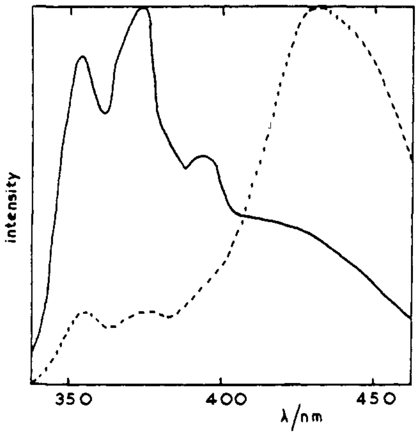

Figure 1. Spectra (uncorrected) of thermoluminescence of 10^{-2} molar zone-refined *trans*-stilbene in squalane after 2 min of γ irradiation: (——) early in glow peak; (- - -) late in glow peak.

not have a "perfect sandwich" structure;[5] the same may be true of excimers formed from them.

Crystalline 2,4-dichloro-*trans*-stilbene gives excimer emission,[6] but there appear to be no reports of excimer emission from stilbene or its derivatives in solution. Stilbene is known to dimerize via the singlet excited state;[7] probably the excimer is an intermediate which reacts in fluid solution much faster than it fluoresces. Similarly, excited diphenylacetylene is known to form products derived from two, three, or four monomer molecules;[8] the excimer is likely to be formed first.

This method is being extended to other compounds and should be a useful one for sufficiently soluble materials. In general, trace impurities are not likely to give spurious results since the ions are not mobile in the solid and only travel short distances (~100 Å) before neutralization. As noted above, impurities able to absorb the fluorescence of the substrate interfere strongly, but their presence is readily detected in photofluorescence.

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(1) The authors thank the Science Research Council (U.K.) for financial support for one of them (D.C.B.) and for an equipment grant.

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Electrogenerated Chemiluminescence. XXII. On the Generation of Exciplexes in the Radical Ion Reaction

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Abstract: Exciplex emission from systems containing tri-*p*-tolylamine (TPTA) as a donor molecule and various acceptor molecules was observed in both acetonitrile (ACN) and tetrahydrofuran (THF) solutions during electrogenerated chemiluminescence (ecl) studies. Systems containing naphthalene as an acceptor and five donor molecules also showed exciplex emission in ACN solutions. Triplet quenching experiments, magnetic field effect measurements, and temperature studies demonstrated that the exciplex is formed directly in the radical ion reaction. The energy of the exciplex emission showed a linear correlation with the cyclic voltammetric peak potentials for reduction of the acceptor molecules and for oxidation of the donor molecules. Studies of the ecl of the dibenzoylmethane (DBM)-TPTA system in six different electrochemical solvents, where only exciplex emission is observed, demonstrated the importance of solvent dielectric constant on exciplex emission intensity. The role of exciplexes in the general ecl scheme is also discussed.

Exciplexes are excited molecular complexes which are dissociated in the ground state.[1] They are usually produced by reaction of a photoexcited singlet species ($^1A^*$) with a ground state molecule, D; exciplex emission is usually structureless and red shifted from that of $^1A^*$ by about 6000 cm^{-1}.[1,2]

$$^1A^* + D \longrightarrow {}^1(A^-D^+)^* \tag{1}$$

$$^1(A^-D^+)^* \longrightarrow A + D + h\nu \tag{2}$$

Previous studies of radical-ion annihilation chemiluminescence (cl)[3,4] reactions and electrogenerated chemiluminescence (ecl)[5,6] in low dielectric constant solvents, such as tetrahydrofuran (THF), have demonstrated the formation of exciplexes by the direct reactions of radical ions

$$A\cdot^- + D\cdot^+ \rightleftarrows {}^1(A^-D^+)^* \tag{3}$$

and it has been suggested that an exciplex may be an intermediate in other cl or ecl reactions, even when exciplex emission is not observed.

It has generally been felt, however, that emission from exciplexes will not be observed in polar solvents, such as acetonitrile (ACN), where dissociation of the exciplex into the radical ions (the reverse of reaction 3) becomes more important.[7] We describe here ecl experiments with a number of acceptor and donor molecules in both THF and ACN which demonstrate the formation of exciplexes and show that the energy of the exciplex emission correlates with the redox potentials of the reactant molecules. Preliminary experiments on the effect of magnetic field, solvent, and temperature variations on the ecl behavior in these systems are also discussed.

Experimental Section

Chemicals. Tri-*p*-tolylamine (TPTA) and tri-*p*-anisylamine (TPAA), kindly provided by Professor R. N. Adams (University of

Table I. Electrochemical, Spectroscopic, and Ecl Results for Various Acceptor/TPTA[a] Systems in ACN Solution

No.	Acceptor molecules	$-E_{pc}$, V vs. SCE	ΔE_{pc}, mV	E_S, eV	E_T, eV	Ecl emission λ_{max}, nm (eV)		$\Delta H°$, eV	Remark
1	Benzophenone (BP)	1.91	80	3.22	2.97[b]	581 (2.13)		2.59	Fairly bright
2	Acetophenone	2.18	180		3.20[b]	560 (2.21)		2.86	Weak
3	Dibenzoylmethane (DBM)	1.55	67		2.77[b]	665 (1.86)		2.23	Very weak
4	Naphthalene	2.66	92	3.99[c]	2.63[c]	379 (3.27)	476 (2.60)	3.34	Bright
5	Benz[*a*]anthracene (BA)	2.17	79	3.35[c]	2.08[c]	391 (3.17) 436 (2.84)	413 (3.00) 529 (2.34)	2.85	Very bright
6	1,1,4,4-Tetraphenyl-1,3-butadiene (TPB)	2.20	86	3.14[d]		550 (2.25)		2.88	Fairly bright
7	1,4-Diphenyl-1,3-butadiene (DPB)	2.12	65	3.6[e]		562 (2.21)		2.80	Fairly bright

[a] For TPTA in ACN, $E_{pa} = +0.84$ V vs. SCE, $E_S = 3.51$ eV, $E_T = 2.96$ eV[4]. [b] D. J. Morantz and A. J. C. Wright, *J. Chem. Phys.*, 54, 692 (1971). [c] R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley-Interscience, New York, N.Y., 1969, p 118. [d] J. B. Berlman, Ed., "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971. [e] J. B. Birks and D. J. Dyson, *Proc. R. Soc. London, Ser. A*, 275 (1360); 135 (1963).

Kansas), were used as received. Fischer certified, reagent grade, benzophenone was recrystallized five times from a 1:1 mixture or diethyl ether and absolute alcohol; the purity was checked by taking its phosphorescence spectrum. Benzaldehyde (Fischer) and acetophenone (Matheson Coleman and Bell, MCB) were purified by vacuum distillation. All other compounds were purified by sublimation, repeated recrystallizations, or a combination of these methods, except for 1,1,4,4-tetraphenyl-1,3-butadiene (Aldrich, 99%) and isoprene (Aldrich, >99%), which were used as received. Polarographic grade tetra-*n*-butylammonium perchlorate (TBAP) of Southwestern Analytical Chemicals, Inc., was dried under vacuum (10^{-5} Torr).

Spectroquality acetonitrile (ACN) (MCB) was used as a solvent after three distillations from phosphorus pentoxide under vacuum without contacting air. Dried ACN was never exposed to the air, but was stored either in an inert atmosphere glove box or under vacuum. The ACN was transferred into the cell on a vacuum line or in the glove box. Tetrahydrofuran (THF) (MCB) was stored over calcium hydride, and then distilled into a storage container containing a sodium mirror. It was allowed to stand for more than 48 hr in contact with the mirror followed by direct distillation into the cell. Spectroquality benzonitrile (MCB) and methylene chloride (Fischer) and dimethyl sulfoxide (DMSO) (MCB) were dried over activated molecular sieves (Linde 4A). *N,N*-Dimethylformamide (DMF) was purified by a previously described technique.[8]

Apparatus and Techniques. Solutions were prepared in the cell directly by vapor transfer on a vacuum line when THF, methylene chloride, or ACN were employed, followed by five freeze-pump-thaw (FPT) cycles to remove oxygen. DMF, benzonitrile, and DMSO were poured directly into the cell either quickly in the air (DMSO and benzonitrile) or in the drybox (DMF), and the cell was then degassed by five FPT cycles.

Cyclic voltammograms were obtained with a Princeton Applied Research Model 170 electrochemistry system (PAR) using a three-electrode cell of conventional design.[9] The same cell was used for the ecl measurements. Ecl was generated by cyclic potential steps generated with the PAR and detected with an Aminco-Bowman spectrophotofluorometer employing a Hamamatsu TV Corp. R456 photomultiplier tube with uv-improved S-20 response and operated at 1100 V to increase the sensitivity. Controlled temperature ecl studies were carried out in the usual type of ecl cell containing two additional tungsten wires sealed in the cell wall connected to a thermistor in the solution. A Victory Engineering Corporation (Springfield, N.J.) Type 51A1 thermistor was used to determine the temperature of the ecl solution, using a Heathkit digital multimeter. Low temperatures were obtained by circulating acetone, the temperature of which was controlled by adding Dry Ice into the cell holder of the spectrophotofluorometer, as described previously.[10] Higher temperature control was accomplished using water heated in a Labline temperature-control bath.

Magnetic field effects were studied using the apparatus and techniques previously described.[6,11]

Results and Discussion

The experiments consisted of electrogeneration of the radical anions of various acceptor molecules, $A\cdot^-$, and studying the emission which resulted upon their reaction with electrogenerated $TPTA\cdot^+$. Electrochemical data, energy levels, and ecl results for a number of acceptors in ACN and THF are given in Tables I and II. Similar results for naphthalene as an acceptor molecule with a number of electrogenerated cation radicals ($D\cdot^+$) are shown in Table III. Typical experimental results for three systems which will be discussed more fully, benzophenone (−)/TPTA (+), naphthalene (−)/TPTA (+), and 1,2-benzanthracene (−)/TPTA (+), are shown in Figures 1-3. The cyclic voltammetry experiments demonstrate that all radical anions are stable, except for benzaldehyde and acetophenone in ACN, which showed anodic peak currents (i_{pa}) on reversal much smaller than the cathodic peak currents. These radical anion species were stable in THF, however. In all cases emission at wavelengths longer than that of either $^1A^*$ or $^1D^*$ and identified as that of the exciplex $^1(A^-D^+)^*$ was observed. The emission maximum for the exciplex was red shifted in ACN as compared to THF, except for the benzophenone (−)/TPTA (+) pair.

Benzophenone (−)/TPTA (+). This system is typical of those where the enthalpy of the radical ion reaction, calculated from the peak potentials using (4),[11a] is significantly

$$-\Delta H° = E_{pa} - E_{pc} - 0.16 \text{ eV} \qquad (4)$$

less than the triplet energies of TPTA or the acceptor molecule (Tables I and II). In these cases only the long wavelength exciplex emission is observed (this scheme can be designated as the "E route" in ecl). Both $TPTA\cdot^+$ and the radical anion of benzophenone are very stable in both ACN and THF as shown by the cyclic voltammograms (Figure 1a). The fairly bright emission observed in THF (λ_{max} = 594 nm) and ACN (λ_{max} = 581 nm) can thus be attributed to an exciplex formed on direct reaction of $A\cdot^-$ and $D\cdot^+$ (reaction 3); Zachariasse[4] reached a similar conclusion in a cl study with THF as a solvent.

To ensure that triplets were not involved in exciplex formation, the triplet quencher isoprene was added to the ecl system in one experiment. Isoprene is a known triplet

Table II. Electrochemical, Spectroscopic, and Ecl Results for Various Acceptor/TPTA[a] Systems in THF Solutions

No.	Acceptor molecules	$-E_{pc}$, V vs. SCE	ΔE_{pc}, mV	E_S, eV	E_T, eV	Ecl emission λ_{max}, nm (eV)	$\Delta H°$, eV	Remark
1	Benzophenone	2.09	83	3.22	2.97	594 (2.09)	2.77	Bright
2	Acetophenone	2.32	89		3.20	523 (2.37)	3.00	Bright
3	Dibenzoylmethane	1.77	89		2.77	615 (2.02)	2.45	Weak
4	Naphthalene	2.79	90	3.99	2.63	378 (3.28) 467 (2.65)	3.48	Bright
5	Benz[*a*]anthracene	2.24	62	3.35	2.08	390 (3.18) 410 (3.02) 435 (2.85) 511 (2.43)	2.92	Bright
6	1,1,4,4-Tetraphenyl-1,3-butadiene	2.21	60	3.14		511 (2.43)	2.89	Bright
7	1,4-Diphenyl-1,3-butadiene	2.26	67	3.6		516 (2.40)	3.03	Bright
8	*trans*-Stilbene[b]	2.34		3.80	2.20	495 (2.50)	3.02	
9	9-Methylanthracene[c]	2.19	90	3.20	1.8	520 (2.38)	2.82	
10	2,5-Diphenyloxazole (PPO)[b]	2.38		3.61		490 (2.53)	3.38	

[a] For TPTA in ACN, E_{pa} = +0.84 V vs. SCE, E_S = 3.51 eV, E_T = 2.96 eV.[4] [b] From ref 5. [c] Taken from H. Tachikawa's Ph.D. Dissertation, University of Texas at Austin, 1973.

Table III. Electrochemical, Spectroscopic, and Ecl Data for Various Donor/Naphthalene[a] Systems in ACN Solution

No.	Donor molecules	E_p(ox), V vs. SCE	ΔE_{pa}, mV	E_S, eV	Ecl emission λ_{max}, nm (eV)	$\Delta H°$, eV	Remark
1	Triphenylamine (TPA)	1.02	138	3.5[b]	409 (3.02)	3.52	Bright
2	*N,N'*-Diphenylbenzidine	0.77 0.92	83 90	3.4[c]	512 (2.41)	3.27	Weak
3	Bis-1,8-(*N,N*-dimethylamino)naphthalene	0.36	137	2.4[c]	581 (2.13)	2.86	Very weak
4	TPTA	0.84	60	3.51	3.79 (3.26) 476 (2.61)	3.34	Bright
5	Tri-*p*-anisylamine	0.70	87	3.26[d]	330 (3.76) 401 (3.09) 500 (2.48)	3.20	Bright

[a] For naphthalene, E_{pc} = −2.66 V vs. SCE (ΔE_p = 92 mV), E_S = 4.0 eV, E_T = 2.64 eV. [b] Estimated from I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", 2nd ed, Academic Press, New York, N.Y., 1971. [c] Estimated from the fluorescence spectra in deaerated cyclohexane under a He atmosphere at room temperature. [d] Taken from ref 4.

quencher[12] and benzophenone triplet has been shown to sensitize the dimerization of dienes via triplet energy transfer.[13] Addition of an excess of isoprene to the benzophenone (−)/TPTA (+) system did not quench the exciplex emission. A magnetic field effect study of this system was not possible because the emission intensity was too small to obtain sufficiently precise measurements in the lower sensitivity field-effect phosphorimeter.

No evidence of a ground state charge transfer complex between A and D, formed as in (5), was obtained from electrochemical experiments.

$$A + D \rightleftarrows (A^- D^+) \qquad (5)$$

Peover[14] showed that complex formation leads to shifts in the potential for oxidation of D upon addition of A, or for reduction of A upon addition of D. An experiment in which E_{pa} for TPTA (1.0 m*M*) was determined in ACN for additions of benzophenone of 12 to 170 m*M* showed no such potential shifts. Similarly the absorption spectrum of a solution of benzophenone and TPTA in ACN did not show any new peaks attributable to a charge transfer complex.

Naphthalene (−)/TPTA (+). The naphthalene radical anion is fairly stable in ACN (E_{pc} = −2.66 V *vs.* SCE) and very stable in THF (E_{pc} = −2.79 V *vs.* SCE) (Figure 2). The reaction enthalpy is sufficient to produce the lowest triplet states of both naphthalene and TPTA and the observed ecl emission in both ACN and THF consists of a band where TPTA fluoresces and a longer wavelength band (λ_{max}(ACN) = 476 nm; λ_{max}(THF) = 467 nm) attributed to exciplex emission. Similar exciplex emission is observed for a solution of naphthalene and TPTA which is photoexcited at wavelengths of naphthalene absorption. When an excess of naphthalene (20 m*M*) is added to a solution of TPTA (0.5 m*M*) in cyclohexane, the fluorescence of the TPTA is quenched, and a new exciplex band appears at wavelengths corresponding to those of the ecl experiment. Exciplex formation between naphthalene and diethylaniline has previously been reported from similar experiments.[15]

Since the reaction energy is sufficient to produce ^3A and ^3D, another possible path to exciplex is via mixed triplet-triplet annihilation (TTA). However, the triplet lifetime of

$$^3A + {}^3D \longrightarrow {}^1(A^- D^+)^* \qquad (6)$$

TPTA is known to be very short (ca. 50 nsec in ethanol at room temperature). Moreover, no emission is observed from naphthalene singlet, which would result from TTA of ^3A, and which is observed during ecl experiments with naphtha-

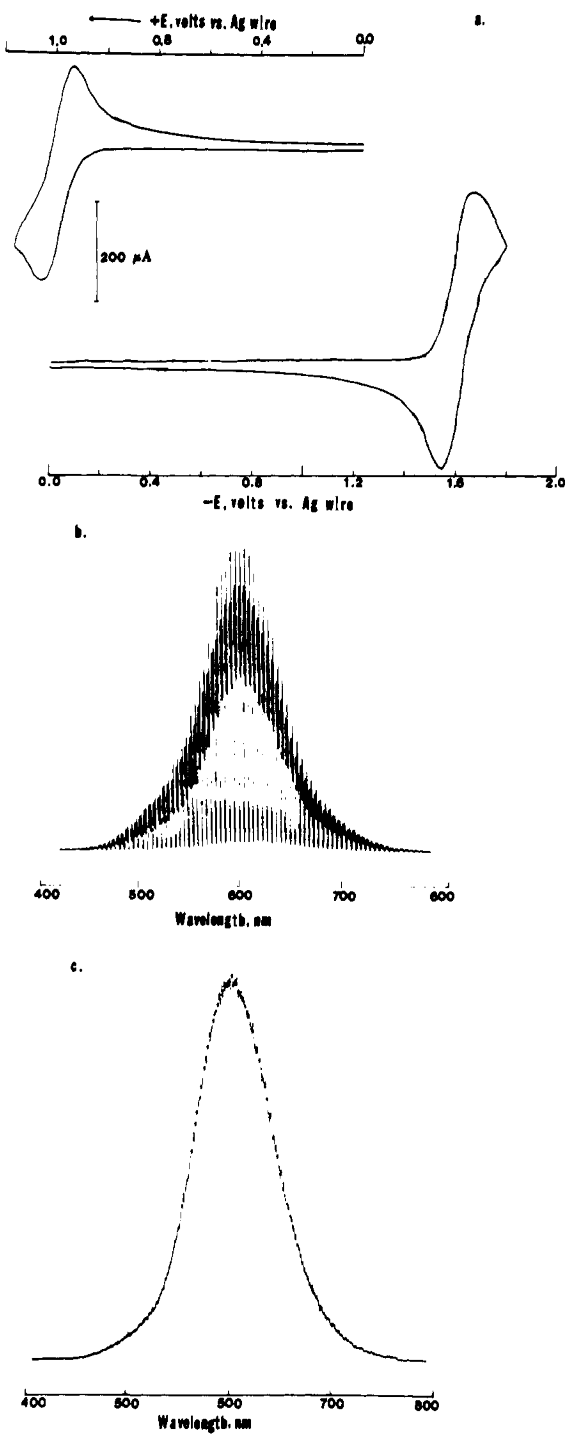

Figure 1. (a) Cyclic voltammograms of 2.2 mM TPTA, 2.5 mM benzophenone, and 0.1 M TBAP in THF at a scan rate of 200 mV/sec at a platinum wire electrode. (b) Ecl spectrum from the above solution; pulse duration 1 sec. (c) The same as (b) with pulse duration 50 msec.

lene (−)/TMPD (+) systems.[16] The origin of the emission from excited TPTA singlet is thus not TTA, but rather thermal activation from the exciplex.[3,4] Weller and Zachariasse[3,4] have invoked this mechanism in the cl of TPTA$\cdot^+$ with the radical anion of 9,10-dimethylanthracene in MTHF and have shown that the energy of activation of the process ($\approx \Delta G_d$) can be approximated by

$$ {}^1(A^-D^+)^* \underset{k_a}{\overset{k_d}{\rightleftharpoons}} A + {}^1D^* \tag{7} $$

$$ \Delta G_d(D) \approx E_s(D) - \Delta H^\circ \tag{8} $$

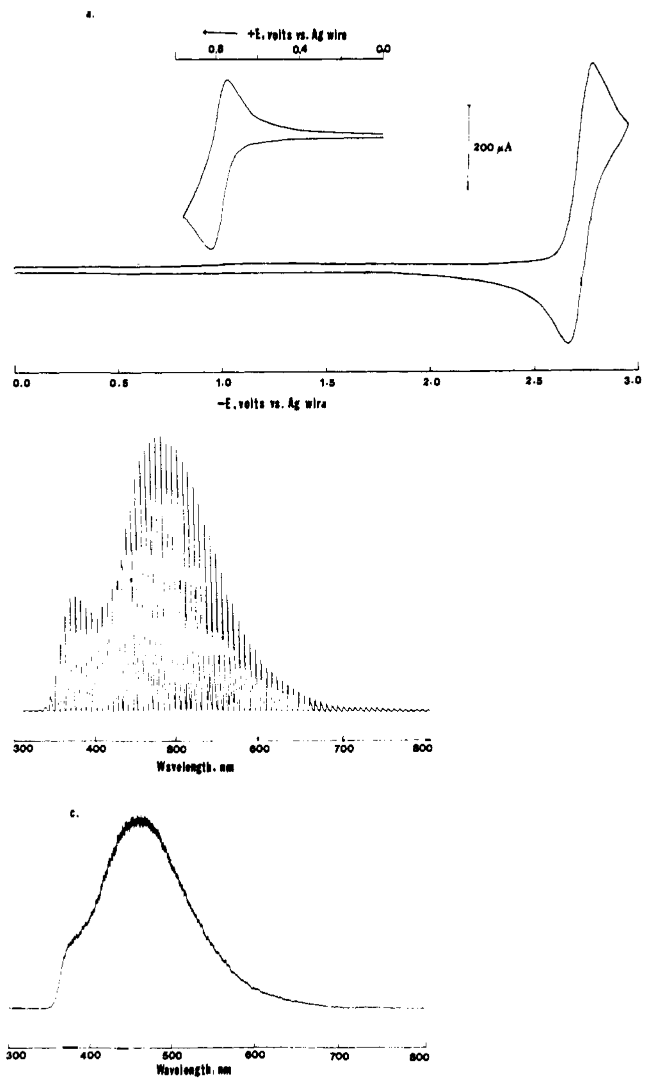

Figure 2. (a) Cyclic voltammograms of 2.0 mM TPTA, 2.5 mM naphthalene, and 0.1 M TBAP in THF at a scan rate of 200 mV/sec at a platinum wire electrode. (b) Ecl spectrum from the above solution; pulse duration 1 sec. (c) The same as (b) with pulse duration 50 msec.

where $E_s(D)$ is the energy of the lowest singlet of D and ΔH° is the enthalpy of the radical ion reaction. From the data in this system we estimate $\Delta G_d(D)$ as 0.17 eV in ACN and 0.03 eV in THF. These authors also pointed out that this quantity could be estimated by studying the relative intensity of ${}^1D^*$ to ${}^1(A^-D^+)^*$ emission $[I(D^*)/I(A^-D^+)^*]$ as a function of temperature, by assuming the reaction scheme

$$\begin{tikzcd}
A\cdot^- + D\cdot^+ \arrow[r, "\gamma_c"] & (A^-D^+) \arrow[r, "\gamma_d"] \arrow[d, "\phi_0'"] & A + {}^1D^* \arrow[d, "\phi_0"] \\
& A + D + h\nu' & D + h\nu
\end{tikzcd} \quad (9)$$

where γ_c and γ_d are yields of exciplex and dissociation and ϕ_0' and ϕ_0 are the intrinsic quantum yields of ${}^1(A^-D^+)^*$ and ${}^1D^*$, respectively. In the absence of production of ${}^1D^*$ by TTA, this leads to

$$ I(D^*)/I(A^-D^+)^* = (k_d/k_f')\phi_0 \tag{10} $$

where k_f' is the radiative rate constant of the exciplex and $k_d = k_a \exp(-\Delta G_d(D)/RT)$. If ϕ_0/k_f' is independent of temperature, a plot of ln $[I(D^*)/I(A^-D^+)^*]$ vs. $1/T$ yields ΔG_d. Such a plot for the naphthalene (−)/TPTA (+) system in Figure 4 yields a value of ΔG_d of 0.12 eV, in good agreement with the value estimated from the singlet energy and peak potentials. Note that the $\Delta G_d(A)$ values (for dis-

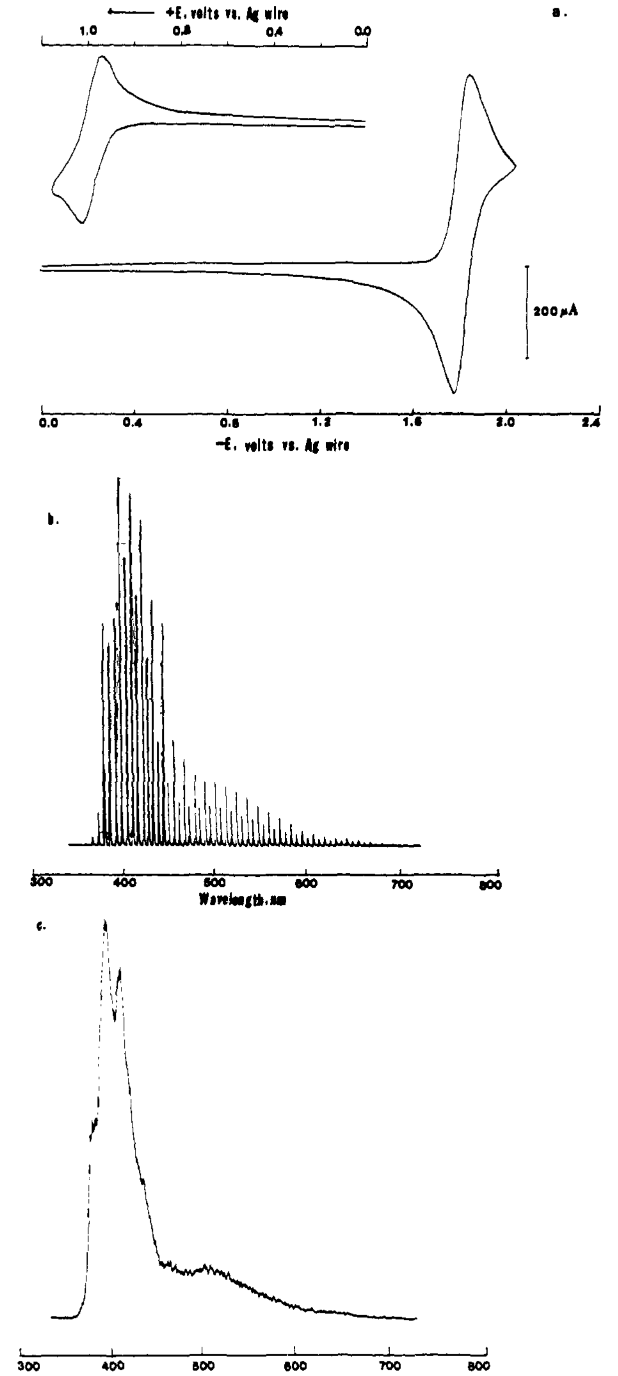

Figure 3. (a) Cyclic voltammogram of 1.3 m*M* TPTA and 2.3 m*M* 1,2-benzanthracene at a platinum wire electrode with 0.1 *M* TBAP (scan rate = 200 mV/sec). (b) Ecl spectrum obtained from above solution; pulse duration 1 sec. (c) The same as (b) with pulse duration 50 msec.

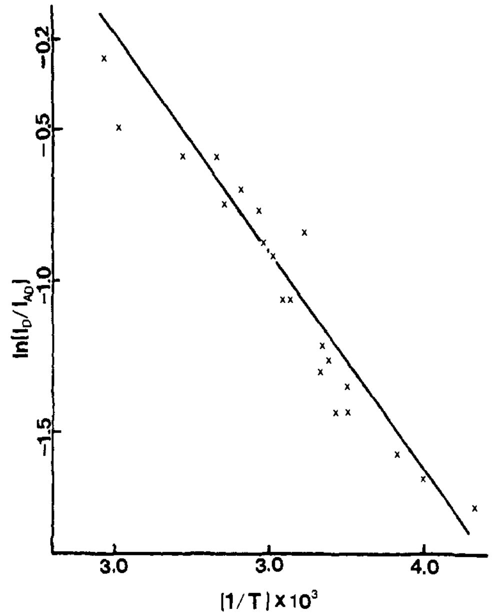

Figure 4. Temperature dependence of the naphthalene/TPTA system in acetonitrile. $I_D/I_{(A^-D^+)}$ was taken from the corrected spectra. Slope corresponds to 2.73 kcal/mol (see text). Data obtained from different solutions.

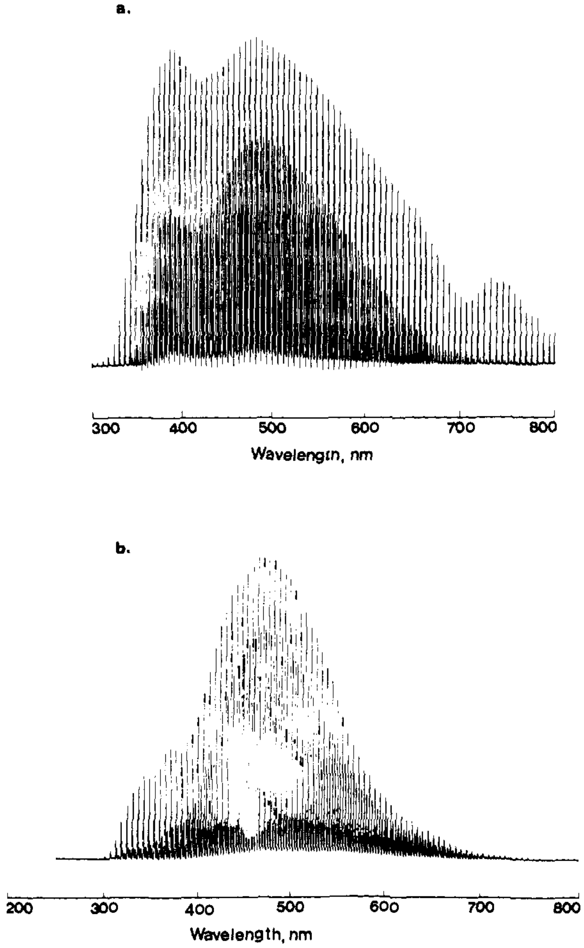

Figure 5. Ecl spectra of the naphthalene/TPTA system in acetonitrile with 1 sec pulse duration at different temperatures: (a) 64°, (b) −33°. The solution contained 2.5 m*M* naphthalene, 1.6 m*M* TPTA, and 0.1 *M* TBAP as a supporting electrolyte. The bumps on the shoulder of the exciplex at approximately 650 and 750 nm in the high temperature ecl are due to the grating second-order scattering of monomer emissions.

sociation of exciplex to $^1A^*$) are 0.65 eV in ACN and 0.51 eV in THF, so that observation of emission from singlet naphthalene is not probable.

This mechanism of direct formation of exciplex and thermal dissociation to form $^1D^*$ is also in agreement with magnetic field effect experiments on this system. Previous studies of magnetic field effects in ecl[6,11] have shown that increases in ecl emission intensities with increasing magnetic field are observed when triplet intermediates play a significant role in the observed ecl. The results for this system (Table IV), when the exciplex emission was monitored, showed essentially no field effect. A field dependent route to the exciplex would involve production of ^3A from the ex-

Table IV. Magnetic Field Effects on Exciplex Emission of Naphthalene (−)/TPTA (+) System in ACN[a]

Field strength, kG	Relative intensity	Field strength, kG	Relative intensity
0	1.00	6.0	1.01
1.5	1.01	7.5	1.01
3.0	0.996	9.0	1.01
4.5	1.00		

[a] The solution contained 2.1 mM naphthalene, 1.6 mM TPTA, and 0.10 M TBAP. The Pt working electrode was pulsed from −2.72 to 0.90 V vs. SCE at a frequency of 1 Hz (500 msec pulse). Total emission through a Kodak No. 2B gelatin filter (cut-off of emission below 390 nm) was monitored.

ciplex in eq 11, TTA of ^{3}A in eq 12, and then reaction of

$$^1(\mathrm{A^-D^+})^* \longrightarrow {}^3\mathrm{A} + \mathrm{D} \qquad (11)$$

$$^3\mathrm{A} + {}^3\mathrm{A} \longrightarrow {}^1\mathrm{A}^* + \mathrm{A} \qquad (12)$$

the ^{1}A* produced with D eq 1, to reform exciplex. The total contribution from this path is probably very small, however. The production of ^{1}A* by this route does occur, however, as evidenced by the appearance of emission at about 330 nm at low temperatures (Figure 5b). Since the formation of ^{3}A is exoenergetic, it persists at low temperatures, where production of ^{1}D*, eq 7, is greatly diminished. At higher temperatures this emission from excited singlet naphthalene is hidden by the shoulder of the TPTA emission.

DMA (−)/**TPTA** (+). The temperature dependence of ecl of the naphthalene (−)/TPTA (+) system can be contrasted with that of the 9,10-dimethylanthracene (DMA) (−)/TPTA (+) system in ACN. Weller and Zachariasse[3d] studied the cl of the DMA (−)/TPTA (+) system in THF and MTHF and found evidence for exciplex formation and a dependency of ln $[I(\mathrm{A}^*)/I(\mathrm{A^-D^+})]$ vs. $1/T$ similar to that shown in Figure 4, providing evidence of thermal production of ^{1}A* from $(\mathrm{A^-D^+})^*$. In ACN solutions at room temperature DMA (−)/TPTA (+) ecl also shows long wavelength emission in addition to that attributable to ^{1}DMA*. The temperature dependence of the intensity of the ^{1}DMA* emission over intensity of long wavelength emission does not follow the monotonic linear relation observed for the naphthalene (−)/TPTA (+) system in ACN. On the contrary the dependency (Figure 6) is more reminiscent of the cl results observed for the DMA (−)/TMPD (+) in THF system.[3b] In this case the exciplex is not observed and the long wavelength emission can be attributed to an excimer produced on TTA, eq 13, in a scheme similar to that observed

$$^3\mathrm{A} + {}^3\mathrm{A} \longrightarrow {}^1\mathrm{A_2}^* \qquad (13)$$

in pyrene (−)/TMPD (+) in ACN ecl.[17] Excimer emission from DMA has also been observed in the ecl of the DMA (−)/DMA (+) system.[18] Thus the interaction energy between DMA$\cdot^-$ and TPTA$\cdot^+$ is probably sufficiently weaker than that between naphthalene$\cdot^-$ and TPTA$\cdot^+$, so that this exciplex may not be formed in high dielectric constant solvents such as ACN. The effect of temperature on the relative monomer/long wavelength emission, as suggested by Weller and Zachariasse, provides a useful way of distinguishing between excimer and exciplex formation in ecl systems.

Benz[*a*]anthracene (−)/**TPTA** (+). This system shows $\Delta H°$ for the radical ion reaction sufficient to produce ^{3}A, and only slightly deficient to produce ^{3}D, but much smaller than that needed to produce the excited singlet states of A or D. The ecl emission at 390 nm corresponds to ^{1}A* while the long wavelength emission can be attributed to excimer and/or exciplex. Delayed fluorescence of BA shows evidence of an excimer formed by TTA.[6,19] However, exciplex formation between ^{1}BA* and diethylaniline has been observed.[15,20] Moreover, in our ecl experiments the ratio of long wavelength emission intensity to that of ^{1}BA* increases from 0.071 in ACN to 0.18 in THF, as would be expected of an exciplex, and the long wavelength emission fits the exciplex correlation described below. The long wavelength emission can thus be attributed to both ^{1}A$_2$* and $^1(\mathrm{A^-D^+})^*$ and the path of the reaction involves direct formation of the exciplex, eq 3, followed by emission and intersystem crossing to form ^{3}A, eq 11. TTA of ^{3}A yields ^{1}A*, eq 12, and ^{1}A$_2$*, eq 13. Some ^{3}D could also be formed from the exciplex, but it is too short lived to undergo appreciable TTA.

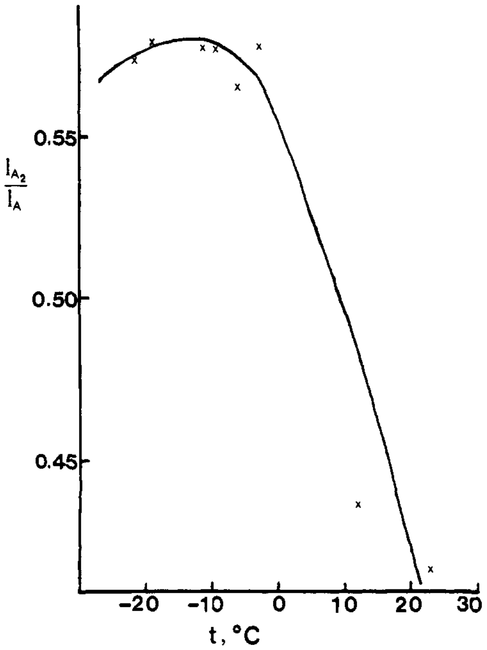

Figure 6. Temperature dependence of the DMA/TPTA system in acetonitrile. $I_{\mathrm{A_2}}/I_{\mathrm{A}}$ obtained from the peak height ratios of uncorrected ecl spectra at different temperatures. Ecl spectra were obtained from solution containing 1.2 mM DMA, 1.3 mM TPTA, and 0.1 M TBAP with a pulse duration of 1 sec by pulsing from −2.00 to 0.95 V vs. Ag at a platinum wire electrode.

Other Systems. The other systems listed in Tables I to III generally follow the behavior of those described above with the ecl depending upon the relative energy of the radical ion reaction and that of the excited states of the reacting species. A very small amount of shorter wavelength emission was observed when 1,1,4,4,-tetraphenyl-1,3-butadiene and 1,4-diphenyl-1,3-butadiene were used as acceptors, which might be attributable to excited singlet A or D emission, but it was so weak that it was difficult to investigate. No emission was observed in the benzaldehyde (−)/TPTA (+) system in either ACN or THF. The radical cations of both triphenylamine (TPA) and bis-1,8-(N,N-dimethylamino)naphthalene show only slight stability in ACN, but the naphthalene (−)/TPA (+) system shows quite bright ecl emission. On the other hand, both the cation and dication of N,N'-diphenylbenzidine are very stable in ACN, as reported by Adams et al.,[21] but only weak ecl is observed with naphthalene$\cdot^-$.

Correlation of Exciplex Emission with Electrode Potentials of Donors and Acceptors. The exciplex energy can be related to the ionization potentials of the donor molecules (IP$_\mathrm{D}$) and the electron affinity of the acceptor molecules (EA$_\mathrm{A}$) by eq 14, where $E(\mathrm{A^-D^+})$ is the transition energy of

$$E(\mathrm{A^-D^+}) = \mathrm{IP_D} - \mathrm{EA_A} - C + \Delta H_\mathrm{S}(\mathrm{A^-D^+}) - \delta E_\mathrm{FC} \qquad (14)$$

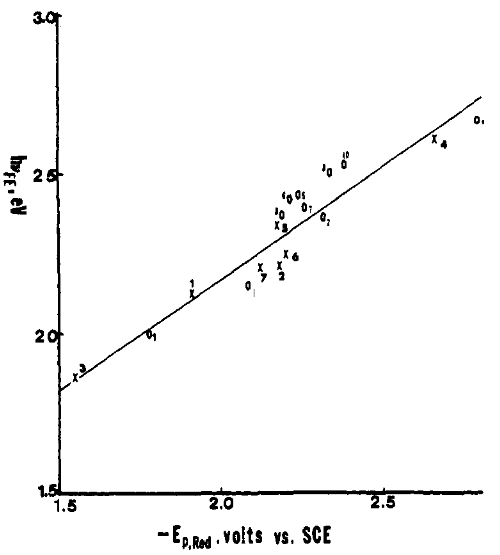

Figure 7. Energy of exciplex emission maximum vs. peak potentials for reduction of acceptor for ecl of TPTA with various acceptors in THF (O) and ACN (X) solutions. The numbers indicate acceptor molecules listed in Table I.

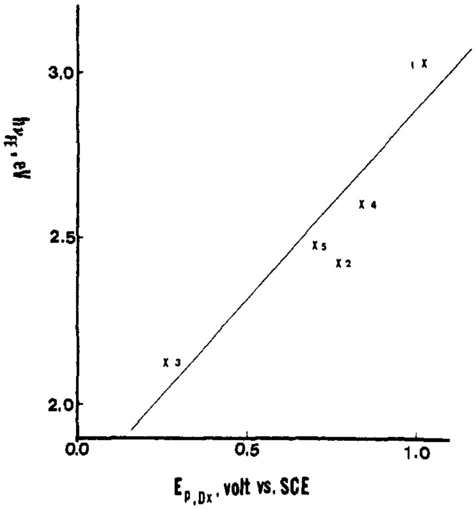

Figure 8. Energy of exciplex emission maximum vs. peak potential for oxidation of donor for ecl of naphthalene with various donors in ACN. See Table III for donor molecules.

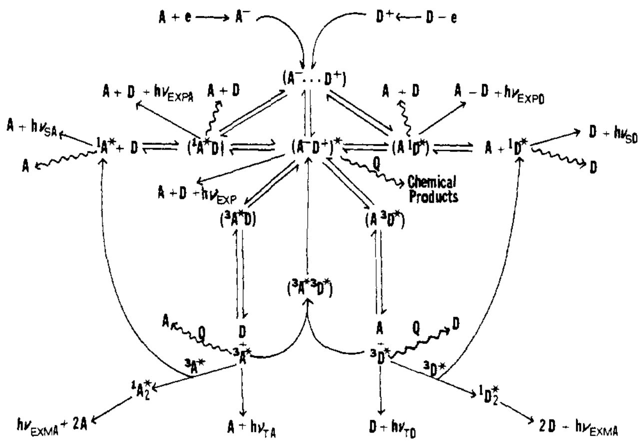

Figure 9. Schematic diagram for reaction paths in ecl. Heavy arrows represent radiative transitions and energy of species decrease (approximately) on proceeding from top to bottom of the figure.

the exciplex, C is the coulombic energy, $\Delta H_S(A^-D^+)$ is the enthalpy of solvation of the exciplex, and δE_{FC} is the energy difference between the product molecules after the Franck-Condon transition and their equilibrium states.[15,22] The electron affinities and ionization potentials vary linearly with the electrode potentials for the reduction of acceptor molecules and oxidation of donor molecules, respectively.[15,23-27] Thus a linear correlation between $E(A^-D^+)$ and both $E_{pc}(A/A^-)$ and $E_{pa}(D/D^+)$ is expected, since the peak potentials are directly related to the standard redox potentials for reversible electrode reactions. A plot of the emission maximum for the exciplex, E_{ex}, against E_{pc} for the different acceptor molecules with TPTA·$^+$ in both ACN and THF (Figure 7) shows a good linear correlation, fitting the relations

$$E_{ex} = -0.65E_{pc} + 0.86 \text{ (in ACN)} \qquad (15a)$$

$$E_{ex} = -0.68E_{pc} + 0.84 \text{ (in THF)} \qquad (15b)$$

This compares well, for example, with the correlation found for the energy of emission of exciplexes formed on photoexcitation of a number of aromatic hydrocarbons in *N,N*-diethylaniline with the half-wave potential for the reduction of the hydrocarbon, E_{A/A^-}.[15]

$$E_{ex} = -0.65E_{A/A^-} + 1.17 \qquad (16)$$

The difference in intercepts found in eq 15 and 16 reflects the differences in the donor molecules and in solvents. Similarly a plot of E_{ex} against E_{pa} for different donor molecules with naphthalene·$^-$ in ACN (Figure 8) shows a linear correlation fitting the equation

$$E_{ex} = 1.27E_{pa} + 1.60 \qquad (17)$$

The fact that the slope of these curves is not exactly unity reflects the nonunity slopes in EA_A vs. E_{pc} and IP_D vs. E_{pa} plots,[23-27] as well as stabilizing and destabilizing interactions in the exciplex.[4,28] The fact that such a correlation exists, however, is strong evidence that the long wavelength emission is attributable to exciplex rather than sensitized impurity or decomposition product emission.

Solvent Effects. In all cases (except for BP/TPTA) the exciplex emission is blue shifted in THF as compared to ACN, reflecting the charge transfer character of the exciplex. The total ecl intensities were always larger in THF compared to ACN and the relative exciplex to monomer emission was higher in THF as well. For example, for naphthalene (−)/TPTA (+), this ratio was 1.96 in ACN and 2.37 in THF, while for BA (−)/TPTA (+) it was 0.076 in ACN and 0.18 in THF. To investigate the effect of solvent further the behavior of the dibenzoylmethane (DBM) (−)/TPTA (+) system was studied in six different solvents. DBM was chosen because it was very easily reducible and formed a stable radical anion, even in CH_2Cl_2 which has a limited cathodic range, and because the DBM (−)/TPTA (+) system shows only exciplex emission ($-\Delta H° < E_T$ of DBM). The results in Table V show that the intensity of ecl emission decreases with increasing dielectric constant of solvent, with no ecl being observed for this system in DMSO. This finding of decreased emission from exciplex in more polar solvents is in agreement with past studies of exciplexes[3,4,7] where higher polarities have been shown to favor dissociation of the exciplex to the solvent separated ion pair. The decrease in $\Delta H°$ with increasing dielectric constant, previously noted in ecl studies, is also observed here (the value in CH_2Cl_2 appears low, perhaps reflecting a strong specific solvation effect).

Conclusion

The results here, along with past ecl and cl studies, demonstrate that radical ion reactions are an effective means of

Table V. Ecl of the Dibenzoylmethane (−)/TPTA (+) System in Various Solvents[a]

Solvent	ϵ	$\Delta H°$, eV	Ecl emission λ_{max}, nm (eV)	i_{pa}/i_{pc}[b]	Relative, ecl intensity
THF	7.6	2.45	615 (2.02)	1.00	1
CH_2Cl_2	9.08	2.23	627 (1.97)	0.93	2
Benzonitrile	25.5	2.28	620 (2.00)	1.00	3
DMF	36.7	2.24	622 (1.99)	0.91	4
CH_3CN	37.5	2.23	665 (1.86)	0.87	5
DMSO	46.6	2.19	No Ecl	0.71	6

[a] Solutions contained 0.10 *M* TBAP and *ca.* 1.5 m*M* DBM and TPTA. [b] i_{pa}/i_{pc} for DBM reduction in each solvent. Calculated from cyclic voltammograms recorded at a 200 mV/sec scan rate.

producing exciplexes in quite polar solvents. The efficiency of producing exciplexes in polar solvents by ecl techniques as compared to photoexcitation methods can be ascribed to: (1) the relatively high concentrations of radical ions, favoring formation of exciplex rather than dissociation (eq 3); (2) the possibility that the solvation of the radical ions ($A\cdot^-$ and $D\cdot^+$) is more like that of the exciplex $^1(A^-D^+)^*$ (compared to the solvation of $^1A^*$ and D (eq 1)), thus yielding a smaller solvent reorganization energy and faster reaction. The overall ecl process can be described as involving primary formation of an ion pair ($A^- \cdots D^+$) and exciplex, which can then undergo various reactions forming excited states, depending upon the relative energies of the species (Figure 9). This should not imply however that a longer distance electron transfer to form excited states of the reactants rather than exciplexes is not possible as well, especially for the case of bulky or sterically hindered radical ions (e.g., those of DPA or rubrene) where dimeric emitters are not observed.

Finally, we should point out that ecl can be employed to produce exciplexes that are not obtainable by the photoexcitation route. For example, benzophenone has close to a unity triplet yield upon photoexcitation, so that reaction of the excited singlet with a donor is very improbable. On the other hand direct production of an exciplex from the radical anion of benzophenone has been demonstrated here. Since exciplexes have been shown to be intermediates in photochemical reactions,[29] ecl offers the possibility of producing the same products, by electrochemical excitation rather than photoexcitation. Work on these kinds of reactions is currently in progress.

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