

ELECTROGENERATED CHEMILUMINESCENCE. XIV. EFFECT OF SUPPORTING ELECTROLYTE CONCENTRATION AND MAGNETIC FIELD EFFECTS IN THE 9,10-DIMETHYLANTHRACENE-TRI-*p*-TOLYLAMINE SYSTEM IN TETRAHYDROFURAN

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A comparison of the efficiency of photon production in the chemiluminescence studies of Weller and Zachariasse and in ECL for the system involving reaction of 9,10-dimethylanthracene (DMA) radical anion and tri-*p*-tolylamine (TPTA) radical cation in tetrahydrofuran (THF) solutions was undertaken. The luminescence intensity increased and the magnitude of the magnetic field effect decreased when the supporting electrolyte (TBAP) concentration was decreased from 0.2 M to 10 mM. The ECL efficiency, extrapolated to low TBAP concentrations, was in good agreement with that of the chemiluminescence studies.

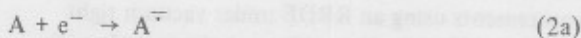
1. Introduction

Weller and Zachariasse [1] described chemiluminescent reactions based on direct reaction of anion radicals, A^- , with solid salts $D^+ClO_4^-$, resulting in the emission of visible photons. Similar reactions have been studied by generating the ions A^- and D^+ in solution electrochemically by alternate pulsing at a platinum electrode or continuously at a rotating ring-disk electrode (RRDE); this method is known as electro-generated chemiluminescence (ECL) [2, 3]. In both cases the overall reaction producing light is:



Although the basic light-producing mechanism represented by eq. (1) applies to both ECL and the type of chemiluminescence (CL) described by Weller and Zachariasse, the reaction occurs under notably differ-

ent experimental conditions in CL and ECL. Aside from the presence of the electrode in ECL, which establishes a definite reaction zone, in electrochemical generation of A^- and D^+ according to



the solvents usually employed have high dielectric constants (e.g., acetonitrile (ACN) and *N,N*-dimethylformamide (DMF), $\epsilon \approx 37$) and the $A^- - D^+$ reaction occurs in the presence of high concentrations (typically 0.1 - 0.2 M) of supporting electrolyte salts. On the other hand, the solvents used in CL studies have much lower dielectric constants ($\epsilon \approx 7$ for the ethers used for the sodium reduction [4]) and the concentration of ionic species are typically about 10^{-4} M after reduction of the hydrocarbon, A, with sodium to form Na^+A^- . Such a difference in the experimental environment could affect both the intensity and efficiency of light production, as well as the spectral distribution of the emitted light. In this paper, we report a comparison of CL and ECL efficiency (where both Φ_{CL} and Φ_{ECL} are based on the number of photons emitted

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per radical ion annihilation) for the 9,10-dimethylanthracene (DMA)/tri-*p*-tolylamine (TPTA) system in tetrahydrofuran (THF) solvent.

The results of Weller and Zachariasse [1] indicated that the system based on the reaction of DMA^- and TPTA^+ in THF gives intense chemiluminescence, and they reported $\Phi_{\text{CL}} = 7.5\%$ based on actinometric measurements. To estimate the reaction enthalpy for eq. (1) when $A = \text{DMA}$ and $D = \text{TPTA}$, they employed thermodynamic $E_{1/2}$ values for these compounds taken in ACN or DMF solvent, corrected for reduced solvation of the ions in THF. The calculated free energy of the ion annihilation reaction, (1), in ACN or DMF is clearly less than that of excited singlet DMA or TPTA (a so-called "energy deficient" reaction), so this efficiency appeared remarkably high. We report here a study of ECL in THF and the effect of supporting electrolyte concentration on Φ_{ECL} and the free energy of the annihilation reaction.

2. Experimental

The experimental technique used in these ECL studies has been previously described [5-7] together with general procedures for preparation of solvents and chemicals. Magnetic field effects on ECL were measured in the manner reported earlier [8]. Φ_{ECL} measurements using an RRDE under vacuum tight conditions [7] utilized a calibrated photodiode with a fairly uniform spectral response from 200 to 1100 nm (UDT-500UV; United Detector Technology, Inc., Santa Monica, California) and a bipotentiostat (Model BIPAD 2; Tacussel Electronique, Villeurbanne, France). Pulsed ECL experiments were conducted in the cell previously shown [6, fig. 1a]. Reproducible positioning of the working electrode in the spectrofluorometer (SPF) is extremely important for obtaining reliable relative intensity values such as those shown in fig. 1; this was achieved by using 5 mm slits in the SPF so that a uniform view of the exposed segment of the 1 cm long vertically held platinum wire electrode was always obtained. Because low supporting electrolyte concentrations were employed in some of these experiments, the cell arrangement in ref. [6] was modified by placing the auxiliary electrode platinum coil close to the working electrode in the small bottom compartment of the cell, without

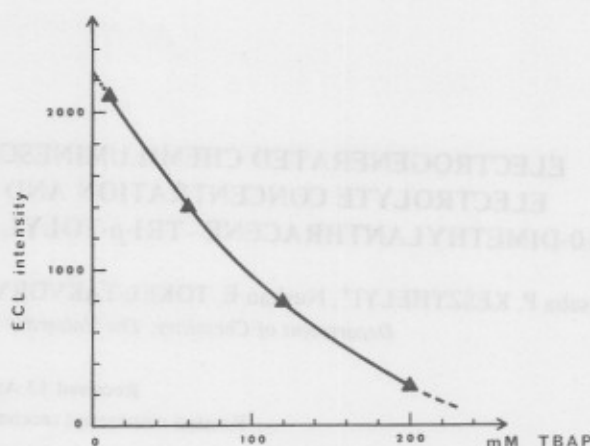


Fig. 1. ECL intensity versus TBAP concentration in the DMA/TPTA mixed system in THF as solvent. $[\text{DMA}] = [\text{TPTA}] = 0.10 \text{ mM}$; frequency of electrogeneration, 0.5 Hz. The chronological order of the experiments, identified by the relevant supporting electrolyte concentration, was 10.0 mM, 200 mM, 60.0 mM, 120 mM.

the customary fritted chamber. Even under this modified cell arrangement precise use of the iR compensation technique in conjunction with the PAR-170 Electrochemistry System (Princeton Applied Research Corporation, Princeton, N.J.) was essential in the pulsed ECL experiments. A detailed description of these experimental arrangements has been given [9].

3. Results

The reaction enthalpy, ΔH_r^0 , for the radical ion electron transfer reaction can be estimated from the equation [8]

$$\Delta H_r^0 = E_{\text{A/A}^-}^0 - E_{\text{D/D}^+}^0 + T\Delta S^0, \quad (3)$$

where $E_{\text{A/A}^-}^0$ and $E_{\text{D/D}^+}^0$ are the standard potentials for reactions (2a) and (2b), respectively, and $T\Delta S^0$ is usually estimated as about 0.1 eV. Emission from the DMA/TPTA system always corresponds to fluorescence of DMA, in agreement with the CL results [1], where the energy of the singlet excited state of DMA, $E_s(\text{DMA})$, is 3.10 eV [4]. For TPTA, $E_s = 3.51 \text{ eV}$ [4]. The reaction is clearly energy deficient in DMF or ACN, where $E_{1/2}(\text{DMA/DMA}^-) = -2.03 \text{ V}$ versus

Table 1
Cyclic voltammetric reduction of DMA and oxidation of TPTA in THF containing different concentrations of TBAP^{a,b}

Concentrations (mM)			Scan rate (mV/sec)	Peak potentials (V)		Peak separation (mV) ^c		$-\Delta H_T^0$ (eV) ^d
TBAP	DMA	TPTA		$-E_{pc}$	E_{pa}	$\Delta E_p(A/A^-)$	$\Delta E_p(D/D^+)$	
200	1.00	1.00	100	2.165	—	70	—	2.85
100	1.00	1.00	200	—	0.856	—	70	—
200	0.100	0.100	200	2.160	0.940	68	80	2.93
200	0.100	0.100	100	2.116	0.921	78	75	2.86
120	0.100	0.100	50	2.155	0.883	70	67	2.87
100	0.100	0.100	100	2.106	0.893	57	73	2.83
60.0	0.100	0.100	100	2.269	0.860	67	83	2.95
10.0	0.100	0.100	100	2.294	1.004	169	116	3.06
10.0	0.100	0.100	100	2.228	1.019	166	134	3.00

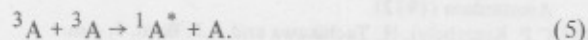
a) Abbreviations: DMA, 9,10-dimethylanthracene; TPTA, tri-*p*-tolylamine; THF, tetrahydrofuran; TBAP, tetra-*n*-butylammonium perchlorate.

b) Satisfactory electrochemistry was not observed for solutions of 1 mM TBAP, nor in solutions of 10 mM TBAP containing 1 mM each DMA and TPTA because of large uncompensated resistance.

c) $\Delta E_p = E_{pc} - E_{pa}$ for A/A⁻ or for D/D⁺ systems; for a reversible electron transfer in the absence of uncompensated resistance effects, $\Delta E_p = 58$ mV.

d) Calculated from eq. (3), estimating E^0 -values from the E_p -values as described in the text; this value can be compared with $E_s(\text{DMA}) = 3.10$ eV.

S.C.E. and $E_{1/2}$ (TPTA/TPTA⁺) = +0.74 V versus S.C.E. [4]. Under these conditions the ion annihilation must produce triplet DMA ($E_T(\text{DMA}) = 1.80$ eV), and excited singlet DMA is produced by triplet-triplet annihilation (TTA):



For TPTA, $E_T = 2.96$ eV [1, 4], so 3D is not accessible via reaction (4) in these solvents. Cyclic voltammetry was employed for obtaining information about the stability and E^0 -values of DMA and TPTA radical ions in THF-TBAP; typical results are shown in table 1. The ΔH_T^0 values were obtained using eq. (3) with $T\Delta S^0 = 0.1$ eV. For a reversible reaction in the absence of uncompensated resistance effects, $E_{1/2}(A/A^-) \approx E^0(A/A^-) \approx E_{pc} + 29$ mV. For these measurements, where uncompensated resistance effects were obviously present, the E^0 -values were estimated as $E^0(A/A^-) \approx E_{pc} + \frac{1}{2}|\Delta E_p(A/A^-)|$, with a similar correction for $E^0(D/D^+)$, i.e., $E^0(D/D^+) \approx E_{pa} - \frac{1}{2}|\Delta E_p(D/D^+)|$. It is clear from these results that ΔH_T^0 in THF is larger than that in DMF or ACN (where $\Delta H_T^0 \approx 2.67$ eV), as predicted by Weller and Zachariasse [1], and that ΔH_T^0

increases at the lower TBAP concentrations in THF.

The ECL efficiency, Φ_{ECL} , was determined at an RRDE with a solution 1.0 mM each DMA and TPTA and 0.2 M TBAP in THF employing techniques previously described [7]; a value of 0.07% was obtained for Φ_{ECL} under these conditions. Since this cell and technique could not be employed for THF solutions containing very small amounts of TBAP, a series of measurements under pulsed conditions were undertaken and the ECL intensity determined for different concentrations of TBAP containing 0.10 mM each DMA and TPTA (fig. 1). Because of the low concentration of TBAP, the switching frequency was limited to low values (0.5 Hz), since resistances were high and charging of the electrical double layer capacitance was slow. For example, for the 10.0 mM TBAP-THF solution a lag of 0.4 sec was observed between the time of potential switching and maximum ECL intensity, while this time lag in 0.1 M TBAP-ACN solutions is only in the order of microseconds. Thus for 10 mM TBAP-THF solutions no ECL emission could be detected for pulse lengths shorter than 0.2 sec, while for less resistive solutions maximum ECL intensities are often observed at frequencies of about 100 Hz [9]. The results in fig. 1 show a strong dependence of ECL intensity on TBAP concentration for this system; ex-

trapolation to solutions containing 10 mM or less TBAP of the Φ_{ECL} value obtained for the 0.2 M TBAP solution leads to an extrapolated Φ_{ECL} of 7%.

Magnetic field effects on ECL intensity have previously been found useful in distinguishing systems that involve TTA from those that do not [8, 10]; in the DMA/TPTA/THF system the presence of a magnetic field resulted in an enhancement of the ECL intensity with increasing field for all concentrations of TBAP (+15% at 0.2 M TBAP, +9% at 0.1 M TBAP, and +6% at 0.01 M TBAP; the field strength for the maximum effect was usually 7.5 kG).

4. Discussion

The ECL efficiency extrapolated to very low concentrations of electrolyte, 7%, is in good agreement with the chemiluminescence value of 7.5% of Weller and Zachariasse [1]. Although quenching of ECL intermediates by TBAP ions may be of some importance, and this effect would be in general agreement with the observed intensity increase with decreasing supporting electrolyte concentration, the increase in reaction enthalpy with decreasing TBAP concentration is probably of more importance. This increase in reaction enthalpy can be traced to either a decrease in the extent of formation of ion pairs, such as $\text{TBA}^+ \cdots \text{DMA}^-$ and $\text{TPTA}^+ \cdots \text{ClO}_4^-$ (formation of ion pairs would facilitate the oxidation of TPTA and the reduction of DMA and hence decrease the magnitude of ΔG_r^0 for the ion annihilation reaction), or to a change in the nature of the solvent system itself, with an effective increase in the dielectric constant of the solvent at higher TBAP concentrations [11]. Thus at high TBAP concentrations in THF, or in ACN or DMF, the reaction is strongly energy deficient and proceeds by the TTA mechanism (or T-route). Here the efficiency is low and a sizeable magnetic field effect is observed. As the TBAP concentration decreases the reaction becomes sufficiently energetic to have appreciable production of singlets directly as well as triplet TPTA, probably involving some thermal activation [1], so

that the mechanism is best described as occurring by the ST-route. The presence of a magnetic field effect even at 10 mM TBAP suggests that TTA is still making a contribution to the emission. Additional evidence suggesting that TTA is involved at higher TBAP concentrations is the fact that the ECL intensity obtained from a solution containing 0.1 mM TPTA and DMA is about the same as that of one containing 1 mM amounts. This can be accounted for by the increased quenching of DMA triplets at higher concentrations of the radical ions, counterbalancing the increased number of triplets produced.

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References

- [1] A. Weller and K. Zachariasse, *Chem. Phys. Letters* 10 (1971) 424, 590.
- [2] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 90 (1968) 6284.
- [3] A.J. Bard, C.P. Keszthelyi, H. Tachikawa and N.E. Tokel, in: *Chemiluminescence and bioluminescence*, eds. M.J. Cormier, D.M. Hercules and J. Lee (Plenum Press, New York, 1973) p. 193.
- [4] K.A. Zachariasse, Ph. D. Thesis, Vrije Universiteit te Amsterdam (1972).
- [5] C.P. Keszthelyi, H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 94 (1972) 1522.
- [6] N.E. Tokel, C.P. Keszthelyi and A.J. Bard, *J. Am. Chem. Soc.* 94 (1972) 4872.
- [7] J.T. Maloy and A.J. Bard, *J. Am. Chem. Soc.* 93 (1971) 5968.
- [8] L.R. Faulkner, H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 94 (1972) 691.
- [9] C.P. Keszthelyi, Ph. D. Thesis, The University of Texas at Austin (1973).
- [10] H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 95 (1973) 1672.
- [11] A. Weller, Comment at Second International Conference on Chemiluminescence and Bioluminescence, Athens, Georgia (1972).