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# Electrogenerated Chemiluminescence

## XI. Electrochemistry and Electrogenerated Chemiluminescence in Scintillator Dye Melts

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### ABSTRACT

Melts of scintillator compounds which are solid at room temperature, such as 2,5-diphenyloxazole (PPO) and 2,5-diphenyloxadiazole (PPD) containing several quaternary ammonium salts as supporting electrolytes, were examined as solvents for electrochemical and electrogenerated chemiluminescence (ECL) studies. Although the resistance of these solutions was high, cyclic voltammetry of 9,10-diphenylanthracene and rubrene in PPO showed the production of stable radical anions and cations for both compounds, and the ECL emission was essentially the same as the fluorescence emission of these compounds in PPO. ECL of rubrene was also observed in molten phenanthrene, PPD, thianthrene, and p-terphenyl, as well as in mixtures of PPO with 1- or 2-methylnaphthalene.

There has been much interest in recent years in the application of nonaqueous solvents in electrochemistry (1). Many of these solvents have the advantage of rather wide potential limits before the solvent itself or the supporting electrolyte undergoes reduction or oxidation at an inert electrode; these solvents are also often less likely to react with electrogenerated species. Most solvents employed are liquid at room temperature [*e.g.*, N,N-dimethylformamide (DMF), acetonitrile (ACN)] while several liquefy at low temperatures ($SO_2$, $NH_3$). Only a few studies of organic systems have employed as solvents compounds which are solid at room temperature; these include dimethylsulfone (mp 127°C) (1, 2), molten ethylammonium chloride (3), and the $AlCl_3$-KCl molten salt system (4). Recent studies involving aprotic solvents include electrogenerated chemiluminescence (ECL) of aromatic compounds, where electrogenerated radical anions ($R^{\overset{-}{\cdot}}$) and radical cations ($R'^{\overset{+}{\cdot}}$) react to form excited state species

$$R^{\overset{-}{\cdot}} + R'^{\overset{+}{\cdot}} \rightarrow R^* + R' \text{ or } R'^* + R \qquad [1]$$

We have recently reported on the ECL of the scintillator material 2,5-diphenyl-1,3,4-oxadiazole (PPD) with thianthrene in acetonitrile solutions (5) and also on the ECL of several other scintillator materials, including 2,5-diphenyloxazole (PPO), 2,5-diphenylfuran (PPF), and p-terphenyl (PTP) (6).

Because PPO has a low melting point (70°C), we thought it of interest to investigate the ECL of molten PPO itself, using a quaternary ammonium salt as a supporting electrolyte. We had additional reason to investigate ECL in molten PPO itself, because, although the ECL of PPO in nonaqueous solvents is of a very unsatisfactory nature (6), showing low intensity, unstable spectral distribution of the emitted light and poor stability of the electrogenerated cation radicals, we have also found that the presence of a 10-fold molar excess of PPO with respect to DPA increases the DPA ECL intensity when only $DPA^{\overset{+}{\cdot}}$ and $DPA^{\overset{-}{\cdot}}$ are electrogenerated in an ACN-0.1M TBAP solution. In the course of these studies we also investigated PPO and related compounds as solvents for electrochemical and ECL studies of other organic species. Although molten scintillator compounds have been used as nuclear reactor coolants (7), to our knowledge they have not been used previously as solvents for electrochemical or spectroscopic studies.

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Key words: nonaqueous solvents, elevated temperature, luminescence, spectroscopy, scintillators, cyclic voltammetry, chemiluminescence.

## Experimental

*Chemicals.*—Scintillation grade 2,5-diphenyloxazole (PPO) was obtained from Aldrich Chemical Company and from Nuclear Equipment Chemical Corporation (NEC). Phenanthrene, 98+%, obtained from Aldrich, was purified by four recrystallizations alternately using spectroscopic grade methanol and hexane. A portion of this purified sample was vacuum sublimed with no detectable improvement in the phenanthrene sample. Thianthrene (TH) was obtained from Aldrich, and it was used without further purification after its properties were compared with specially purified thianthrene samples (5). The p-terphenyl (PTP), scintillation grade, was supplied by NEC. Scintillation grade 2,5-diphenyl-1,3,4-oxadiazole (PPD), rubrene (puriss), and one of the 9,10-diphenylanthracene (DPA) samples were obtained from Aldrich. A second sample of DPA was obtained from City Chemical Corporation. The 1- and 2-methylnaphthalene were obtained from Aldrich, and together with the scintillation grade compounds, they were used without further purification after no electrochemical or fluorescent impurities could be detected. Because vacuum sublimation actually leads to considerable decomposition of rubrene and DPA, that technique was abandoned in favor of recrystallization from spectrograde hexane. Several experiments were conducted using as-received rubrene or DPA and there was no observable difference between these results and data obtained using samples purified by recrystallization from spectrograde hexane. Tetraphenylporphin (TPP) was obtained from Mad River Chemical Company and was used without furthur purification. Tetra-n-butylammonium perchlorate (TBAP), tetraethylammonium perchlorate (TEAP), tetramethylammonium perchlorate (TMAP), tetra-n-butylammonium fluoborate ($TBABF_4$), and tetramethylammonium fluoborate ($TMABF_4$), all polarographic grade, were obtained from Southwestern Analytical Chemicals, Inc., and used without further purification; they were dried for 48 hr at 90°C in a vacuum oven and stored in a desiccator over anhydrone. In most experiments TBAP was used as a supporting electrolyte, although all other supporting electrolytes (except those containing chloride anion) behaved satisfactorily in molten PPO.

*Apparatus.*—For preliminary and spectroscopic experiments a cell having a detachable Pyrex or quartz ground glass bottom compartment, a central electrode compartment, and a vacuum adapter (8) was used; when luminescence was a result of optical excitation, the central section housing the electrodes was removed, so that the possibility of interference with the right angle excitation process could be eliminated. The cell used in most ECL experiments is shown in Fig. 1 (a silver wire reference electrode, similar in size and position to the platinum working and auxiliary electrodes, is not shown in the drawing). Through a vacuum adapter the cell can readily be evacuated to $10^{-6}$ Torr when empty due to the absence of the more numerous ground glass joints used in usual cell construction. Since the solvent-supporting electrolyte system is solid at room temperature, the usual freeze-pump-thaw deaeration procedure is replaced by a pump-melt-freeze (PMF) cycle; the pressure over the ECL mixtures was reduced to $<10^{-5}$ Torr by several PMF cycles. We have previously reported (9) that a silver wire was an acceptable reference electrode in the case of dimethylformamide-TBAI solutions; the use of a silver reference electrode in molten salt electrochemistry has also been described (10). The applied potential or current was controlled using a PAR Model 170 Electrochemistry System (Princeton Applied Research Corporation) which could be linked with a Wavetek Model 114-G function generator for fast electrogeneration. The ECL emission was detected using an Aminco-Bowman spectrophotofluorometer (SPF) in conjunction with a Hamamatsu TV Corporation R-456 photomultiplier tube (PMT) which is required for spectral measurements extending beyond 580 nm. To detect the very low intensity ECL of TPP the SPF was modified to allow operation of the PMT at 1100V d.c. rather than at the original 700V d.c. The ECL cell was placed in a temperature-controlled cell compartment (Aminco-Bowman part No. 4-8262) and hot water was circulated using a Labline-controlled temperature bath. In the case of phenanthrene it was found necessary to boost the heating rate obtained from the constant temperature bath by using a heating tape powered by an auto transformer, around the constant temperature cell compartment in addition to the hot water. The signal from the SPF was fed either into a Moseley 7005A X-Y recorder, or to a Tektronix storage oscilloscope equipped with a Polaroid camera. An alternate heating arrangement, mainly used for electrochemistry and visual observation of ECL, involved use of a small Pyrex bath filled with water or mineral oil, and heated with an immersed Nichrome coil. In a typical experiment the constant temperature bath and the controlled temperature cell compartment of the SPF are heated to reach the desired temperature (commonly 95°-97°C for the Labline bath and 75°-80°C for the cell compartment heated by the circulating hot water) while the clean cell is evacuated on a vacuum line to a pressure less than $10^{-6}$ Torr. The solid compounds are next introduced (usually 1.000g PPO, 0.100g TBAP, and 10.0 mg DPA or rubrene), and the cell is evacuated again. Several PMF cycles are carried out before the cell is permanently sealed using a natural gas-oxygen torch. Cells so prepared remain in an apparently contamination-free state for as long as 18 months as attested by essentially identical electrochemical and ECL results obtained at various time intervals. The stability of the silver wire reference electrode in these systems appeared very satisfactory.

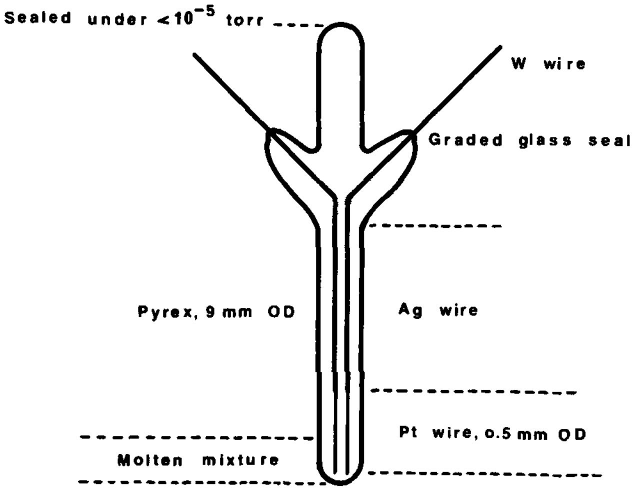

Fig. 1. Electrochemical and ECL cell.

## Results and Discussion

*Electrochemistry of the melts.*—In selecting a solvent for electrochemical work, it is necessary that the potential limits of the solvent-supporting electrolyte system, *i.e.*, the potentials at which the electrode-solvent system shows reduction and oxidation, are wide enough to encompass the potential region of interest. The potentials at which several of the scintillator compounds and solutes of interest reduce and oxidize in ACN solutions containing 0.1M TBAP are shown in Fig. 2. (The structures of these compounds and other compounds that are discussed in this work are shown in Fig. 3.) These potentials suggest that the pure scintilator compounds, such as PPO and PPD, will have sufficiently wide potential ranges to be useful solvent systems. Some of the more useful molten solvents and their approximate potential ranges are given in Table I.

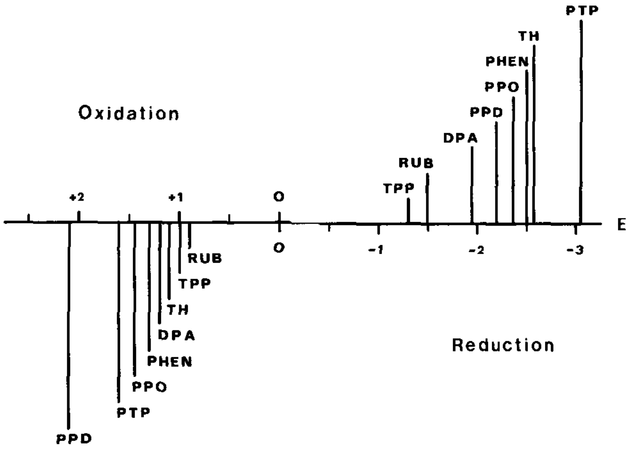

Fig. 2. Oxidation-reduction potentials of scintillator dyes and solutes. Electrochemistry in solutions of 0.1M TBAP in $CH_3CN$ at a platinum electrode vs. a Ag wire reference electrode (except for PTP which was reduced in propylene carbonate-0.1M TBAP). The oxidation and reduction limits of DMF and ACN vs. the Ag reference electrode are +1.7 to −2.8 (DMF) and +2.3 to −2.9 (ACN-TBAP).

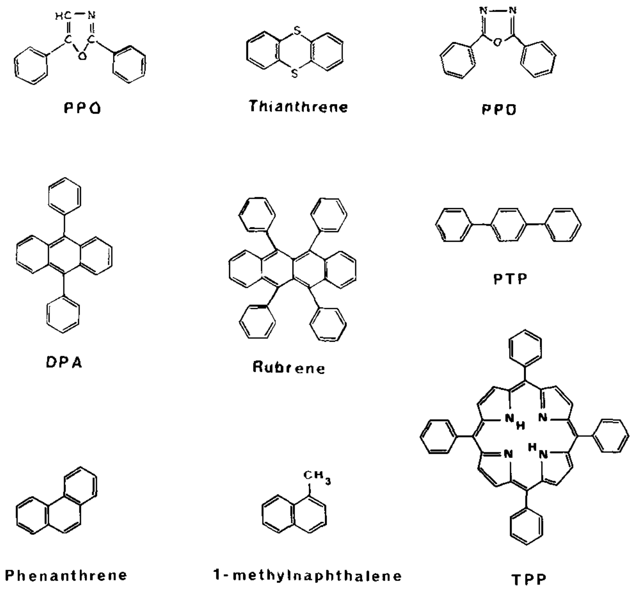

Fig. 3. Structural formulas. Accepted abbreviations (11) are used where possible in naming the compounds.

In ECL experiments attempted in the molten scintillator solvent systems without added solutes other than supporting electrolytes (*e.g.*, Table II, 5 and 18), no light emission was observed.

*Electrochemistry of rubrene and DPA in melts.*—The melts could be employed as solvents for the aromatic hydrocarbons rubrene and DPA conventionally used in ECL studies. Typical cyclic voltammograms in molten PPO-TBAP are shown in Fig. 4 and 5. These voltammograms are similar in shape to those found in DMF and ACN and show that the radical anion and cation of rubrene and DPA are stable in PPO under these conditions. The differences of the peak potentials of the forward and reversal waves are larger than those for nernstian electrode reactions at these temperatures (*e.g.*, for rubrene reduction $E_{pc} - E_{pa} = 400$ mV (exp); compared to 67 mV [theoretical]). However, the resistance of these solutions is high so that uncompensated resistance effects are probable. The cyclic voltammograms all show an increase in peak currents under continuous cycling (which is opposite to the usual behavior observed for multiple scans) as well as a decrease in the separation of the forward and reversal $E_p$-values. This effect may be caused by some kind of filming of the platinum wire electrode in molten PPO, a film which is being removed under continuous cycling, accompanied by an increase in the active area on the electrode. It is also possible that the stable electrogenerated cations and anions make a contribution to the total ionic population of the solution, especially in the vicinity of the electrode and decrease the uncompensated *iR*.

Table I. Some of the molten solvents used and their useful potential ranges

| Solvent (MP) | Electrolyte | Oxidation-reduction limit (V *vs.* Ag reference electrode) |
|---|---|---|
| PPO (70-72) | TBAP | +1.5/−2.2 |
| PPD (140-141) | TBAP | +1.8/−2.0 |
| TH (154-6) | TBAP | +1.1/−2.4 |
| TBAP (217-8) | — | +2.8/−3.0 |
| PHEN (100-1) | TBAP | +1.4/−2.2 |

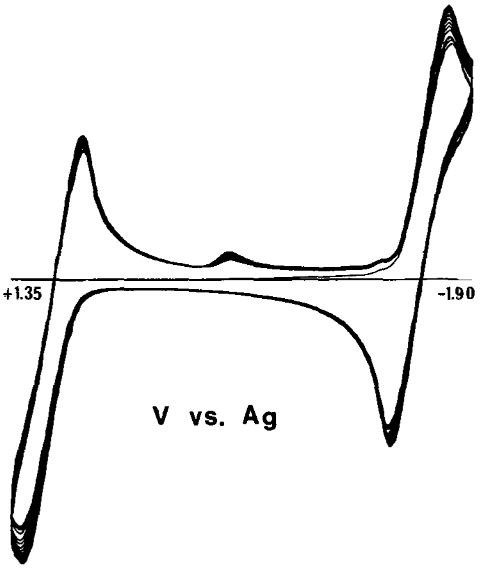

Fig. 4. Cyclic voltammogram of rubrene in molten PPO-TBAP. Sweep rate was 100 mV/sec; rubrene concentration was 3 mM.

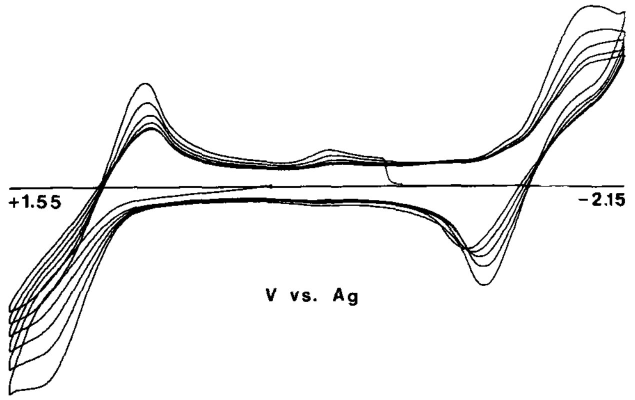

Fig. 5. Cyclic voltammogram of 9,10-diphenylanthracene in molten PPO-TBAP. Sweep rate was 100 mV/sec; DPA concentration was 3 mM.

The relatively high resistance of these molten solutions was evidenced by very high uncompensated *iR* losses; for example, when currents as low as 200 $\mu$A were passed, the full *iR* compensation of the PAR had to be applied.

*ECL in molten solvents.*—The major effort in this research was directed toward a study of ECL in the molten systems. Important requirements in observing ECL are that the excited state species formed by the radical ion annihilation reaction [1], are not quenched to a large extent by the solvent molecules and that the solvent does not absorb the emitted radiation. To investigate these effects a study of the fluorescence of the solvent PPO, and of solutions of rubrene and DPA in PPO was undertaken. The fluorescence spectrum obtained in molten PPO itself, shown in Fig. 6, consists of a single peak shifted to the red with respect to PPO emission obtained in dilute solutions at 3800 nm. In cyclohexane solutions upon change of the PPO concentration from 0.1 to 25 g/liter, the fluorescence emission peak decreases in height and broadens toward the red region of the spectrum (11); this broadening, which is usually attributed to excimer formation, is not found in the pure PPO melt. The attenuation of certain wavelengths of the emission beam in traversing the *ca.* 6 mm of molten PPO from the center of the cuvette where excitation occurs may also be a factor. It is also possible that the observed fluorescence is caused by a trace impurity in the PPO, although the shape of the fluorescence emission spectrum is independent of excitation wavelength from 2800-3800 nm. Both DPA and rubrene exhibit fluorescence spectra in PPO (Fig. 7 and 8) which are very similar to those seen for these compounds in dilute solutions of ACN.

When the platinum working electrode in a molten PPO-TBAP solution containing either DPA or rubrene is pulsed between potentials where $\overset{-}{\mathrm{R}\cdot}$ and $\overset{+}{\mathrm{R}\cdot}$ are formed ECL results; typical ECL emission spectra for pulse lengths of 0.05-1 sec are shown in Fig. 9 and 10. The ECL spectra are virtually the same as the fluorescence spectra in PPO and hence, nearly the same as the ECL spectra in ACN and DMF, so that there is no evidence for interaction between the PPO and the excited states. Neither is there a temperature effect on the ECL spectra for DPA or rubrene in PPO as compared to ECL in ACN or DMF, although there is a small shift of the rubrene ECL peak toward the red. The emitted ECL light was very steady with time on repeated cycling for both rubrene (Fig. 11a) and DPA (Fig. 11b), showing stability of the radical ion species in this medium. Experiments involving other supporting electrolytes (TBABF$_4$, TEAP, TMAP) in PPO and other scintillator melts (PPD, PTP, TH, PHEN) are shown in Table II. We also tried molten supporting electrolytes (*e.g.*, TBAP, TBACl) themselves as solvents. The electrochemical behavior of rubrene and

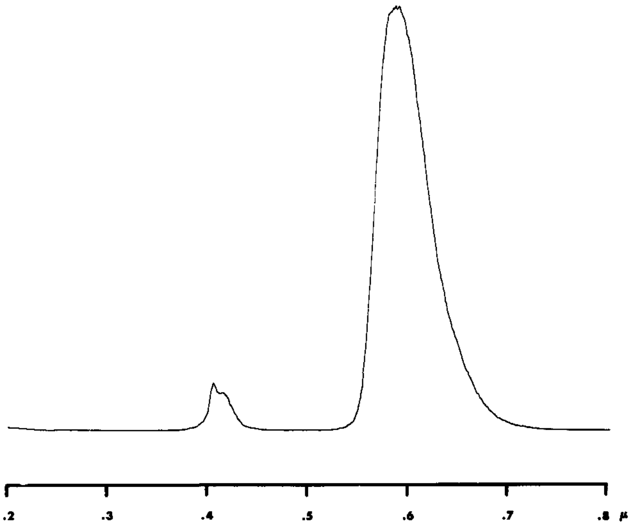

**Fig. 8.** Fluorescence spectrum of rubrene in molten PPO. Rubrene concentration was 3 mM; peak at 0.40μ represents scatter of λ excitation.

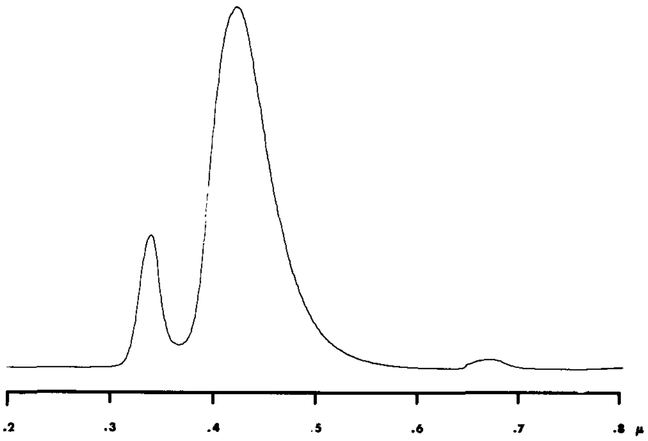

**Fig 6.** Fluorescence spectrum of molten PPO. Peak at 0.34μ represents scatter of λ excitation.

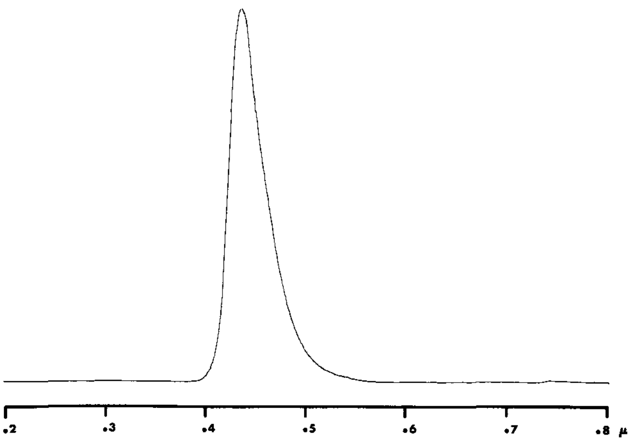

**Fig. 7.** Fluorescence spectrum of 9,10-diphenylanthracene in molten PPO. DPA concentration was 3 mM; λ excitation = 400 nm.

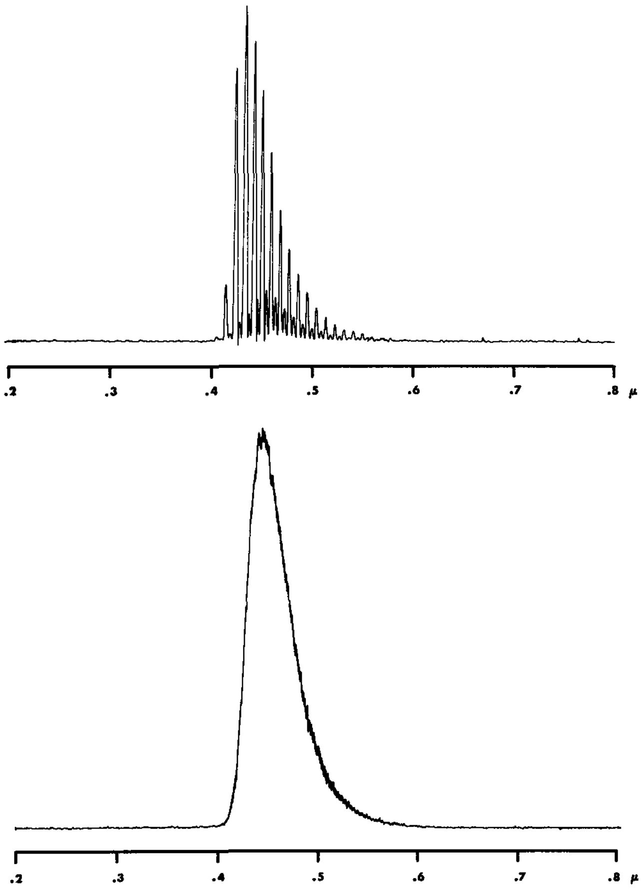

**Fig. 9.** Spectral distribution of the 9,10-diphenylanthracene ECL emission in molten PPO-TBAP. Potential steps between −2.15 and +1.55 (V *vs.* Ag reference electrode) at 0.5 Hz (top) and 5 Hz (bottom); DPA concentration was 3 mM.

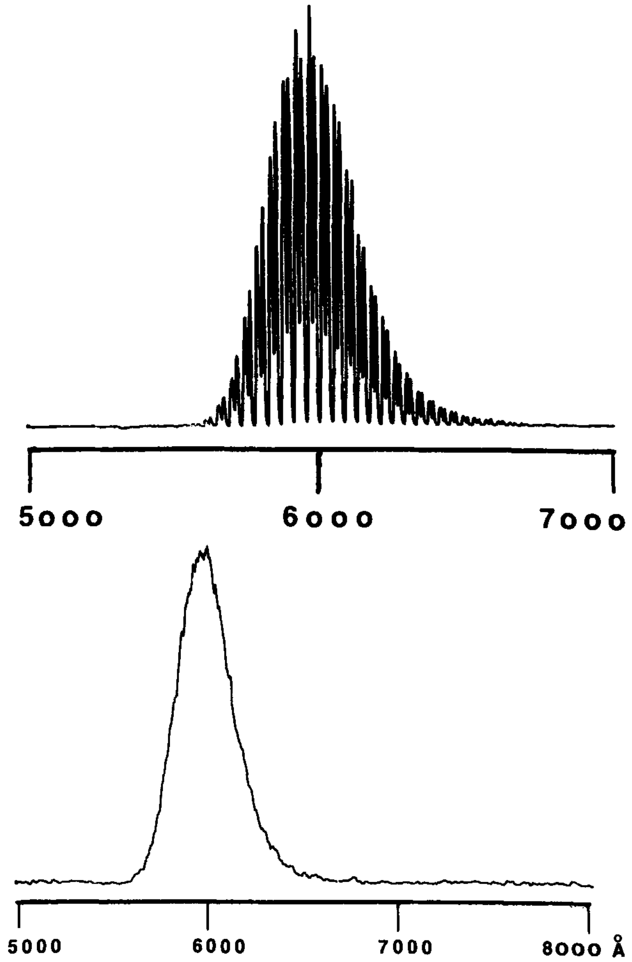

**Fig. 10.** Spectral distribution of the rubrene ECL emission in molten PPO-TBAP. Rubrene concentration was 3 mM. Top: voltage pulses with $+4.00/-2.50$ limits at 1 Hz; bottom: potential steps between $-1.90$ and $+1.40$ (*V vs. Ag reference electrode*) at 10 Hz.

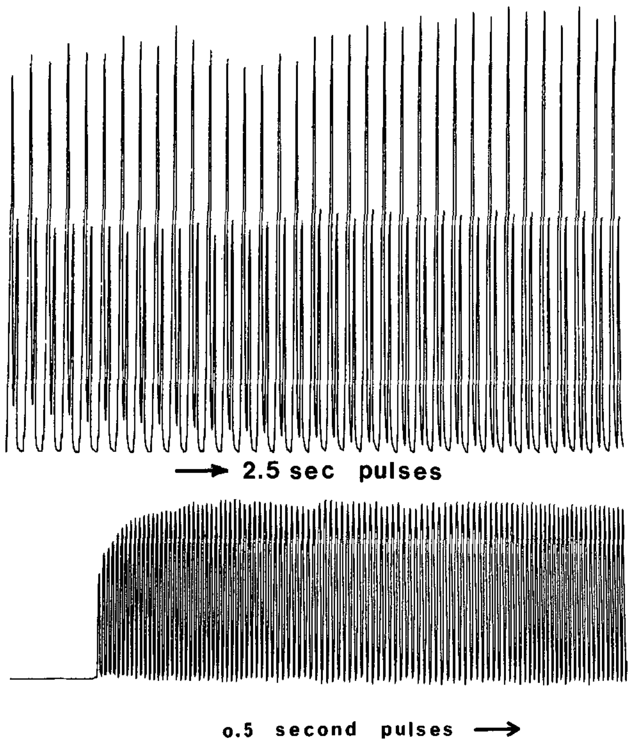

**Fig. 11.** Intensity-time characteristics of the rubrene (a, top) and 9,10-diphenylanthracene (b, bottom) ECL emission at the wavelength of spectral maximum in molten PPO-TBAP.

DPA in these was generally unsatisfactory and no ECL was observed with them. In molten TBAP the cyclic voltammetric behavior of both DPA and rubrene was characterized by irreversible waves and unstable radical ions. In molten TBACl the reduction of DPA shows reversible cyclic voltammetric behavior at $-1.4$V *vs.* Ag reference electrode; the oxidation background limit of TBACl occurs at $+1.5$V *vs.* Ag reference electrode, so that oxidation of DPA or rubrene to the cation radical cannot be observed. As shown in Table II, all of the following molten scintillator-TBAP-rubrene systems produced ECL: PPD, TH, PHEN, and PTP. Not all compounds with seemingly acceptable properties were usable, however; N,N-diphenylformamide, for example, was found to be unsuitable to observe rubrene ECL. Also, the $PPD^-/TH^+$ pair, which has good ECL characteristics in ACN-TBAP (5), was found to yield no detectable luminescence in molten PPO-TBAP. No luminescence was observed in binary PPO-TBAP, PPD-TBAP, TH-TBAP, or PHEN-TBAP under any conditions in the absence of DPA or rubrene.

In some experiments "pre-annihilation" ECL was observed for PPO-TBAP solutions containing rubrene or DPA, when the potential was stepped to one where the anion (or cation) radical was produced and then stepped to potentials insufficient to produce the oppositely charged species. For example, when rubrene cation radical was produced first, light could be detected when the electrode was stepped back to potentials more negative than $-1.0$V *vs.* Ag, although rubrene anion radical is not produced until $-1.7$V. Similar pre-annihilation effects were found for initial production of rubrene anion and DPA ion radicals. Some unusual effects on the pre-annihilation ECL, such as the variation of the ECL intensity with applied potentials that are still short of the foot of the wave, similar to what we have found in the case of thianthrene pre-annihilation ECL (5), may also involve nonuniform current densities and uncompensated *iR* effects in these highly resistive media.

As seen from experiments 23 and 24 in Table II, the addition of 25% by weight of 1- or 2-methylnaphthalene to the PPO-TBAP solution resulted in an approximately two-fold increase in rubrene ECL emission compared to PPO solutions not containing methylnaphthalene. We have noticed similar increases in ECL intensities upon addition of less polar solvents, such as benzene or toluene, to ACN solutions (6). A systematic investigation of the effect of solvent on ECL efficiency is currently under way.

Although the experiments described using the usual three-electrode, potential step, technique are most appropriate for obtaining electrochemical data, ECL can also be produced in the two-electrode mode, employing voltage or current steps. In fact in some circumstances, particularly at higher frequencies or when reaction products can cause shifts in the potential of the silver wire reference electrode, the two electrode mode, with the voltage span adjusted empirically to give maximum light output and the applied program an asymmetric square wave with the potentiostat reference and auxiliary leads connected together, can produce larger light intensities than the three-electrode mode. In practical devices employing ECL, the two-electrode mode would, of course, be preferred.

Although this work was not concerned with the construction of ECL devices, some possible applications of molten scintillator systems can be mentioned. The melting point of these compounds, or of their mixtures, is constant within a few degrees centigrade, and a range from room temperature to over 200°C can be covered by varying the composition. The ohmic resistance of a frozen mixture is very high while the melts have a much lower resistance (less than 1000 ohms in the cells used here) so that a circuit incorporating one or several of these mixtures can behave as a temperature sensing device. Addition of DPA or rubrene to

Table II. Summary of electrogenerated chemiluminescence experiments

| No. | Solvent[a] | Electrolyte | Solute(s)[b] | Temperature[c] (°C) | Experimental conditions[d] | Results and remarks[e] |
|---|---|---|---|---|---|---|
| 1 | TBAP | — | — | 220 | CV; potential steps; voltage pulses | No luminescence detected |
| 2 | TBAP | — | RUB | 220 | CV; potential steps; voltage pulses | No luminescence; unstable RUB cation & anion |
| 3 | TBAP | — | DPA | 220 | CV; potential steps; voltage pulses | No luminescence; unstable DPA cation & anion |
| 4 | TBACl | — | DPA | 80 | CV; potential steps | No luminescence; stable $DPA^-$, TBACl unsuitable for $DPA^+$ |
| 5 | PPO | TBAP | — | 80 | Potential steps; voltage pulses | No luminescence |
| 6 | PPO | TBAP | RUB | 80 | CV | Stable $R^+$ and $R^-$ |
| 7 | PPO | TBAP | RUB | 80 | Potential steps | RUB ECL detected |
| 8 | PPO | TBAP | RUB | 80 | Voltage pulses | RUB ECL, brighter than above |
| 9 | PPO | TBAP | RUB | 80 | Voltage pulses (sine wave) at 60 cps | RUB ECL for 30 days continuous, intensity fell |
| 10 | PPO | $TBABF_4$ | RUB | 80 | Voltage pulses | RUB ECL |
| 11 | PPO | $TMABF_4$ | RUB | 80 | Voltage pulses | RUB ECL |
| 12 | PPO | TEAP | RUB | 80 | Voltage pulses | RUB ECL |
| 13 | PPO | TMAP | RUB | 80 | Voltage pulses | RUB ECL |
| 14 | PPO | TBAP | TH & PPD | 80 | Potential steps | No luminescence |
| 15 | PPO | TBAP | DPA | 80 | CV; potential steps; voltage pulses | Stable $R^+$ & $R^-$; DPA ECL;[g] DPA ECL |
| 16 | PPO/PPD | TBAP | RUB | 115 | Voltage pulses | RUB ECL |
| 17 | PPO/PTP | TBAP | RUB | 95 | Voltage pulses | RUB ECL |
| 18 | TH | TBAP | — | 150 | CV; potential steps | No luminescence |
| 19 | TH | TBAP | PPD | 150 | Potential steps | No luminescence |
| 20 | PHEN | TBAP | RUB | 100 | Voltage pulses | RUB ECL[f] |
| 21 | PPD | TBAP | RUB | 140 | Voltage pulses | RUB ECL |
| 22 | PTP | TBAP | RUB | 220 | Voltage pulses | RUB ECL |
| 23 | PPO/1-methylnaphthalene | TBAP | RUB | 80 | Potential steps; voltage pulses | RUB ECL; brighter than using PPO alone |
| 24 | PPO/2-methylnaphthalene | TBAP | RUB | 80 | Potential steps; voltage pulses | RUB ECL; brighter than using PPO alone |
| 25 | N,N-diphenylformamide | TBAP | RUB | 80 | Voltage pulses | No luminescence |
| 26 | PPO | TBAP | TPP | 80 | CV; potential steps; voltage pulses | TPP ECL of very low intensity |

[a] The typical ratio of solvent to electrolyte to solute was 100:10:1, resulting in solutions approximately 5 mM in solute. When a mixed solvent was used, the component added to PPO was approximately 25% by weight.

[b] RUB = rubrene; DPA = 9,10-diphenylanthracene.

[c] Estimated sample temperatures in the vicinity of the electrode. The bath temperature was considerably higher than these values, *e.g.*, in the case of molten TBAP the bath had to be higher than 235°C to prevent solidification of the sample in the vicinity of the electrode. Since the electrodes are good heat conductors, the temperature in the vicinity of the electrode is lower than that of the rest of the ECL solution.

[d] Voltage pulses: two electrode mode of electrogeneration (see text); CV: cyclic voltammetric experiment; potential steps; three electrode mode; potential is stepped between first reduction and first oxidation process.

[e] Visual observations in case of high-temperature experiments by the dark adapted eye.

[f] Molten phenanthrene was found to sublime excessively in the ECL cell during experiments.

[g] DPA ECL in PPO is approximately twice as intense as that obtained in ACN under similar conditions.

these mixtures would also result in the emission of light upon melting when a cyclic signal is applied to the electrode and this process is a reversible one following the solid-liquid phase transitions.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1973 JOURNAL.

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