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ABSTRACT

The ECL emission from energy-deficient mixed aromatic hydrocarbon (AHC) acceptor and tetrathiafulvalene (TTF) donor systems has been investigated in acetonitrile. Radical ion annihilation involving TTF radical cations and AHC radical anions was found to result entirely in acceptor fluorescence emission. Energy considerations show that AHC triplet formation followed by triplet-triplet annihilation to produce the AHC first excited singlet state is the most probable mechanism for the observed ECL. The intermediacy of exciplexes in the ECL process was not observed experimentally.

Tetrathiafulvalene (TTF) has been the subject of intense investigation for its role as a donor in highly conducting one-dimensional solid-state complexes (1-3), such as, for example, its simple salt with tetracyanoquinodimethane (TTF-TCNQ) (4). These conducting salts form a class of ground state organic charge transfer complexes. Less is known about the potential of TTF as a donor in excited state reactions such as: (*i*) the formation of excited state complexes (exciplexes) via direct photoexcitation; and (*ii*) the formation of excited states via radical ion annihilation involving electron transfer from acceptor radical anions ($A^{-\cdot}$) to donor radical cations ($D^{+\cdot}$), electrogenerated chemiluminescence (ECL). As judged from its ionization potential (6.95 ± 0.1 eV) (5) and oxidation potential ($+0.33$V *vs.* SCE, 0.1M TEAP in acetonitrile) (6) the donor strength of TTF should be comparable to that of amines (*e.g.*, IP = 6.86 eV for triphenylamine and 7.50 eV for triethylamine) (7) which as a donor class have been observed to form exciplexes efficiently in both the photoexcitation (8-11) and ECL (12-17) modes. Many examples of ECL generation in mixed systems using amines as donors have been investigated (12-15) and on a purely speculative basis, behavior similar to that using N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) as a donor ($E_{p,a} = +0.24$V *vs.* SCE, 0.1M TBAP in DMF) (12) might be expected for TTF.

In addition a major goal in ECL studies has been to search for donors and acceptors which form highly stable radical ions in an attempt to extend the long-term lifetime of ECL systems (18, 19). The stability of the TTF radical cation by controlled potential reversal bulk coulometry on a time scale of a few hours has previously been observed (20) which makes it considerably more stable than amine oxidation in general [TMPD (16) and tri-*p*-tolylamine (TPTA) (17) are exceptions]. The stability of mixed TTF donor-acceptor ECL systems is therefore of interest. The following work represents a survey of mixed ECL systems consisting of TTF as the donor and various aromatic hydrocarbons as acceptors in acetonitrile solution undertaken as an initial effort to characterize TTF as a donor in excited state reactions.

Experimental

Chemicals.—Rubrene (Aldrich) was dissolved in hot xylene and precipitated with cold ethanol under nitrogen in subdued light twice. Ru(bipy)$_3$(ClO$_4$)$_2$ was prepared by metathesis with excess NaClO$_4$ in a water-ethanol mixture from Ru(bipy)$_3$Cl$_2 \cdot 6$H$_2$O purchased from G. F. Smith Chemical Company. Further purification of Ru(bipy)$_3$(ClO$_4$)$_2$ was accomplished by two recrystallizations from acetonitrile. Anthracene (Matheson, Coleman, and Bell) was recrystallized once from benzene and sublimed twice. Diphenylanthracene (DPA; Aldrich) was sublimed twice and then zone-refined. Dimethylanthracene (DMA; Aldrich, 99%) was sublimed twice under vacuum at 120°C. *Trans*-stilbene was sublimed twice before use. Tetrathiafulvalene (Aldrich) was either sublimed twice under high vacuum at 60°C or was first recrystallized once from dry, degassed hexane and then sublimed twice. No difference in experimental results was observed between the two purification procedures. Tetra-*n*-butylammonium perchlorate (TBAP) purchased from Southwestern Analytical Chemical Company was used as received after drying under vacuum at 100°C for 24 hr. Benzonitrile and acetonitrile were both purchased from Matheson, Coleman, and Bell. A previously reported procedure was used to purify benzonitrile (21). Acetonitrile was dried and degassed by three transfers from dry P$_2$O$_5$ under vacuum. The solvent was stored under vacuum or in an inert helium atmosphere. Benzene (Fisher) and tetrahydrofuran (Matheson, Coleman, and Bell) were refluxed over sodium-benzophenone and subsequently distilled and stored in an inert nitrogen or helium atmosphere.

Apparatus and procedures.—Cyclic voltammetry and ECL experiments were carried out in the controlled potential mode using a Princeton Applied Research (PAR) Model 173 potentiostat and a Model 175 universal programmer. The voltage analog output from a PAR Model 176 current follower was either recorded directly using a Houston Instrument Model 2000 X-Y recorder or monitored and subsequently recorded via a Nicolet Model 1090A digital oscilloscope. Electrochemical cells of a conventional three-electrode design were used for cyclic voltammetry and ECL and were similar to ones previously described (22,23). Emission spectra, fluorescence, and ECL were obtained using an Aminco-Bowman spectrophotofluorometer.

Solutions were prepared under an inert helium atmosphere in a Vacuum Atmospheres Model HE-43-2 dry box. Since TTF was found to undergo photodecomposition in dry degassed solutions of acetonitrile, ECL solutions were exposed to a minimum of room light. A background cyclic voltammogram was taken of the solvent-supporting electrolyte (0.1M TBAP) system before each study to insure the absence of residual oxygen and electroactive trace contaminants. ECL was generated in the pulse mode (cyclic double

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Table I. Electrochemical parameters for various acceptors in the presence and absence of TTF

Compound	Oxidation[a]			Reduction[a]		
	E_{pa} (V)[b] ±0.02	ΔE_p (mV) ±5	i_{pc}/i_{pa} ±5%	E_{pc} (V)[b] +0.02	ΔE_p (mV) ±5	i_{pa}/i_{pc} ±5%
Anthracene	+1.22	—	—	−2.12	70	0.91
	(+1.25)	—	—	(−2.09)	(70)	(0.87)
Rubrene[c]	+0.83	110	0.99	−1.60	100	0.92
	(+0.83)	(100)		(−1.65)	(100)	(0.93)
DMA	+1.07	80	0.83	−2.12	70	0.93
	(+1.07)	(80)	(0.87)	(−2.14)	(80)	(0.94)
DPA	+1.17	70	0.93	−2.04	70	0.99
	(+1.17)	(70)	(0.79)	(−2.03)	(70)	(0.98)
trans-stilbene[d]	+1.43	—	—	−2.37	70	0.98
	(+1.45)	—	—	(−2.30)	(60)	(0.66)
Ru(bipy)$_3$$^{+2}$	+1.28	70	1.0	−1.41	70	0.90
	(+1.25)	(70)	(0.94)	(−1.46)	(70)	(0.85)

[a] Values in parenthesis are for the acceptor in the presence of TTF. Solutions contain 0.1M TBAP in acetonitrile unless otherwise noted. Acceptor concentrations are in the range 3.4 × 10⁻³-1.2 × 10⁻²M. TTF concentrations are in the range 2.1 × 10⁻³-7.1 × 10⁻³M.
[b] Cyclic voltammetric peak potentials using a Pt disk electrode in V *vs.* Ag QRE corrected to V *vs.* SCE using $E_{pa}(TTF^+/TTF)$ = +0.34V *vs.* SCE.
[c] In benzonitrile.
[d] [*Trans*-stilbene] = 8.2 × 10⁻³M; [TTF] = 2.1 × 10⁻³M.

potential step waveform) and in general ECL experiments were carried out on the same solutions previously characterized by cyclic voltammetry.

Results

Electrochemistry.—The electrochemical parameters listed in Table I show that except for the case of *trans*-stilbene and TTF, the interaction of donor and acceptor neutral and radical ion species on the cyclic voltammetric time scale is small. Values of E_p and ΔE_p, cyclic voltammetry peak potentials and peak separations, and i_{pc}/i_{pa} or i_{pa}/i_{pc}, peak current ratios for oxidation and reduction, respectively, were monitored for the acceptor in the presence and absence of TTF and show only slight variations. Deviations from ideal electrochemical behavior (*e.g.*, $\Delta E_p > 60$ mV) or slight shifts in values of E_p can be attributed to: (*i*) uncompensated cell resistance as in the case of using benzonitrile as a solvent; or (*ii*) the use of an unshielded Ag quasireference electrode in contact with the bulk electrochemical solution. For most of the systems examined, including *trans*-stilbene and TTF, values for ΔE_p and i_{pc}/i_{pa} for the two reversible one-electron oxidations of TTF were 70 mV and 1.00 ± 0.02, respectively, both in the absence and presence of the various acceptors. The only exception occurred for TTF in benzonitrile in which the second TTF oxidation wave overlapped with the first oxidation wave of rubrene and a large cathodic current spike was observed for dication reduction upon potential reversal. Large cathodic current spikes for the reduction of the TTF dication were frequently observed in nonpolar solvents and nonpolar solvent mixtures, such as tetrahydrofuran and benzene-acetonitrile (50:50). Unfavorable electrochemistry for TTF oxidation prevented ECL experiments in pure tetrahydrofuran. Under the experimental conditions of cell design and at a potential scan rate of 200 mV sec⁻¹, a value of 70 mV represents the peak separation expected for a reversible one-electron transfer in acetonitrile.

Examination of Table I reveals that in some cases values of i_{pa}/i_{pc} for reduction of the acceptor in the presence of TTF are significantly less than in the absence of TTF. Such behavior is represented in the extreme case by the *trans*-stilbene-TTF system in which increasing the concentration of TTF results in increasing values of i_{pc} and decreasing values of i_{pa}/i_{pc}. Limiting behavior for [TTF] > [*trans*-stilbene] is characterized by the complete absence of anodic current upon potential reversal following *trans*-stilbene reduction and by values of $i_{pc}/v^{1/2}$ which are approxi-

mately 2.8-3.0 times larger than those in the absence of TTF. A plot of $i_{pc}/v^{1/2}$ *vs.* log v was approximately linear (slight curvature was observed for extreme high and low values of v) for a solution consisting of 5.4 × 10⁻³M TTF, 1.2 × 10⁻²M *trans*-stilbene, and 0.1M TBAP in acetonitrile. The reaction(s) represented by these results have not been thoroughly investigated but the electrochemical data is consistent with a reaction of the *trans*-stilbene radical anion with TTF neutral as a first step forming a product which undergoes further reduction. A similar reaction may occur to a much lower degree in some of the other aromatic hydrocarbon acceptor-TTF systems.

Figures 1 and 2 illustrate the cyclic voltammograms resulting from the two extreme cases of electrochemical behavior observed in this investigation: (*i*) slightly interacting, anthracene-TTF; and (*ii*) strongly
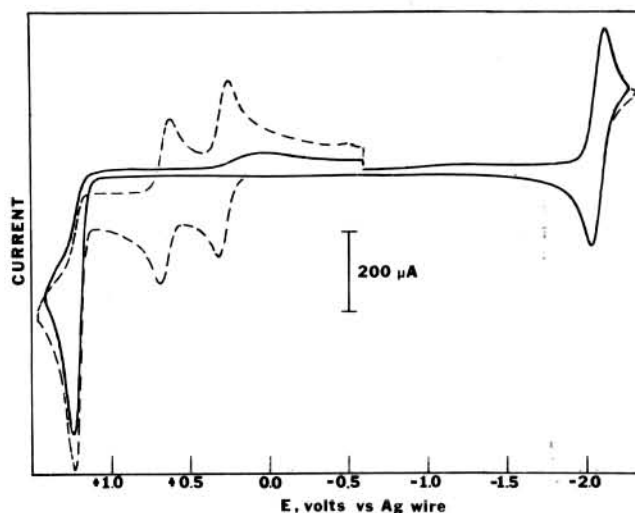

Fig. 1. First scan cyclic voltammograms of (———) 1.2 × 10⁻²M anthracene and (− − −) 1.2 × 10⁻²M anthracene and 7.1 × 10⁻³M TTF in a 0.1M TBAP-acetonitrile supporting electrolyte-solvent system using a scan rate of 200 mV sec⁻¹.

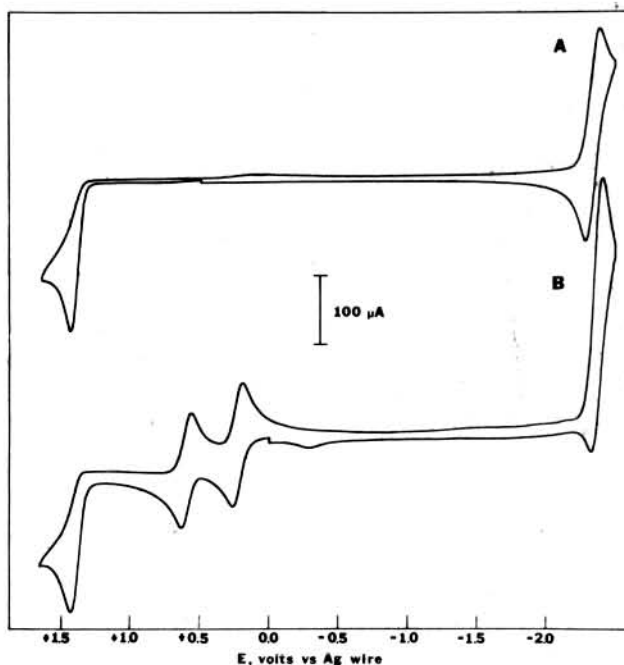Fig. 2. First scan cyclic voltammograms of (A) 1.1 × 10⁻²M *trans*-stilbene; and (B) 1.1 × 10⁻²M *trans*-stilbene and 4.9 × 10⁻³M TTF in a 0.1M TBAP-acetonitrile supporting electrolyte-solvent system using a scan rate of 200 mV sec⁻¹.

interacting, *trans*-stilbene-TTF. In Fig. 1 and 2 a small cathodic wave in the range 0.0-+0.50V *vs.* Ag QRE is observed upon potential reversal following the anodic scan in the absence and presence of TTF. These waves can be attributed to the reduction of an oxidation product of the unstable anthracene and *trans*-stilbene radical cations. An anodic wave at −0.4V *vs.* Ag QRE found after potential reversal following *trans*-stilbene reduction is also observed for *trans*-stilbene in the presence of TTF. For all of the systems examined except *trans*-stilbene and TTF no additional product waves are observed when the applied potential limits are set to allow only the one electron oxidation of the donor (TTF) and the one electron reduction of the acceptor (AHC).

ECL.—Of the six donor-acceptor systems examined in this work, four exhibited ECL. The ECL was generated in the controlled potential mode employing a cyclic double potential step waveform alternately generating the acceptor radical anion and the donor radical cation. The ECL spectra obtained for three of the systems in Table II are shown in Fig. 3. The luminescence in all three cases can be attributed entirely to DPA, DMA, and rubrene fluorescence when reabsorption at the appropriate donor-acceptor concentrations is taken into account. In the case of DMA an additional component due to excimer emission contributes to the ECL spectrum. The observed spectral distributions, relative peak intensity ratios, and peak energies compare well with previously published ECL spectra of the isolated acceptors (12, 24, 25). The ECL spectra also essentially match the fluorescence spectra taken of the original electrochemical bulk solutions either at full concentration or diluted by a factor of 1/10 in a 1.00 cm path length fluorescence cell taken using a right angle illumination geometry. In addition fluorescence spectra of the bulk electrochemical solutions compare well in spectral distribution and peak energies with fluorescence spectra of the isolated acceptors taken in acetonitrile or other solvents (24, 26). The ECL spectrum of TTF and DMA was also taken in a relatively nonpolar acetonitrile-tetrahydrofuran (40:60) solvent mixture, and within experimental error it was identical in spectral distribution with the spectrum obtained in pure acetonitrile. A complete ECL spectrum of anthracene-TTF could not be obtained due to rapid decay of the ECL emission; however, emission was observed at a wavelength of 400 nm when the working electrode was pulsed between potential limits corresponding to the generation of

TTF^+ and the anthracene radical anion.

In all cases where ECL is observed, emission is clearly the result of TTF radical cation-acceptor radical anion annihilation as the anodic potential is varied from a point where no faradaic oxidation processes occur toward more positive potentials. The onset of spectrophotofluorometric detection of ECL always corresponded to the onset of anodic current for TTF oxi-
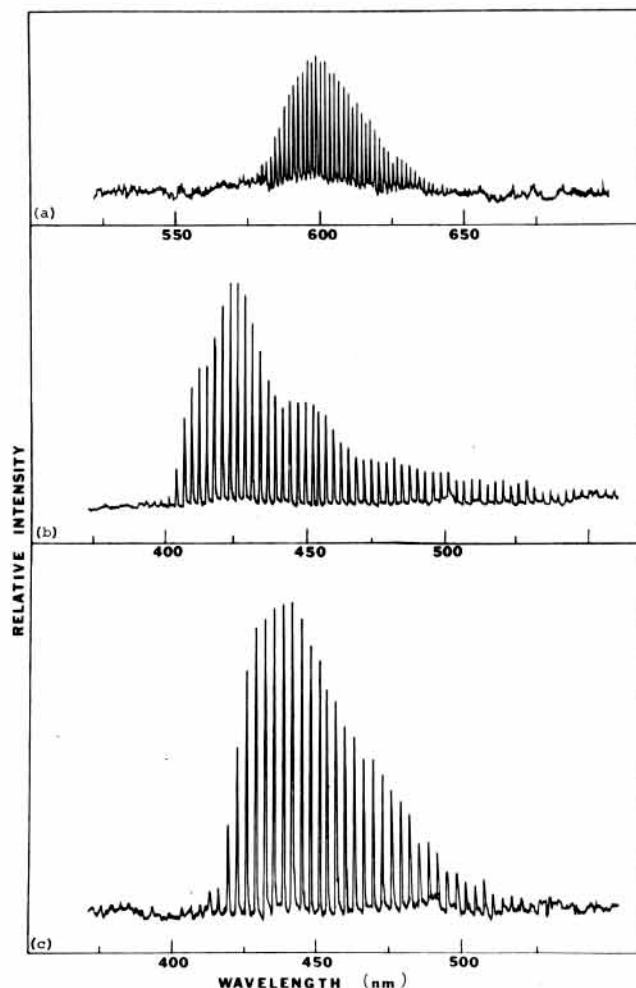

Fig. 3. ECL spectra of (a) 5.0×10^{-3}M rubrene and 2.2×10^{-3}M TTF, pulse width = 500 msec; (b) 2.4×10^{-3}M DMA and 1.9×10^{-3}M TTF, pulse width = 500 msec; and (c) 4.3×10^{-3}M DPA and 5.9×10^{-4}M TTF, pulse width = 500 msec; all in acetonitrile containing 0.1M TBAP; spectrophotofluorometer bandpass = 5 nm.

dation. Extending the anodic potential limit to values which cause TTF dication or acceptor radical cation formation resulted in either a rapid decrease in the peak ECL intensity as a function of potential, as in the case of DPA-TTF, or in a gradual decrease in ECL intensity, as in the case of DMA-TTF. Intensity enhancements at potentials more positive than TTF^+ production were never observed.

Peak ECL intensities for all the TTF-aromatic hydrocarbon systems monitored under continuous pulsing conditions on a time scale of a few minutes to 1 hr

Table II. Electrochemical and excited state energy parameters for TTF-acceptor ECL systems

Compound	$E_p(A^+/A)$[a] (V *vs.* SCE)	$E_p(A/A-)$[a] (V *vs.* SCE)	$E(^1A^*)$[b] (eV)	$E(^3A^*)$[d] (eV)	$-\Delta H^\circ$ (A-...D+)[f] (eV)	ECL
Anthracene	+1.25	−2.09	3.3	1.8	2.27	Yes (unstable)
Rubrene	+0.83	−1.65	2.2	1.2	1.83	Yes
DMA	+1.07	−2.14	3.10[c]	1.80[c]	2.32	Yes
DPA	+1.17	−2.03	3.0	1.8	2.21	Yes
Trans-stilbene	+1.45	−2.30	3.8	2.0	2.48	No
Ru(bipy)₃+²	+1.25	−1.41	—	2.04[e]	1.59	No

[a] Cyclic voltammetry peak potentials from Table I.
[b] Singlet energies from Ref. (38), unless otherwise noted.
[c] Reference (13).
[d] Triplet energies from Ref. (31) unless otherwise noted.
[e] Reference (39).
[f] Free enthalpy for radical ion annihilation in eV taking $E_{pa}(D^+/D)$ for TTF as +0.34V *vs.* SCE in acetonitrile (0.1M TBAP) and using $-\Delta H^\circ = E_p(D^+/D) - E_p(A/A-) - 0.16$, see Ref. (15).

decayed to zero intensity in a few hundred pulses or less. ECL emission in these mixed systems in acetonitrile was always observed to occur on only one pulse polarity which was usually, but not consistently, anodic. Emission could not be observed on the opposite polarity pulses except under the most sensitive spectrophotofluorometric conditions. Observation of emission only on anodic pulses might be attributed to instability of the TTF radical cation relative to that of the aromatic hydrocarbon radical anion; however, on the cyclic voltammetric time scale such instability is not observed. Only the aromatic hydrocarbon radical anions exhibited significant instability as judged by peak current ratios (see Table I). Correlated to the decrease in ECL intensity with time under continuous pulsing conditions was the buildup of a layer of colored material in the solution surrounding the working electrode. Cyclic voltammetry showed no new peaks or product waves associated with the colored material and presumably it arises from the accumulation of excess stable radical ion (TTF$^+\cdot$ or AHC$^-\cdot$) with time. Prolonged pulsing resulted in product formation observed as a gray precipitate of unknown composition in the TTF-DMA and TTF-DPA systems.

Discussion

Listed in Table II are the cyclic voltammetric peak potentials for the first oxidation and reduction waves of several acceptor compounds deemed suitable for study in this work. Also tabulated are the acceptor singlet and triplet energies and the enthalpies for radical ion annihilation for the reaction between the TTF radical cation and the acceptor radical anion to produce ground state products. The calculated enthalpies for radical ion annihilation are based on experimental data obtained in this work and represent the maximum excess energy available for donor or acceptor excited state production in the radical ion annihilation reaction.

Examination of the data in Table II reveals several important aspects of ECL production using TTF as a donor. Note that the cyclic voltammetry peak potentials for the first oxidation wave of all the acceptors fall well outside the first oxidation wave for TTF; therefore, no interference is to be expected from the acceptor in generating TTF$^+\cdot$. In only one case (TTF-rubrene) does overlap occur between the acceptor first oxidation and TTF second oxidation waves. In addition, TTF is not reduced within the potential range available for the acetonitrile-TBAP solvent-supporting electrolyte system and therefore cannot interfere with acceptor reduction. These conditions insure that with the appropriate selection of potential limits the reaction between the donor radical cation and the acceptor radical anion may be probed exclusively.

Comparison of $\Delta H°$ values with the excited state energies listed in Table II shows that in no case is the energy release during radical ion annihilation sufficient to populate the acceptor excited singlet state; however, in most systems (the first five in Table II) the acceptor first excited triplet state may be attained. The situation for TTF is less clear since the excited state singlet and triplet energies for this molecule are not well defined. To our knowledge fluorescence and low temperature phosphorescence studies of TTF are absent in the literature. Our own fluorescence studies at room temperature show weak emission from 10^{-3} to $10^{-4}M$ deaerated acetonitrile solutions of TTF in the range 300-500 nm. The spectral distribution of this emission was dependent on excitation wavelength and irradiation time (photolysis of $10^{-4}M$ acetonitrile solution via the unfiltered output of a 450W Xe lamp) and can be attributed predominantly to impurity fluorescence. The disappearance of TTF as a function of irradiation time can be followed by absorption spectroscopy and correlates

with increasingly efficient Rayleigh scattering and formation of cloudy photolysis solutions. Results of a low temperature phosphorescence study of $10^{-4}M$ TTF in methyltetrahydrofuran at 77°K were similarly inconclusive. Although phosphorescence was observed, the spectral distribution of the emission was again a function of excitation wavelength and irradiation time. It should be mentioned that the fluorescence observed in TTF solutions was too weak to contribute significantly to fluorescence spectra of mixed TTF-acceptor solutions and was never observed in ECL spectra.
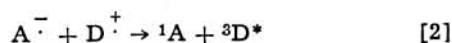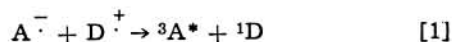
Attempting to estimate the singlet energy of TTF from its absorption spectrum also presents problems. The longest wavelength low molar absorptivity coefficient band of TTF at 450 nm has been variously assigned to: (i) an $n \rightarrow \pi^*$ transition of the sulfur lone pair electrons (27); (ii) a symmetry forbidden singlet-singlet $\pi \rightarrow \pi^*$ transition of B_{1g} symmetry (28); and (iii) a composite of two weakly allowed spin-forbidden singlet-triplet $\pi \rightarrow \pi^*$ transitions of B_{2u} and B_{3u} symmetry (29). Self-consistent statistical exchange multiple-scattering calculations also lead to the prediction of a spectroscopically unobserved triplet state at approximately 1.7 eV (29). The discrepancy in the assignments for the low energy TTF absorption band has so far not been resolved by spectroscopic means.

If indeed the lowest lying excited singlet state in TTF can be correlated with the lowest energy absorption band ($E_s = 2.58$-2.8 eV), then the TTF singlet will be inaccessible in all the ECL systems examined in this study. The TTF triplet, which has been estimated to be 0.20-0.68 eV lower than the singlet by $X\alpha$-scattered wave calculations (30), could be accessible in several systems. If, however, the lowest energy TTF absorption band correlates with the lowest energy triplet, then neither the TTF singlet or triplet states could be populated in the systems examined. Population of a TTF excited state cannot be probed by ECL since no emission which could be attributed to TTF (or an impurity) was ever observed in the ECL spectra monitored in acetonitrile solution.

The observed ECL behavior for the six systems in Table II can be divided into two categories: (i) ECL is observed and corresponds entirely to emission from the aromatic hydrocarbon acceptor (first four systems); and (ii) ECL is not observed [TTF-*trans*-stilbene and TTF-Ru(bipy)$_3$(ClO$_4$)$_2$]. Of the systems in the first category the absence of emission other than acceptor fluorescence in the ECL rules out the formation of stable emitting excited state complexes (exciplexes) (although not exciplex formation itself). Exciplex emission in the long wavelength region of the TTF-DMA ECL spectrum in acetonitrile can be ruled out by the observation that within experimental error the spectral distribution is identical to that in the ECL spectra of DMA alone in acetonitrile and DMA-TTF in an acetonitrile-tetrahydrofuran (40:60) solvent mixture. An enhancement in the exciplex/monomer intensity ratio and a blue shift in exciplex emission would otherwise be expected in the less polar solvent ($\epsilon = 7.4$ for tetrahydrofuran and $\epsilon = 36.7$ for acetonitrile) (15). Excimer emission is considerably less affected by solvent polarity. The DMA excimer emission observed in the TTF-DMA ECL spectra is produced probably via triplet-triplet annihilation of ^{3}DMA* as in the previously studied DMA$^-\cdot$/TPTA$^+\cdot$ (15) and DMA$^-\cdot$/TMPD$^+\cdot$ (16) systems. In addition, fluorescence studies of 10^{-3}-$10^{-4}M$ aromatic hydrocarbon solutions containing 10^{-3}-$10^{-1}M$ concentrations of TTF in acetonitrile, benzene, and tetrahydrofuran failed to produce definitive evidence for exciplex emission. Although apparent long wavelength emission was observed in solutions containing the highest TTF concentrations, reabsorption of acceptor fluorescence emission by TTF, not exciplex emission, was found to be

responsible. Both competitive absorption and reabsorption caused serious experimental difficulties in carrying out energy transfer studies in these systems.

Since the acceptor excited triplet states are accessible in all systems exhibiting ECL triplet-triplet annihilation is adequate to account for acceptor fluorescence in every case. Numerous investigations, including the study of magnetic field effects and energy deficient systems, have demonstrated the intermediacy of triplets in the ECL of rubrene (31, 32), DPA (31, 33), DMA (13, 16), and anthracene (31, 33) mixed systems. An over-all mechanism for ECL emission can be represented as follows

$$A^{\overline{\cdot}} + D^{+}_{\cdot} \to {}^3A^* + {}^1D \qquad [1]$$

$$A^{\overline{\cdot}} + D^{+}_{\cdot} \to {}^1A + {}^3D^* \qquad [2]$$

$${}^3A^* + {}^3A^* \to {}^1A^* + {}^1A \to 2{}^1A + h\nu \qquad [3]$$

Again note in Eq. [1] that the formation of acceptor excited singlet states can be omitted on the basis of energy considerations. Equation [2] necessarily includes the possibility of forming donor triplets; however, formation of TTF singlets cannot occur in the four systems exhibiting ECL.
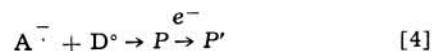
The relatively rapid degradation of ECL intensity over a period of time under continuous pulsing conditions makes it amply clear that the reactions in Eq. [1]-[3] are not the only pathways available for donor-acceptor interaction. Numerous possibilities exist for chemical reactions leading to ECL degradation including: (i) direct interaction of neutral donor and acceptor molecules to form ground state complexes or other products; (ii) chemical reaction of radical ions either by first-order degradation processes or by reaction with neutral donor and acceptor molecules or other solution constituents including impurities; (iii) chemical reactions via radical ion annihilation; and (iv) photochemical reactions of donor and acceptor excited states produced by radical ion annihilation. The formation of ground state complexes incorporating TTF as a donor are well known and as previously mentioned form an important and highly studied class of conducting solid-state DA complexes. Formation of such DA complexes commonly occurs via reaction of the neutral substituents but can also occur as a radical ion reaction as, for example, in the reaction of electrogenerated $TTF^{+}_{\cdot}$ with X^- to form TTF halide salts (34, 35). Ground state complex formation by either method, however, or any other reaction between neutral donor and acceptor molecules is unsupported in the systems examined in this study by the electrochemical evidence. In addition, formation of strong DA complexes with the acceptors in this study is unlikely due to their relatively weak electron accepting ability. Furthermore, electrochemical data show that donor radical cations in the presence of neutral acceptor and acceptor radical anions in the presence of neutral donor are stable on a cyclic voltammetric time scale, with the one exception of *trans*-stilbene$^{\overline{\cdot}}$ in the presence of TTF neutral. However, even though evidence for a chemical reaction cannot be observed in initial mixed donor-acceptor solutions, product formation is observed after electrochemistry, possibly indicating the contribution of radical ion reactions on a long-time scale. The possible contribution of photochemical reactions to over-all ECL degradation cannot be easily probed; however, the reactivity of TTF excited state(s) appears to be established in this and other studies (5, 36) and must be taken into account. An analysis of the products formed in the ECL systems examined in this study will be necessary to elucidate precisely the specific pathway(s) involved in the observed degradation behavior. It should be noted that in general studies defining the stabilities of radical ions

on a cyclic voltammetric or even bulk coulometric time scale will not necessarily be of use in predicting the stability of ECL systems.

Of the two systems which did not exhibit ECL the TTF-*trans*-stilbene system was chosen as a possibility for exhibiting exciplex emission. Observation of exciplex emission in the ECL from *trans*-stilbene radical anion and amine radical cation annihilation has been observed (15) enhancing the possibility of observing exciplex emission using TTF as a donor. The complete absence of emission from the *trans*-stilbene-TTF system seems to rule out the formation of a stable emitting exciplex. The *trans*-stilbene triplet state is accessible in this system; however, the short triplet lifetime at room temperature in fluid solution (37) is adequate to explain the absence of stilbene fluorescence via triplet-triplet annihilation. The most compelling reason for not observing ECL is the extreme reactivity of the *trans*-stilbene radical anion in the presence of TTF. A new product-forming route is opened for the radical anion which competes with radical ion annihilation and excited state formation. As stated previously, the evidence at this point indicates a reaction of the stilbene radical anion with neutral TTF forming a further reducible product

$$A^{\overline{\cdot}} + D^\circ \xrightarrow{e^-} P \to P' \qquad [4]$$

The $Ru(bipy)_3(ClO_4)_2$-TTF system was chosen as a test case. No ECL was expected for reaction with the TTF radical cation, although reaction with TTF^{+2} would just barely be energetic enough to produce the Ru(II) triplet state. No ECL is observed, however, pulsing between potential limits sufficiently anodic to produce $TTF^{+}_{\cdot}$, TTF^{+2}, or the Ru(III) complex. The lack of emission from the Ru(I)-Ru(III) reaction in the presence of TTF indicates that efficient quenching of either the Ru(I)-Ru(III) radical ion annihilation and/or of the Ru(II) excited triplet state takes place. A possible explanation for the lack of emission in the TTF^{+2}-Ru(I) annihilation reaction is the presence of the TTF radical cation in the solvent cage complex immediately after electron transfer leading to efficient quenching

$$D^{+2} + A^- \to (D^{+}_{\cdot} \ldots {}^3A^*) \to D^{+}_{\cdot} + A \qquad [5]$$
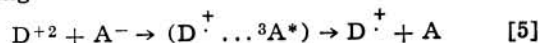
Acknowledgment

REFERENCES

1. B. A. Scott, S. J. LaPlaca, J. B. Torrance, B. D. Silverman, and B. Welber, *J. Am. Chem. Soc.*, **99**, 6631 (1977).
2. E. M. Engler, *Chem. Technol.*, 274 (1976).
3. A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
4. J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
5. C. E. Klots, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.*, **60**, 1177 (1974).
6. D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett, and N. D. Canfield, *J. Am. Chem. Soc.*, **93**, 2258 (1971).
7. J.-P. Blanchi and A. R. Watkins, *Chem. Comm.*, 265 (1974).
8. H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **72**, 257 (1968).
9. D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

10. J. Saltiel, E. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, *J. Am. Chem. Soc.,* **99,** 884 (1977).
11. N. C. Yang, D. M. Shold, and B. Kim, *ibid.,* **99,** 6587 (1977).
12. J. T. Maloy and A. J. Bard, *ibid.,* **93,** 5968 (1971).
13. C. P. Keszthelyi, N. E. Tokel-Takvoryan, H. Tachikawa, and A. J. Bard, *Chem. Phys. Lett.,* **23,** 219 (1973).
14. H. Tachikawa and A. J. Bard, *ibid.,* **26,** 568 (1974).
15. S. M. Park and A. J. Bard, *J. Am. Chem. Soc.,* **97,** 2978 (1975).
16. A. Weller and K. Zachariasse, *Chem. Phys. Lett.,* **10,** 197 (1971).
17. A. Weller and K. Zachariasse, *ibid.,* **10,** 424 (1971).
18. S. M. Park and A. J. Bard, *J. Electroanal. Chem.,* **77,** 137 (1977).
19. D. Laser and A. J. Bard, *This Journal,* **122,** 632 (1975).
20. M. R. Suchanski, Ph.D. Dissertation, Northwestern University, Evanston, Ill. (1977).
21. R. C. Larson and R. T. Swamoto, *J. Am. Chem. Soc.,* **82,** 3239 (1960).
22. N. E. Tokel, C. P. Keszthelyi, and A. J. Bard, *ibid.,* **94,** 4872 (1972).
23. T. H. Teherani, L. A. Tinker, and A. J. Bard, Paper submitted to *J. Electroanal. Chem.*
24. T. C. Werner, J. Chang, and D. M. Hercules, *J. Am. Chem. Soc.,* **92,** 763 (1970).
25. C. P. Keszthelyi and A. J. Bard, *This Journal,* **120,** 241 (1973).
26. C. P. Keszthelyi, N. E. Tokel-Takvoryan, and A. J. Bard, *Anal. Chem.,* **47,** 249 (1975).
27. R. Zaradnik, P. Carsky, S. Hunig, G. Kiesslich, and D. S. Scheutzow, *Int. J. Suljur Chem., C,* **6,** 109 (1971).
28. R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, *J. Electron Spectrosc. Relat. Phenom.,* **2,** 207 (1973).
29. B. I. Bennet and F. Herman, *Chem. Phys. Lett.,* **32,** 334 (1975).
30. P. S. Bagus and B. I. Bennet, *Int. J. Quant. Chem.,* **9,** 143 (1975).
31. L. R. Faulkner, H. Tachikawa, and A. J. Bard. *J. Am. Chem. Soc.,* **94,** 691 (1972).
32. H. Tachikawa and A. J. Bard, *Chem. Phys. Lett.,* **26,** 246 (1974).
33. L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.,* **91,** 209 (1969).
34. J. Q. Chambers, D. C. Green, F. B. Kaufman, E. M. Engler, B. A. Scott, and R. R. Schumaker, *Anal. Chem.,* **49,** 802 (1977).
35. F. B. Kaufman, E. M. Engler, D. C. Green, and J. Q. Chambers, *J. Am. Chem. Soc.,* **98,** 1596 (1976).
36. B. A. Scott, F. B. Kaufman, and E. M. Engler, *ibid.* **98,** 4342 (1976).
37. A. Weller and K. Zachariasse, *Chem. Phys. Lett.,* **24,** 300 (1974).
38. D. J. Freed and L. R. Faulkner, *J. Am. Chem. Soc.,* **93,** 2097 (1971).
39. N. E. Tokel-Takvoryan, R. E. Hemmingway, and A. J. Bard, *ibid.,* **95,** 6582 (1973).