

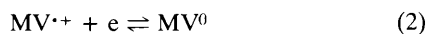
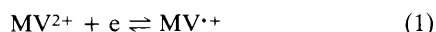
## The Electroreduction of Methyl Viologen

Michael Heyrovský

*Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 118 40 Prague 1, Czechoslovakia*

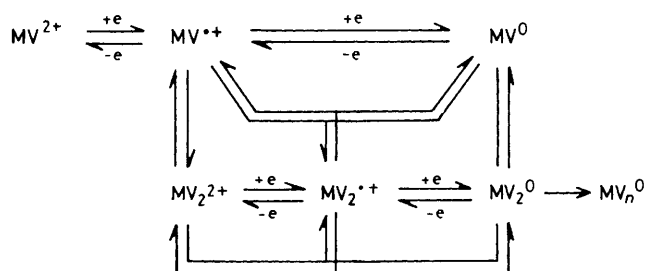
In electroreduction, after the transfer of the first electron to methyl viologen,  $MV^{2+}$ , resulting in formation of the radical cation,  $MV^{\cdot+}$ , the electron transfer to  $MV^{\cdot+}$  without chemical complications occurs only under special conditions: the species more readily reduced than  $MV^{\cdot+}$  are the dication or monocation dimers,  $MV_2^{2+}$  or  $MV_2^{\cdot+}$  formed in reactions in solution near the electrode.

It is well known<sup>1</sup> that the methyl viologen (1,1'-dimethyl-4,4'-bipyridinium) dication,  $MV^{2+}$ , changes into the blue radical cation,  $MV^{\cdot+}$ , by accepting one electron from an electrode in the fast reversible reaction (1) which in aqueous solution is accompanied by adsorption of  $MV^{2+}$  and  $MV^{\cdot+}$  at the electrode surface.<sup>2,3</sup> For the half-wave potential of this electrode reaction in aqueous solutions the value of  $-0.69$  V vs. saturated calomel electrode (S.C.E.), identical with the corresponding standard redox potential,<sup>4</sup> has been accepted.<sup>5</sup> The actual course of the second reduction step of  $MV^{2+}$ , generally considered to be as represented in reaction (2), where  $MV^0$  symbolizes the reduced molecular form of methyl viologen (1,1'-dimethyl-1,1'-dihydro-4,4'-bipyridine), has been the subject of detailed research, the important results of which are reported in the present note.



When studied by linear sweep voltammetry with a stationary mercury drop electrode, the electroreduction of  $MV^{\cdot+}$  to  $MV^0$  in neutral aqueous solutions occurs as a simple reversible process at  $-1.35$  V vs. S.C.E. at  $MV^{2+}$  concentrations of  $1 \times 10^{-5}$  M and lower and at voltage scan rates of  $200$  mV s<sup>-1</sup> and higher.<sup>3</sup> Under these conditions two pairs of peaks about  $0.7$  V apart can be observed on the cyclic voltammetric curve, due to the two reversible redox steps in equations (1) and (2). The asymmetry of the curve indicates that part of the reduction product  $MV^0$  undergoes an inactivating reaction, presumably an association (3), where  $n$  denotes the degree of association.

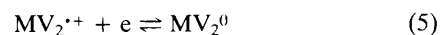
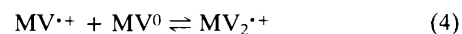
In d.c. polarography a reduction process, which, as its half-wave potential,  $E_{1/2} -1.35$  V vs. S.C.E., shows, corresponds to the voltammetric  $MV^{\cdot+}/MV^0$  redox reaction, is marked on the polarographic curve by a well-defined wave only when the rate of flow of mercury into the electrode is



Scheme 1

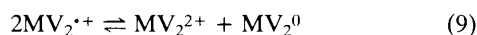
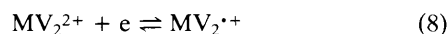
sufficiently high (however, still within laminar limits). With a slow drop growth and low  $MV^{2+}$  concentration the polarographic curve shows a reduction wave with its half-wave potential more positive by  $0.15$  V than the  $MV^{\cdot+}/MV^0$  redox, *i.e.*, at  $-1.2$  V vs. S.C.E. When the pressure of mercury above the capillary tip is increased above a certain limit, there appears, on top of the existing wave, the  $MV^{\cdot+}/MV^0$  wave at  $-1.35$  V which increases linearly with the mercury pressure. This effect can be explained in the following way.

The radical cation  $MV^{\cdot+}$  produced in the first reduction step is adsorbed at the negatively charged electrode. Similarly, the reduced molecular form  $MV^0$  is also adsorbed on mercury, although less strongly. Following the electron transfer reaction the adsorption of the reduced species continues, irrespective of its adsorbability, until full coverage of the electrode is attained; only then do the products begin to diffuse towards the bulk of the solution. When the pressure of mercury exceeds a certain limit, the rate of increase of the electrode surface becomes higher than the rate of occupation of the newly forming surface by adsorbing product of the electrode reaction, and hence no reduction product can appear in the solution for secondary reactions to take place. With a high rate of growth of the mercury drop neither  $MV^{\cdot+}$  nor  $MV^0$  appear beyond the electrode surface and thus, under these special conditions, the second stage of the electroreduction of  $MV^{2+}$  proceeds in the simplest way, according to equation (2). With a lower rate of growth of mercury surface, after the electrode becomes fully covered by the products and  $MV^{\cdot+}$  and  $MV^0$  appear in solution, the monocation dimer<sup>6,7</sup>  $MV_2^{\cdot+}$ , when formed [reaction (4)] by encounter of these two species near the electrode, is reduced [reaction (5)] to  $MV_2^0$ , the dimer of  $MV^0$ , in the wave at  $-1.2$  V vs. S.C.E. In the negative potential range when  $MV^{2+}$  is reduced directly to  $MV^0$ , the cation radical  $MV^{\cdot+}$  is produced in solution by the conproportionation reaction<sup>8</sup> (6), and the formation of the monocation dimer  $MV_2^{\cdot+}$  and its reduction proceed according to reactions (4) and (5). Thus in d.c. polarography under normal conditions and at low concentrations of  $MV^{2+}$  the reduction wave corresponding to the second stage of electroreduction of  $MV^{2+}$  is due to electron transfer to the dimeric species  $MV_2^{\cdot+}$ . In voltammetry with a slow scan rate, there appear two negative peaks at  $-1.2$  and  $-1.35$  V vs. S.C.E., pertaining to the reduction of  $MV_2^{\cdot+}$  and  $MV^{\cdot+}$  respectively.



In the potential range between the  $MV^{2+}/MV^{\cdot+}$  and  $MV_2^{\cdot+}/MV_2^0$  redox reactions there occurs one more faradaic

process in aqueous solutions, at  $-1.0$  V vs. S.C.E. It becomes apparent when the concentration of  $MV^{2+}$  in the solution is sufficiently high or, with solutions of low concentration of  $MV^{2+}$ , when the time of contact of the solution with the electrode is sufficiently long. In d.c. polarography a reduction wave at  $-1.0$  V can be distinguished on the curve with a  $5 \times 10^{-5}$  M solution when the drop-time is 3 s; in linear sweep voltammetry a peak at  $-1.0$  V is clearly defined with a  $2 \times 10^{-5}$  M solution at a potential scan rate of  $50$  mVs $^{-1}$  and lower. With higher concentrations and faster scans the peak is reversible. With increasing concentration of  $MV^{2+}$  or with prolonged drop-time the d.c. polarographic wave at  $-1.0$  V increases at the expense of the more negative  $MV_2^{*+}/MV_2^0$  wave at  $-1.2$  V: with  $5 \times 10^{-4}$  M solution and a drop-time of 3 s or with  $2 \times 10^{-4}$  M solution and a drop-time of 10 s the negative wave is almost completely replaced by the more positive one.



The species primarily produced by electroreduction of  $MV^{2+}$  at  $-1.0$  V is the radical cation  $MV^{*+}$  which is adsorbed at the electrode. After complete coverage of the electrode surface has been attained the radical cations are free to diffuse towards the bulk of the solution or to combine to form the dication dimer  $MV_2^{2+}$  according to reaction (7) which is presumably slower than reaction (4). As soon as this dimer appears near the electrode at  $-1.0$  V vs. S.C.E. it accepts an electron and is reduced [reaction (8)] to the monocation dimer  $MV_2^{*+}$ . When accumulated the monocation dimer disproportionates [reaction (9)] and the reduction of  $MV_2^{2+}$  at  $-1.0$  V continues with the dimer  $MV_2^0$  as product. The total height of the polarographic wave is determined by the rates of reactions (7) and (9) with the limit at high  $MV^{2+}$  concentrations of a diffusion-controlled two-electron process, as is found

experimentally. The polarographic wave or the voltammetric peak of  $MV^{2+}$  observed at  $-1.0$  V vs. S.C.E. is thus due to reduction of the dication dimer  $MV_2^{2+}$  formed in solution near the electrode by dimerization of the radical cation  $MV^{*+}$  and not to the direct reduction of this radical which takes place in a potential range more negative by 0.35 V.

The paths along which the two-electron electroreduction of  $MV^{2+}$  can proceed in aqueous solutions are summarized in Scheme 1, where the adsorption steps and the reactions of catalytic evolution of hydrogen have not been included. The species  $MV^0$  and  $MV_2^{*+}$  are oxidized by hydrogen ions and hence the second reduction stage of  $MV^{2+}$  is pH-dependent<sup>1,11</sup> in solutions of pH < 7.

Received, 27th May 1987; Com. 715

## References

- 1 O. H. Müller, *Ann. N.Y. Acad. Sci.*, 1940, **40**, 91; R. M. Eloffson and R. L. Edsberg, *Can. J. Chem.*, 1957, **35**, 646; R. N. F. Thorneley, *Biochim. Biophys. Acta*, 1974, **333**, 487.
- 2 J. Volke in 'Die Polarographie in der Chemotherapie, Biochemie und Biologie,' ed. H. Berg, Akademie-Verlag, Berlin, 1964, p. 70; E. Steckhan and T. Kuwana, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 253; L. Pospíšil, J. Kůta, and J. Volke, *J. Electroanal. Chem.*, 1975, **58**, 217; V. N. Grachev, S. I. Zhdanov, and G. S. Supin, *Elektrokhimiya*, 1978, **14**, 1353; A. Régis and J. Corset, *J. Chim. Phys.*, 1981, **78**, 687; W. J. Albery and P. N. Barlett, *J. Electroanal. Chem.*, 1985, **182**, 7; O. Enea, *Electrochim. Acta*, 1986, **31**, 789.
- 3 M. Heyrovský and L. Novotný, *Coll. Czech. Chem. Commun.*, 1987, **52**, 1097.
- 4 L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, 1933, **16**, 859.
- 5 C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, 1981, **10**, 49.
- 6 A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **13**, 211.
- 7 K. Chandrasekaran and D. G. Whitten, *J. Am. Chem. Soc.*, 1981, **103**, 7270.
- 8 M. Ito and T. Kuwana, *J. Electroanal. Chem.*, 1971, **32**, 415.
- 9 E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524.
- 10 A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1787.
- 11 M. Heyrovský, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 585.