# Evidence for the Product of the Viologen Comproportionation Reaction being a Spin-paired Radical Cation Dimer

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The mechanism of the bipyridylium comproportionation reaction has been determined using the redox states of methyl viologen (MV). The reaction, hitherto presumed to follow the stoichiometry $MV^{2+} + MV^0 \longrightarrow 2\ MV^+$, has been investigated using *in situ* electrochemical EPR and UV–VIS spectroscopy and been shown to proceed *via* an intermediate step forming a spin-paired radical cation dimer $(MV)_2^{2+}$. Dimer dissociation occurs as a subsequent reaction stage.

Bipyridylium-based electrochromic devices are currently being investigated for the production of *e.g.* flat TV-type displays.[1,2] The most fully documented member of this group is methyl viologen: 1,1′-dimethyl-4,4′-bipyridylium as the dichloride salt, $MV^{2+}$. This dication is a colourless species, but cathodic reduction yields the blue radical cation, as in eqn. (1), which can

$$MV^{2+} + e^- \longrightarrow MV^+ \qquad (1)$$

equilibrate with the red (spin-paired) radical cation dimer $(MV)_2^{2+}$,[3] as in eqn. (2). Organic solvents, such as propylene

$$2\ MV^+ = (MV)_2^{2+} \qquad (2)$$

carbonate or acetonitrile, favour the monomer and solutions are blue, while aqueous solutions are purple owing to a substantial presence of both species.[4]

The monomer can be reduced to neutral $MV^0$, which is slightly brown,[5,6] as in eqn. (3).

$$MV^+ + e^- \longrightarrow MV^0 \qquad (3)$$

$MV^0$ is a powerful reducing agent and will react with the $MV^{2+}$ dication in a comproportionation reaction which has, to date, been cited as eqn. (4).

$$MV^{2+} + MV^0 \longrightarrow 2\ MV^+ \qquad (4)$$

During recent kinetic investigations of the comproportionation reaction,[7] it was necessary to postulate that the reaction proceeded *via* the dimer $(MV)_2^{2+}$ following reaction (2) rather than the monomer.[7] This was argued following an observed loss of electroactivity following comproportionation; the radical cation dimer/dication redox couple is known to be quasi-reversible.[7]

We now present further evidence that dimer is indeed the product of comproportionation. We have used a water-based solvent in this study to allow both the monomer and dimer species to exist in solution. The polyAMPS polyelectrolyte was chosen since its high viscosity enables the individual steps of fast reactions to be resolved.

## Experimental

Several electrochromic cells of the form ITO/polyAMPS, KCl, $(MV^{2+}\ 2Cl^-)$/ITO were constructed using ITO (indium tin-oxide) covered glass (supplied by Sanyo, Japan), as an optically transparent electrode. (ITO is a mixture of indium and tin oxides.)

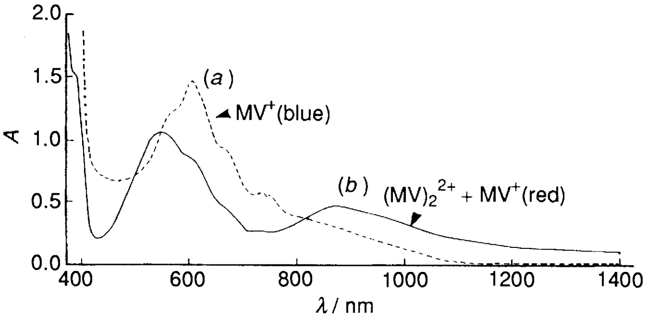

**Fig. 1** Optical spectrum of the cell ITO/polyAMPS, KCl, $(MV^{2+}\ 2Cl^-)$/ITO recorded after applying a potential of 1.0 V for 3 s (*a* (- - - -); and (*b*) (——) 3.0 V for 3 s. Some monomeric $MV^+$ is apparent in spectrum (*b*)

The polyelectrolyte polyAMPS [poly(acrylamido-3-methylpropanesulfonic acid)] (Aldrich) was used as received, *i.e.* as a 10% w/w solution in water. KCl (Analar, BDH) was 0.1 mol kg$^{-1}$ and methyl viologen dichloride (Aldrich) was 0.04 mol kg$^{-1}$.[8] Lower concentrations of the electrochromic methyl viologen would not produce colour. The electrolyte was degassed on a vacuum line, and stored in a Schlenk tube under $N_2$.

Electrochromic cells were assembled in a sandwich arrangement, and hermetically sealed with epoxy resin to prevent polyAMPS losing water.

External electrical contacts were made with conducting silverdag paint (Acheson Colloid Co., Plymouth Rock, Plymouth). A Schlumberger 1186 electrochemical interface was used as a two-electrode potentiostat with the reference and counter electrodes connected. (We have used a two-electrode device since 'real' devices will use this array.)

For EPR studies, the cells (width <8 mm) were sealed with adhesive tape to avoid difficulties arising from radical generation within the epoxy resin sealant. The cell was suspended in the resonant cavity of a Varian E109 X-band instrument, and the intensity of the EPR signal followed with time, using a WPA CQ95 Y-t chart recorder.

The change in optical absorbance during electrolysis was followed with an electrochromic cell placed in the sample beam of a Shimadzu UV-3100 spectrometer. The spectrum of the cell prior to colouration was used as the reference.

## Results and Discussion

A potential of *ca.* 1.0 V, applied across the cell, was sufficient to generate only radical cations, $MV^+$, [eqn. (1)]. The spectrum of

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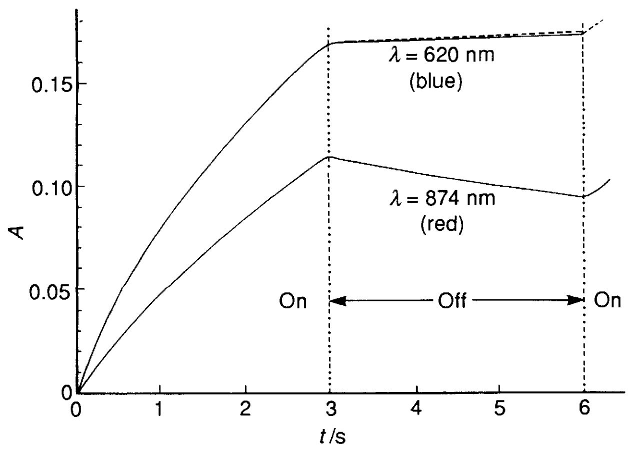

**Fig. 2** Trace of optical absorbance at 620 nm and 874 nm during a 3 s pulse at 3.0 V, and subsequently, for the cell ITO/polyAMPS, KCl, ($MV^{2+}$ $2Cl^-$)/ITO. Absorbances have been adjusted after setting to zero for $t = 0$. The broken line is eqn. (A3).

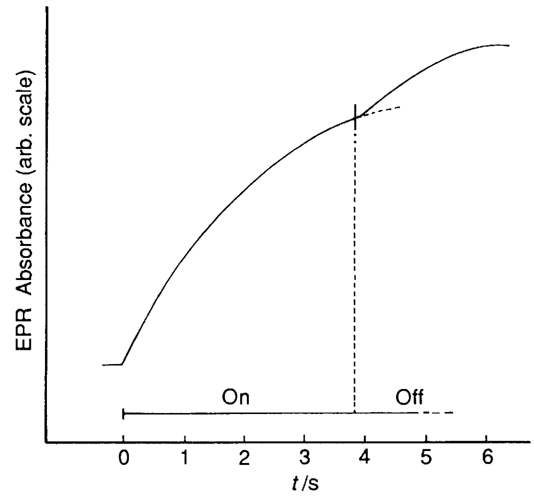

**Fig. 3** Trace depicting the time-dependence of EPR intensity for the cell, both during and after electrolysis

the resulting blue solution is shown in Fig. 1(*a*). With a larger potential (3.0 V), sufficiently negative to generate $MV^0$ [eqn. (3)], a rich crimson colour developed, Fig. 1(*b*), which, during electrolysis, turned to red–purple and thence to blue–purple. Following disconnection of the cell from the potentiostat, the colour turned wholly blue within <2 min.

The spectrum of the crimson solution [curve (*b*) in Fig.1] closely resembles that of the methyl viologen radical cation dimer $(MV)_2^{2+}$.[3] The resulting blue solutions were found to have spectra identical with the initial blue solution *i.e.* akin to Fig. 1(*a*), indicating that the colour change crimson ⟶ blue resulted from the conversion of dimer to monomer. The cell behaved with excellent reproducibility.

Generation of the red $(MV)_2^{2+}$ dimer can be followed by observing the increased optical absorbance at 874 nm, Fig. 1(*b*). Fig. 2 shows the increase during a 3 s pulse at a potential of 3.0 V, thereby ensuring the generation of the $MV^0$ species. During the 3 s interval succeeding the pulse, the cell was on open-circuit. The absorbance at 874 nm is seen to have decreased somewhat (Fig. 2), indicating some removal of the dimer. Simultaneously, there was a slight increase in the absorbance in the blue region (we choose 620 nm); and this is close to the increase predicted on the basis of dimer being converted to monomer (see Appendix).

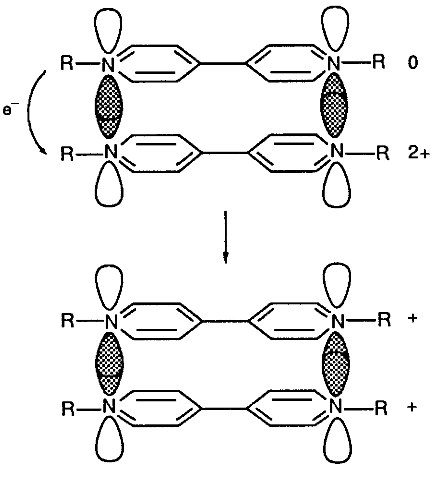

**Fig. 4** Schematic to show the mechanism of bipyridylium comproportionation: intramolecular electron transfer yields a radical cation dimer, which may subsequently dissociate to form monomer

The cell was uncoloured after electrochemical oxidation of the coloured radical cation-containing species. No gas had been electrogenerated. We assume, therefore, that any products of electrolysis at the counter electrode are innocent and are produced in low quantities. Clearly our device is only a prototype, and any working device would require an additional redox couple to be placed adjacent to the counter electrode.

The EPR derivative spectrum of the generated $MV^+$ monomer was found to be similar to that reported in the literature.[3] Using a constant field, a simple intensity–frequency plot was produced; the frequency of maximum intensity was noted, and followed as a function of time during electrolysis within the EPR cell. The potential was again 3.0 V, to generate $MV^0$ [eqn. (2)] which is, like the spin-paired $(MV)_2^{2+}$, 'EPR invisible'.[9,10] The EPR intensity is thus a function of $[MV^+]$ monomer concentration, and its trace during electrolysis is shown in Fig. 3.

When the current was switched off (*i.e.* open circuit), the EPR intensity increased rapidly for *ca.* 1.5–2.0 s (Fig. 3) *even though no current flowed.* This again indicates that the generation of the $MV^+$ monomer occurs through a mechanism other than direct electrolysis. That the EPR intensity *increased* after the cessation of current is simply because the dimer dissociates [*i.e.* the reverse of eqn. (2)].

We postulate that the comproportionation reaction proceeds as follows. The $MV^0$ and $MV^{2+}$ species approach in solution. A sandwich-type structure is formed rapidly between the two redox species *via* an overlap of π-clouds. Intramolecular electron transfer then occurs to form dimer, which may then dissociate (see Fig. 4, in which only the orbitals on nitrogen are shown). It should be noted that the radical cation dimer is always stated to have a 'sandwich' configuration of this type.[3,10]

## Conclusions

The immediate product of the bipyridylium comproportionation reaction is a spin-paired radical cation dimer. Dissociation of this dimeric species yields the characteristic colour of the $MV^+$ monomer.

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## Appendix

The increase in absorbance, $A$, at 620 nm is observed to be only slight. This artifact arises from the overlapping nature of monomer and dimer bands at this wavelength; the concentration of monomer increases while the dimer concentration decreases. From the reaction stoichiometry: dimer $(1 - x) = 2$ monomer $(2x)$ where $x$ is the extent of dimer dissociation, it follows from Beer's law that, eqns. (A1) and (A2) hold, where

$$A^{620}/cl = 2x\varepsilon^{620}_{\mathrm{mon}} + (1 - x)\varepsilon^{620}_{\mathrm{dim}} \qquad \text{(A1)}$$

$$A^{874}/cl = 2x\varepsilon^{874}_{\mathrm{mon}} + (1 - x)\varepsilon^{874}_{\mathrm{dim}} \qquad \text{(A2)}$$

$cl$ = concentration × path length. Extinction coefficients, $\varepsilon$, for monomer and dimer are in ref. 3.

Rearrangement of eqn. (A2) and (A1), yields, eqn. (A3);

$$A^{620}/cl = (A^{874}/cl - \varepsilon^{874}_{\mathrm{dim}}) \times \left\{\frac{(2\varepsilon^{620}_{\mathrm{mon}} - \varepsilon^{620}_{\mathrm{dim}})}{(2\varepsilon^{874}_{\mathrm{mon}} - \varepsilon^{874}_{\mathrm{dim}})}\right\} + \varepsilon^{620}_{\mathrm{dim}} \qquad \text{(A3)}$$