The Photochemical Reduction of 2,1,3-Benzothiadiazole-4,7-dicarbonitrile by Ethylenediaminetetra-acetic acid in the Presence of Micelles

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Photolysis of solutions of 2,1,3-benzothiadiazole-4,7-dicarbonitrile (1) containing ethylenediaminetetra-acetic acid disodium salt (EDTANa2) and cetyltrimethylammonium bromide (CTAB) micelles at pH 5—5.5 causes formation of (1)·-, identified by its visible and e.s.r. spectra.

Micelles have been shown to have a number of possible roles in photochemical electron transfer reactions.[1] Amongst these are (a) the inhibition of ground state complexation between electron donor or acceptor and chromophore,[2] and (b) effects on the relative rates of forward and energy wasting back electron transfer reactions by promoting charge separation.[3]

During the course of studies aimed at identifying possible neutral electron transfer catalysts[4] for use in the photochemical decomposition of water, we have discovered a reaction in which the micelle fulfils both these roles simultaneously and apparently protects an unstable radical anion from the environment, in which it is unstable.

Compound (1)[5] has a strong u.v. absorption centred at 320 nm and irradiation at this wavelength causes weak emission at 3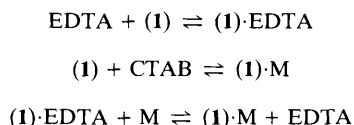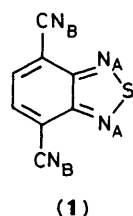80 nm. On addition of ethylenediaminetetra-acetic acid disodium salt (EDTANa2), this emission is increased ca. 10 fold.‡ The intensity of the emission in the presence of EDTA is highly pH sensitive, decreasing dramatically in intensity from pH 4—5.5 and then increasing slowly at high pH.

At pH 5.5, the emission intensity in the presence of EDTA can be reduced by addition of cetyltrimethylammonium bromide (CTAB) at concentrations greater than the critical micelle concentration, although the intensity of the emission remains higher than that of solutions of (1) in the absence of EDTA.

We interpret these results as arising from complex formation between (1) and EDTA [(1·EDTA)] and that complexation causes a reduction in the efficiency of non-radiative decay processes of the excited state of (1). On addition of CTAB,

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‡ Such stimulated emissions have been observed e.g. where complexation by cyclodextrin occurs [see S. Scypinski and J. C. Love, Int. Lab., 1984, 14, (3) 60, and refs. therein].

$$\text{EDTA} + (1) \rightleftharpoons (1)\cdot\text{EDTA}$$

$$(1) + \text{CTAB} \rightleftharpoons (1)\cdot\text{M}$$

$$(1)\cdot\text{EDTA} + \text{M} \rightleftharpoons (1)\cdot\text{M} + \text{EDTA}$$

Scheme 1. Equilibria existing in solutions containing (1), EDTA, and CTAB.

Table 1. Major features in the visible spectrum of (1)·⁻ in CTAB micelles (400—800 nm).

| λ/nm	ε/dm³ mol⁻¹ cm⁻¹	Width at half height/nm
760	5395	20
688	4477	32
625	2257	
490	4750	102
452	4775	88

this complex is broken down and some (1) enters the micelles [(1·M)], see Scheme 1. Its absorption spectrum is apparently unaffected.

Continuous photolysis with light from a 500 W tungsten lamp of solutions containing (1) (2.5×10^{-4} mol dm⁻³), CTAB (0.4% w/w), and EDTA (0.1 mol dm⁻³) at pH 5—5.5 produces brown solutions, the visible spectra of which (see Table 1) are almost identical to those of (1)·⁻ produced by pulse radiolysis. The presence of (1)·⁻ is confirmed by e.s.r. studies which show a 17 line signal. This can be attributed to an overlapping 1:2:3:2:1 quintet of 1:2:3:2:1 quintets from a radical with a (N$_A$) = 0.255 and a (N$_B$) = 0.075 mT.

This electron transfer reaction is evidently highly efficient since, despite the very low extinction coefficient of (1) in the visible region of the spectrum, up to 50% conversion into (1)·⁻ can be observed in *ca.* 30 min.§

The formation of the radical anion can *only* be detected under conditions of pH where there is a significant proportion of (1) inside the micelles. This is because electron transfer apparently does not occur within the (1)·EDTA complex (as evidenced by the strong emission intensity of this complex) and hence can only occur when the complex is separated, *e.g.* if (1) is in the interior of the micelle and EDTA is electrostatically bound to its surface. This will also inhibit back electron transfer between EDTA·⁺ and (1)·⁻ sufficiently for EDTA·⁺ to decompose, see Scheme 2.

In addition, the micelle serves a third function in this system by protecting the formed radical from the protic environment, in which it is unstable. This instability is demonstrated by the observation that, whereas cyclic voltammograms of aqueous methanolic solutions of (1) show⁶ a quasi-reversible 1 electron couple with $E°$ = −0.49 V (*vs.* normal hydrogen electrode), in
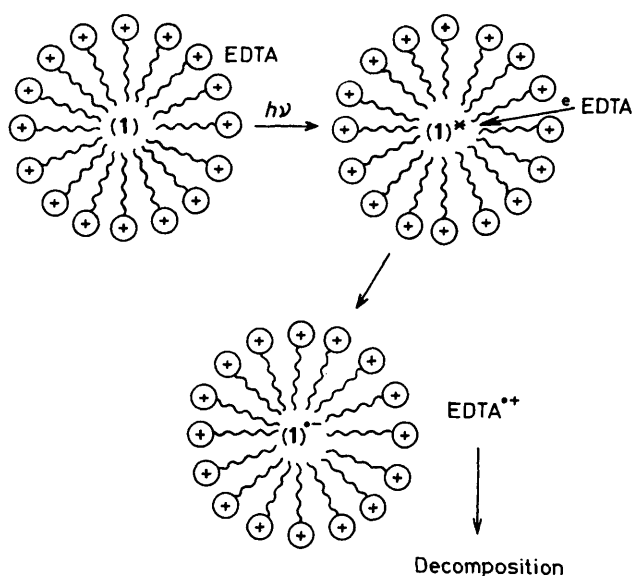
Scheme 2. Role of the micelle in formation of (1)·⁻ on irradiation of solutions containing (1), EDTA, and CTAB.

acetate buffer at pH 4.5 a 1 electron reduction wave with E_{max} = −0.53 V is observed with no accompanying wave corresponding to reoxidation.

Although its decay kinetics are currently under investigation, the stabilisation of (1)·⁻ is evidently highly efficient since spectrophotometric studies show that for a solution of (1)·⁻ (8 × 10⁻⁵ mol dm⁻³), only half has decayed in 12 h, and the colour is still clearly visible after 24 h. Similar stabilisations *e.g.* of esters from hydroxide ion by negative micelles are well known.⁷

The observation⁴ that (1) is a highly efficient quencher of the excited state of [Ru(bipyridyl)₃]²⁺ suggests it might have importance as an electron transfer agent. Studies of its use in this way are being actively pursued.

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References

1 'Micellisation, Solubilization and Microemulsions,' ed. K. L. Mittal, Plenum Press, New York, 1977, and refs. therein.
2 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978, and refs. therein.
3 J. Kiwi, K. Kalyanasundaram, and M. Grätzel, *Struct. Bonding (Berlin)*, 1982, **49**, 39, and refs. therein.
4 J. S. Clayton, D. W. Bruce, D. J. Cole-Hamilton, and P. Camilleri, *Inorg. Chim. Acta*, in the press.
5 K. Pilgram and R. D. Skiles, *J. Heterocycl. Chem.*, 1974, **11**, 777.
6 P. Camilleri, J. R. Bowyer, M. T. Clark, and P. O'Neill, *Biochim. Biophys. Acta*, 1984, **765**, 236.
7 F. M. Menger and C. E. Portnoy, *J. Am. Chem. Soc.*, 1967, **89**, 4698.

§ Quantum yields for this reaction have not yet been measured.