the ozonolysis of alkenes has recently been reviewed by Murray.[1] The most extensive mechanistic scheme previous to 1960 was proposed by Criegee.[2] According to his proposal (Scheme I), the initial ozone–alkene adduct I fragments to give a zwitterion II and a carbonyl compound III. The normal ozonide is formed by the recombination of II and III. Experimental data have accumulated which cannot be rationalized on the basis of the Criegee mechanism. In particular, the discovery that cis–

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