ELECTROGENERATED CHEMILUMINESCENCE. THE PRODUCTION OF BENZOPHENONE PHOSPHORESCENCE IN FLUID SOLUTION BY RADICAL ION REACTION

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Observation of benzophenone triplet emission in fluid solution by an electrogenerated chemiluminescence (ECL) technique from the benzophenone(−)/thianthrene(+) system and related mixed systems is reported. The triplet character of the ECL was confirmed by experiments involving energy transfer from the benzophenone triplet to naphthalene.

1. Introduction

The triplet state has played an important role as an intermediate in photochemical reactions and in photophysical processes [1–4]. Although the triplet state is usually produced by photoexcitation, previous studies of electrogenerated chemiluminescence (ECL) have demonstrated that the electron transfer reaction between radical ions can produce the triplet state directly and with good efficiency [5–9]. This is particularly true for "energy deficient" ECL systems where the enthalpy of the homogeneous electron transfer reaction

$$A^- + D^+ \rightarrow {}^3A + D \text{ (or } A + {}^3D) \tag{1}$$
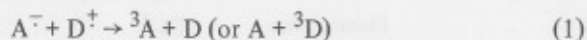
provides only enough energy to produce the triplet states of one or both reactants, which then may undergo triplet–triplet annihilation

$$^3A + {}^3A \rightarrow {}^1A^* + A \tag{2}$$
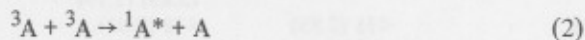
to produce singlet excited states which emit. Direct emission from the triplet state is usually not observed in ECL because of the relatively long radiative lifetimes of the triplets and rapid quenching of them under the usual ECL conditions (fluid solution at room temperature). Several reports of triplet emission in ECL have appeared, but in most of these cases emission at wavelengths longer than that from $^1A^*$ or $^1D^*$ can be ascribed to exciplexes or reaction

products derived from unstable radical ions. Thus Zweig et al. [10] ascribed the longer wavelength emission in their studies of phenanthrene ECL to phosphorescence of phenanthrene; the system is an unstable one, however, and the existence of triplet emission in this case has been disputed [11,12]. Zachariasse [9] suggested that long wavelength emission during the chrysene(−)/TMPD(+) (TMPD = N,N,N′,N′-tetramethyl-*p*-phenylenediamine) chemiluminescence reaction might originate from triplet chrysene, but later studies suggest that this is not the case [13]. Triplet emission is observed during ECL from the Ru(bipy)$_3^{2+}$ system (bipy = bipyridyl) [14], but in this case the radiative lifetime is decreased in the presence of the heavy metal ion.

In searching for an organic triplet emitter in ECL, benzophenone appears to be an especially favorable candidate. There is a very small energy difference between the singlet and triplet excited states and the quantum yield for intersystem crossing approaches unity. Moreover, benzophenone shows phosphorescence in fluid solution even at room temperature [15–17] and forms a stable radical anion. In the studies of the ECL of mixed systems of benzophenone(−)/tri-*p*-toylamine(TPTA)(+), only exciplex emission resulting from direct formation upon cation–anion recombination was observed [18]. In this case the reaction enthalpy was not sufficient to produce the triplet excited state of benzophenone. In this

paper we describe ECL experiments involving reaction of several different radical cations with benzophenone radical anion and energy transfer experiments which support a mechanism involving direct triplet emission.

2. Experimental

2.1. Chemicals

Dibenzo-*p*-dioxin (DBPD), provided by Professor H.J. Shine (Texas Tech University), and TPTA provided by Professor R.N. Adams (University of Kansas) were used without further purification. 1,4,6,9-tetramethylthianthrene (TMTH) and 4,4′-dimethoxybiphenyl were synthesized by reported methods [19,20] and were purified by repeated recrystallizations from benzene (TMTH) or methanol (4,4′-dimethoxybiphenyl). Thianthrene (TH) (Aldrich), phenoxathiin (Eastman Organic), benzophenone (BP) (Fischer certified, reagent grade), naphthalene (Eastman Organic, ethanol recrystallized), and rubrene (Aldrich) were purified by repeated recrystallizations from appropriate organic solvents or by repeated sublimations. Fluoranthene (Aldrich, 99%+)

and 9,10-diphenylanthracene (DPA) (Aldrich, 99%) were used as received.

Spectroquality acetonitrile (ACN) (Matheson, Coleman, and Bell; MCB) was used as a solvent after three distillations from P_2O_5 under vacuum. This purified and dry 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 by a vapor transfer method or directly in the glove box. Spectroquality benzene (MCB) was stored over metallic sodium, and then distilled either into a storage container or the cell.

2.2. Apparatus and procedures

Solutions were prepared by the method previously described [18]. Electrochemical and ECL experiments employed a Princeton Applied Research Model 170 electrochemistry system (PAR) and a three-electrode cell of conventional design [21]. The ECL was generated by cyclic potential steps and detected with an Aminco–Bowman spectrophotofluorometer. Details of the apparatus and techniques are available [22]. Unless otherwise specified, all solutions were ACN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP).

Table 1
Electrochemical, ECL, and fluorescence data [a]

	Compounds, D	E_{pa} [b] V versus SCE	$-\Delta H^0$, eV [c]	Fluorescence maximum, nm (eV)	ECL [d] nm(eV)
1.	TMTH	1.20	2.95	438 (2.83)	437.504 (2.83) (2.19)
2.	thianthrene	1.26	3.01	435 (2.85) 450 (2.76)	438 (2.83) 570 (2.18)
3.	phenoxathiin	1.25	3.00	376 (3.30)	470 (2.64) 570 (2.18)
4.	DBPD	1.43	3.18	408 (3.04) 427 (2.90)	410 (3.02)
5.	4,4′-dimethoxy- biphenyl	1.28	3.03	344 (3.59)	none

a) For benzophenone, E_s = 3.22 eV, E_T = 2.99 eV, E_{pc} = −1.91 V versus SCE in ACN.
b) E_{pa}, anodic peak potential in cyclic voltammetry.
c) Estimated by $-\Delta H^0 = E_{pa} - E_{pc} - 0.16$ (eV) [5]; E_{pc} for benzophenone being −1.91 V.
d) For system BP(−)/D(+).

3. Results and discussion

3.1. ECL of mixed systems containing BP

Electrochemical and ECL data are summarized in table 1. Because the energy of the lowest triplet (n, π^*) state of benzophenone (BP) is near 3.0 eV and the reduction peak potential of BP (E_{pc}) is -1.91 V versus SCE, only compounds such as TMTH, phenoxathiin, TH, 4,4′-dimethoxybiphenyl, and DBPD, which are oxidized above +1.20 V versus SCE will produce radical cations which react with

BP⁻ in an annihilation reaction which is sufficiently energetic to produce ^{3}BP. The systems containing molecules having sulphur atoms between benzene rings (compounds 1–3) form very stable radical cations upon oxidation and show very similar ECL behavior. The reaction enthalpy of the electron transfer reactions of these cation radicals with BP⁻ ranges from 2.95 to 3.01 eV as shown in table 1, which is, within experimental error, barely energy sufficient for the benzophenone triplet. The reaction enthalpy provides enough energy to promote TH and TMTH to their lowest excited singlet state; however, it is too small to produce excited singlet phenoxathiin, where E_S is estimated to be at least 3.3 eV in ACN based on its fluorescence spectrum.

A typical ECL spectrum for the BP(−)/TH(+) systems, shown in fig. 1a, has two emission peaks at about 450 and 560 nm. The BP(−)/TMTH(+) system shows very similar behavior (fig. 2). The assignment of the 450 nm peaks is ambiguous, since
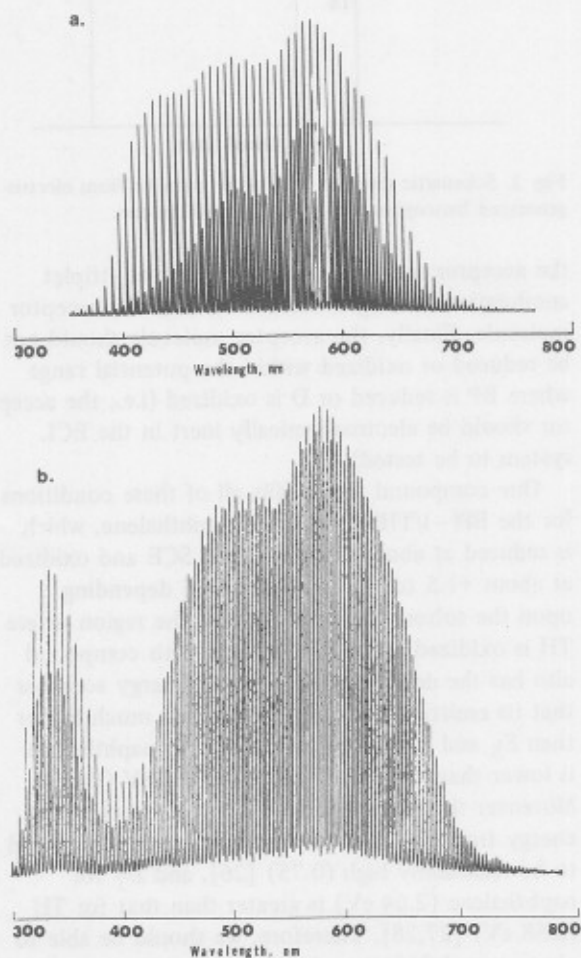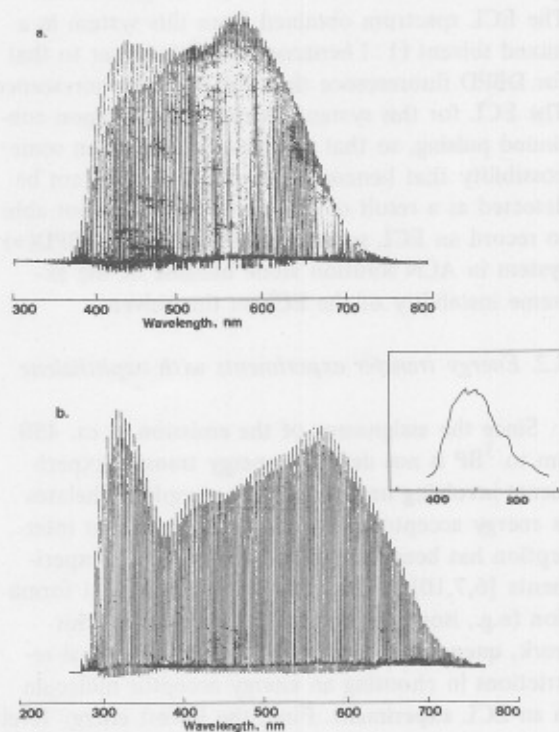

Fig. 1. ECL spectrum of (a) BP–TH system containing 2.9 mM of TH and 3.7 mM of BP in ACN and (b) BP–TH system in the presence of naphthalene, containing 1.2 mM BP, 1.3 mM TH, and about 7 mM naphthalene in ACN; pulse duration, 1 s.

Fig. 2. (a) ECL spectrum of the BP(1.6 mM) (−)/TMTH (1.4 mM) (+) system in ACN. (b) ECL spectrum after addition of 4.9 mM naphthalene to above solution. Difference spectrum is shown in the inset at twice the sensitivity.

the energy levels of the singlet excited state of TH and TMTH and that of triplet excited state of BP are both near this energy. For phenoxathiin, the singlet emission energy is higher than that of BP phosphorescence, and the fluorescence of phenoxathiinn was not observed, while the spectrum is very similar to the one shown in fig. 1a. The origin of the longer wavelength peak at 560 nm is not clear, but it probably originates from an impurity in the TH or TMTH or from some decomposition product derived from their radical cations [22].

The systems involving the reaction of BP^- and the radical cations of 4,4′-dimethoxybiphenyl or DBPD did not produce satisfactory ECL. The BP(−)/4,4′-dimethoxybiphenyl(+) system did not give any detectable ECL, although the radical cation is very stable [23] and the reaction enthalpy should be sufficient to form ^3BP. DBPD is oxidized at +1.43 V versus SCE, forming a very stable cation radical [24]. The reaction enthalpy for the BP(−)/DBPD(+) system is therefore sufficient for ^3BP generation. The ECL spectrum obtained from this system in a mixed solvent (1 : 1 benzene−ACN) is closer to that for DBPD fluorescence than for BP phosphorescence. The ECL for this system decayed rapidly upon continued pulsing, so that there might have been some possibility that benzophenone triplet could not be detected as a result of fast decay. We were not able to record an ECL spectrum for the BP(−)/DBPD(+) system in ACN solution alone because of the extreme instability of the ECL in this solvent.

3.2. Energy transfer experiments with naphthalene

Since the assignment of the emission at ca. 450 nm to ^3BP is not definite, energy transfer experiments involving naphthalene or europium chelates as energy acceptors were undertaken. Triplet interception has been employed before in ECL experiments [6,7,10], with observation of product formation (e.g., isomerization of stilbene) or, for this work, quenching of emission. There are several restrictions in choosing an energy acceptor molecule in an ECL experiment. First, the lowest energy level of the acceptor molecule should be lower than that of the donor molecule (^3BP), as is required in spectroscopic experiments. Secondly, the efficiency of triplet−triplet energy transfer should be high with
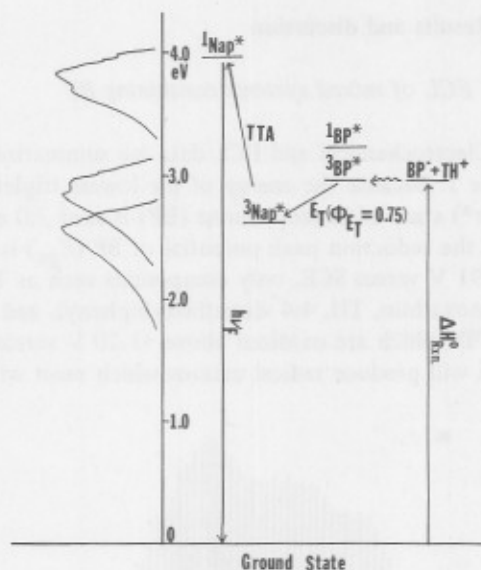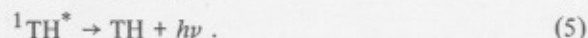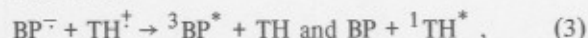

Fig. 3. Schematic diagram for energy transfer from electro-generated benzophenone triplet to naphthalene.

the acceptor molecule undergoing triplet−triplet annihilation leading to fluorescence of the acceptor molecule. Finally, the acceptor molecule should not be reduced or oxidized within the potential range where BP is reduced or D is oxidized (i.e., the acceptor should be electrochemically inert in the ECL system to be tested).
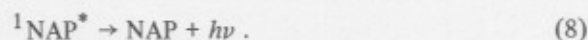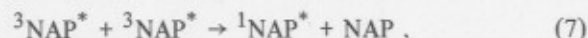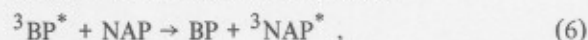
One compound that fulfils all of these conditions for the BP(−)/TH(+) system is naphthalene, which is reduced at about −2.6 V versus SCE and oxidized at about +1.5 to +1.7 V versus SCE depending upon the solvent [25], far beyond the region where TH is oxidized and BP is reduced. This compound also has the desirable feature as an energy acceptor that its emitting singlet energy level is much higher than E_S and E_T for BP, while E_T for naphthalene is lower than that of BP by about 0.4 eV (fig. 3). Moreover the relative probability of triplet−triplet energy transfer from ^3BP to naphthalene is reported to be reasonably high (0.75) [26], and E_T for naphthalene (2.64 eV) is greater than that for TH (2.58 eV) [27,28]. Therefore, we should be able to observe naphthalene emission from a system containing TH and BP by pulsing the potential at the working electrode in such a range that only TH^+ and BP^- are produced alternately, only if ^3BP is produced in the electron transfer reaction. The ex-

perimental result, shown in figs. 1b and 2b, upon addition of naphthalene to the BP(−)/TH(+) and BP(−)/TMTH(+) systems is a new emission located at approximately 330 nm attributable to singlet naphthalene emission, and a quenching of some, but not all, of the emission at 437 nm. To ensure that it was not the triplet excited state of TH or TMTH which transferred its energy to naphthalene, a control experiment was performed using fluoranthene (FL) as the source of the anion radical. Because the triplet energy level of fluoranthene is lower than that of naphthalene by about 0.3 eV (E_T of fluor-Anthene = 2.3 eV), the only possibility of having energy transfer to naphthalene for the FL(−)/TH(+) system is from the TH. The ΔH^0 for the electron transfer reaction between $FL^{\bar{\cdot}}$ and $TH^{\dot{+}}$ is about the same as that in the TH(+)/BP(−) system. When an ECL experiment was performed with a solution containing 1.4 mM TH, 1.6 mM FL, 9.0. mM naphthalene in ACN there was no emission from naphthalene indicating that no energy transfer occurs from ^{3}TH to naphthalene.

These experimental observations are consistent with production of both ^{3}BP and ^{1}TH* in the ECL experiment:

$$BP^{\bar{\cdot}} + TH^{\dot{+}} \rightarrow {}^3BP^* + TH \text{ and } BP + {}^1TH^* , \quad (3)$$

$$^3BP^* \rightarrow BP + h\nu , \quad (4)$$

$$^1TH^* \rightarrow TH + h\nu . \quad (5)$$

In presence of naphthalene (NAP):

$$^3BP^* + NAP \rightarrow BP + {}^3NAP^* , \quad (6)$$

$$^3NAP^* + {}^3NAP^* \rightarrow {}^1NAP^* + NAP , \quad (7)$$

$$^1NAP^* \rightarrow NAP + h\nu . \quad (8)$$

In this energy transfer experiment we noticed that the lower the naphthalene concentration was, the better resolved was the naphthalene fluorescence and the higher was the relative intensity of naphthalene emission. No quantitative studies of this phenomenon were carried out.

Additional evidence that direct emission from ^{3}BP is observed was obtained by finding the difference spectrum by subtraction of the ECL spectrum between 380 and 600 nm in the presence of naphthalene (fig. 2b) from that in its absence (fig. 2a). This difference spectrum, shown as an inset to fig.

2b, closely resembles the phosphorescence spectrum of BP in fluid solution at room temperature [15–17]. The general behavior of ECL systems with TH or phenoxathiin as the radical cation source was very similar to that described for TMTH both in the absence and presence of naphthalene.

4. Conclusions

The existence of an emitting benzophenone triplet in some ECL systems involving $BP^{\bar{\cdot}}$ and radical cations appears established. The observation of electrogenerated phosphorescence in fluid solution suggests that the efficiency of production of the triplet is high. Since triplet benzophenone is used as a sensitizer in photochemical reactions, its production in ECL leads to the possibility of "photochemistry without light" [29] via electrogeneration.

Acknowledgement

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