Mechanisms of Chemiluminescent Electron-Transfer Reactions. II. The Triplet Yield of Electron Transfer in the Fluoranthene–10-Methylphenothiazine System

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Abstract: The yield of triplets from the electron-transfer reaction occurring in *N*,*N*-dimethylformamide between the anion radical of fluoranthene and the cation radical of 10-methylphenothiazine has been measured by intercepting the triplet species with *trans*-stilbene. The average yield obtained was 0.7%. The results are discussed in terms of possible process mechanisms.

Certainly one of the fundamental quantities of interest for any reaction generating excited states is the yield of those states. As a result of their short lifetimes and generally low concentrations, such species often elude detection, and quantitative measurements are rarely achieved. Recent mechanistic studies of chemiluminescent electron-transfer processes have indicated that the direct generation of intermediate excited-state molecules during an electron transfer is fundamental to the overall luminescence process.[1,2] The assessment of these excited-state yields has become quite important because they obviously bear significantly upon the overall efficiency of the luminescence process. In addition, such knowledge can clarify the relative importance of the various kinetic steps leading to emission.

The demonstration that a triplet species is a necessary intermediate for luminescence from certain energy-deficient systems[2] has suggested the possibility of measuring the triplet yield by a quenching technique. It seems clear that if one could use as a triplet quencher a molecule which undergoes an irreversible photochemical transformation from its lowest triplet state, one could effectively measure the number of triplets generated during electron transfer by determining the number of photoproduct molecules arising from the reaction.

Previous work has shown that *trans*-stilbene acts as an effective quencher of the chemiluminescence arising from the reaction between the fluoranthene anion radical and the 10-methylphenothiazine (10-MP) cation radical.[2] This observation has been interpreted in terms of triplet–triplet energy transfer from the fluoranthene triplet to *trans*-stilbene, an act which inhibits the normal generation of the emitting fluoranthene singlet *via* triplet–triplet annihilation.

Since the *trans*-stilbene triplet undergoes isomerization to the cis form, the fluoranthene–10-methylphenothiazine–*trans*-stilbene system seems well suited for a measurement of the triplet yield of electron transfer. The sensitized cis–trans isomerization of stilbenes has been studied extensively,[3] and quantum yields have been obtained for a wide variety of sensitizers. Moreover, the facile separation of the two isomers *via* vapor-phase chromatography offers a distinct advantage in the measurement of low excited-state yields. Finally, one can produce a known number of reaction events by generating reactants coulometrically at controlled potential.

We have executed experiments of the type outlined here, and we wish to report what we believe to be the first data pertaining to the excited-state yield of any electron-transfer reaction in a fluid medium.

Experimental Section

The *trans*-stilbene employed in this work was Eastman scintillation grade material which was further purified by recrystallization from ethanol. Vapor-phase chromatography showed no detectable *cis*-stilbene in the recrystallized trans compound. *cis*-Stilbene (used only to establish chromatographic retention times) was purchased from the Aldrich Chemical Co. and was employed without further purification. Scintillation grade fluoranthene produced by Eastman Organic Chemicals was used as received. Eastman also manufactured the 10-methylphenothiazine used in these experiments, but it was recrystallized three times from benzene beforehand.

N,*N*-Dimethylformamide (DMF) served as the solvent in all experiments. It was furnished by Matheson Coleman and Bell (bp 152–154°) and was purified extensively by a previously published procedure.[4] Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) manufactured by Southwestern Analytical Chemicals was employed as the supporting electrolyte after drying *in vacuo*.

Gas chromatographic analyses were performed using a 4-ft column of 20% Apiezon L on 60–80 Chromosorb W operated at 220°. Detection was *via* thermal conductivity and chromatograms were displayed on a Sargent Model MR recorder equipped with a Disc Integrator.

Electrochemical generation of the reactant radical ions was carried out in a cell designed to hold about 50 ml of solution and capable of being evacuated to less than 10^{-5} Torr. The anode was a three-turn helix about 2.5 cm in diameter which was fabricated from 22-gauge platinum wire. Its helical axis was oriented normal to the face of a 5-cm-diameter mercury pool, which served as the cathode. The apparent surface area of the cathode was about three times that of the anode. An aqueous Ag|AgCl, KCl (saturated) reference electrode was centered in the anode spiral, and solution contact was made by an integral agar bridge and an asbestos fiber. The solution was stirred by a magnetic bar floating on the mercury surface. A Wenking Model 61RS potentiostat exercised control over the electrolysis, and current–time curves were displayed on the same recorder used for gas-chromatographic analysis.

Results

The trapping of excited states by means of energy transfer places several requirements on the acceptor

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(3) 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).

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molecule. Since, in the system studied here, the excited states are generated by radical ion annihilation, the acceptor must be chemically inert toward these ions. It must also be neither reduced nor oxidized at the electrodes in the potential range of interest. Finally, the energy levels should be such that the rate of energy transfer is diffusion controlled, thereby ensuring effective trapping.

Table I summarizes the pertinent redox potentials and triplet energy levels for the compounds employed in this study. It is clear from the table that *trans*-stilbene fulfills quite satisfactorily these requirements for an effective, but chemically inert, quenching agent to be used in the fluoranthene–10-MP system. Triplet–triplet energy transfer between fluoranthene and *trans*-stilbene has been demonstrated.[5] Since the triplet state of fluoranthene lies some 6 kcal above that of *trans*-stilbene[3,6] but 4 kcal below that of *cis*-stilbene, energy transfer should occur nearly at the diffusion-controlled rate to *trans*-stilbene, but very inefficiently to the cis isomer.[7] The cyclic-voltammetric peak potential for reduction of *trans*-stilbene is 0.4 V more cathodic than that of fluoranthene, and the stilbene oxidation, as is that for fluoranthene, is so anodic that it is obscured by the anodic background limit of the DMF–TBAP system. In contrast, 10-MP is easily oxidized, but it is not reduced before the cathodic background limit. The reductions of fluoranthene and *trans*-stilbene and the oxidation of 10-MP are reversible, so one can be confident that generation of the desired ion radical of fluoranthene and 10-MP occurs without simultaneous (or subsequent) generation of the corresponding ions of *trans*-stilbene. Earlier studies of these radical ions indicate a high degree of stability in DMF and other aprotic solvents. No significant decay of the 10-MP cation or the fluoranthene anion would be expected in this work. Finally, cyclic-voltammetric studies performed earlier show no side reactions between *trans*-stilbene and either reactant radical ion.[2]

Table I. Voltammetric Peak Potentials[a] and Triplet Energy Levels

Compound (R)	E_p (R/R$\cdot^+$)	$-E_p$ (R/R$\cdot^-$)	E_T, kcal
Fluoranthene	NO[b]	1.70	53
10-MP[c]	0.90	NR[d]	54[e]
trans-Stilbene	NO	2.11	47
cis-Stilbene	NO	2.16	57

[a] All values are taken from ref 2. The data are for DMF solutions with 0.1 *M* TBAP supporting electrolyte and are referred to Ag|AgCl; KCl (saturated). [b] NO = not oxidized. [c] 10-MP = 10-methylphenothiazine. [d] NR = not reduced. [e] Estimated from value for phenothiazine. See ref 8.

Solutions containing fluoranthene, 10-MP, and *trans*-stilbene were prepared in DMF containing 0.1 *M* TBAP as the supporting electrolyte. These solutions were subjected to several freeze–pump–thaw cycles to remove oxygen. In each case the final pressure over the frozen solution was never more than 5×10^{-5} Torr. The reference electrode was placed in the cell under a positive pressure of helium, then the cell was sealed, leaving the solution under a helium blanket.

During the electrolysis the anode potential was controlled potentiostatically to +1.00 ± 0.01 V *vs.* Ag|AgCl, KCl (saturated); thus only the 10-MP radical cation was generated at the anode. The cathode potential was not controlled potentiostatically. Nevertheless the experimental system was designed such that the cathode was maintained at a potential somewhat anodic of the mass-transfer-limited region of the current–potential curve for fluoranthene reduction. Two design factors, the large surface area of the cathode and the effectiveness of stirring in the cathode region, tend to reduce the average current density at that electrode to a value below that of the anode. In addition, a large fluoranthene concentration served to improve the buffering action by making the mass-transfer-controlled region less accessible. These conditions ensured that the only reaction occurring at the cathode was that of fluoranthene reduction. Thus in each experiment, equal numbers of fluoranthene anions and 10-MP cations were generated per unit time, and the stirring served to bring them together for reaction in the bulk. The total number of reaction events could be derived from the charge passed, which was measured by integrating the current–time curve.

At the end of the electrolysis the solution was removed from the cell and was concentrated to a tenth its former volume *in vacuo*. Portions were then subjected to vapor-phase chromatography, and from the ratios of the integrated peak areas for the *cis*- and *trans*-stilbenes, the total number of triplet states formed during electrolysis was calculated. For the purpose of this calculation, the quantum yield for the isomerization (trans → cis) was taken to be 0.41. This value was obtained by Hammond, *et al.*,[3] in a study of the *trans*-stilbene isomerization sensitized by fluorenone, a sensitizer with nearly the same triplet energy as fluoranthene.

From the coulometric data and the assessment of the total number of triplets formed, the triplet yield of the electron-transfer reaction was calculated. The results are shown in Table II together with additional pertinent experimental data. In the table, Q represents the charge passed during electrolysis, trans/cis is the ratio of *trans*- to *cis*-stilbene in the electrolyzed solution (ratio of chromatographic peak areas), and ϕ_T is the calculated triplet yield for electron transfer.

Table II. Triplet State Yields and Pertinent Experimental Data

Initial concentrations, m*M*						
Fluoranthene	10-MP	*trans*-S[a]	Time,[b] min	Q, C	Trans/cis	ϕ_T
49.4	19.8	29.9	130	86	600	0.007
30.4	20.9	30.0	83	70	600	0.008
30.2	20.4	30.8	530	274	240	0.005

[a] *trans*-Stilbene. [b] Electrolysis time.

Several precautions were taken to ensure that *cis*-stilbene was generated neither photochemically nor thermally from ambient conditions. All electrolyses and measurements were performed in subdued light at a temperature of 24–27°. A control experiment involving the solution used in the third run shown in Table II failed to show the presence of *cis*-stilbene after the solution was carried through all of the experimental steps except the electrolysis. During any particular ex-

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periment, the observed current was exceptionally constant. This fact provides notable evidence for a high degree of reversible radical annihilation to starting products and for the absence of any important side reactions.

Discussion

The experimental results shown in Table II indicate that the triplet yield is about 0.7%, thus 1000 electron-transfer events produce only about 7 triplets. Chemiluminescence in this system is therefore seemingly quite inefficient, especially since the electron transfer is just the initial step toward the formation of the emitting fluoranthene singlet as a final product.

One particularly interesting aspect of the fluoranthene–10-MP system is that the triplet states of both product molecules are apparently accessible to the electron transfer. The redox reaction yields 2.6 eV per event or about 60 kcal/mol.[2] The fluoranthene triplet energy is 53 kcal/mol, but similar data do not exist for 10-MP. However, the lowest triplet of phenothiazine lies at about 54 kcal/mol,[8] and it seems reasonable to assume that the 10-MP triplet is near this value.

Certainly the fate of any 10-MP triplets produced in the system is an issue of importance to this study. If, as is indicated, the fluoranthene triplet does lie below that of 10-MP, it is possible that the fluoranthene molecule generated in each product pair acts as a rapid and effective quencher for the nearby 10-MP triplet. Thus the effect of this view is that only fluoranthene triplets emerge from the electron-transfer process. On the other hand, it is possible that energy transfer is not effective between fluoranthene and 10-MP, in which case both triplets exist independently if both are formed.

The chemiluminescence spectrum definitely has the structure of fluoranthene fluorescence,[2] so the fluoranthene triplet is apparently the predominant precursor to emission. This fact may support fluoranthene's role as an effective quencher of 10-MP triplets, but it can be alternately explained in terms of exclusive generation of fluoranthene triplets during electron transfer or in terms of a failure by 10-MP to undergo triplet–triplet annihilation. In the interest of completeness, it is worth noting here that a minor emission component resulting from 10-MP cannot be resolved from the fluoranthene emission because the fluorescence spectra of the two species overlap extensively. Thus at this time one cannot exclude the 10-MP triplet as a possible product of electron transfer.

The essential elements of these thoughts are summarized in the following reaction scheme.

$$\mathrm{FA}\cdot^{-} + \text{10-MP}\cdot^{+} \longrightarrow {}^{3}\mathrm{FA}^{*} + \text{10-MP} \tag{1}$$

$$\mathrm{FA}\cdot^{-} + \text{10-MP}\cdot^{+} \longrightarrow \mathrm{FA} + {}^{3}\text{10-MP}^{*} \tag{2}$$

$$\mathrm{FA}\cdot^{-} + \text{10-MP}\cdot^{+} \longrightarrow \mathrm{FA} + \text{10-MP} \tag{3}$$

$$\mathrm{FA} + {}^{3}\text{10-MP}^{*} \longrightarrow {}^{3}\mathrm{FA}^{*} + \text{10-MP} \tag{4}$$

$${}^{3}\mathrm{FA}^{*} + {}^{3}\mathrm{FA}^{*} \longrightarrow {}^{1}\mathrm{FA}^{*} + \mathrm{FA} \tag{5}$$

$${}^{3}\mathrm{FA}^{*} \longrightarrow \mathrm{FA} \tag{6}$$

$${}^{3}\text{10-MP}^{*} \longrightarrow \text{10-MP} \tag{7}$$

$${}^{1}\mathrm{FA}^{*} \longrightarrow \mathrm{FA} + h\nu \tag{8}$$

In this scheme, FA and 10-MP represent fluoranthene and 10-methylphenothiazine, respectively. The fluoranthene anion radical is written as $\mathrm{FA}\cdot^{-}$, and $\text{10-MP}\cdot^{+}$ symbolizes the 10-MP cation radical. An asterisk denotes electronic excitation to either the lowest triplet or the first excited singlet, the states being distinguished by numeric superscripts. If a 10-MP emission component is needed present, one can easily rationalize it by including the additional reactions.

$${}^{3}\text{10-MP}^{*} + {}^{3}\text{10-MP}^{*} \longrightarrow {}^{1}\text{10-MP}^{*} + \text{10-MP} \tag{9}$$

$${}^{1}\text{10-MP}^{*} \longrightarrow \text{10-MP} + h\nu \tag{10}$$

This system also presents an interesting opportunity for the "mixed" annihilation of ${}^{3}\mathrm{FA}^{*}$ with ${}^{3}\text{10-MP}^{*}$. Parker has shown that such a reaction takes place between anthracene and naphthacene triplets;[9] but both present compounds have large Stokes' shifts in their fluorescence spectra, hence their singlet energies are poorly defined. As a consequence, it is not clear what product state would result from the mixed annihilation if it did occur.

Regardless of the role that ${}^{3}\text{10-MP}^{*}$ plays in the overall emission scheme, large concentrations of *trans*-stilbene (*trans*-S) should effectively quench both triplets by the reactions

$${}^{3}\text{10-MP}^{*} + \textit{trans}\text{-S} \longrightarrow \text{10-MP} + {}^{3}\textit{trans}\text{-S}^{*} \tag{11}$$

$${}^{3}\mathrm{FA}^{*} + \textit{trans}\text{-S} \longrightarrow \mathrm{FA} + {}^{3}\textit{trans}\text{-S}^{*} \tag{12}$$

$${}^{3}\textit{trans}\text{-S}^{*} \longrightarrow \textit{cis}\text{-S} \tag{13}$$

Since both triplets are intercepted, ϕ_{T} should be regarded as the overall triplet yield of the electron-transfer process.

Obviously any critical assessment of the value of this estimate for the triplet yield must involve a careful examination of the experimental conditions to be certain that ϕ_{T} is indeed that which it represents. One prerequisite for an accurate measurement of ϕ_{T} by the method used here is that essentially all triplet species generated in the electron-transfer step be quenched by the *trans*-stilbene. This requirement means that the quenching rate must be at least an order of magnitude greater than the sum of the rates of all other processes depleting the donor triplet supply. Hence the pseudo-first-order quenching rate constant, given by the product of the second-order quenching rate constant and the *trans*-stilbene concentration, must be considerably greater than the reciprocal lifetimes of the donor triplets in the absence of *trans*-stilbene. Since the quenching rate is likely to be diffusion controlled or nearly so, one can estimate the value of k_{q} from the von Smoluchowski–Debye equation.[10,11] For DMF at 25°, one obtains $k_{\mathrm{q}} = 8.3 \times 10^{9}$ l./(mol sec). Thus the pseudo-first-order quenching constant, $k_{\mathrm{q}}[\textit{trans}\text{-stilbene}]$, is about $2 \times 10^{8}\ \mathrm{sec}^{-1}$ for these experiments.

One does not know the triplet lifetimes in the absence of *trans*-stilbene, of course, but ordinarily they are likely governed primarily by quenching from trace impurities in the solvent system, most particularly by oxygen.[12,13] In solutions which are degassed painstakingly, such lifetimes can be as great as 10 msec,[12,14]

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but one usually would expect them to be in the range from 10 μsec to 1 msec. Of course very rapid internal processes in the fluoranthene and 10-MP molecules could conceivably deactivate their triplets, but delayed fluorescence studies of fluoranthene indicate that its triplet lifetime is reasonably long in deoxygenated fluid solutions.[13] Unfortunately, such data are not available for 10-MP, but phosphorescence studies of phenothiazine do not indicate that fast, internal triplet deactivation processes are operative in that species.[8]

One additional complication encountered in this reaction system is the fact that the radical ions are themselves very efficient triplet quenchers.[14] They will therefore compete with *trans*-stilbene for the available triplet species. The magnitude of this effect can be assessed on the basis of simple calculations performed with the data in Table II. The ratio of the charge passed, Q, to the product of the electrolysis time and the Faraday gives the average rate of reactant generation at each electrode in moles per unit time. Since the current was nearly constant throughout each experiment, this average does not significantly deviate from the instantaneous rate of generation at any time. For the three experiments tabulated above, the rate is about 10^{-7} mol/sec. If one assumes that the reaction takes place uniformly throughout the 50-ml solution volume, and if one takes the mixing and reaction time to be 1 sec, one achieves an estimate for the steady-state radical-ion concentration of about 10^{-6} M. This figure probably can be taken as a fairly reliable upper limit. The ions probably quench at the diffusion-controlled rate; perhaps even faster if possible long-range effects arising from their paramagnetism or from resonance energy transfer apply. Taking these possibilities into account by using an upper-limit rate constant for radical-ion quenching of 10^{11} l./(mol sec), one arrives at a pseudo-first-order quenching rate of 10^{5} sec^{-1}. This figure is not comparable to the *trans*-stilbene quenching rate of 2×10^{8} sec^{-1} calculated above. All of these factors considered, it seems quite likely that the fluid-solution triplet lifetimes are a good deal greater than 100 nsec in the absence of *trans*-stilbene. One must therefore expect a stilbene quenching efficiency approaching 100%.

These considerations coupled with the fast and very complete redox reaction certainly support the contention that the ϕ_T values reported in Table II are truly representative of the system studied. It is also worth noting that they suggest a fundamental reason underlying the low emission efficiencies reported for other systems.[15,16]

In searching for reasons to explain the inefficient production of excited states, the fundamental issue seems to be the actual rate at which an electron is transferred from the anion to the cation. One reason is that if the electron transfer is slower than the time scale of molecular vibrations, the reaction enthalpy has a strong likelihood of being dissipated in the molecular vibrations and subsequently by collisional transfer to solvent molecules.[17] On the other hand, if the electron transfer could be made to occur more rapidly, more efficient production of excited states could result. Two possibilities for speeding up this reaction involve increasing the coulombic attraction between the reactants. One of these is to use solvents of lower solvating power (*i.e.*, lower dielectric constant than DMF), and the other is to employ radical dications and dianions as reactants. In this regard it is interesting to note that Helfrich and Schneider have observed efficient exciton production from electron–hole recombinations in anthracene crystals, where dielectric effects tending to reduce coulombic attraction may be minimized.[18]

On the other hand, it is possible that the low triplet yield obtained in this study merely reflects large alterations in molecular structure accompanying excitation in this particular system. In the vibrational structure of absorption and fluorescence spectra and in the relatively large Stokes' shifts for fluorescence, one has substantial evidence that both fluoranthene and 10-MP undergo considerable molecular reorganization upon excitation to the first excited singlet state. If, in a similar manner, large changes in geometry accompanied the conversion of the radical ions of these compounds to the lowest molecular triplet states, it would not be at all surprising that the triplet yield of electron transfer is low.

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