Electrochemistry of the Viologens

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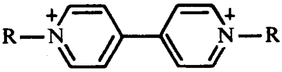
1 Introduction

It is nearly half a century since Michaelis[1] first reported on the electrochemical behaviour of a class of compounds which he christened the 'viologens', formally known as 1,1′-disubstituted 4,4′-bipyridinium ions (1). Since that time there have been successive waves of interest in this class of compounds, each wave producing its corresponding literature and yet with little or no links between them, and much information has been lost as a result. The present review is an attempt to link together the literature from the various sources.



(1)

The viologens were originally investigated as redox indicators in biological studies,[1] and they retain their importance here as possessing one of the lowest (most cathodic) redox potentials of any organic system showing a significant degree of reversibility. Subsequently they were the parent compounds for one of the most exciting new types of herbicide discovered for many years, the 'paraquat' family. Herbicidal activity was found to be linked to the redox potential.[2,3] More recently there has been an attempt to construct electrochemical display devices as substitutes for LEDs and LCDs, and the viologens have been one of the most strongly favoured candidate compounds in this, with their electrochemically reversible behaviour and the marked colour change between the two oxidation states. Later still they have been adopted as 'mediating compounds' in a range of biological studies, which are discussed in the section on applications. It has been found that compounds that are not themselves electroactive can still be reduced by electrochemically reducing the viologen, which then chemically reduces the other compound. Further evidence of their reversibility lies in their having been seriously considered as one component of secondary batteries.

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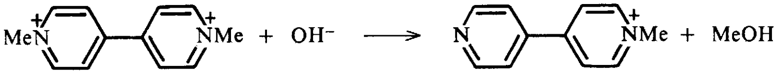
[1] L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, 1933, **16**, 859.
[2] J. Volke, *Collect. Czech. Chem. Commun.*, 1968, **33**, 3044.
[3] L. Pospisil, J. Kuta, and J. Volke, *J. Electroanal. Chem. Interfacial Electrochem.*, 1975, **58**, 217.

Finally, as their cation radicals have a strong optical absorption band in the visible region of the spectrum, the viologens are, *de facto*, candidates for the investigation of photoelectrochemical processes. However, the effect of light irradiation on viologens falls outside the scope of this review. Two other reviews should be mentioned here, which, although much broader in scope than this exercise, are highly relevant in that they provide the general context of the chemistry discussed here. Bard, Ledwith, and Shine[4] have written about 'Formation Properties and Reactions of Cation Radicals in Solution'. Kosower[5] has published 'Pyridinyl Radicals in Biology'.* The various contributions reviewed below are derived from many of these interests. Although we have tried whereever possible to assign the relevant portion of each contribution into the appropriate sections of this review, this separation has not always been possible. In addition a major collation of polarographic data, hitherto unpublished, has been included; because of its importance it was decided to allow it to stand alone.

2 General Considerations

A. Simple Chemistry and Electrochemistry.—The viologens exist in three main oxidation states, namely $V^{2+} \rightleftharpoons V^{+\cdot} \rightleftharpoons V^0$. The first reduction step is highly reversible and can be cycled many times without significant side reaction. The further reduction to the fully reduced state is less reversible, not least because the latter is frequently an insoluble species as well as being an uncharged one. The compounds are also very stable chemically, although in more alkaline solutions they will dealkylate according to equation (1) as reported by Farrington, Ledwith, and Stam.[6]


(1)

Because the methanol resulting from the dealkylation can be a reducing agent, solutions of methyl viologen in alkali can spontaneously be reduced and will then turn blue as the monocation radical is formed. The process can be catalysed, it is reported, by platinized platinum in weakly alkaline solutions.[7]

It is further suggested, on the basis of plots of open-circuit potential *versus* time, that the reduction in the presence of platinum is accompanied by oxidation of the dication. This will be pursued in a later section.

The viologens may also be incorporated into polymers, the resulting materials retaining to a large extent the chemical and electrochemical properties of the monomeric species. Simon and Moore[8] have reported the chemical and electro-

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*It is also worth reading 'The Bipyridinium Herbicides', L. A. Summers, Academic Press, London and New York, 1980.

[4] A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, 1976, **13**, 155.

[5] E. M. Kosower in 'Free Radicals in Biology', ed. W. A. Pryor, Academic Press, 1976, Vol. 2.

[6] J. A. Farrington, A. Ledwith, and M. F. Stam, *J. Chem. Soc., Chem. Commun.*, 1969, 259.

[7] I. V. Shelepin and O. A. Ushakov, *Zh. Fiz. Khim.*, 1975, **49**, 1736.

[8] M. S. Simon and P. T. Moore, *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 1.

chemical behaviour of a range of these, also showing u.v.-visible spectra. Subsequent studies in this area have been reported by Factor and Heinsohn[9] and recently by Sato and Tamamura.[10] The latter authors stress the small potential gap between first and second viologen reductions and the problems this causes, particularly in electrochromic displays, on account of the relative irreversibility of the second reduction. By using polyviologens they claim that the first reduction occurs at a more anodic, the second at a more cathodic potential. They make much of the fact that their polymers have a much narrower molecular-weight range than those of Factor *et al.* or Noguchi,[11] but they do not refer to Simon and Moore. In this paper they show how E_{rev} (both for first and second reduction) changes as a function of chain length. They also show u.v., visible, and near-i.r. spectra of monomers, dimers, and oligomers of stated chain length. The synthesis of polymerizable viologens with a terminal vinyl group is reported by Kamogawa and Mizuno.[12] Redox-potential data as well as u.v.-visible spectra are included. Yamana and Kawata[13] have also studied viologen polymers, their interest being in the electrochromic characteristics.

It might be noted that cathodic-reduction studies of the unquaternized 4, 4′-bipyridyls have also been reported, with details of product analysis.[14]

B. Synthesis.—Michaelis and Hill[1] describe the syntheses of the methyl, ethyl, and benzyl viologens and the betaine derived from chloracetic acid. Other authors who discuss preparative details include Evans and Evans[15] (diethyl, dipropyl, dibutyl, dibenzyl) and Van Dam and Ponjee,[16] who refer to the Menschutkin reaction in which an amine is quaternized with an alkyl halide. Hunig and Schenk[17] have published on the synthesis of bipyridinium salts (as distinct from details mentioned in passing). Bruinink[18] has reported synthesis details for both the 1,1′-diheptyl bipyridinium dibromide and the tetramethylene bis[4-(1-benzylpyridine-4′-yl)pyridinium] perchlorate as well as the tetrafluoroborate analogue of the same species. N.m.r. and other analytically useful information is included.

When investigating alternative anions most workers synthesize or purchase the bromide and prepare other salts by ion exchange.

C. Effect of the 1,1′-Substituents.—The observation that the 1,1′-substituents affect both the solubility of the cation radical and the reversible potential of both reduction steps has influenced the choice of viologens for herbicidal applications and for electrochromic displays.

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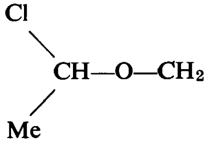
[9] A. Factor and G. E. Heinsohn, *Polym. Lett.*, 1971, **9**, 289.
[10] H. Sato and T. Tamamura, *J. Appl. Polym. Sci.*, 1979, **24**, 2075.
[11] H. Noguchi, *Proc. 35th Nat. Meet. Chem. Soc. Jpn.*, 1976.
[12] H. Kamogawa and H. Mizuno, *J. Polym. Sci.*, 1979, **17**, 3149.
[13] M. Yamana and T. Kawata, *Nippon Kagaku Kaishi*, 1977, **7**, 941.
[14] Yu. N. Forestyan, *Sov. Electrochem.*, 1971, **7**, 691.
[15] A. G. Evans, J. C. Evans, and M. W. Baker, *J. Chem. Soc., Perkin* 2, 1977, 1787.
[16] H. T. Van Dam and J. J. Ponjee, *J. Electrochem. Soc.*, 1974, **121**, 1555.
[17] S. Hunig and W. Schenk, *Liebigs Ann. Chem.*, 1979, 727.
[18] J. Bruinink, C. G. A. Kregting, and J. J. Ponjee, *J. Electrochem. Soc.*, 1977, **124**, 1854.

Inevitably much effort has gone into the optimum choice of substituent, usually in conjunction with the choice of anion. However, when considering the implications of the various findings for the general electrochemistry of the viologens it is important at each stage to draw the distinction between those systems having soluble cation radicals and those in which a precipitate is formed.

In illustration of the latter case Table 1, taken from reference 16, shows a range of substituents forming a permanent film (precipitate) in the presence of bromide ion.

Table 1 *Electrochemical reduction of viologens in aqueous solutions of dibromides for preparation of permanent film*[16]

R	*Effective length of R in* CH_2 *units*	*Permanent film*
Me	1	–
Et	2	–
Pr	3	–
Bu	4	–
C_5H_{11}	5	+
C_6H_{13}	6	+
C_7H_{15}	7	+
C_8H_{17}	8	+
iso-C_5H_{11}	4	+
Ph—CH_2	4—5	+
 $\mathrm{(Cl)(Me)CH{-}O{-}CH_2}$	4	–
Me—CH=CH—CH_2	4	–
CH_2=CH—C_3H_6	4—5	–
NC—C_3H_6	4—5	–

Variations of the 1,1′-substituents have also appeared in the patent literature relating to electrochromic displays.[19] In this case the basic substituent is an aryl group; further substitution of this influences the colour and other characteristics of the radical-cation film.

Barltrop and co-workers have also carried out some studies on the effects of varying the 1,1′-substituents.[20]

D. Effect of the Anion.—It is apparent that when the viologen cation radical forms a precipitate the anion not only affects the precipitation process but also the nature of the aggregate.

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[19] Ger. Pat. 25 27 638 (equiv. Br. Pat. 1 514 466).

[20] J. A. Barltrop, personal communication.

Motivated by display considerations, Van Dam and Ponjee[16] selected the combination of heptyl viologen with the bromide anion. Chloride was also found to induce precipitation. With a similar interest in electrochromic displays Jasinski[21] investigated a number of anions with heptyl viologen and mentioned that he was not successful in isolating solid salts of the dication other than with bromide ion. Anions found by him to be compatible with the viologen dication and its reduction products were Br^-, $H_2PO_4^-$, SO_4^{2-}, F^-, formate, and acetate. Van Dam *et al.*[16] have studied Cl^-, BF_4^-, and ClO_4^-. The following ions were not found useful by Jasinski[21] (for various reasons that he covers): HCO_3^-, BH_4^-, CN^-, PF_6^-, SbF_6^-, AsF_6^-, and SCN^-. The precipitation of dodecyl viologen with CN^- ion has been reported by Winters.[22] The $MeSO_4^-$ ion is referred to in references 23 and 24, and the $H_2PO_2^-$ ion in reference 25.

It is suggested by Jasinski[26] that divalent mono-hydrogen phosphate ions suppress formation of the monocation film on Au and degrade the adherence of the film that was formed. In reference 21 a number of anion effects are mentioned. Thus COO^--based films on Au and Ag are said to recrystallize rapidly at open circuit.[21] The same was true when formate ion was added to phosphate solution that had hitherto not shown the same effect. Bicarbonate was said to form 'well behaved' films free from recrystallization effects. However, the minimum pH possible was 7.5, and slow hydrolysis of the viologen was apparent after a few days. The same ion is discussed in reference 26. Acetate gave a stable film if the concentration exceeded 0.5 mol dm^{-3}, but at lower concentration film loss due to blue-haze formation took place.

3 Thermodynamic Aspects

A. Reversible Electrode Potentials.—Taking the reactions (2), we may measure

$$V^{2+} \underset{E_1}{\rightleftharpoons} V^{+\cdot} \underset{E_2}{\rightleftharpoons} V^0 \qquad (2)$$

the reversible potentials for each step for a given viologen. We may also formulate here the so-called 'conproportionation' and 'disproportionation' reactions [equations (3) and (4)].

$$2V^{+\cdot} \rightarrow V^{2+} + V^0 \text{ (disproportionation)} \qquad (3)$$

$$V^0 + V^{2+} \rightarrow 2V^{+\cdot} \qquad \text{(conproportionation)} \qquad (4)$$

These reactions can take place both in solution and at the surface of an electrode. In the latter case the process is presumably a combination of the homogeneous reaction and coupled anodic and cathodic reactions on the common metal [equations (5)—(7)].

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[21] R. J. Jasinski, *J. Electrochem. Soc.*, 1977, **124**, 637.
[22] L. Winters and A. Borror, *Tetrahedron Lett.*, 1976, **24**, 2313.
[23] R. Fielden and L. A. Summers, *Experientia*, 1974, **30**, 843.
[24] A. L. Black and L. A. Summers, *J. Heterocycl. Chem.*, 1971, **8**, 29.
[25] European Published Patent Application 0001912.
[26] R. Jasinski, Abstr. 205 ECS Meeting, Las Vegas, Oct. 1976.

$$V^0 - e = V^{+\bullet} \qquad \text{(anodic)} \qquad (5)$$

$$V^{2+} + e = V^{+\bullet} \qquad \text{(cathodic)} \qquad (6)$$

$$V^0 + V^{2+} = 2V^{+\bullet} \qquad \text{(overall)} \qquad (7)$$

The conproportionation constants for a number of the viologens have been obtained from the two redox potentials by using equation (8), and the values

$$E_2 - E_1 = \frac{RT}{F} \cdot \ln k_{\text{conp}} \qquad (8)$$

obtained are quite large, suggesting that little disproportionation occurs. k_{conp} for the 1,1′-dimethyl compound has been variously quoted as 6 × 10^6 in acetonitrile;[27] in reference 28 the value is given as 1 × 10^7 in both acetonitrile and DMF. Shelepin and Ushakov[7] give K as 4 × 10^6 but do not indicate whether the solvent is DMF or water. Hunig and Sauer[29] have quoted the expression (9), where K_{sem} is equivalent to k_{conp}.

$$\% \text{ semiquinone form} = \frac{K_{\text{sem}}^{\frac{1}{2}} \times 100}{K_{\text{sem}}^{\frac{1}{2}} + 2} \qquad (9)$$

B. Values for E_1 and E_2.—A range of values of the redox potentials may be found in the literature. This is summarized in Table 2. Some authors, such as Hunig, obviously feel that reversible potentials can only be obtained in organic solvents in which all the reactants and products are highly soluble. Others would not agree with this. Redox potentials have been obtained either by static, *i.e.* potentiometric, methods or by using cyclic voltammetric data, where E_1 is taken as the mean value between the oxidation (outward scan) and reduction (homeward scan) peaks. Other authors have used $E_{\frac{1}{2}}$ values from polarographic methods. In theory such approaches are only valid if the reaction is truly reversible, but in practice acceptable values for the redox potential can be obtained even when a reaction is somewhat less than fully reversible. Finally, where one of the components of an electrochemical equilibrium is a solid it would be expected that the free energy of formation of this species, and therefore the reversible potential, would depend on the morphology of the solid state. It will be seen that such differences have indeed been observed in respect of the heptyl viologen radical cation.

Ito and Kuwana[30] quote the potential of the first reduction for methyl viologen as −0.446 *vs.* NHE, citing the work of Elofsen and Edsberg,[33] Osa and Kuwana,[34] Michaelis and Hill,[1] and Volke.[2] They state that the value is pH-independent in the range pH 5—13, while Jasinski[21] states that though the Br$^-$ salt of the heptyl

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[27] S. Hunig, B. J. Garner, G. Ruider, and W. Schenk, *Liebigs Ann. Chem.*, 1973, 1036.
[28] S. Hunig, J. Gross, and W. Schenk, *Liebigs Ann. Chem.*, 1973, 324.
[29] S. Hunig and G. Sauer, *Liebigs Ann. Chem.*, 1971, **748**, 189.
[30] M. Ito and T. Kuwana, *J. Electroanal. Chem. Interfacial Electrochem.*, 1971, **32**, 415.
[31] T. Kawata and M. Yamamoto, *Jpn. J. Appl. Phys.*, 1975, **14**, 725.
[32] W. R. Boon, *Chem. Ind.*, 1965, 782.
[33] R. M. Elofson and R. L. Edsberg, *Can. J. Chem.*, 1957, **35**, 646.
[34] T. Osa and T. Kuwana, *J. Electroanal. Chem. Interfacial Electrochem.*, 1969, **22**, 389.

homologue is pH-independent the phosphate potential does depend on pH. Bard[4] quotes authorities to suggest that there is slight pH dependence for the second reduction of methyl viologen, but no dependence for the first stage. Kuwana's quoted value is the mean of the four workers they cite, ± 0.005 V. The second reduction potential is given as −0.88 V.

In Table 2 are listed published values for a range of viologens, such values being dependent on solvent, substituent radical, and anion as well as temperature.

A correlation with Hammett values was first attempted in 1970[35] and showed a close fit between these and $E_{\frac{1}{2}}$ (or E_{rev}) values. More recently the exercise was repeated by Hunig[36] using his own data for viologens in acetonitrile. It is noteworthy that even though the aqueous data are not 'reversible' in the polarographic sense the E_{rev} values are real and reproducible, unlike many others found in organic electrochemistry. Thus the values may be used with Hammett functions in that they do represent genuine thermodynamic measurements.

Table 2 *Published reversible potentials in aqueous media*

Compound	*Anion*	E_1	E_2	d*E*/dpH	*Ref.*
Methyl	Cl^-[c]	−0.446[a]	−0.88	–	30
Methyl	Cl^-[c]	−0.446[a]	–	0	1
Methyl	$MeSO_4^-$	−0.36[a]	−0.70	0	24
Ethyl	Cl^-[c]	−0.449[a]	–	0	1
Propyl	Br^-	−0.690[b]	−0.965	–	31
Hexyl	Br^-	−0.710[b]	−0.930	–	31
Heptyl	Br^-	−0.600[b]	−0.800	–	31
Octyl	Br^-	−0.705[b]	−0.945	–	31
Benzyl	Cl^-[c]	−0.359[a]	–	0	1
Benzyl	Cl^-	−0.350[a]	–	–	32
Benzyl	Br^-	−0.570[b]	−0.790	–	31
Benzyl	Cl^-	−0.573[b]	−0.790	–	31
Benzyl	I^-	−0.568[b]	−0.775	–	31
Betaine	Cl^-[c]	−0.444[a]	–	0	1
n-Propyl	I^-	−0.438[a]	–	–	32
n-Hexyl	Br^-	−0.439[a]	–	–	32
Ethoxycarbonyl-methyl	Cl^-	−0.422[a]	–	–	32
2-Hydroxyethyl	Br^-	−0.408[a]	–	–	32
2-Ethoxyethyl	I^-	−0.386[a]	–	–	32
2-Carboxyethyl	Cl^-	−0.431[a]	–	–	32
2,2′-Dicyano-1,1′-dimethyl	$MeSO_4^-$	+0.09[a]	–	0	23 (suggest other values avail to −0.7 V)

[a] *vs.* NHE. [b] *vs.* SCE. [c] In phosphate buffers.

[35] B. G. White, *Proc. Br. Weed Control Conf.* (10*th*), 1970, 997.

[36] S. Hunig and W. Schenk, *Liebigs Ann. Chem.*, 1979, 1523.

For the n-heptyl viologen Jasinski[21] quotes Table 3 for first and second reduction potentials, showing the effect of both anion and electrode material. The least negative number relates to the first reduction, the more negative number to the full reduction. (E_{rev} from the hydrogen evolution reaction at pH 5.5 was found to be -520 mV with the same reference.)

Table 3 *First and second reduction potentials for the n-heptyl viologen*

	Potentials (mV vs. *Perma Probe*) ($+520$ mV vs. H_2/H^+ *at* pH 5.5[21])					
Anion	Au		Pt		Ag	
Br^- (0.3M)	-420	-730	-430	(< -600)	-430	-700
$H_2PO_4^-$ (2M)	-390	-770	-390	(< -600)	-390	–
Formate (0.4M)	-570	-650			-550	-670
HCO_3^- (1M)	-490	-680			-500	-670
Acetate (0.5M)	-550	-650				
F^- (1M)*	-540	-600	-590		-530	
	no colour					
SO_4^{2-} (0.3M)	-540	-650	-570*	-620*	-520	-640
	no colour					

*Millimolar viologen.

Unfortunately we must resist the temptation to seek a correlation of the data in Tables 2 and 3. The variation of conditions is wide, and the available information is insufficient to correct for these differences. It is notable in this respect that the buffer or supporting electrolyte used is rarely quoted. In view of the fact that there can be no indifferent electrolyte with the viologen system, this is a serious omission. There is an obvious need for a systematic approach to correlating reversible potential data over as wide a range of viologens as possible, and such an approach was in fact made by White and co-workers over ten years ago. These results are reported below for the first time.

C. Further Data on the Effects of Substituent Variation on Potentials.—At ICI's Jealott's Hill Laboratories (Plant Protection Ltd.) Dr. B. G. White and colleagues have over the years studied some 400 compounds of the 4,4′-bipyridinium type with a view to examination of their herbicidal activity. A part of this effort was devoted to polarographic studies on these compounds. The majority of these results have never previously been published, and the authors are extremely grateful to Dr. White and ICI Ltd. for permission to do so.

The compounds tested fell into the following categories:

(i) asymmetric quaternaries in which one substituent was always the methyl group,

(ii) symmetric quaternaries,

Table 4 *Asymmetric quaternaries*

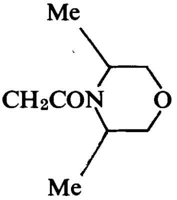
R^1	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
$\rightarrow O$	−490	$CH_3SO_4^-$	6.8
Me	−443	Cl^-	6.8
$CH_2CH=CH_2$	−426	I^-	6.8
CH_2CH_2OH	−422	Cl^-	6.8
CH_2Ph	−408	Br^-	6.8
$CH_2CH=CHCO_2Me$	−381	I^-	6.8
CH_2COMe	−380	I^-	1.5
	−374	Cl^-	6.8
CH_2CONH_2	−371	I^-	6.8
	−371	I^-	6.8
$CH_2CH=CHCN$	−369	Br^-	6.8
CH_2CO_2Et	−362	I^-	6.8
$CH_2CSNHPh$	−357	I^-	6.8
$CH=C(SMe)_2$	−330	I^-	6.8
CH_2CN	−287	Cl^-	6.8
$CH(CN)CO_2Et$	−287	I^-	1.5

Table 5 *Symmetric quaternaries* (*R*, *R*)

R^1	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
OMe	−651	I^-	6.8
NH_2	complex behaviour	I^-	varied
H	−485	Cl^-	1.5
Ph	−288	Cl^-	6.8

(iii) symmetric quaternaries where the substituent was —CH_2R^1,

(iv) symmetric quaternaries where the substituent was —$(CH_2)_2R^1$,

(v) symmetric quaternaries of type —$(CH_2)_3R^1$, and

(vi) miscellaneous compounds.

Results obtained are given in Tables 4—12. Tables 10—12 show a more recent series of measurements completed by White and his co-workers. These tables also show σ^* values and compare observed with calculated $E_{\frac{1}{2}}$ values.

Table 6 *Symmetric compounds of type* [$R^1(CH_2)$, —$(CH_2)R^1$]

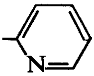
R^Q	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
Me	−443	Cl^-	6.8
CH_2COO^-	−410	Cl^-	5.0
CH_2Ph	−340	Br^-	6.8
CH_2- 	−325	Cl^-	6.8
CH_2SEt	−308	Cl^-	6.8
CH_2COMe	−305	Br^-	1.5
CH_2CONMe_2	−302	Cl^-	6.8
CH_2CONH_2	−296	Cl^-	6.8
CH_2COOEt	−267	Br^-	6.8
$CH(Ph)COOEt$	−188	Br^-	6.8
CH_2CN	−150	I^-	6.8
$CH(Ph)CN$	− 73	Br^-	1.5, 7.0

Table 7 *Symmetric compounds of type* [$R^1(CH_2)_2$, —$(CH_2)_2R^1$]

R^Q	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
CH_2CH_2OH	−399	Cl^-	6.8
$CH_2CH_2CONMe_2$	−385	Cl^-	6.8
CH_2CH_2OEt	−386	I^-	6.8
CH_2CH_2COOEt	−376	Br^-	6.8
$CH_2CH(OEt)_2$	−373	Cl^-	6.8
CH_2CH_2Cl	−335	Cl^-	6.8
$CH_2CH_2\overset{+}{N}Me_3$	−280	Br^-	6.8

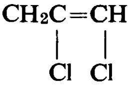
Experimentally, quaternary salts were usually 10^{-3} mol dm^{-3}, but occasionally this was reduced to avoid absorption peaks. Solutions were buffered at 6.8, but for systems with strong electron-attracting groups more acidic solutions were used to prevent interaction with the solvent and betaine formation. Buffer solutions were either phosphate 10^{-2} mol dm^{-3}, KCl 10^{-1} mol dm^{-3}, 1:1 water–methanol with borax buffer (pH = 9.8) 4.2×10^{-2} mol dm^{-3}, or KCl–NaOH 5.1×10^{-2} mol dm^{-3}, with added polyethyleneglycol-100 at 0.01% as a suppressor. White and co-workers fully recognized these effects, which are described by us elsewhere in the text. However, they normally operated in a region where the half-wave potentials were concentration independent.

It was recognized by these authors[3] long before others who published subsequently that a body of data such as the above could be used to determine σ^* values that would otherwise be extremely difficult to obtain. They also found that under all conditions used by them the E data did conform to the

Table 8 *Symmetrical quaternaries of type* [$R^1(CH_2)_3$, —$(CH_2)_3R^1$]

R^Q	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
$(CH_2)_3COOEt$	−433	Br^-	6.8
$(CH_2)_3CONMe_2$	−399	Cl^-	6.8
$(CH_2)_3CN$	−362	Cl^-	6.8
$(CH_2)_3N^+Me_3$	−331	Br^-	6.8

Table 9 *Miscellaneous quaternaries*

R^Q	$E_{\frac{1}{2}}$/mV (*NHE*)	*Anion*	*pH*
$(CH_2)_4\overset{+}{N}Me_3$	−367*	Br^-	8.0—10.0
$CH_2CH{=}N{-}OH$	−325	Br^-	6.8
 $CH_2\underset{Cl}{C}{=}\underset{Cl}{C}H$	−266	Cl^-	6.8

*Value obtained potentiometrically.

linear free-energy relationship. The equation $E_{\frac{1}{2}}(1) = 0.241(\sigma^*) - 0.443$ (*vs.* NHE) held. They obtained the further relationship $E_{\frac{1}{2}}(2) = 0.6[E_{\frac{1}{2}}(1) + 0.1]$, as did Hunig,[36] and concluded this phase of their work with calculations of the semiquinone formation constants from the relationship $E_{\frac{1}{2}}(1) - E_{\frac{1}{2}}(2) = 0.059\log K$. They were able to test all this by comparing predicted and actual $E_{\frac{1}{2}}$ values, using literature σ^* values for the former purpose; to within 1—5 mV agreement was good.

D. pH Dependence.—From the stoicheiometry of the redox equations it would appear that the reversible potentials should be pH-independent, and this is indeed found in almost all cases where the test has been made. However, Jasinski[21] states that the di-n-heptyl viologen phosphate system does show pH dependence. The trends were in agreement with the mechanism of Van Dam and Ponjee discussed below, based on the sole involvement of the monophosphate anion in controlling the concentration of $V^{+\cdot}$. This is perhaps less surprising when one considers that phosphate buffers contain more than one anion, in an equilibrium which itself determines the pH. Fitting the potentials of ten viologen dihydrogen phosphate solutions (pH 5.5—7.5), Jasinski obtained Nernstian behaviour with an E_0 − 0.147 *vs.* NHE ± 6 mV (the value of $pK_{1,2}$ for the $H_2PO_4^-$–HPO_4^{2-} equilibrium was taken as 6.71). The potential of E_0^2 was −0.540 to −0.690 *vs.* NHE, independent of pH, viologen concentration, and total phosphate concentration.

E. Anion Dependence.—Van Dam and Ponjee[16] have made a study of the effect of anion concentration on half-wave potential and the reversible potential of the

Table 10 *Asymmetric compounds of type* [R—(CH_2), —(CH_2)R′] (*aqueous*)

X	Y	σ^* X	σ^* Y	$\Sigma\sigma^*$	$-E_{\frac{1}{2}}$ (1) mV vs. *NHE*	$-E_{\frac{1}{2}}$ (2) mV vs. *NHE*	$-E_{\frac{1}{2}}$ (1) mV vs. *NHE* *calculated*
Et	$CH_2CH{=}CH_2$	−0.100	+0.233	0.133	428	733	427
$(CH_2)_2OH$	C_5H_{11}	+0.197	−0.145	0.042	438	758	438
$CH_2CH{=}CH_2$	$(CH_2)_3CN$	+0.233	+0.165	0.398	383	678	395
n-Pr	$(CH_2)_2CO_2Me$	−0.115	+0.255	0.140	408	743	416
$(CH_2)_3F$	$CH_2CH{=}CHMe$	+0.141	+0.130	0.271	418	663	410
$CH_2CH{=}CH_2$	$(CH_2)_2CONEt_2$	+0.233	+0.240	0.473	383	691	386
Et	$(CH_2)_2SEt$	−0.100	+0.200	0.100	428	688	431
$(CH_2)_3CN$	$(CH_2)_2CH{=}CH_2$	+0.165	+0.083	0.248	394	677	413
$CH_2{—}\underset{\substack{\vert \\ Me}}{C}{=}CH_2$	CH_2CONH_2	?	+0.600	0.820[a]	336	652	–
$CH_2CH{=}CH_2$	CH_2COO^-	+0.233	?	0.370[a]	390	755	–
$CH_2{—}\underset{\substack{\vert \\ Et}}{C}{=}CH_2$	$(CH_2)_2OMe$	?	+0.185	0.325[a]	396	671	–
$CH_2CH{=}\underset{\substack{\vert \\ Cl}}{C}Me$	$(CH_2)_2OMe$	?	+0.185	0.350[a]	393	658	–

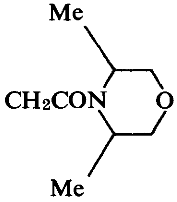
[a] Values derived from the plot of $E_{\frac{1}{2}}(1)$ *vs.* $\Sigma\sigma^*$.

Table 11 *Second asymmetric series (as before but in water–methanol mixtures)*

X	Y	$-E_{\frac{1}{2}}$ (1) mV vs. *NHE*	$-E_{\frac{1}{2}}$ (2)
Me	Me	361	780
Et	$CH_2CH{=}CH_2$	333	668, 808
$(CH_2)_2OH$	n-C_5H_{11}	–	–
$CH_2CH{=}CH_2$	$(CH_2)_3CN$	286	697
n-Pr	$(CH_2)_2CO_2Me$	–	–
$(CH_2)_3F$	$CH_2CH{=}CHMe$	320	718
$CH_2CH{=}CH_2$	$(CH_2)_2CONEt_2$	293	718
Et	$(CH_2)_2SEt$	325	718
$(CH_2)_3CN$	$(CN_2)_2CH{=}CH_2$	298	710
$CH_2C(Me){=}CH_2$	CH_2CONH_2	257	678
$CH_2CH{=}CH_2$	$CH_2CO_2^-$	328[a]	758
$CH_2C(Et){=}CH_2$	$(CH_2)_2OMe$	293	723
$CH_2CH{=}C(Cl)Me$	$(CH_2)_2OMe$	–	–

[a] Almost certainly this compound is displaced through differential ionization

Table 12 *Symmetric types* (R—CH_2, CH_2—R) (*aqueous, buffered*)

	$-E_{\frac{1}{2}}$ (1) mV vs. *NHE*	$-E_{\frac{1}{2}}$ (2)
Me	443	793
$(CH_2)_2OH$	399	749
CH_2CO_2Et	270	564
$(CH_2)_2NH_2$	280	556
$(CH_2)_2Cl$	335	605
$CH_2CO_2^-$	410	764
CH_2CN	150	408
$CH(CN)Ph$	73	218
$CH_2CH{=}CH_2$	408	689
CH_2CONH_2	295	628
$CH_2CH{=}NOH$	325	629
	305	670
$CH_2C{\equiv}CH$	435	850
Et	451	848
$C_6H_4(NO_2\text{-}p)$	70	240
n-C_7H_{15}	415	695

n-heptyl compound. A plot of half-wave potential *versus* log anion concentration is linear over some three decades of concentration, for both the first and the second reduction step, while a similar plot for the e.m.f. of the Pt|viologen solution|AgCl|Ag cell is likewise linear for chloride and bromide salts of the n-heptyl viologen.

Van Dam and Ponjee analyse their results in terms of the Nernst equation, writing $L = [V^{+\cdot}]\,[X^-]$, where L is the solubility product, X^- the anion in question,

$$E(1) = E_0(1) + 0.059\log\frac{[V^{2+}]\,[X^-]}{L} \quad \text{first step}$$

$$E(2) = E_0(2) + 0.059\log\frac{L}{[X^-]\,[V^0]} \quad \text{second step}$$

but rightly pointing out that half-wave potentials are not to be equated with reversible potentials. Using these equations they find L values of 8.5×10^{-6} for heptyl viologen chloride and 3.9×10^{-7} for the corresponding bromide.

F. Non-aqueous Media.—There are numerous reports of $E_{\frac{1}{2}}$ for various viologens in non-aqueous media. The major collation of values in acetonitrile is due to Hunig and Schenk,[36] who list E_1 and E_2 values for some 17 4,4′-bipyridyls as well as a further eight that are only stable in the reduced form. They then plot the first and second reduction potentials against σ or σ^* values, obtaining an excellent straight-line plot in each case.

They also show – as the former fact implies – that a straight-line relationship is given between E_1 and E_2.

With this range of substituents one might suppose that Hunig has virtually exhausted this area. Surprisingly, the collation of eight compounds reported by Van Dam and Ponjee[16] reproduced in Table 13 contains only one substituent – ethyl – in common with those studied by Hunig and Schenk, although their compounds are all long-chain aliphatics. It must be stated that the reported values for ethyl viologen, both apparently measured *versus* AgCl|Ag, do not appear to agree at all well.

Table 13 *Half-wave potentials for viologen tetrafluoroborates in acetonitrile*[16]

R	$-E_{\frac{1}{2}}$/V *1st. reduction step* vs. Ag|AgCl	$-E_{\frac{1}{2}}$/V *2nd. reduction step* vs. Ag|AgCl
Ethyl	0.48	0.89
n-Propyl	0.47	0.90
Allyl	0.44	0.85
n-Butyl	0.45	0.98
n-Amyl	0.46	0.89
iso-Amyl	0.46	0.90
Hexyl	0.49	0.93
Heptyl	0.41	0.88

Shelepin and Ushakov[7] quote half-wave potentials for methyl viologen in DMF with $NaClO_4$ or TEAP as supporting electrolyte, and certain other data are also quoted for these systems, such as E_{peak}. Hunig[37] quotes polarographic data for the same compound also in DMF.

G. Calorimetric Data.—Gundry[38] gives the standard free enthalpy of the 1,1′-dimethyl cation as 183.2 kJ mol^{-1}, and other thermodynamic information for the same species is also quoted.

4 Kinetics of Reduction

The cathodic reduction of the viologens has been studied both by classical dropping mercury electrode polarography and also by other methods of electrode kinetic study. As is so often the case it is unfortunate that very little tie-in between the two bodies of work can be made. In both cases we must differentiate between work done in dilute (*ca.* 10^{-3} mol dm^{-3}) solutions and that done in much stronger (*ca.* 1 mol dm^{-3}) supporting electrolytes.

A. Solid-electrode Kinetic Studies.—Results have been reported using Ag, Pt, Au, and SnO_2 or In_2O_3 electrodes, both stationary and, in one or two cases, rotating.

Where the cation radical is completely soluble the kinetics are straightforward and usually diffusion controlled since almost all workers appear to have used millimolar solutions. An exception is Leest[39] who shows an exponentially shaped current–voltage curve for 0.01 mol dm^{-3} viologen. Cyclic voltammetry and polarography on the dropping mercury electrode both show traces in which not less than two peaks (first and second reductions) are seen and frequently others too, which have been explained in terms of adsorption. These will be discussed in the section on 'Polarography' (Section 4D). The mechanism becomes more complex when the cation radical is a solid, the solubility of which is controlled, as we have seen, by the nature of the substituents in the 1,1′-positions and also by the anions used. Here it is mainly the electrochromic display oriented studies that are relevant, since the need for a solid deposit forms the basis of most of such devices.

B. Cyclic Voltammetric Studies.—This technique has been the most widely used in the study of the viologens, predominantly in work on the heptyl homologue for electrochromic display purposes. Analysis of data can be subdivided as follows:

(i) qualitative inspection of scans, and effect of scan rates and scan limits,

(ii) quantitative measurements, *e.g.* testing i_p as a function of scan rate, and comparison of Q_a and Q_c,

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[37] S. Hunig and J. Gross, *Tetrahedron Lett.*, 1968, **21**, 2599.
[38] H. A. Gundry, D. Harrop, and A. J. Head, *J. Chem. Thermodyn.*, 1978, **10**, 203.
[39] R. E. Leest, *J. Electroanal. Chem. Interfacial Electrochem.*, 1973, **43**, 251.

(iii) association of cyclic voltammetric data with another technique.

Bruinink[18] shows cyclic voltammograms on tin dioxide electrodes as a function of sweep speed and sweep limits. With a fast scan (100 mV sec^{-1}) up to four peaks are seen on the anodic sweep, three (including a shoulder) on the cathodic. The authors suggest that the peak due to V^0 formation is not seen on the anodic side at slow scan rate because of the conproportionation reaction, but nevertheless there are more peaks than the simple stoicheiometry of the reaction will account for, and the authors suggest that oxidation of charge-transfer complexes between V^0 and $V^{+\cdot}$ might explain these. Interesting results are also obtained by arrest of the scan in the cathodic region for 1 min. The subsequent anodic peak is displaced to a more anodic potential in the case of 'unstable' species such as the heptyl viologen cation radical bromide, and the authors ascribe this to oxidation of 're-oriented' parts of the cation radical film, which can also, it is stated, be seen microscopically.

Turning now to the $Q_a{:}Q_c$ ratios, Bruinink and Kregting find that this ratio is unity so long as the cathodic limit is not too extreme. When it is, that ratio drops. The critical cathodic potential depends on the viologen used and is less cathodic for the 'unstable' heptyl viologen bromide. It is accepted that these findings contradict those of Belinko[40] who explored the effect of progressively more extreme cathodic excursions and plotted the results as $Q_a{:}Q_c$. He also shows relative transmission on an optically transparent electrode (OTE) as it is associated with these potential sweeps. As the cathodic limit is increased beyond *ca.* -1.0 V *vs.* SCE the transmission, which drops as the cation radical is formed, fails to increase again as the scan returns to the anodic region, so indicating the breakdown of reversibility. One can offer explanations involving V^0, hydrogen evolution, $V^{+\cdot}$ dissolution, and impurities. A comprehensive explanation of $Q_a{:}Q_c$ ratios would however require consideration not only of the behaviour of the deposit but also of the erase mechanism itself.

Gavrilov and Ushakov[41] studied methyl viologen perchlorate and chloride in both water and DMF and mixtures of the two. The contrast between the solvents is interesting. In the organic solvent with perchlorate anion the system is reversible (defined in that the anodic and cathodic peaks in the cyclic voltammogram are only slightly displaced); much less so in water, with results in the mixed solvent having intermediate values. Open-circuit decay curves are plotted as E *vs.* log time. Whereas in aqueous media the potential is known to be steady until virtually all the surface film has been oxidized, this was decreasingly true as the proportion of DMF increased, and the authors explain this in terms of the Nernstian response of concentration with time. The authors explain the difference in reversibility in terms of the low solubility of the reduced form in aqueous media containing perchlorate. They describe the film as grey in colour, turning black with time. Shelepin[7] shows that $i_p \propto (\text{scan rate})^{\frac{1}{2}}$ for millimolar viologen solutions. He also compares scans in sulphuric acid with and without 6 mmol

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[40] K. Belinko, *Appl. Phys. Lett.*, 1976, **29**, 363.

[41] V. I. Gavrilov, O. A. Ushakov, and I. V. Shelepin, *Sov. Electrochem.* (*Engl. Transl.*), 1978, **14**, 958.

dm^{-3} methyl viologen and suggests that the latter is adsorbed because the hydrogen peaks are suppressed. However in the anodic region there is no sign of the V^{2+} oxidation propounded elsewhere.

The work of Ito and Kuwana[30] tells us little about mechanism, partly because a submillimolar methyl viologen (MV) solution is used, although the cyclic voltammograms and potential step (coupled with optical transmission recording) conform closely to theory for diffusion-controlled processes. However, they do quote a value for the rate of the conproportionation reaction $MV^{2+} + MV^0 = 2MV^{+\bullet}$, with $K_{eq} = 4 \times 10^7$ and $k_f = 3 \times 10^9$ (quoting Winograd and Kuwana[42]). Steckhan and Kuwana[43] continue the work in equally dilute solutions but with both benzyl and methyl viologens and quote $K_{eq}(MV) > 10^3$. Cyclic voltammograms on SnO_2 OTE are shown, and chronopotentiometric data are reported. They summarize their studies on methyl and benzyl viologens in Table 14.

Table 14 *Various parameters for methyl and benzyl viologens*

Parameter	*Methyl viologen*	*Benzyl viologen*
$\Delta E_{peak}/mV^a$	52	55
E^0/V^b	−0.449	−0.358
$D/cm^2\ sec^{-1c}$	0.86 ± 0.02	0.43 ± 0.02

[a]From cyclic voltammetry (0.033—16.5 V s^{-1}). [b]Formal potential *vs.* NHE; solutions are *ca.* 1 mmol dm^{-3} and all data are on tin oxide electrodes. [c]From chronopotentiometry, using i *vs.* $t^{\frac{1}{2}}$ plot slope ($\times 10^5$).

It is stated, although not precisely how, that all values are corrected for i_R drop. E^0 = formal potential *vs.* NHE and is obtained from the cyclic voltammogram at 0.85 of i_p (cathodic). The peak-separation data are obtained by plotting ΔE_p and $E_{0.85}$ *vs.* square root of scan rate and extrapolating to zero. The plots were linear over a 20-fold range. Ratios of i_p (anodic:cathodic) are stated to be unity except for benzyl viologen where i_p (c:a) = 0.76; i_p *vs.* (scan rate)$^{0.5}$ was linear over a wide range.

Chronoabsorptiometric experiments were also reported. In this paper the authors dwell on surface-adsorption phenomena. Analysis of A–t curves (absorption *vs.* time) shows three cases, namely the ideal case (benzyl viologen on SnO_2), adsorption of product (methyl viologen on In_2O_3), and adsorption of both reactant and product (benzyl viologen on Pt). Dication concentrations were 0.2 mmol dm^{-3}; raising this to 0.4 for the benzyl case caused cation-radical adsorption on SnO_2 to become evident. Differences in pzc values are invoked to explain the dependence on the nature of the electrode.

Vargalyuk[44] investigated the effect of electrode material on kinetics of heptyl viologen bromide reduction in DMF. D_0 was found to be 1.24×10^{-6} $cm^2\ sec^{-1}$

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[42] N. Winograd and T. Kuwana, *J. Am. Chem. Soc.*, 1970, **92**, 224.

[43] E. Steckhan and T. Kuwana, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 253.

[44] V. F. Vargalyuk, T. I. Starokozheva, Yu. M. Losharev, and E. A. Nechaev, *Sov. Electrochem.*, 1979, **15**, 108.

by chronoamperometric methods where $it^{0.5}$ was constant. The electrode material exerted a considerable effect, the reaction becoming irreversible with PbO_2 but quasi-reversible on Pt and vitreous carbon. Pre-treatment of PbO_2 with $BaCl_2$ led to a 6 × rate increase (explained in terms of ζ potentials and Br^- adsorption), and it is suggested that similar effects might occur on SnO_2.

Jasinski[21] uses chronopotentiometry as well as cyclic voltammetry to study heptyl viologen. The chronopotentiogram shows plateaux of unequal length on the anodic and cathodic sides, explained in terms of charge loss due to the conproportionation reaction. In his cyclic voltammetric data the charge recovery is explored under a variety of conditions. With phosphate electrolytes he found the cathodic charge recoverable. This was not so in bromide solutions.

The emphasis of Jasinski's paper is largely on side reactions and the occurrence of 'spotting'. Presumably this is another manifestation of the 'recrystallized' cation radical as discussed by Bruinink.[18] The anion, potential limits, and electrode material are all stated by Jasinski to affect this phenomenon, as they do also the question of adherence of the solid film to the electrode surface. Thus Au and Ag electrodes at pH 7.5 show a 'blue haze' instead of a coherent film, and this is explained in terms of micellization phenomena. Other products reported include a 'yellow oily film obtained by pulsing to +600 mV which could be wiped off though it was electrochemically inactive' (after anodic treatment) and (after pulsing on Pt to +1.2 V) a green-yellow material. These results are apparently with phosphate ion. With bromide ion the yellow tribromide salt is known to be formed.[45]

The most detailed cyclic voltammetric study is due to Bruinink and Kregting,[46] who compare the behaviour of the heptyl viologen with analogues based on metal deposition and other models and conclude that the deposition of the radical does indeed involve a nucleation process. At lower concentrations they, like Shelepin,[7] obtain a linear i_p *vs.* (scan rate)$^{\frac{1}{2}}$ plot up to 10^{-3} mol dm^{-3} and from this obtain a value for D of 7.4×10^{-6} cm^2 sec^{-1}. Their conclusion that the mechanism was indeed a nucleation process rather than solution precipitation is the starting point of an equally important paper by Barradas.[47] He shows how an overall sequence of charge transfer–nucleation–hemispherical diffusion–linear diffusion occurs and points out that loss of $V^{+\cdot}$ from electrode surface to solution is a significant process. This paper is also interesting because it is shown that 'Tafel slope' data can be obtained (using minute current densities) for the reduction of n-heptyl viologen, thus also electrochemical reaction order plots.

C. Potential-step Transients.—This well known technique is reported by Bruinink and Van Zanten.[48] After the initial double-layer charging, the log$i$–log$t$ plots show a plateau followed by a current decay, which gives a slope of $-\frac{1}{2}$ and

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[45] US Pat. 3912368.

[46] J. Bruinink and C. G. A. Kregting, *J. Electrochem. Soc.*, 1978, **125**, 1397.

[47] S. Fletcher, L. Duff, and R. G. Barradas, *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **100**, 759.

[48] J. Bruinink and P. Van Zanten, *J. Electrochem. Soc.*, 1977, **124**, 1232.

suggests diffusion control; the plateau suggests an initially reversible process. The greater the overvoltage, the shorter is the plateau, and it seems possible (though the authors do not attempt this) that Q_{plateau} might be constant in all cases shown by them. The work is done on SnO_2 with 10^{-2} mol dm^{-3} diheptyl viologen bromide, for which the diffusion coefficient is found to be 7×10^{-6} cm^2 s^{-1}.

The potentiostatic (or galvanostatic) step function is used in electrochromic displays. Kawata[13] has shown the 'write-time' (an arbitrarily defined absorption density) *versus* applied potential for heptyl viologen and a polymeric viologen. In a plot of optical density *versus* time a curious and large inflection is seen at one voltage. There is a linear relationship between log(write-time) and log(concentration) from 10^{-3}—10^{-1} mol dm^{-3} viologen. The 'erase' process is also considered, and erase-time is proportional to applied potential. Potential-step data are also given in reference 49, where step length and applied potential are plotted *versus* reflectance, the latter probably referring to $\lambda_{\max}$ (545 nm). This explains the assertion by the authors that 2 mC cm^{-2} can give a contrast ratio (CR) of 5:1, a higher value for this charge density than might be expected. It is also interesting to re-plot their data so that change of CR with time, at a series of potentials, is shown. The authors also quote data for Q (applied charge density) and reflectance R, simultaneously, over a complete cycle of write, hold, erase, *i.e.* cathodic pulse, open-circuit and anodic pulse.

D. Polarographic Studies.—Many of these studies are aimed simply at establishing a quantitative analytical technique. Only very few are mechanistically oriented. Hunig and Gross[37] explore the effect of structure on some twenty-three examples of Weitz-type salts, using polarographic techniques in DMF and acetonitrile. For methyl viologen the following data are quoted for E *vs.* AgCl|Ag reference [slope = $i/(i_{\text{lim.}} - i)$]:

(*a*) in water $E(1) = -0.640$ (slope = 60 mV),
$E_{\frac{1}{2}} \approx -0.680$ *vs.* SCE (from ref. 33)

(*b*) in DMF $E(1) = -0.38$ (slope 59 mV; semiquinone formation constant = 10^7),
$E(2) = -0.80$ (system reversibility good)

(*c*) in MeCN $E(1) = -0.40$ (slope 62 mV; semiquinone formation constant = 10^7),
$E(2) = -0.82$ (slope 61 mV; good reversibility).

In a further paper Hunig, Gross, and Schenk[28] use both a.c. and d.c. polarography to study the methyl viologen and several further related Weitz-type molecules. Using the 'K' value first introduced by Michaelis,[50] *i.e.* the formation constant for the semi-quinone, $V^0 + V^{2+} = 2V^{+\cdot}$, obtained from the equation $E_2 - E_1 = 0.059 \log K$ (at 25 °C), they show, using calculated models, that as K

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[49] C. J. Schoot, P. T. Bolwijn, H. T. Van Dam, R. A. Van Doorn, and J. J. Ponjee, *Appl. Phys. Lett.*, 1973, **23**, 64.

[50] L. Michaelis, *Chem. Rev.*, 1935, **16**, 243.

decreases in magnitude it becomes increasingly difficult to resolve polarographically. While a.c. polarography allows values as low as $K = 50$ to be resolved, the limit for the d.c. method is closer to 100 or 150. Half-wave potentials (saturated KCl in DMF) obtained by them are seen to be in good agreement with the literature, from which they quote Boon[32] and other authors.[51]

In aqueous media it is normally assumed that only the first reduction step is reversible, whereas in organic solvents both values are accessible, probably because the fully reduced compound is soluble in the medium.

The study of Kawata[31] has previously been considered and is mainly of interest in respect of the $E_{\frac{1}{2}}$ values quoted earlier. Pospisil and Volke[3] have studied the adsorption coupled kinetics of reduction of the 1,1′-dibenzyl viologen and the dimethyl analogue. Admittance data, differential capacitance values, and d.c. polarography all on the DME are reported, all at very low concentrations (*ca.* 10^{-4} mol dm^{-3}). Elsewhere[52] they report the interaction of dipyridinium ions with adsorbed halides. More recently two Russian papers along similar lines have appeared. Grachev and Zhdanov[53] show the considerable effect of the anion on the polarograms. Using both a.c. and d.c. polarography, they show that both the concentration of the anion and its nature can drastically alter the polarograms. They correlate the molecular weight of the anion with first, second, and third diffusion wave potentials. Grachev, Zhdanov, and Supin[54] earlier used both a.c. and d.c. methods to study in depth the *NN*-dimethyl-4,4′-bipyridinium bis-(*OO*-dimethyl phosphate). Leduc, Thevenot, and Buvet[55] present perhaps the most thorough polarographic study of benzyl viologen in the millimolar concentration range. They show a.c. and d.c. polarography on the DME, differential capacitance, and work on platinum and gold RDEs.

The d.c. polarogram shows five peaks at 0.5 mmol dm^{-3} buffered at pH = 9.8. These peaks correspond to five in-phase a.c. peaks and two out-of-phase peaks. Two additional a.c. peaks are also seen both in and out of phase and yet another out of phase. At lower benzyl viologen concentrations some of these disappear. Cyclic voltammetry on the DME shows two reversible steps and one irreversible. The effect of benzyl viologen concentration on the polarographic peak heights is reported fully. On this basis the peaks are assigned in terms of adsorption prewaves or diffusion-controlled peaks. It is noteworthy that on the RDE (where Au and Pt are stated to give the same results) the general pattern of results is said to be more complex and harder to interpret. Volke and Volkova have studied not only the bipyridinium ion (reference 56 and references quoted) but also the uncharged species itself.[57] Others papers of a purely analytical nature, either for

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[51] L. Michaelis, *J. Am. Chem. Soc.*, 1933, **55**, 1481; R. F. Homer and T. E. Tomlinson, *J. Chem. Soc.*, 1960, 2498; L. A. Summers, *Nature*, 1967, **214**, 381; R. F. Homer, T. E. Tomlinson, and G. C. Mees, *J. Sci. Food Agric.*, 1960, **11**, 309.

[52] L. Pospisil and J. Kuta, *J. Electroanal. Chem. Interfacial Electrochem.*, 1978, **90**, 231.

[53] V. N. Grachev and S. I. Zhdanov, *Sov. Electrochem.*, 1979, **15**, 1154.

[54] V. N. Grachev, S. I. Zhdanov, and G. S. Supin, *Sov. Electrochem.*, 1978, **14**, 1353.

[55] P. Leduc, D. Thevenot, and R. Buvet, *Bioelectrochem. Bioenerg.*, 1976, **3**, 491.

[56] J. Volke and V. Volkova, *Collect. Czech. Chem. Commun.*, 1969, **34**, 2037.

[57] J. Volke and V. Volkova, *Collect. Czech. Chem. Commun.*, 1972, **37**, 3686.

quantitative estimation of the 4,4′-bipyridinium salt or the simultaneous estimation of this and the 2,2′-compound, are given in references 58 and 59. Schwarz[60] has studied the polarographic behaviour of the diethyl viologen and interpreted the results, both reductive and oxidative, in terms of the monomer–dimer equilibrium. An interested observation relates to the way in which the blue cation radical is attracted to the Hg electrode, and as the latter (a pool) is withdrawn the blue colour follows it. Bearing in mind what is visible to the eye, this shows not only the adsorptive forces, metal–viologen, but also the solution association.

The two recent papers[53,54] by Grachev and co-workers on dropping mercury electrode polarography of the viologens, both d.c. and a.c., show the various diffusion- and adsorption-controlled peaks. The second of these is the more important in that it investigates the role of the anion. Suffice to say here that three different types of polarogram are found, differing in respect of the number of diffusion-controlled and adsorption-controlled waves, depending on the anions used. The authors relate this behaviour to the solubility of the cation-radical film, as has been discussed earlier in this review for solid-electrode studies, and plot half-wave potential *versus* molecular weight of anion, obtaining two straight lines, one for simple inorganic ions and the other for organic anions, mainly aromatic. The relationship so found recalls that of ionic radius reported by Van Dam and Ponjee.[16] Grachev *et al.* go on to suggest that ohmic resistance of the cation-radical film causes some of the observed phenomena, and they draw an analogy with anodic dissolution of Hg drops in halide media, where without doubt such a resistive film does occur. The resistivity of heptyl viologen films is a subject which occurs elsewhere in this review.

5 Reactions and Properties

A. Dimerization, Oligomerization, Micellization, and Clustering.—It has been shown, for any of the three oxidation states of the viologens, that association occurs, or that there are good grounds for expecting that it would do so.

Where the 1,1′-substituents are long-chain alkyl groups, the dication solution would be expected to show micellization at higher concentrations, as discussed, for example, by Fendler.[61] Unpublished work using a variety of the normal techniques has shown the existence of a c.m.c. for heptyl viologen.[61a] The electrolytic conductance of the heptyl viologen dibromides has been measured in water and methanol by Van Dam[62] but not up to sufficient concentrations to reveal the c.m.c. In water, up to the highest concentration quoted (93×10^{-4} equiv. l^{-1}), it

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[58] Yu. F. Balyabin and A. V. Kotova, *Zavod. Lab.*, 1967, **33**, 24.

[59] N. G. Sheremet and G. S. Supin, *Zh. Anal. Khim.*, 1973, **28**, 1422.

[60] W. Schwarz, Ph.D. Thesis, University of Wisconsin, 1961.

[61] J. H. Fendler and E. J. Fendler, 'Catalysis in Micellar and Macromolecular Systems', Academic Press, New York, 1975.

[61a] A. C. Lowe, personal communication.

[62] H. T. Van Dam, *J. Electrochem. Soc.*, 1976, **123**, 1181.

is reported that the dicationic species was the only form present. Measurement of D, the diffusion coefficient for the dication, provides one method for monitoring the onset of association. Table 15 gives data from Jasinski[63] and others. In addition, Jasinski plots a graph of D *vs.* concentration for phosphate and bromide over a concentration range from 0.1 mmol dm^{-3} to 0.1 mol dm^{-3}.

Table 15 *Diffusion coefficients for viologen solutions*

Molarity	*Anion*	$D(\times 10^6$ cm^2 s$^{-1})$	*Species*	*Ref.*
1 (pH 4)	$H_2PO_4^-$	0.2	heptyl	63
2 (pH 4)	$H_2PO_4^-$	1.4	heptyl	63
1 (pH 5)	$H_2PO_4^-$	0.15	heptyl	63
2 (pH 5)	$H_2PO_4^-$	0.2	heptyl	63
1 (pH 7)	Br^-	3.1	heptyl	63
10^{-3}	Br^-	7.4	heptyl	46
0 (inf. dilution)	$H_2PO_4^-$	6	heptyl	63
0.01 (0.1M-KBr)	Br^-		heptyl	64
water				
water (40%)		4.10		
+ DMF (60%)		2.91		
DMF		1.24		

Vargalyuk,[65] in common with many other authors, discusses association of the cation radical and also points out that the V^0 species should be considered a candidate for dimerization. His open-circuit decay studies are intended to support this hypothesis.

B. Association of the Cation Radical.—There is a great deal of evidence for some form of association of the cation radical. In their review on 'Cation Radicals' Bard, Ledwith, and Shine[4] point out that, as a class, one expects dimerization of these compounds. However, such dimers may be either monocation dimers or dication dimers, $M^{+\cdot} + M = M_2^{+\cdot}$ or $2M^{+\cdot} = M_2^{2+}$, although Vargalyuk rejects the second of these on grounds of electrostatic repulsion forces. Other authors have discussed ideas such as 'pi-dimerization'[5] or clustering.[66]

E.s.r. or u.v.–visible spectroscopy is the basis for most of the evidence for radical-cation dimerization or association. Thus Ivanov *et al.*[67] have shown that heptyl viologen radical cations dimerize and that such dimers do not give e.s.r. signals.

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[63] R. Jasinski, *J. Electrochem. Soc. (Accelerated Commun.)*, 1979, **126**, 167.

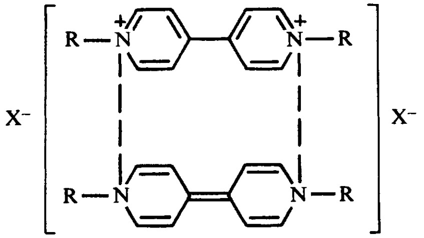
[64] V. F. Vargalyuk, T. I. Starokozheva, and Yu. M. Loshkarve, *Sov. Electrochem.*, 1979, **15**, 1337.

[65] V. F. Vargalyuk, T. I. Starokozheva, Yu. M. Loshkarev, and N. Yu. Savel'eva, *Sov. Electrochem.*, 1979, **15**, 200.

[66] M. J. Blandamer, J. A. Brivati, and M. C. R. Symons, *Trans. Faraday Soc.*, 1967, **63**, 1850; M. J. Blandamer and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1965, 629.

[67] V. F. Ivanov, A. D. Grishnia, and B.I. Shapiro, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1383.

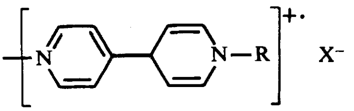
Mel'nikov, Novikov, and Khaskin[68] suggest a quinhydrone structure for the dimer. These 'dipyridyl violets' are known to exist in solution in equilibrium with cation radicals (2).



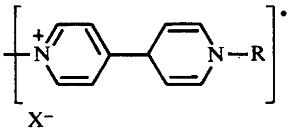
(2)

Van Dam and Ponjee[16] propose a sandwich-type ion-pair structure for the heptyl viologen cation-radical dimer. A rather different hypothesis is advanced by Vargalyuk, Starokozheva, and Loshkarev.[64] They suggest that cation-radical association with the anion takes place at the electrode surface and base their finding on a chronoamperometric study of the di-*N*-heptyl bromide at three different electrodes, Pt, vitreous carbon, and SnO_2, where they find very different chronoamperometric data.

Sato and Tamamura,[10] though their work deals ostensibly with viologen-based polymers, also report u.v., visible, and near-i.r. spectra of monomers. From these they draw the important conclusions that in the case of the monomeric viologen cation radicals there exists a strong intermolecular interaction and the 'deterioration' of films of such radicals is caused by this and can be depicted as a transformation from the ion-pair state (3) to the ion-bonding state (4).



(3)



(4)

Recently Furue and Nozakura[69] have obtained spectroscopic evidence that 1′,1″-trimethylenebis-(1-methyl-4,4′-bipyridinium) perchlorate can be photoreduced to form exclusively the intramolecular radical-cation dimer.

An interesting general conclusion running through these studies is that water promotes association far more than any other solvent.

Thus Kosower and Cotter,[70] drawing largely on the work of Schwarz,[60] show how a decrease in temperature can favour dimer formation. Spectral data from Schwarz's work clearly show formation of a new peak at 8700 Å and a shift in

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[68] N. N. Mel'nikov, E. G. Novikov, and B. I. Khaskin, 'Chemistry and Biological Activity of Bipyridyls and Their Derivatives', Gosimdat, Moscow, 1975, p. 35.

[69] M. Furue and S.-I. Nozakura, *Chem. Lett.*, 1980, 821.

[70] E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524.

both u.v. and visible regions to shorter wavelengths. They postulate the equilibrium $(V^{+\bullet})_2 \rightleftharpoons 2V^{+\bullet}$, with a dissociation constant of 2.6×10^{-3} at 1 mol dm^{-3} salt concentration. That the observed colour changes are seen only in water and not in acetonitrile is explained in terms of ion-pair formation in the organic solvent, precluding dimerization. Kosower also shows energy-level diagrams for all the species under discussion. He dismisses the idea that the dimer might be a complex of the oxidized and reduced forms of the cation radical. However, it is interesting to note that a solid complex consisting of two $MV^{+\bullet}$ and the dication (iodide as anion) has been isolated and analysed and is stable in dry air.[71] Dimerization has been studied by Evans and Evans[15] largely using e.s.r., who show the process to be favoured at low temperatures. Full thermodynamic data for a number of bipyridyls are quoted by these authors, and the equilibrium constant for the monomer$\leftrightarrow$dimer process gave good straight-line plots against $1/T$ for several of these compounds in methanolic solution. Two points emerge from this work. Firstly, a second undetermined but paramagnetic species is detected at low temperatures. Secondly, while dimerization is clearly only important at low temperatures in the methanol solutions used in this work, there is a strong argument to suggest that when an 'insoluble' cation-radical film is formed on an electrode the existence of this as a condensed phase would favour dimerization or higher-order aggregation. A similar study by Ivanov and Grishina[72] used methyl and heptyl viologens in a PVA matrix. U.v.–visible spectra show a hypsochromic shift, and e.s.r. measurements were used to determine the dimer concentration. Optical densities for the monomer and dimer are plotted, as are the dimer dissociation constants as a function of temperature. The removal of water is seen to favour dimerization, again an observation with apparent implications for electrochemically formed deposits. However, Gavrilov and Ushakov,[41] in contrast to other authors, suggest that methyl viologen can associate in aprotic solvents, such as DMF. In the same paper they use spectroscopic data to show that in concentrated solutions association is almost complete, and the spectrum resembles closely that of an evaporated methyl viologen film formed in vacuum. They also go on to suggest, quoting the work of Kosower and Cotter,[70] that dimerization may be a precursor to more extensive aggregation.

The dissociation constant of 2.6×10^{-3}, quoted above, corresponds to a ΔG of -14.7 kJ mol^{-1}. This value is consistent with those quoted by Evans[15] for various viologens: ΔG^0 ranges from -10.6 to -16.37 kJ mol^{-1}, the latter figure being the methyl viologen value.

When the dimerization – or higher-order aggregation – is accompanied by precipitation, further complications can ensue. Thus Bruinink[18] refers to the 'instability' of heptyl viologen bromide films and discusses this in terms of reorientation or recrystallization of the film. The point is illustrated by an open-circuit potential decay plot, showing a shift of some 35 mV in the reversible potential. This value, corresponding to -3.4 kJ mol^{-1}, is obviously indicative of

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[71] B. Emmert and H. Haffner, *Chem. Ber.*, 1924, **57**, 1792.

[72] V. F. Ivanov and A. D. Grishina, *Izv. Akad. Nauk SSR, Ser. Khim.*, 1977, **8**, 1873.

a more subtle process than the dimerization itself. The ΔG value is comparable with conformational free-energy changes.

C. Mechanistic Considerations.—It has been seen that the cation radical may either be soluble or form a film at the electrode surface, and this will be a function of the solvent, the alkyl substituent, and the anion. If the radical is soluble then the kinetics are simple and appear to be reversible. However, if a film is formed then the kinetics of both its formation and reoxidation are complex. It appears that its formation involves a nucleation-type process.

To date most mechanistic investigations have employed dilute solutions. In order to form a more complete picture of the processes operating, particularly when the cation radical undergoes deposition, a greater volume of data is required. These data must cover the concentration dependencies, particularly in view of the use of stronger solutions in display applications.

Once the film is formed one sees abundant evidence that changes take place, and this is presumably some form of aggregation. Colour and texture (both features of 'spotting') form part of this evidence. Potential changes at open circuit and changes in the reoxidation kinetics as shown by potential-step data afford other evidence. Whether one can explain all these effects in 'change-of-state' terms or whether one must invoke chemical explanations is unresolved. The longer the film is allowed to exist on the electrode surface the greater will be such effects. However, one must recall that dissolved oxygen can never be wholly absent from these systems, and, if present, there is evidence that it can react irreversibly with the cation radical.[73]

Jasinski[74] formulates a mechanism for the electrochemical process. The film is formed, either in one or two steps, from bulk solution. (Whether there is a first step being the formation of a soluble radical cation, followed by precipitation of the salt, is debatable.) The film so formed is non-porous since undercutting and peeling of the film are not found on anodic oxidation. Finally there appears to be an equilibrium between the radical cation in the film and the same species in bulk solution.

Jasinski returns in reference 63 to the growth processes of heptyl viologen dihydrogenphosphate films on gold electrodes. Some comparison measurements were made with viologen bromide. Looking at the time interval from 60 ms to 40 s after application of the potential sweep (during which time the film grew from 0.5 mC cm^{-2} to more than 40 mC cm^{-2}) his main findings were as follows. Firstly, i_{peak} *vs.* (sweep rate)$^{0.5}$ gave linear plots over a large range, that range being greatest in bromide, or in phosphate of pH 4, but somewhat more restricted in phosphate of pH 5. Jasinski calculates diffusion coefficients in a number of ways and finds that values obtained from cyclic voltammetry and chronocoulometry agree well. In a figure he shows how the value of D is the same for phosphate and bromide at low concentrations and how the value drifts slowly down with increasing concentration over the range 0.2 mmol dm^{-3} to 0.01 mol dm^{-3}. At

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[73] R. N. F. Thorneley, *Biochim. Biophys. Acta*, 1974, **333**, 487.

[74] R. J. Jasinski, *J. Electrochem. Soc.*, 1978, **125**, 1619.

this point, however, while the bromide continues the slow decrease phosphate plunges rapidly down, decreasing by a full order of magnitude in the concentration range 0.01—0.1 mol dm^{-3}. At infinite dilution $D = 6 \times 10^{-6}$ cm^2 s^{-1} for both anions. On the basis of the magnitude of D and its dependence on solution properties Jasinski argues that the diffusion control must be from solution and not diffusion in the film as it is formed. Plots of charge, Q, *vs.* $t^{0.5}$ are also linear, again supporting the diffusional process. However, the intersection at $Q = 0$ occurs at a finite time, varying from 10 to 120 ms.

In his conclusion Jasinski poses a key question. Since film growth is diffusion limited the film itself must be either electronically conducting or porous. In the latter case further deposition could only result from diffusion of the dications through the pores to the electrode surface, followed by diffusion out of the radical cation, presumably to nucleate onto the existing deposit. Furthermore, oxidation, too, would have to occur at the metal surface, so detaching the outer layers of radical cation from the electrode surface, and this has not been seen in practice. Jasinski therefore opts for the electronically conducting model and points out that charge flow through it need only be as fast as the inward diffusion of dications. From the spectrophotometric data of Schwarz[60] and Chang[75] he estimates film thickness as 90 Å mC^{-1} cm^2. A simple calculation reveals this thickness to be equivalent to a density of 5.0 g cm^{-3}, a value which seems surprisingly high. However, from this thickness and the measured diffusion coefficient he uses the Cottrell equation to obtain a resistivity of 10^4 Ω cm for the film grown in phosphate at pH 4 and the higher value of 10^5 in phosphate at pH 5.5. Cyclic voltammetric i–$v^{\frac{1}{2}}$ plots show a fall-off at the higher pH, which Jasinski attributes to higher ohmic resistance, but it must be noted that a film of the thickness reported should not produce a large ohmic drop. The film formed by reduction of the di-n-heptyl cation is stated[46] to have negligible resistances even at a charge density of 2 mC cm^{-2}. Nevertheless it appears to block further deposition of cations either from concentrated viologen solutions or when recovery time is allowed to replenish the diffusion layer.

Murano and Kamura[75a] have studied the electrical and spectroscopic properties of an evaporated methyl viologen film in vacuum. They obtained resistance values of 10^5—10^6 Ω for a thickness of 10^3—10^4 Å. Their deduction was that conductivity is electronic not ionic.

Barna[75b] has studied the open-circuit reorientation of deposited heptyl viologen films, finding that the film reorients to a phase with a higher degree of ordering and hence a greater optical anisotropy. The same birefringence measurements showed that higher deposition overpotentials resulted in a less ordered film and that the number of active sites available for film nucleation was potential dependent, thereby confirming previous arguments.[46,74]

D. Oxidation of the Cation Radical.—Once formed, the kinetics of the cation-

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[75] I. F. Chang, B. L. Gilbert, and T. I. Sun, *J. Electrochem. Soc.*, 1975, **122**, 955.
[75a] K. Murano and Y. Kamura, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2407.
[75b] G. G. Barna, *J. Electrochem. Soc.*, 1980, **127**, 1317.

radical reoxidation have been studied mostly with cyclic voltammetry. However, Jasinski[74] has applied a potential step to a previously formed film. His conclusions can be summarized: that, firstly, the greater the overvoltage the faster the reoxidation and, secondly, the more material on the electrode surface as a film the longer the oxidation requires. He also observes a definite 'tail' and suggests that this corresponds to the 0.03 mC cm^{-2} of charge associated with the monolayer immediately adjacent to the electrode surface, which is expected to behave differently. Finally he shows at some length that in the case of SnO_2 the history of the surface has a profound effect on these results, and washing or chemical pre-treatment are all examined. However, there are no indications here that similar effects would apply on metallic surfaces, assuming these were reasonably clean.

E. Reaction with Oxygen.—The viologen cation radical reacts rapidly with oxygen. The reaction has been proposed as a means for determination of oxygen dissolved in water in low concentrations. Sweetser[76] uses proflavine and EDTA to generate the $MV^{+\cdot}$ photochemically. Leest[39] generates the radical electrochemically. He formulates the overall reaction as

$$2MV^{+\cdot} + \tfrac{1}{2}O_2 = 2MV^{2+} + 2OH^-$$

which might be followed by de-alkylation (*q.v.*).

It is now recognized that the reaction is not quite so simple. It appears that in a fast first step oxygen is reduced to hydrogen peroxide or its ion, followed by a slower step in which the hydroxyl ion is formed with the O—O bond being broken. Workers who have used excess oxygen observe only the first of these two steps, by monitoring the rate of disappearance of the monocation radical. So we have the data of Farrington,[77] who quotes rate constants of 7.7 × 10^8 dm^3 mol^{-1} for the reaction of $PQ^{+\cdot}$ with O_2 and 6.5 × 10^8 dm^3 mol^{-1} for reaction with O_2^-, and Rauwel[78] quotes a rate 'in excess of 10^8 dm^3 mol^{-1} s^{-1}', citing Farrington in support of this.[79] Pulse-radiolysis techniques were used for the studies by Farrington, a ring-disc electrode by Rauwel.

White,[35] quoting unpublished work of Farrington, shows how the first step (reaction with molecular oxygen) has a pH-independent half-life of less than 1 microsecond, while the second step has a half-life from *ca.* 200 s at pH 4 to 0.2 s at pH 8. This analysis is supported and extended by the work of Thorneley,[73] who quotes data for rate constants of the second (slow) step over the pH range 7.5—9. The latter author, however, raises an interesting question that remains unanswered. There appears to be controversy as to whether the oxidation of the cation radical is reversible or not. On the one hand it is suggested that the oxidation by air is reversible in the sense that as much cation radical can be regained by re-reduction as was originally present. On the other hand there seems to be evidence from both Thorneley himself and other workers he cites that oxidation of the

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[76] P. B. Sweetser, *Anal. Chem.*, 1967, **39**, 979.
[77] J. A. Farrington, *Biochim. Biophys. Acta*, 1973, **314**, 372.
[78] F. Rauwel, *J. Electroanal. Chem. Interfacial Electrochem.*, 1977, **75**, 579.
[79] J. A. Farrington and M. Ebert, *Biochim. Biophys. Acta*, 1973, **314**, 372.

cation radical by dissolved H_2O_2 does lead to an irrecoverable loss of some 15% or so that cannot be re-reduced.

All the foregoing relates to homogeneous reactions. In the presence of an electrochemically active metal surface, such as Ag, there is every reason to think that a pair of coupled reactions can take place in which oxygen is reduced and the cation radical is oxidized.

F. Reaction with Molecular Hydrogen.—Molecular hydrogen can, when catalysed, react with viologens. Considering this as a pair of redox reactions, one of which has a pH-dependent value (H_2 oxidation) and the other of which is pH-independent (viologen reduction), a pH can be selected where the reaction $MV^{2+} + \frac{1}{2}H_2 \rightleftharpoons MV^{+} + H^{+\cdot}$ may go either forwards or backwards, and indeed whatever the bulk pH it will be seen that the reaction itself causes a pH change that will act locally.

This reaction was studied by Beresin *et al.*[80] using methyl viologen at pH 7.2—7.8 at a concentration of 4×10^{-4} mol dm^{-3} up to 4×10^{-3} mol dm^{-3} and using enzymes to catalyse it in both the forward and backward direction. A later study by Okura,[81] who does not cite Beresin, is very similar and uses near-u.v. light to form hydrogen by reduction of water with oxidation of the $MV^{+\cdot}$ previously formed. Interestingly colloidal Pt is also shown to act as a catalyst for this reaction.

Beresin obtains the expression (10) as an equilibrium constant for the reaction. Other work is quoted in reference 82.

$$K_p\,(H_2 = 1\text{ atm}) = \frac{[MV^{+\cdot}][H^+]}{[V^{2+}]} = 8 \pm 2 \times 10^{-9}\text{ mol dm}^{-3} \qquad (10)$$

G. Oxidation of the Viologen Dication.—Air oxidation of V^{2+} has been discussed by Shelepin and Ushakov.[7] Apart from the observation that the products can be detected by their green fluorescence in u.v. light, little more is known. According to them methyl viologen is stable in acid and neutral solution. The rate of oxidation depends on concentrations of dissolved oxygen, OH^- ions, and viologen. A 2 mmol dm^{-3} solution in 0.1 mol dm^{-3} alkali is stable in air for three days. Trebling the viologen concentration results in a yellow coloration in one day. Jasinski[74] states that de-aerated solutions which were stored in air "developed a pungent odour within a few days unless contained in 'actinic' glass". Shelepin's work does, however, suggest that the rate of anodic oxidation even on platinized platinum electrodes is extremely small.

The wavelength of the radiation used by Shelepin and Ushakov is not stated, but they describe how illumination of 1.5 mmol dm^{-3} MV^{2+}–0.13 mol dm^{-3} KH_2PO_4 (pH 4.7) gives the cation radical as well as oxidation products. Open-circuit potential measurements of a platinized Pt electrode again indicated that

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[80] I. V. Beresin, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 1975, **225**, 105.

[81] I. Okura and N. Kim-Thuan, *J. Mol. Catal.*, 1979, **6**, 449.

[82] J. Kiwi and M. Graetzel, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 624.

oxidation and reduction were occurring simultaneously. However, it is not quite clear whether air was present in these experiments.

The effect of light irradiation on viologens falls outside this review. It has been extensively documented by Calderbank,[83,84] and in considering this effect the presence or absence of air is crucial but not always clear in the primary literature. An interesting comment by Shelepin[85] is that the photo-oxidation of methyl viologen by air is increased by phosphate anions, but for an unknown reason. His paper reviews the degradation products of illumination, as do those of Calderbank[84] and Shchegoleva.[86]

H. Effect of the Substrate.—This section is of particular relevance to electrochromic displays. Previous references have been made to the effect of the substrate on the appearance of a heptyl viologen film[21] and to the effects that cleaning and pretreatment have on the behaviour of the deposited monocation. There are other references in the literature to substrate effects. For example in reference 26 Jasinski suggests that on Au, with F^- or SO_4^{2-}, pale yellow films are formed, presumably the fully reduced species (V^0). To what extent this observation reflects the colour of the metal itself is not certain. He also states that in the same fluoride solutions that gave the yellow films on Au the cation radical (presumably blue) was formed on Pt. Jasinski quotes Kosower,[70] Volke,[56] and Schwarz[60] in support of the idea that pre-adsorption of the radical cation or the dication might explain these effects. He also suggests that the substrate might affect the reversibility of the electrochemical oxidation-reduction in that on Pt the reduction to V^0 followed by its reoxidation to the dication could be repeatedly done without leaving a residue on the electrode surface, a reversibility not found on Ag or Au electrodes with the solutions used. On these metals polarization into the V^0 region altered the shape of the cyclic voltammograms and also gave rise to black discoloration of the purple film. It is hard to explain such differences, and certainly with other anions the effects reported by Jasinski are not seen. On the active noble metals such as Pt, where hydrogen evolution would be most favoured, one might expect the greatest resulting change in pH with the damaging consequences of alkalization. But of the other side reactions that can be envisaged it is hard to see how Au, a singularly inactive metal in the catalytic or electrocatalytic sense, might exert the effects suggested above.

6 Colour and Spectrum

A. Visual Appearance of Solid Films.—The solid cation film deposited on the cathode appears violet, and, at extreme thicknesses, black and can in this form be shiny and crystalline. However, more unusual departures from these norms have been reported. Jasinski[21] reports a red/violet film on Pt, using heptyl

[83] A. Calderbank, *Adv. Pest Control Res.*, 1968, **8**, 127.
[84] A. Calderbank and J. A. Farrington, *J. Chem. Soc., Perkin Trans.* 1, 1972, 138.
[85] I. V. Shelepin, V. A. Barachevskii, and N. I. Kunavin, *Zh. Fiz. Khim.*, 1975, **49**, 1731.
[86] I. S. Shchegoleva, *Khim. Vys. Energ.*, 1976, **10**, 398.

viologen fluoride, and also on Pt and Ag in sulphates. However, neither anion, he states, produced a coloured film on Au cathodes, although electrochemical data confirmed that reduction was taking place. Phosphate/formate anions do give the same colour on Au. Addition of F^- suppresses it. In addition it is suggested that the combination of an Ag cathode with F^- anion gives a less stable or more soluble film. Reduction of *NN'*-di(*p*-cyanophenyl)-4,4'-dipyridinium dichloride gives a green film (Brit. Pat. 1314049).

The second phenomenon that can be visually observed is 'spotting', the formation of small islands of a lighter colour and having a crystalline appearance. These have been reported by Bruinink[18] and other authors. When an attempt is made to reoxidize the cation radical back to the V^{2+} state these 'spots' are harder to oxidize, taking longer or requiring a more anodic potential to do so. Gavrilov again reports similar effects.[41]

Bruinink *et al.* have added further observations on this 'spotting'. It is reported to be sensitive to factors such as (*a*) the amount of V^0 formed during the reduction (*i.e.* cathodic limit), (*b*) electrode material, (*c*) electrolyte, (*d*) electrode texture, and (*e*) viologen structure. Thus the 1,1'-diheptyl viologen bromide showed spotting after 10 seconds or so, while a tetramethylene bis[4-(1-benzylpyridine-4'-yl)pyridinium] tetrafluoroborate showed similar effects only after several minutes; the perchlorate analogue is also stable.

As discussed in the preceding section on dimerization, the 'spotting' has been linked with changes in open-circuit potential, and Bruinink[18] shows how the onset of spotting in the less stable heptyl viologen bromide film is associated with an anodic potential shift of *ca.* 35 mV after 30 seconds, which is not shown by the more stable viologens such as those listed above. (There is also a much smaller and slower anodic shift seen in all cases, which is because of the restoration of the V^{2+} concentration at the interface after its depletion due to the reduction.)

Point (*b*) above was largely confirmed by Jasinski,[74] who showed that pretreatment of the electrode surface (mainly SnO_2) was critically important and that properly treated (degreased, *etc.*) surfaces showed much less charge loss after a minute or so at open circuit.

B. Colour and Spectrum of Monocation Radicals.—As has been seen, some of the monocation radicals are soluble in aqueous media while others form a precipitated film at the electrode surface. Almost all, whether dissolved or solid, are blue to reddish-purple in colour. The questions with which we may concern ourselves relate to the colour, the spectrum in the u.v.–visible region, and the extinction coefficient.

The literature has many examples of recorded spectra of the viologens. Michaelis[1] shows that of the methyl, ethyl, benzyl, and betaine viologen as well as the 4,4'-dipyridyl the first two are similar to one another. In the benzyl a secondary peak at 550 nm is more intense than the primary one at 600 nm. Van Dam and Ponjee show[16] transmission spectra of ethyl viologen chloride in water and that of the n-heptyl as the tetrafluoroborate in acetonitrile and as the bromide on SnO_2. There are many other examples in papers cited elsewhere in this review. A factor which besets the interpretation of all these spectra is the dimerization, which has been discussed elsewhere. Kosower and Cotter,[70] also quoting Schwarz,[60] show how dimerization can cause the appearance of a separate shoulder in the visible region of the spectrum. Kawata[31] has recorded similar observations. Warming and cooling the solution[70] also reveals the monomer–dimer transition, but only in water and not in acetonitrile. Thorneley[73] extends the point by showing that the apparent extinction coefficient of methyl viologen cation radical decreased as concentration increased (in the millimolar range). Though many other values of ϵ are quoted for methyl viologen, only he appears to have taken this factor into account, and this must cast doubt on the others. The same question of dimerization has been used by Kawata to explain colour changes of both methyl viologen (quoting the work of Kosower) and benzyl viologen.[31] This author studied benzyl viologen bromide in water and in methanolic solution, as well as the iodides and chlorides and the cation radical in glycerin.

Other spectra recorded in various solvents including water, acetonitrile, and ethanol are reported by Hunig[87] and Kosower and Cotter[70] as well as Guerin-Ouler[88] and Winograd and Kuwana[89,42].

Thanks to the data of Kawata[31] on the one hand and of Hunig and Schenk[36] on the other some order can be brought to the field. Kawata shows a relationship between peak wavelength and solution polarity, using propanol, methanol, and DMSO, which have dielectric constants from 20 to 45 to show that a wavelength shift occurs from 605 nm to 614 nm. Hunig, on the other hand, shows that peak wavelength may be correlated with $E_{\frac{1}{2}}$ and so with Hammett functions. All these data, both spectral and electrochemical, relate to acetonitrile as a solvent. As a result of the work of Hunig and also Kawata a measure of prediction can be brought to bear in respect of systems as yet unstudied.

In respect of cation radicals which form solid films there are again some data, all obtained using SnO_2. Kawata[31] reports that peaks are shifted to shorter wavelengths when solid films are formed. It is well known that the visible spectrum of organic dyes is a function of their aggregation state, and such observations are not therefore surprising.[90]

Viologen can be used as the basis of a copolymer, and the spectrum of this, both infrared and u.v.–visible, is reported by Simon and Moore[8] and more recently by Sato and Tamamura.[10] Gavrilov and Ushakov[41] use an In_2O_3 electrode to record spectra for methyl viologen with both Cl^- and ClO_4^- anions.

Malpas and Bard[91] have recently published a report on the use of a new technique, 'photoacoustic spectroscopy', to measure heptyl viologen bromide

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[87] S. Hunig and D. Scheutzow, *J. Chem. Phys.*, 1971, **75**, 335.

[88] D. Guerin-Ouler and C. Nicollin, *Can. J. Spectrosc.*, 1974, **19**, 69.

[89] N. Winograd and T. Kuwana, *J. Am. Chem. Soc.*, 1964, **86**, 5524; N. Winograd and T. Kuwana, *J. Electroanal. Chem. Interfacial Electrochem.*, 1969, **23**, 33.

[90] S. F. Mason in 'The Chemistry of Synthetic Dyes', ed. K. Venkataraman, Academic Press, 1970, Vol. 3.

[91] R. E. Malpas and A. J. Bard, *Anal. Chem.*, 1980, **52**, 109.

spectra on metal films. They state that their data agree with classical spectrophotometric measurements on SnO_2 quoted by Chang *et al.*[75]

C. Extinction Coefficients.—These have been quoted for methyl viologen by Beresin,[80] Bard,[4] Hunig,[27] Steckhan and Kuwana (benzyl and methyl),[43] Downes,[92] and Krumholtz.[93] Other authors are Winograd and Kuwana,[42] Schoot for the n-heptyl solid film,[49] Barclay,[94] and Eisenstein and Way.[95] However, the most impressive reference, precisely because values are quoted as a function of concentration and because errors in previous estimates are discussed, is due to Thorneley,[73] and his value for methyl viologen, extrapolated to zero concentration, is 1.3×10^4 at 600 nm.

However, Kawata[13] has plotted absorbance *versus* charge density. He obtains a straight line (absorbance = 0.8 for 5 mC cm^{-2} at 545 nm) for heptyl viologen with just over half this value for the polymeric viologen at 595 nm.

In respect of solid viologen films the whole concept of extinction coefficient is a hazy one, and it would seem that much depends on the state of aggregation of the solid and quite possibly, bearing in mind dimerization, the 'age' of the film. No careful measurements appear to have been reported here.

D. Other Spectroscopic Data.—E.s.r. data are reported by Shchegoleva,[86] Guerin-Ouler,[96,88] and Johnson and Gutowski[97] as well as Kosower[70] and Blandamer.[66] In many cases the data are used to support evidence of oligomerization (*q.v.*). Semi-empirical MO calculations of some viologens and their correlation with experimental spectra are reported by Hunig[87] and Guerin-Ouler.[96]

7 Newer Aspects

A. Viologen-modified Electrodes.—Hawkridge and co-workers[98,99] have published papers in which a gold or platinum electrode is subjected to an extended cathodic step in viologen solution. As a result of this, it is claimed, a modified form of viologen, possibly akin to the polymers reported by Simon and Moore,[8] is formed at the electrode surface. They also claim that this polymeric form of the viologen is stable in air for some days but at the same time is electro-active in that it can act as a mediator. In the latter role it can heterogeneously reduce spinach ferrodoxin many times faster than an untreated gold electrode does in the classical electrochemical mode. The authors recognize the three oxidation states of viologens but maintain that once a given potential (*e.g.* −0.950) has been exceeded on the cathodic side the subsequent regeneration of the higher oxidation

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[92] J. E. Downes, *J. Chem. Soc. (C)*, 1967, 1491.
[93] P. Krumholtz, *J. Am. Chem. Soc.*, 1951, **73**, 3487.
[94] D. J. Barclay, C. L. Bird, D. H. Martin, *J. Electron. Mater.*, 1979, **8**, 311.
[95] K. K. Eisenstein and J. Way, *J. Biol. Chem.*, 1969, **244**, 1720.
[96] D. Guerin-Ouler and C. Nicollin, *Mol. Phys.*, 1977, **34**, 161.
[97] C. S. Johnson and H. S. Gutowski, *J. Chem. Phys.*, 1963, **39**, 58.
[98] H. L. Landrum, R. T. Salmon, and F. M. Hawkridge, *J. Am. Chem. Soc.*, 1977, **99**, 3154.
[99] J. F. Stargardt, F. M. Hawkridge, and H. L. Landrum, *Anal. Chem.*, 1978, **50**, 930.

states is no longer possible, or at least not readily so. SEM studies reveal an amorphous deposit on the gold electrodes. It is pointed out that a similar product could not be reproduced on an Hg electrode – a very different, brown species was formed which rapidly turned blue in air. Another remarkable feature of these deposits is their ability to store 'reducing power' even in air. Thus after such exposure they are still capable of reducing the methyl viologen dication to produce a blue colour in solution. This inertness to air is in very striking contrast to the reactivity of the cation radical to oxygen, discussed elsewhere. In their second paper[99] benzyl and methyl viologens were compared in this role. They behaved very differently and gave different deposits on electrodes as shown by the SEM. However, the earlier behaviour was confirmed.

A viologen-modified electrode – but in a very different sense – is also described by Cieslinski and Armstrong.[100] It is now well known that all manner of molecules can be bonded to glass surfaces (and others) by silyl linkages. These authors so bonded heptyl viologens onto a SnO_2 or indium–tin oxide optically transparent electrode (OTE) and showed the cyclic voltammograms and also spectral intensity at fixed wavelength during reduction and reoxidation. Little difference is seen in the case of the cyclic voltammetric data. However, there are clear indications that silylated surfaces show greater intensity of absorption, and react faster, than their untreated analogues. The converse is also true in that reoxidation appears to be slower.

B. Technological and other Applications of Viologen Electrochemistry.—It was indicated at the beginning of this review that the electrochemical behaviour of the viologens had been found useful in a wide range of practical applications. The relationship between electrochemical and herbicidal properties has been noted, as has the use of the viologens for estimation of dissolved oxygen.[78] Still in the realm of analytical chemistry, their use as redox indicators was recognized very early on by Michaelis and Hill.[1]

There is a growing emphasis on physico-chemical studies of biological systems. It is frequently found that a given compound cannot be directly reduced electrochemically, although application of electrochemical techniques, with their many advantages, would be highly desirable. In such a situation the use of a 'mediating compound' has become widespread, and the viologens, with their ready reversibility, are among the most widely used mediators. The mediating compound is reduced electrochemically, and then chemically reduces the compound to be studied. Because the process is 100% efficient, one can thus use the idea to apply coulometric analyses or spectroelectrochemical methods. The method is now so widely used that one can only quote a few examples. Fielden and Summers list many of these,[23] and the work of Hawkridge[98,99] applied to spinach ferrodoxin or sperm-whale myoglobin has been quoted earlier. Stombaugh[101] studies proteins in this way, while Beresin[80] has also used methyl viologen as a mediator in the oxidation of hydrogen *via* enzyme catalysis.

[100] R. C. Cieslinski and N. R. Armstrong, *J. Electrochem. Soc.*, 1980, **127**, 2605.
[101] N. A. Stombaugh, *Biochemistry*, 1976, **15**, 2633.

Rauwel[78] has studied cytochrome *c*, as have Mackey and Kuwana, who also studied cytochrome oxidase.[102] Anderson[103] used pulse radiolysis to study electron-transfer rates between various heterocyclic compounds including viologen and biologically important species.

The reversibility of viologens has led to their consideration as candidates for battery half cells.[50]

Photochemical effects fall outside the scope of the present review, but references 104 and 105 indicate the role which could be played by methyl viologen and its homologues in the direct conversion of sunlight to electrical energy.

Last but not least is the interest in the use of viologens to create electrochromic displays. These (used, for example, in the seven-segment display mode) could be used to display time in watches or wherever a passive display is called for. A more detailed discussion of such devices is to be found elsewhere, but the majority of scientific literature relating to them has been quoted in this review. More applied publications, such as that of Shapiro *et al.*,[106] compare the heptyl, decyl, and benzyl viologens in terms of cycle life and contrast ratio found. Heptyl and decyl gave 10^4—10^5 cycles, and the contrast ratio was marginally superior for the heptyl. However, too little is known about the test conditions to evaluate these data. It is interesting to note, in conclusion, that in respect of electrochromic displays the first patents involving heptyl viologen were filed in 1970.

The authors wish to thank Dr. D. J. Barclay for his advice and assistance.

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[102] L. N. Mackey and T. Kuwana, papers presented at 4th Bioelectrochem. Symp., Jülich, West Germany, 27th Oct., 1975.

[103] R. F. Anderson, *Z. Phys. Chem.*, 1976, **80**, 969.

[104] A. B. Bocarsley, D. C. Bookbinder, *et al.*, *J. Am. Chem. Soc.*, 1980, **102**, 368.

[105] A. J. Bard, A. B. Bocarsley, *et al.*, *J. Am. Chem. Soc.*, 1980, **102**, 3671.

[106] B. I. Shapiro and I. N. Savkina, *Prib. Sist. Upr.*, 1977, **2**, 45.