Electrogenerated Chemiluminescence

XXVI. Systems Involving Tetraarylpyroles, Tetraphenylfuran, and Tetraphenylthiophene

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ABSTRACT

The production of light upon the electron transfer reaction of electrogenerated radical ions of tetraarylpyroles [aryl = anisyl (TAP), phenyl (TPP), p-chlorophenyl (TCPF), p-tolylaminophenyl (TPA)], tetraphenylfuran (TPF), and tetraphenylthiophene (TPT) in systems containing these compounds alone in acetonitrile solutions or in mixed systems containing naphthalene, 2,5-diphenyl-1,3,4-oxadiazole, benzophenone, and tri-p-tolylamine is reported. Emission which corresponds to the fluorescence of the TAP, TPP, TPF, and TPT, as well as longer wavelength emission attributed to exciplex emission for some mixed systems, is observed. The singlet and triplet level energies of the compounds of interest are estimated and their cyclic voltammetric behavior described briefly.

The usual basic requirements for a system which produces light upon the electron transfer reaction of electrogenerated species, e.g., A- and D+ (electrogenerated chemiluminescence or ECL), include the formation of stable radical ions, the fluorescence of at least one of the parent species (A and D), and sufficient free energy release in the A-+D+ reaction to form an excited state. Moreover, efficient ECL systems, such as those involving 9,10-diphenylanthracene and rubrene, involve bulky molecules in which steric effects appear to hinder formation of complexes between the reactant species. Previous studies (1-6) have shown that tetra-aryl substituted five-member ring compounds (pyrroles, furans, and thiophenes)

X = NH
Ar = p-C6H4
Ar = p-C6H4OH
Ar = p-C6H4CH3
Ar = p-C6H4Cl

X = O
Ar = C6H5

X = S
Ar = C6H5

form stable radical cations upon electrochemical oxidation. Although their luminescent properties and their behavior upon reduction have not been previously investigated, they appeared to be interesting compounds for ECL studies either as the source of both radical ions or as the radical cation source in mixed systems.

Experimental

The preparation and purification of the pyrrole, furan, and thiophene compounds has been described (1-6). Tri-p-tolylamine (TPTA), naphthalene (NAP), benzophenone (BP), 2,5-diphenyl-1,3,4-oxadiazole (PPD), acetonitrile (ACN), and tetra-n-butylammonium perchlorate (TPAP) were obtained and treated as previously reported (7, 8). The benzene was treated with sodium for 48 hr and then distilled and degassed by four freeze-pump-thaw cycles. All solutions were prepared in an inert atmosphere glove box. Solution preparation, experimental procedures, apparatus, and instrumentation were as previously described (7, 8).

Results and Discussion

Fluorescence spectra of these compounds have not been previously described. These were obtained for millimolar solutions in acetonitrile and the position of the emission maxima are listed in Table I along with the u.v. absorbance maxima obtained in previous studies (1-6). The observed emission spectra were not as well defined as those reported for similar, less sterically hindered compounds, such as 4,5-diphenylimidazole (14) so that location of the 0–0 band was not possible. The reported singlet energies (Eₐ) in Table I were obtained by averaging the energies of the emission spectra and absorption maxima. This method gives Eₐ = 3.45 eV for TPF as compared to a value of 3.55 eV for 2,5-diphenylfuran as obtained from the well-resolved 0–0 band in the spectrum given by Berlman (14). Cyclic voltammetry (CV) and ECL experiments were generally performed in 2-3 mM solutions of the compound of interest in 0.1M TBAP-ACN. For TTP and TCPF, which were not soluble in ACN, a 1:1 mixture of ACN-benzene was employed as solvent. A typical cyclic voltammogram, that for TPF, is shown in Fig. 1. The CV results, given in Table I, show that the radical cations of the pyrroles are very stable while those of the furan and thiophene are moderately stable.

Table I. Electrochemical and spectroscopic data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation</th>
<th>Reduction</th>
<th>Cyclic Voltammetry</th>
<th>Spectroscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_a/ E_c</td>
<td>I_p</td>
<td>E_a/ E_c</td>
<td>I_p</td>
</tr>
<tr>
<td>TAP</td>
<td>+0.66</td>
<td>1.0</td>
<td>&lt;2.9</td>
<td>0</td>
</tr>
<tr>
<td>TPP</td>
<td>+0.90</td>
<td>1.0</td>
<td>2.78</td>
<td>0</td>
</tr>
<tr>
<td>TCPF</td>
<td>+0.91</td>
<td>1.0</td>
<td>3.38</td>
<td>0</td>
</tr>
<tr>
<td>TTF</td>
<td>+1.02</td>
<td>0.8</td>
<td>2.42</td>
<td>=1</td>
</tr>
<tr>
<td>TPT</td>
<td>+1.38</td>
<td>0.9</td>
<td>2.30</td>
<td>=1</td>
</tr>
</tbody>
</table>

* For other compounds in this study: Naphthalene; E_a = -2.88 V/SCE (7), E_c = 3.99 eV, E_e = 1.91 eV (10); PPD: E_a/ E_c = -2.17 V/SCE; BP: E_a = 3.25 eV, E_e = 3.06 eV; ACN: E_a/ E_c = 2.97 eV (11). For 0.1M TBAP/ACN solutions (except for TTP and TCPF) which used 1:1 ACN:benzene; scan rate, 200 mV/sec, I_p and I_c are anodic and cathodic peak potentials, I_a and I_c are anodic and cathodic peak currents.

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during the time scale of the experiment. For the pyrroles, the reductions occur close to the background reduction process with no anodic current observed on scan reversal. For TPF and TPT, a clear anodic peak is observed in CV, with $i_{pa}$ ~ $i_{pc}$ (where $i_{pa}$ and $i_{pc}$ are the anodic and cathodic peak currents).

One series of ECL experiments consisted of electrogeneration of the radical cations of the compounds of interest ($R^+$) and observing the emission during generation of the radical anion of the same molecule ($R^-$) or of NAP, PPD, or BP ($A^-$) (all of which form relatively stable anion radicals). In another series of experiments, the emission from the reaction of the compound radical anion ($R^-$) with the stable electrogenerated radical cation of TPTA (7, 12) ($D^+$) was studied. The ECL results for typical systems are shown in Table II. Except for TCPP, the systems involving the pyrrole, TPF, or TPT alone, i.e., as the source of both $R^+$ and $R^-$, showed emission similar to that of the fluorescence of the parent compound. The reaction enthalpy (13), $\Delta H^*$, in these cases was about the same as $E_a$, so that direct population of the excited singlet state upon electron transfer is possible. In reactions with NAP, PPD, or BP as acceptors or with TPTA as donor, as well as for TTP, TPF, and TPT alone, emissions at longer wavelengths were also observed. These will be discussed in more detail for a few of the cases investigated.

**TPP(-)/TPP(+).**—The cyclic voltammogram of TPP in 0.1M TBAP/ACN (Fig. 1) illustrates the stability of $TPP^+$ and the instability of the radical anion. After a cathodic scan in which the radical anion is produced, a reverse scan shows the appearance of a reversible system of $-0.23$ V vs. SCE. The nature of this system, probably originating from a reaction of the radical anion, was not investigated further, but was observed with all of the pyrroles investigated in this study. The ECL emission observed in this case was quite bright and stable with time for a frequency of pulsing of 500 Hz (Fig. 1).

**NAP(-)/TPP(+).**—The reaction enthalpy for the reaction of the rather stable NAP radical anion with $TPP^+$ is somewhat less than $E_a$ of TPP and much less than $E_a$ of NAP. The observed emission consists of a band at 400 nm, where TPP fluoresces, and a longer wavelength band at 445 nm. The former could originate via triplet-triplet annihilation of TPP while the latter band can be ascribed to a TPP-NAP exciplex. NAP has been shown to form exciplexes with various donors in ECL in ACN solutions with the energy of the exciplex emission, $E_{ex}$ correlating with the $E_{ex}$ of the donor according to Eq. [1] [note that the same spectrophotofluorometer and photomultiplier tube were employed in this study and the previous one (7)]

$$E_{ex} = 1.27E_{ex} + 1.60$$

The $E_{ex}$ of TPP of 0.90 V vs. SCE yields an $E_{ex}$ of 2.73 eV (equivalent to emission at 450 nm) with this equation, which is very close to the experimentally observed value. The longer wavelength emission observed for the PPD(-)/TPP(+) can probably also be ascribed to an exciplex. To examine if TPP-NAP exciplexes could be observed in photoexcitation experiments, the quenching of NAP fluorescence by TPP was investigated. Although TPP was an effective quencher of NAP fluorescence in both ACN and CHCl$_2$ solutions, no longer wavelength emission was observed. Thus, as has been observed previously (7), formation of the exciplex on direct reaction of the radical ions is

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**Table II. Summary of ECL results**

<table>
<thead>
<tr>
<th>Compound as donor and following acceptors</th>
<th>Systems with compound as donor and following acceptors</th>
<th>Naphthalene</th>
<th>PPD</th>
<th>Benzophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>System alone</td>
<td>$\Delta H^*$</td>
<td>$\lambda_{max}$</td>
<td>$I_{rel}$</td>
</tr>
<tr>
<td></td>
<td>$R^-(+)$</td>
<td>(eV)</td>
<td>(nm)</td>
<td></td>
</tr>
<tr>
<td>TAP ($&gt;3.4$)</td>
<td>3.16</td>
<td>400 (3.08)</td>
<td>3</td>
<td>0.51</td>
</tr>
<tr>
<td>TTP ($&gt;3.5$)</td>
<td>3.31</td>
<td>400 (2.93)</td>
<td>3</td>
<td>0.51</td>
</tr>
<tr>
<td>TCPP ($&gt;3.3$)</td>
<td>3.45</td>
<td>400 (2.93)</td>
<td>3</td>
<td>0.51</td>
</tr>
<tr>
<td>TPF ($&gt;3.5$)</td>
<td>3.50</td>
<td>400 (2.93)</td>
<td>3</td>
<td>0.51</td>
</tr>
<tr>
<td>TPT ($&gt;3.5$)</td>
<td>3.50</td>
<td>400 (2.93)</td>
<td>3</td>
<td>0.51</td>
</tr>
</tbody>
</table>

- **Note:** $\Delta H^*$ is the enthalpy of the radical ion reaction, calculated using the data in Table I and the equation (Ref. 13): $\Delta H^* = E_{ex} - E_{ex} - 0.16$ (eV); $I_{rel}$ is the approximate relative intensity of the ECL (dependent also on frequency and solution conditions) with respect to the PPD(-)/thianthrene(+) system, taken as having $I_{rel} = 100$; $\lambda_{max}$ ECL is position of ECL peak(s), generally with uncertainty of ±24 nm.

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**Fig. 1. TPP(-)/TPP(+) system.** (a) Cyclic voltammogram of 3.4 mM TPP in 0.1M TBAP-ACN at Pt electrode; scan rate, 200 mV/sec. (b) ECL of the above solution at 500 Hz. (c) Fluorescence spectrum of 3.4 × 10⁻⁵M TPP in ACN; $\lambda_{exc} = 323$ nm.
a more efficient route than production via photoexcitation. The low intensity of the ECL in this case probably results from dissociation of the exciplex to the ions or to TTP which undergoes quenching and triplet-triplet annihilation reactions.

**TTP(--)/TTP(+)**—A cyclic voltammogram of TTP (Fig. 2) shows formation of a stable radical cation but the reduction of TTP can hardly be distinguished from the background reduction at ca. -2.85 V, and the TTP radical anion is quite unstable. Just as with TPP, a new reversible system appears during CV at -0.26 V following a reduction scan. In spite of the instability of the anion, the system shows quite stable ECL consisting of two peaks (Fig. 2). The more intense at 410 nm corresponds to \( \text{TTP}^* \) formed directly upon the energy sufficient radical ion reaction; this peak consists of emission during the cathodic pulses and shows maximum intensity at higher frequencies (ca. 500 Hz). The second peak consists of emission only on anodic pulses and appears only at low frequencies, showing a maximum intensity at 1 Hz. After about 1 hr of ECL experiments, the CV and the fluorescence spectrum are essentially the same as the starting solution. While the longer wavelength peak could be attributed to an excimer, this doesn't appear to be reasonable since it is only found on anodic pulses, it disappears at higher frequencies, and it is not observed for the structurally similar TTP. A better explanation for this emission invokes the production of a reactant during the cathodic pulse which reacts with radical cation to produce light. At high frequencies the extent of the TTP- decomposition reaction would be small, but at lower frequencies appreciable side-product would be produced. Evidence of this side-product is not obtained by fluorescence measurements after extended ECL, as is usually found for cases in which emission is observed from radical ion decomposition products (15, 16), so that the side-product, if formed, decomposes during or after the electron transfer reaction.

**TPT(--)/TPT(+)**—Both radical cation and anion of TPT are stable on the CV time scale (Fig. 3) and the ECL emission which results from the radical ion electron transfer reaction is rather intense with an emission maximum located between 412 and 438 nm, varying from experiment to experiment. Similar results are obtained when NAP, PPD, or BP are the sources of the radical anions. For the BP(--)/TPT(+) system two separate peaks at 418 and 433 nm can be distinguished. In all cases the electrodes are filmed after extended ECL experiments (ca. half-hour), resulting in changes in the CV. This filming might account for the lack of reproducibility of the observed emission peak location, if the ECL intensity was changing with time while the spectrum was being recorded. The emission at 410-415 nm is probably that of \( \text{TPT}^* \) formed either directly, or for the case of NAP and BP, via triplet-triplet annihilation. The emission at 437 nm could be from a
decomposition product of TPT$^+$. Previous studies (6) have shown that cis-dibenzoylestilbene can form from decomposition of the radical cation. A solution of this species, prepared by a previously published procedure (17) did not show fluorescence, however.

\[ TPT^-(\text{-})/TPTA^+(\text{+}) \]

The ECL in this case shows two distinct peaks: one at 418 nm for anodic pulses and one at 520 nm for cathodic ones. The first peak is again attributable to $^1\text{TPT}^*$ formed on triplet-triplet annihilation while the longer wavelength emission can be attributed to an exciplex. The emission maximum observed in this case agrees quite well with the relation found for exciplexes formed in ECL resulting from reaction of TPTA$^+$ with various acceptors (7).\[ E_{ex} = -0.65E_{pc} + 0.86 \] Triplet levels.—Although TPF and TPT show ECL with BP as the source of radical anion, none of the pyrroles do. One possible explanation might be that the enthalpy of the radical ion reaction (2.4-2.6 eV) is insufficient to produce the corresponding pyrrole triplet. To estimate the triplet energies, phosphorescence measurements of TPP and TTP contained in an ethanol glass at 77K were performed. The triplet energies found for TTP and TTP, 2.48 and 2.46 eV, respectively (with corresponding lifetimes under those conditions of 2.9 and 2.7 sec), demonstrate that the triplets could be formed in the BP$^-(\text{-})$/TPT$^+(\text{+})$ and BP$^-(\text{-})$/TPT$^+(\text{+})$ systems.

A more probable explanation is suggested by the CV of the pyrrole/BP systems. Upon addition of TPP or TTP to a system containing BP, the reverse current following a reductive sweep forming BP$^-$ is strongly decreased compared to the behavior of BP$^-$ in the absence of these species (Fig. 4). The reversible system centered at $-0.23$V appears when BP is reduced in the presence of TTP (just as it does for the TTP alone system) even when the negative limit of the cathodic sweep is not sufficiently negative to cause TTP reduction. Thus BP$^-$ reacts in some way with TTP decreasing its lifetime and preventing ECL. Although we did not investigate the nature of this reaction, a possible one involves abstraction of a proton by the BP$^-$.

![Cyclic voltammetry of 1.8 mM BP in 0.1M TBAP-ACN at PT electrode with scan rate of 100 mV/sec (a) in presence of 1.7 mM TPP and (b) in absence of TPP.](image)

This system could also be formed by reaction of TPT with TPT$^-$, thus explaining the appearance of the reversible systems upon reduction of TPT in the absence of BP. This proton abstraction reaction could not occur, however, with TPF or TPT. Moreover, this explanation is consistent with a previous study (18) which showed that in the presence of a base, e.g., acetate, CV of a TTP solution results in the appearance of a reduction peak at $-0.3$V, attributed to the reduction of the neutral radical.

**Conclusions**

A number of systems involving the compounds of interest are capable of producing ECL. While several rather intense systems were found, the lifetime of the systems under the conditions used here were not particularly good and electrode filming frequently occurred. We might note that Zweig et al. (19) noticed that the ECL from simple arylfurans was less satisfactory than that obtained from isoazofuran derivatives. Exciplex formation has been demonstrated on direct radical ion reaction in ACN solutions under conditions where photolysis or acetate, CV of a TPP solution results in the appearance of a reduction peak at $-0.3$V, attributed to the reduction of the neutral radical.

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**REFERENCES**

Anodic Oxidation of Anhydrous Methanol

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ABSTRACT

The electrooxidation of anhydrous methanol was studied with several electrochemical techniques. The effect of controlled amounts of water in the nonaqueous system was followed. The product analysis confirmed the production of formaldehyde as the predominant reaction product in this nonaqueous system. The addition of controlled quantities of water brings about changes in the polarization curves presumably owing to the formation of oxides on the platinum surface and to the production of formate ions. Strongly adsorbed species are observed at low anodic polarizations in the completely anhydrous system as well as in the presence of water. The exact nature of these species could not be identified but the formation of a polymeric inert film is suspected. The effect of adsorbed sulfur on the platinum working electrode was also examined; the adsorbed sulfur layer is unstable at high anodic potentials and causes an inhibition of the anodic oxidation of methanol or methoxide ion.

Electrooxidation reactions in nonaqueous solvents have been widely studied, in particular with respect to high energy density batteries and electroorganic synthesis. The electrooxidation of methanol in aqueous solutions has been extensively investigated since this material can be a very attractive fuel in a methanol-air fuel cell (1-3). However, relatively few studies have been carried out to elucidate the anodic reactions of pure anhydrous methanol. Recently such work has been published by Sundholm (4) and Iwakura et al. (5); the residual water content was rather high (120 ppm) in the work of Iwakura, and also appreciable in the experiments reported by Sundholm. No special procedures seem to have been undertaken to remove the last traces of water and also to work under conditions where the reacting solutions could be kept anhydrous (4,5). In the present work the residual water content was kept as low as possible (below 10 ppm) and the experiments were carried out in a controlled atmosphere enclosure where the anhydrous conditions remained unchanged.

In recent years, attempts have been made to increase the electrochemical activity of electrodes for the electrooxidation by adsorbing sulfur, among other materials, on the working electrode (6-9). Here, the effect of this additive on the electrooxidation of methanol is explored further.

Experimental

The purification of methanol and the electrochemical polarization experiments were carried out in a controlled atmosphere chamber supplied by Vacuum/Atmospheres Corporation, Model HE454. Under a dynamic flow of argon, the residual water and oxygen content could be maintained in the few ppm range. The methanol was dehydrated according to the following procedure (10): commercial spectro-grade methanol was distilled once after the dissolution of metallic sodium in it; this distilled methanol was then refluxed for one day over magnesium turnings with traces of iodine; this solution was then distilled and the distillate kept in a glass bottle in the controlled atmosphere chamber. All these procedures were carried out under controlled atmosphere. Determination of the residual water was performed with a modified automatic Karl-Fischer titration apparatus, the Aquastat II; the result of this analysis indicated a residual water content below 10 ppm. The desired concentration of sodium methoxide (the electrolyte solute) was obtained by the dissolution of metallic sodium in the purified methanol.

The steady-state automatic polarization curves were obtained for 20 mV potential steps using electrochemical apparatus and method described previously (11); the electronic apparatus were located outside the controlled atmosphere chamber and the electrical contacts were made via appropriate feedthroughs. A separate electrochemical system was used outside the chamber to carry out the electrode coverage experiments in aqueous solutions. This second electrochemical cell was equipped with a system allowing the electrode to be rinsed thoroughly with deoxygenated 1N Uitrex sulfuric acid. This second aqueous system is required to provide a source of oxygen in the oxidation of the species adsorbed on the electrode in the nonaqueous medium. The transfer of the electrode from the dry box to the aqueous system was performed under argon atmosphere, keeping the exposure of the electrode to the ambient air to a strict minimum.

The description of the instruments and the method used for the determination of the electrode coverage are described elsewhere (12). The integration of the current for the determination of the electrode coverage during anodic or cathodic potential sweeps was performed either by a manual method or electronically as described previously (12).

The analysis of formaldehyde in concentrated methanol requires a method different from the one...