

## EFFECT OF CONCENTRATION AND MAGNETIC FIELD ON RADICAL ION (WURSTER'S BLUE CATION AND BENZOQUINONE ANION) QUENCHING OF ANTHRACENE TRIPLETS IN FLUID SOLUTION\*

Hiroyasu TACHIKAWA and Allen J. BARD

*Department of Chemistry, The University of Texas at Austin,  
Austin, Texas 78712, USA*

Received 1 February 1974

The effect of magnetic field on the delayed fluorescence (DF) of anthracene in methylene chloride solutions in the presence of the radical cation of *N, N, N', N'*-tetramethyl-*p*-phenylenediamine (TMPD) and the radical anion of *p*-benzoquinone (BQ) has been studied. The results show strong quenching of anthracene triplets by both  $\text{TMPD}^{\ddagger}$  and  $\text{BQ}^{\cdot-}$  as well as a decrease in the rate of the triplet-radical ion reaction rate (and hence an increase in DF intensity) with increasing magnetic field. An equation for the effect of magnetic field on DF intensity in the presence of paramagnetic quenchers is proposed.

### 1. Introduction

Faulkner and Bard [1] previously reported that the radical cation of *N, N, N', N'*-tetra-*N*-methyl-*p*-phenylenediamine (TMPD) (also called Wurster's Blue cation) was an effective quencher of anthracene triplets. Moreover, the rate of the quenching reaction, a doublet-triplet interaction, was decreased by an external magnetic field, so that the delayed fluorescence of anthracene showed an increase in intensity with increasing magnetic field, instead of the negative field effect observed for the delayed fluorescence in the absence of paramagnetic quenchers [2]. These results for methylene chloride solutions were consistent with the field effects observed in solid-state studies [3-5] and were useful in interpreting the effect of a magnetic field on electrogenerated chemiluminescence (ECL) emission [6]. The previous study was limited to quenching with a single concentration of  $\text{TMPD}^{\ddagger}$ . This paper extends that study for different concentrations of  $\text{TMPD}^{\ddagger}$  and also demonstrates similar quenching and magnetic field effects for the radical anion of

*p*-benzoquinone (BQ).

### 2. Experimental

The cell used for these experiments is shown in fig. 1. Anthracene, TMPD and tetra-*n*-butylammonium perchlorate (TBAP) were placed in chamber c of the cell, the cell was attached to a vacuum line via the 24/40 joint and evacuated. The solvent, methylene chloride, was distilled into chamber c from a reservoir on the vacuum line. The resulting solution was deaerated by subjecting it to eight freeze-pump-thaw cycles. Helium gas (0.5 atm) was introduced into the cell, the stopcock was closed, and the solution was transferred into chamber b. This vessel contains a platinum foil (36 mm × 40 mm) working electrode; a platinum helix, which is separated from the bulk solution by a medium porosity frit, is used as the auxiliary electrode. A silver wire, which is separated from the test solution by a medium porosity frit, serves as a reference electrode (Ag ref.). A 7 mm length of platinum wire located very close to the frit of reference electrode, was used to monitor the concentrations in the solution after bulk electrolysis. A small amount of  $\text{TMPD}^{\ddagger}$  radical cation was produced coulometrically by electrolysis. After the electrolysis, the solution containing

\* Work supported by the U.S. Army Research Office-Durham. Funds for the purchase of the electromagnet were supplied by Research Corporation and the University Research Institute of the University of Texas.

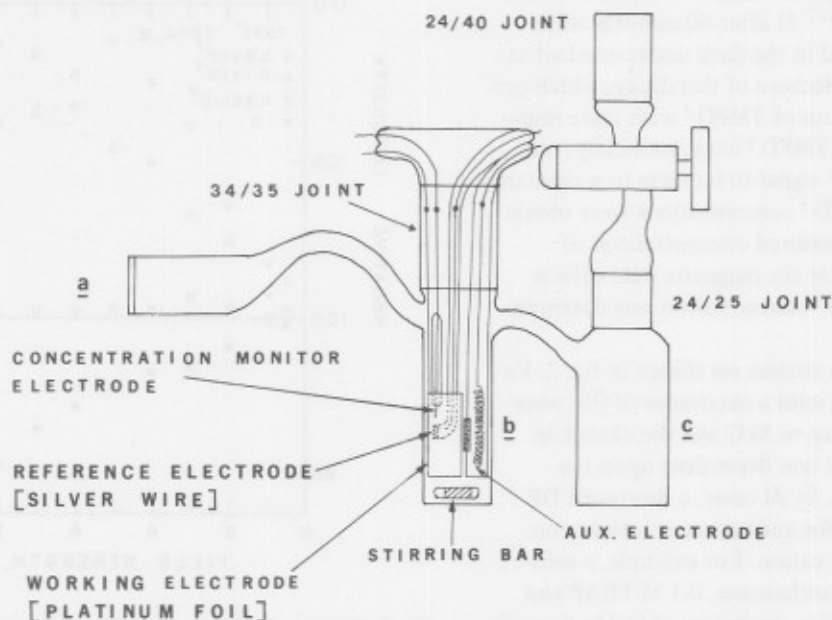


Fig. 1. Cell used for radical ion quenching studies in delayed fluorescence, consisting of (a) chamber for spectroscopic observations, (b) electrolysis chamber, and (c) solution preparation chamber.

anthracene,  $\text{TMPD}^{\ddagger}$  and TBAP was transferred to cuvette a for the delayed fluorescence measurements employing right-angular illumination; this cuvette is of the same form as that described previously [7]. A similar technique was employed for preparation of the anthracene, BQ, TBAP solutions containing  $\text{BQ}^{\cdot-}$ . The phosphorimeter was the same as that previously described [8], except that it was modified to include circular graded filters (Barr and Stroud, Ltd.) [8] in the emission beam and a higher power source, a 200 watt PEK high-pressure mercury lamp and associated power supply. The photomultiplier output of the delayed fluorescence signal was measured with a Model HR-8 lock-in amplifier (Princeton Applied Research Corp.) and was recorded on a Model 1060 signal averager (Fabri-Tek, Inc.). The magnet was a Varian Model V-3400 electromagnet with a 9-inch pole diameter and 3-inch gap, powered by a Model V-2500 power supply. The delayed fluorescence intensity at a given field strength was divided by the average of the zero field intensity values determined immediately before and immediately after the field effect measurement to

yield the relative intensity. The resulting relative intensities were the same for measurements made with increasing, decreasing or random field strengths. A detailed description of the apparatus, chemicals, and techniques has been given [8].

### 3. Results

#### 3.1. Quenching by $\text{TMPD}^{\ddagger}$

Measurements of delayed fluorescence (DF) intensities at different magnetic field strengths were carried out for methylene chloride solutions containing 1 mM anthracene, 0.1 M TBAP and  $\text{TMPD}^{\ddagger}$  at concentrations between 0 and  $3.6 \times 10^{-7}$  M. The presence of supporting electrolyte (TBAP) in these studies was required, because the radical cation was produced by electrogeneration. Although the stability of  $\text{TMPD}^{\ddagger}$  in methylene chloride is exceptionally good compared to other radical ion solvent systems, it still decays slowly at low concentration. For example, a

$1.07 \times 10^{-6}$  M solution of  $\text{TMPD}^+$  decayed to a concentration of  $2.6 \times 10^{-7}$  M after 80 minutes when the solution was stored in the dark under one-half atmosphere of helium. Because of this decay, which perhaps arises from reaction of  $\text{TMPD}^+$  with trace impurities, after producing  $\text{TMPD}^+$  coulometrically, one had to wait for the DF signal to increase to a constant, stable value. The  $\text{TMPD}^+$  concentrations were obtained by averaging the measured concentrations of  $\text{TMPD}^+$  before and after the magnetic field effects were measured;  $\text{TMPD}^+$  concentration was determined electrochemically.

The results of these studies are shown in fig. 2. Enhanced DF intensities, with a maximum of 9%, were observed for fields of up to 8kG and the change in DF intensity with field was dependent upon the  $\text{TMPD}^+$  concentration. In all cases, a shortened DF lifetime was observed for anthracene solutions containing  $\text{TMPD}^+$  radical cation. For example, a solution containing 1 mM anthracene, 0.1 M TBAP and  $0.95 \times 10^{-7}$  M  $\text{TMPD}^+$  in methylene chloride showed a DF lifetime of 1.45 msec as compared to a DF lifetime for a 1 mM anthracene solution without radical ions of 3.4 msec. Since the triplet lifetime is twice the delayed fluorescence lifetime, the corresponding triplet lifetimes were 2.9 msec and 6.8 msec. From these measurements, the rate constant for triplet quenching by  $\text{TMPD}^+$ ,  $k_D$ , was calculated to be  $2 \times 10^9$  l/mole sec using the equation [9]:

$$1/\tau = 1/\tau^0 + k_D [\text{TMPD}^+]. \quad (1)$$

The quenching rate constant of  $2 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$  obtained and the lifetime in the absence of  $\text{TMPD}^+$  are the same as those previously reported [1] for methylene chloride solutions without TBAP. Hence, these results confirm that the quenching rate constant is smaller than the calculated diffusion-limited rate constant (ca  $2.6 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ) and that quenching of the triplets by TBAP is unimportant.

### 3.2. Quenching by $\text{BQ}^-$

The anion radical of BQ was chosen as the quencher because BQ is reduced quite easily ( $E_{1/2} = -0.49$  V versus S.C.E.), so that it could be produced by electrochemical reduction without difficulties arising from the reduction of solvent, supporting electrolyte or anthracene itself, even for a concentration ratio of

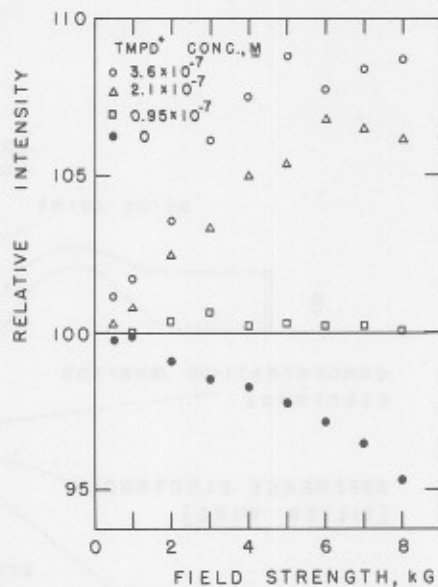


Fig. 2. Magnetic field effects on delayed fluorescence of anthracene from a solution containing 1mM anthracene and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) in methylene chloride, with different amounts of  $\text{TMPD}^+$ .

anthracene to BQ of  $10^4$ .  $\text{BQ}^-$  is also quite stable in the system under study: 1mM anthracene and 0.1 M TBAP in methylene chloride solution.

Although a 1 mM anthracene solution in 0.1 M TBAP-methylene chloride showed a strong DF signal, addition of a small amount of the parent BQ itself significantly quenched the DF intensity of anthracene. For example, the DF signal for a solution of  $10^{-3}$  M anthracene in  $\text{CH}_2\text{Cl}_2$  was completely quenched by  $2 \times 10^{-5}$  M BQ and only one-fiftieth of the initial DF intensity was observed when  $1.5 \times 10^{-6}$  M BQ was added. The prompt fluorescence of anthracene is not quenched by BQ at this level of concentration. Since the triplet energy level of anthracene, 1.8 eV [10], is lower than that of BQ, 2.3 eV [11], direct triplet energy transfer from triplet anthracene ( $^3\text{A}$ ) to BQ cannot occur. However, this quenching may occur through the formation of a charge transfer complex ( $\text{A}^+\text{BQ}^-$ ), on reaction of  $^3\text{A}$  and BQ, based on the oxidation potential of ground state anthracene (ca +1.4 V versus S.C.E.), the energy level of  $^3\text{A}$  and the reduction potential of BQ. Although the triplet state of anthracene was quenched by BQ, the magnetic field effects on

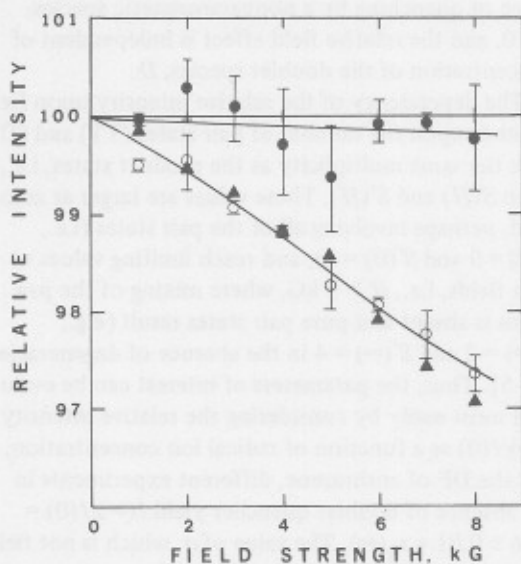


Fig. 3. Magnetic field effects on delayed fluorescence of anthracene in the presence and absence of BQ and BQ<sup>-</sup>, in methylene chloride solutions containing 0.1 M TBAP and  $\blacktriangle$  1 mM anthracene,  $\circ$  1 mM anthracene and  $1.5 \times 10^{-6}$  M BQ,  $\bullet$  1 mM anthracene and  $1.6 \times 10^{-7}$  M BQ<sup>-</sup>.

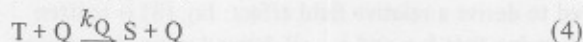
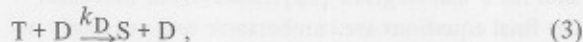
DF from a solution containing only 1 mM anthracene and 0.1 M TBAP in methylene chloride was exactly the same as that of a similar solution containing  $1.5 \times 10^{-6}$  M BQ; the anthracene DF intensity decreased several percent for magnetic fields up to 8 kG (fig. 3). Thus, as expected, there is no field effect on the <sup>3</sup>A-BQ interaction.

However, for a solution containing  $4 \times 10^{-6}$  M BQ and 1 mM anthracene in 0.1 M TBAP-CH<sub>2</sub>Cl<sub>2</sub> which was electrolyzed coulometrically by setting the potential at -0.58 V versus Ag ref. to produce the anion radical BQ<sup>-</sup>, a change in the DF behavior with field is observed. After electrolysis the DF signal from the solution was barely detectable on the lock-in amplifier; the intensity was roughly one-fiftieth of the DF intensity from the solution before electrolysis. As shown in fig. 3, the DF intensity from this solution is essentially unaffected by magnetic fields up to 8 kG. These results can be interpreted as an enhancement of the DF intensity (a decrease in BQ<sup>-</sup> quenching of <sup>3</sup>A) with magnetic field which compensates for the negative field effects on triplet-triplet annihilations. Studies with higher concentrations of BQ<sup>-</sup> could not be carried out be-

cause the DF intensity became too small under these conditions for precise measurements, even when both phase-sensitive detection and signal averaging were used.

#### 4. Discussion

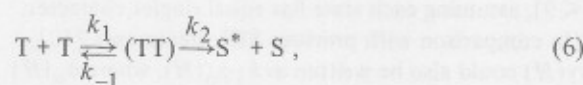
The effect of radical ion concentration and magnetic field on the delayed fluorescence intensity can be described by combining the familiar equations for DF [9] with the theoretical treatments of Merrifield and co-workers [3-5]. Thus, for the reaction scheme



(where D represents a quencher in a doublet state (e.g., a radical ion), Q, a nonparamagnetic quencher, T, the triplet and S, the singlet states), the rate equation for T, using italics here to represent concentrations, is

$$dT/dt = R_T - 2\gamma T^2 - k_D DT - k_Q QT. \quad (5)$$

$R_T$  is the rate of triplet formation, which for DF studies is  $\phi'_t I_a$ , where  $\phi'_t$  is the fractional transfer of singlets to the triplet state and  $I_a$  is the intensity of exciting radiation absorbed (in einstein  $\ell^{-1} \text{ sec}^{-1}$ ). The term  $\gamma$ , following the treatment of Merrifield et al. [3-5], represents the annihilation rate constant, derived in terms of the mechanism



which admits only the possibility of scattering or annihilation to form excited singlet after formation of the pair (TT). A more complete treatment would include the possibility of formation of two ground state singlets, of T and S, of quintet states, etc., upon reaction of two triplets (see, for example, Bezman and Faulkner [12]). With the assumption made below of a triplet lifetime governed by quenching, these additional reactions will not affect the derived steady state triplet concentration. Although one usually includes all quenching reactions in a single equation involving a triplet lifetime,  $\tau$ , we here divide such reactions into those involving paramagnetic quenchers and those



ment will hold for systems with 'Feldberg' slopes close to  $-2.96$  [12,13]. For the general case, which is probably of greater importance in ECL, where higher triplet concentrations are involved, the triplet concentration must be obtained from the steady state solution of eq. (5), and in that case a more careful consideration of the various possible paths during triplet-triplet annihilation is probably warranted.

### References

- [1] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 91 (1969) 6497.
- [2] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 91 (1969) 6495.
- [3] R.C. Johnson and R.E. Merrifield, *Phys. Rev.* 1B (1970) 896;
- R.C. Johnson, R.E. Merrifield, P. Avakian and R.B. Flippen, *Phys. Rev. Letters* 19 (1967) 285.
- [4] R.E. Merrifield, *J. Chem. Phys.* 48 (1968) 4318.
- [5] V. Ern and R.E. Merrifield, *Phys. Rev. Letters* 21 (1968) 609.
- [6] L.R. Faulkner, H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 94 (1972) 691.  
L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 91 (1969) 209.
- [7] L.R. Faulkner and A.J. Bard, *Chem. Instr.* 2 (1970) 337.
- [8] H. Tachikawa, Ph.D. Thesis, The University of Texas at Austin (1973).
- [9] C.A. Parker, *Photoluminescence of solutions* (Elsevier, Amsterdam, 1968).
- [10] J.S. Brinen and J. G. Karen, *Chem. Phys. Letters* 2 (1968) 671.
- [11] M. Zander, *Phosphorimetry* (Academic Press, New York, 1969).
- [12] R. Bezman and L.R. Faulkner, *J. Am. Chem. Soc.* 94 (1972) 3699.
- [13] S.W. Feldberg, *J. Phys. Chem.* 70 (1966) 3928.