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Comment on: 'Dimer Formation of Viologen Derivatives and their Electrochromic Properties' [1]

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INTRODUCTION

The title paper [1] was recently published in *Dyes and Pigments*. It was received for publication on 12 February 1996 and accepted for publication a month later on 11 March 1996.

The paper discusses the radical cation of bipyridilium compounds ('bipm' named formally as 1,1'-disubstituent-4,4'-bipyridilium), formed by one electron reduction of the respective dication:

$$\text{bipm}^{2+} + e^{-} \rightarrow \text{bipm}^{+\bullet} \tag{1}$$

The radical is paramagnetic (the spins are unpaired) as shown by the radical having an electron paramagnetic resonance (EPR) signal [2]. The dication is colourless but the radical is brilliantly coloured, hence the viologens are electrochromic [3]. On an elementary level, the colour may be explained in terms of photon absorption to effect optical charge transfer between the heterocyclic nitrogen atoms of (formal) charge +1 and 0. (In fact, the electron is more-or-less delocalised throughout the entire molecule [2].)

Dimerisation and structure of the dimer

In water, the radical cation moieties spin pair [2] to form a diamagnetic dimer:

$$2\ \text{bipm}^{+\bullet} \rightarrow (\text{bipm})_2^{2+} \tag{2}$$

The dimer has a 'sandwich' type structure [2,4] with the π-clouds of each viologen radical overlapping. The viologen dimer is stable in water, but is unstable in *all* non-aqueous solvents unless the temperature is lowered below [2] *ca* 10°C. This solvent dependence is usually explained in terms of columbic repulsion between the two cationic charge; only in water is the energy of solvation great enough that ΔG^0 for dimerisation is larger (more negative) than is $(\Delta H^0 - T\Delta S^0)$ for Coulomb repulsion.

The structure in Fig. 1 of the title paper (Ref. 1, p. 171) is unlikely to be correct as orbital overlap is not maximised: a consideration of the entropy change on dimerisation necessitates that the dimer occupies a small volume of space i.e. both the two rings overlap entirely [2]. Even if only one ring of each viologen was interacting, the structure in the paper would still be wrong as the two rings bearing a radical electron are not spin pairing; and the two rings bearing a cationic charge are adjacent: the spin-pairing energy is minimised and the charge-repulsion energy is maximised.

Colours seen at different times and potentials

The dimer has a different colour from that of the monomer owing to (i) the formation of a new optical band for the dimer at *ca* 900 nm; and (ii) changes in energy, causing the UV–vis spectroscopic bands for the monomer undergoing a blue shift (λ_{max} for methyl viologen radical cation monomer, $MV^{+\cdot}$ = 600 nm and λ_{max} for the methyl viologen radical dimer = 560 nm [3]). Alkyl-substituted viologens are blue as a monomer and the respective dimer is red, so a mixture of monomer and dimer looks violet [4].

The authors assert that dimer was formed at high (negative) potentials; and certainly the spectra show that dimer was the ultimate product. There is no recorded instance of a concerted two-electron uptake to form dimer:

$$2\ \mathrm{bipm}^{2+} + 2\mathrm{e}^{-}(\mathrm{bipm})_2^{2+} \tag{3}$$

In fact, the reaction seen by these authors is a multi-step process. First, single viologen dications are di-reduced

$$\mathrm{bipm}^{2+} + 2\mathrm{e}^{-}\mathrm{bipm}^{0} \tag{4}$$

Following formation, this di-reduced (or 'di-hydro') viologen species diffuses into the solution bulk. On encountering unreduced dication, electron transfer occurs:

$$\mathrm{bipm}^{2+} + \mathrm{bipm}^{0} \rightarrow (\mathrm{bipm})_2^{2+} \tag{5}$$

This redox reaction is termed 'comproportionation'. It is this separate, *homogeneous* reaction which causes the colour of the dimer to be seen.

Comproportionation may be followed by EPR [5], UV–vis spectroscopy [6] or by electrochemical means such as cyclic voltammetry [7]. Dimer is the true product of comproportionation but, since dimer is unstable in non-aqueous solutions, the dimer species dissociate to form two monomeric radicals. The violet colour seen is a composite: that of red dimer and blue monomer.

The dimer dissociates at open circuit since the equilibrium-constant K dicates the ratio of monomer to dimer, and K is relatively small e.g. K is 380 (mol $dm^{-3})^{-1}$ for aqueous ethyl viologen in the presence of iodide [4]. This difference of colour in open circuit and when colour is applied has been observed many times before [8–10].

Spectra of radical cations

Finally, there are Figs 1 and 3 [1] to analyse. The spectra of viologen radical cations and of radical cation dimers are very similar (see above), the major difference being the peaks at 550 nm (dimer) and 600 nm (monomer) have difference absorbances. The spectra in Figs 1 and 3 of the title paper [1] are therefore surprising: only the traces obtained with the highest voltage looks anything like the spectrum of $bipm^{+\bullet}$; it is to be assumed that the other bands (which are apparently gaussian) refer to other coloured species than viologens.

All alkyl-substituted viologen radical cations in solution have the same spectra as the trace in Fig. 1 of the title paper (at 3.7 V) [1]. This is because the electron resides within the bipyridine 'core' and electronic interactions beyond the first carbon of the alkyl chain are minimal. It is thus not the case that the colour is a function of the ethyl substituent.

SUMMARY

The authors assert (in their abstract) that a monomer dimer equilibrium is proposed to explain the observation that the electrochromic colour at 1.7–3.0 V is violet, but is blue on open circuit. This is why the authors see the colour of the viologen dimer. The author's statement that the colour is owing to the ethyl group is shown to be incorrect.

REFERENCES

1. Kim, S. H., Bae, J. S., Hwang, S. H., Gwon, T. S. and Doh, M. K., *Dyes and Pigments*, 1997, **33**, 167.
2. Evans, A. G., Evans, J. C. and Baker, M. W., *J. Chem. Soc., Perkin Trans. II*, 1979, 1797.

3. Monk, P. M. S., Mortimer, R. J. and Rosseinsky, D. R., *Electrochronlism: Fundamentals and Applications*. VCH, Weinheim, 1995.
4. Kosower, E. and Cotter, J. L., *J. Am. Chem. Soc.*, 1964, **86**, 5524.
5. Compton, R. G., Monk, P. M. S., Rosseinsky, D. R. and Waller, A. M., *J. Electroanal. Chem.*, 1989, **267**, 309.
6. Monk, P. M. S., Fairweather, R. D., Ingram, M. D. and Duffy, J. A., *J. Chem. Soc., Perkin Trans. II*, 1992, 2039.
7. Datta, M., Jansson, R. E., and Freeman, J. J., *Appl. Spectrosc.*, 1986, **40**, 251.
8. Sammells, A. F. and Pujaru, N. U., *J. Electrochem. Soc.*, 1986, **133**, 1270.
9. Belinko, K., *Appl. Phys. Lett.*, 1976, **29**, 363.
10. Monk, P. M. S., Fairweather, R. D., Ingram, M. D. and Duffy, J. A., *J. Electroanal. Chem.*, 1993, **259**, 301.