

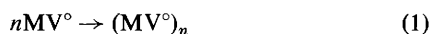
Catalytic and Photocatalytic Reduction of Water by the Reduced Forms of Methylviologen

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Polarographic results show that the reaction between water and the methylviologen redox system in the absence of catalyst is due to reduced methylviologen in its molecular form or in the form of its monocation dimer and that it is enhanced by light absorbed by these forms.

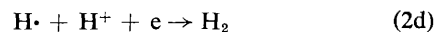
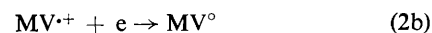
In studies of redox reactions of the methylviologen dication (1,1'-dimethyl-4,4'-bipyridylium ion), MV^{2+} , in aqueous solutions, the electron transfer between the radical cation, $MV^{•+}$, and the neutral reduced form, MV° , is considered to be irreversible.¹ We have found by cyclic voltammetry at a hanging mercury drop electrode that the electron transfer proper occurs reversibly, but that the primary reduced form MV° undergoes a fast inactivation which we assume to be an association [reaction (1)] favoured by the difference in solvation of the ionic and molecular forms, where n is the



degree of association. The association reactions of reduction products of MV^{2+} are the cause of the spectral, chemical, and electrochemical complexity of the methylviologen redox system;²⁻⁴ a relatively simple picture is obtained at a low concentration of the parent species.

With 1×10^{-5} M $MVCl_2$ in 0.1 M $NaClO_4$ and with a scan rate of 300 mV/s the potential on the cyclic voltammetric curve of the reversible peak couple corresponding to the $MV^{•+}/MV^{\circ}$ redox reaction is about 700 mV more negative than that of the $MV^{2+}/MV^{•+}$ process. MV° is therefore a much stronger reducing agent than $MV^{•+}$ and should be much more reactive towards water. This is proved to be so by d.c. polarography of 2×10^{-5} M $MVCl_2$ in aqueous solution where MV^{2+} is reduced in two steps with half-wave potentials about 700 mV apart corresponding to the separate uptake of 2 electrons; when the acidity of the solution is

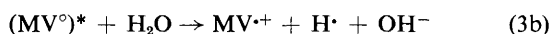
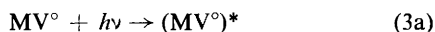
gradually increased, at pH < 7 the second cathodic wave of MV^{2+} due to reduction to MV° begins to increase above the height of the first wave until at pH ca. 4 it exceeds it by about 4 times; henceforth with further acidification it does not increase any more. This increase is obviously due to the catalytic process in reactions (2a—d), (2e) overall, which



competes with the inactivation (1). While the evolution of hydrogen from water by the reaction with $MV^{•+}$ takes place in acidic solutions and in the presence of catalysts,⁵⁻⁷ MV° is able to react spontaneously in aqueous solutions irrespective of pH, the only hindrance being its inactivation. With low concentrations of MV° in an acidic medium, the rate of reaction of MV° with water can prevail over the rate of its self-association.

On the d.c. polarographic curve of 2×10^{-5} M $MVCl_2$ in aqueous solutions the second cathodic wave, which at pH ≥ 7 is of the same height as the first wave, increases by more than 200% when the dropping mercury electrode

(D.M.E.) is irradiated by light from a high-pressure mercury lamp. With increasing concentration of MV^{2+} the ratio of the photocurrent to the 'dark' current decreases, and in 2×10^{-4} M solution it only amounts to 20%. The dependence of photocurrent on the wavelength of the light incident upon the D.M.E. indicates that the light-absorbing species is the reduction product MV° , the absorption spectrum of which is known.⁸ This means that the homogeneous reduction of water by MV° , reaction (2a), is accelerated by light [reactions (3a) and (3b)]. The absorption of light by MV° obviously

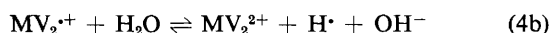


does not increase the rate of inactivation (1) and hence aided by photons of wavelength between 300 and 400 nm, MV° can decompose water also in the pH range above 7.

In buffer solutions of pH >7 the presence of $MV^{\cdot+}$ in concentration as small as 10^{-7} M produces a marked effect on the limiting current of the second d.c. polarographic reduction wave of MV^{2+} . Such an effect is typical for catalytic evolution of hydrogen at the D.M.E.⁹ We explain it by formation (4a) near the electrode of the monocation dimer¹⁰ in competition



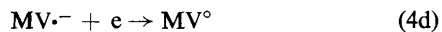
with the inactivation (1). The monocation dimer MV_2^{2+} is a stronger reductant than the cation radical $MV^{\cdot+}$ and is not prone to inactivation unlike the strongest reductant MV° . With water it presumably reacts analogously to $MV^{\cdot+}$ or MV° [reaction (4b)] forming MV_2^{2+} , the dication dimer,^{2-4,8}



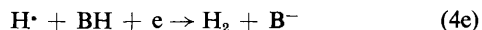
which at concentrations less than 10^{-4} M dissociates into cation radicals [reaction (4c)]. These either reach the electrode



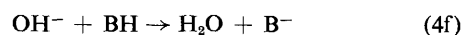
and are reduced [reaction (4d)], or react with MV° in the



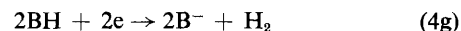
flux of products from the electrode [reaction (4a)], and regenerate the monocation dimer MV_2^{2+} . The H^\cdot radicals formed in the homogeneous process (4b) are consumed in the electrode reaction (4e), where BH is the acid and B^- the base



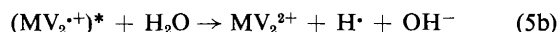
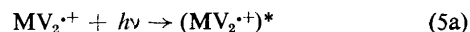
component of the buffer. The acid component reacts also with OH^- [reaction (4f)], and the net catalytic process is then



given by the sum of reactions (4a–f), reaction (4g).



The polarographic catalytic current described increases when the D.M.E. is irradiated with the mercury lamp. The effect of light is stronger here than in the case of the second reduction wave at low concentrations of MV^{2+} . The photocurrent reaches its maximum, about 6 times the value of the 'dark' current, in buffers of pH ca. 9 containing 2×10^{-4} M MV^{2+} . The photocatalytic reaction follows a path presumably analogous to reaction (3) [reactions (5a) and (5b)]. With



higher concentration of MV^{2+} the active monomers $MV^{\cdot+}$ and MV° as primary reduction products undergo higher and more complex associations^{3,4} and the species thus formed are obviously less active in the reaction with water. It is possible that at higher concentrations of MV^{2+} , i.e., at a higher rate of hydrogen production, an irreversible hydrogenation of the methylviologen redox forms observed in other systems^{7,11} also takes place near the electrode.

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