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Radical Cations of some Low-potential Viologen Compounds

Reduction Potentials and Electron-transfer Reactions

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The one-electron reduction potentials (E^1) of certain pyrazinediium, diazepinediium and diazocinediium viologen compounds substituted with methyl groups, V^{2+}, have been determined from the position of the one-electron transfer equilibria with reference compounds using pulse radiolysis. E^1 ranges from -491 ± 6 mV (*vs* NHE) for 6,7-dihydro-2,11-dimethyldipyrido-[1,2-*a*:2′,1′-*c*]pyrazinediium dibromide ($V21^{2+}$) to -832 ± 11 mV for 6,7,8,9-tetrahydro-2,3,12,13-tetramethyldipyrido[1,2-*a*:2′,1′-*c*][1,4]diazocinediium dibromide ($V42^{2+}$).

The rates of reduction by e^-_{aq} were found to be independent of E^1 whereas the rates of electron transfer from $CO_2^{\cdot -}$ and $(CH_3)_2\dot{C}OH$ species do show a dependence on E^1 for V^{2+} compounds of lowest E^1. Marcus-type treatment of the rate-constant data yields a rate constant of electron exchange between propan-2-oxyl radicals and acetone in the range (2–6) × 10^6 dm^3 mol^{-1} s^{-1} and between the radical cation of 6,7-dihydro-2,3,10,11-tetramethyldipyrido[1,2-*a*:2′,1′-*c*]-pyrazinediium dibromide ($V22^{\cdot +}$) and its unreduced form ($V22^{2+}$) of 5 × 10^7 dm^3 mol^{-1} s^{-1}.

Since the discovery of the first viologen-type herbicide, diquat (6,7-dihydrodipyrido-[1,2-*a*:2′1′-*c*]pyrazinediium dibromide),[1] much interest has been shown in this class of compound. The electrochemistry of the related 1,1′-disubstituted 4,4′-bipyridinium compounds had been known for some time in that stable highly coloured radical cations are formed upon one-electron reduction.[2] The correlation between the reduction potential of both classes of viologen compounds and the degree of herbicidal action has been made.[3,4] This early work promoted the use of diquat, methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride) and benzyl viologen (1,1′-dibenzyl-4,4′-bypyridinium dichloride) as redox indicators. Recent work has shown that viologen compounds can be used as electron-transfer agents in the photoreduction of water.[5]

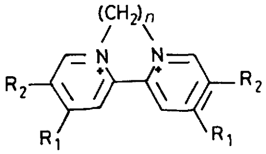
The pulse-radiolysis method of measuring equilibrium constants (K^1) of free-radical electron-transfer reactions[6,7]

$$S^{\cdot -} + R \rightleftharpoons S + R^{\cdot -} \qquad (1)$$

has been extended to measure one-electron reduction potentials (E^1) of compounds (S) using redox indicators (R) of known potential.[8,9] Recently low-potential viologen compounds (V^{2+}) have been used to determine the low-lying E^1 of the $NAD^+/NAD^{\cdot}$ couple[10,11] and also E^1 of the cancer chemotherapeutic acridine, amsacrine.[12] Full details of the radical spectra ($V^{\cdot +}$) of the V^{2+} compounds, their E^1 determinations and rates of electron transfer have not been published and are included in this study.

EXPERIMENTAL

All V^{2+} compounds were prepared from their 2,2′-dipyrido precursors as dibromide salts by the general quaternisation procedure of Homer and Tomlinson,[13] but using 1,2-dichlorobenzene as the solvent.[14] 2,2′-Dipyridine,[15] 5,5′-dimethyl-2,2′-dipyridine[16] and 4,4′,5,5′-tetramethyl-2,2′-dipyridine were prepared by the action of Rayney nickel on pyridine, 4-methylpyridine and 4,5-dimethylpyridine, respectively. Pure salts were obtained following several recrystallizations from aqueous methanol + acetone. The prepared compounds are designated Vxy^{2+} where x is the number of methylene groups bridging the pyridine rings and y is the number of methyl groups substituted on each pyridine ring (see table 1). The general structure is shown below.



6,7-Dihydro-2,11-dimethyldipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium dibromide ($V21^{2+}$), 7,8-dihydro-2,12-dimethyl-6*H*-dipyrido[1,2-*a*:2′,1′-*c*][1,4]diazepinediium dibromide ($V31^{2+}$) and 6,7,8,9-tetrahydro-2,13-dimethyldipyrido[1,2-*a*:2′,1′-*c*] [1,4]diazocinediium dibromide ($V41^{2+}$) were prepared by the method of ref. (14). 6,7-Dihydro-2,3,10,11-tetramethyldipyrido-[1,2-*a*:2′,1′-*c*]pyrazinediium dibromide ($V22^{2+}$): m.p. 281 °C; elementary analysis 6.8% N (calc. 6.4%); $C_{16}H_{20}N_2Br_2 \cdot H_2O$, λ_{max} $(H_2O) = 252$ and 316 nm ($\varepsilon = 12150$ and 24600). 7,8-Dihydro-2,3,11,12-tetramethyl-6*H*-dipyrido[1,2-*a*:2′,1′-*c*][1,4]diazepinediium dibromide ($V32^{2+}$) was prepared by the method of ref. (17). 6,7,8,9-Tetrahydro-2,3,12,13-tetramethyl-dipyrido[1,2-*a*:2′,1′-*c*][1,4]diazocinediium dibromide ($V42^{2+}$): m.p. > 300 °C; elementary analysis 6.4% N (calc. 6.0%); $C_{18}H_{24}N_2Br_2 \cdot H_2O$, $\lambda_{max}(H_2O) = 281$ nm ($\varepsilon = 13200$).

1-(2-Hydroxy-3-methoxypropyl)-2-methyl-4-nitroimidazole (AM-1) was donated by Dr A. Michalowski, Instytut Onkologii, Warsaw, Poland; 1-methylnicotinamide (MN^+) was obtained from Sigma and all other reagents used were of AnalaR grade.

Details of both the Linac[18] and Van de Graaff[19] accelerator pulse-radiolysis and radical-detection systems have been published. Dosimetry was carried out using aerated KSCN solution assuming the $(SCN)_2^{\cdot -}$ radical produced had a radiation chemical yield, G, of 0.29 μmol J^{-1} with a molar absorptivity, ε, of 7600 $dm^3\ mol^{-1}\ cm^{-1}$ at 480 nm.[20] Radical absorption spectra are presented as the product of the radiation chemical yeild, G, and the molar absorptivity.

Pulse radiolysis [*ca.* 0.3 Gy(J kg^{-1}) in 0.05–0.2 μs] was carried out in oxygen-free distilled water which was purified by a Milli-Q system (Millipore Inc.) and adjusted to pH 7.0 using phosphate buffers (2 mmol dm^{-3}). The oxidizing radical species formed on the radiolysis of water

$$H_2O \rightsquigarrow e_{aq}^-, {}^{\cdot}OH, H^{\cdot}, H_2O_2, H_2, H_3O^+ \qquad (2)$$

were either scavenged by added 2-methylpropan-2-ol (0.2 mol dm^{-3}) to form a radical that does not undergo electron transfer

$${}^{\cdot}OH(H^{\cdot}) + (CH_3)_3COH \rightarrow {}^{\cdot}CH_2(CH_3)_2COH + H_2O(H_2) \qquad (3)$$

or converted into the reducing species $CO_2^{\cdot -}$ and $(CH_3)_2\dot{C}OH$ by their reaction with added sodium formate (0.1 mol dm^{-3}) or propan-2-ol (0.2 mol dm^{-3}):

$${}^{\cdot}OH(H^{\cdot}) + HCOO^- \rightarrow CO_2^{\cdot -} + H_2O(H_2) \qquad (4)$$

$${}^{\cdot}OH(H^{\cdot}) + (CH_3)_2CHOH \rightarrow (CH_3)_2\dot{C}OH + H_2O(H_2). \qquad (5)$$

The reactions of $CO_2^{\cdot -}$ and $(CH_3)_2\dot{C}OH$ species were studied in saturated solutions of N_2O, which effectively converts e_{aq}^- into $CO_2^{\cdot -}$ and $(CH_3)_2\dot{C}OH$ species through

$$N_2O + e_{aq}^- \rightarrow {}^{\cdot}OH + N_2 + OH^- \qquad (6)$$

followed by reaction (4) or (5).

Choosing suitable concentrations of V^{2+} and R ensures that the reducing species are scavenged quickly enough to enable the establishment of equilibrium (1) to be studied. At constant radiation dose $(G\varepsilon)_{\mathrm{obs}}$ is proportional to the optical density observed when both $S^{\cdot-}$ and $R^{\cdot-}$ are present at equilibrium and is proportional to the optical density of solutions containing only S or R, $(G\varepsilon)_{S^{\cdot-}}$ and $(G\varepsilon)_{R^{\cdot-}}$, by

$$K^1 = \frac{[R^{\cdot-}][S]}{[S^{\cdot-}][R]} = \left(\frac{(G\varepsilon)_{\mathrm{obs}} - (G\varepsilon)_{S^{\cdot-}}}{(G\varepsilon)_{R^{\cdot-}} - (G\varepsilon)_{\mathrm{obs}}}\right)\frac{[S]}{[R]}. \tag{7}$$

The position of equilibrium (1) will be influenced by the ionic strength (I) of the solution if either both reductants or products are charged.[21] The difference in one-electron reduction potential, ΔE^1, between two redox compounds is given by

$$\Delta E^1 = (RT/nF)\ln(K^1 f_r) = 59(\log K^1 + \log f_r) \tag{8}$$

at $T = 295$ K, where f_r is the activity-coefficient ratio. The activity of individual ions cannot be determined, but the mean activity coefficient, $f_\pm$, of ions of charge z_1 and z_2 in a fully dissociated aqueous electrolyte can be estimated using the Debye–Hückel formulation:[22]

$$\log f_\pm = -0.507\,|z_1 z_2|\,I^{1/2}(1+3.28a_i I^{1/2})^{-1} \tag{9}$$

where a_i is the ion-size parameter (taken as 0.5 nm).

RESULTS

RADICAL SPECTRA AND ONE-ELECTRON REDUCTION RATES OF THE V^{2+} COMPOUNDS

All of the V^{2+} compounds scavenged e^-_{aq}, $CO_2^{\cdot-}$ and $(CH_3)_2\dot{C}OH$ species to form radical spectra which were measured a few microseconds after the pulse see (fig. 1):

$$e^-_{aq} + V^{2+} \rightarrow V^{\cdot+} \tag{10}$$

$$CO_2^{\cdot-} + V^{2+} \rightarrow V^{\cdot+} + CO_2 \tag{11}$$

$$(CH_3)_2\dot{C}OH + V^{2+} \rightarrow V^{\cdot+} + (CH_3)_2CO + H^+. \tag{12}$$

The concentration of V^{2+}(0.25 mmol dm^{-3}) and the small dose size (*ca.* 0.3 Gy) were used to minimise any dimerisation through

$$V^{\cdot+} + V^{\cdot+} \rightleftharpoons V_2^{2+}. \tag{13}$$

Similar radical absorption bands were produced by all 3 reductants upon their reaction with each V^{2+} compound. The positions of the absorption bands of the methyl-substituted radical cations, $V^{\cdot+}$, are similar to those of the non-methyl-substituted $V^{\cdot+}$ reported earlier.[23,24] At any given wavelength the measured $G\varepsilon$ following reduction by $CO_2^{\cdot-}$ is slightly more than double that arising from reduction by e^-_{aq}, as the yield of $^{\cdot}OH$ radicals which escape the radiation spur is increased in N_2O-saturated solution and $H^{\cdot}$ atoms contribute to the formation of $CO_2^{\cdot-}$ by reaction (4). Electron transfer from $(CH_3)_2\dot{C}OH$ to the V^{2+} compounds gave $G\varepsilon$ values slightly lower than for $CO_2^{\cdot-}$, except for $V42^{\cdot+}$ where all absorption bands are markedly smaller.

The rates of e^-_{aq} scavenging and electron transfer from $CO_2^{\cdot-}$ and $(CH_3)_2\dot{C}OH$ to the V^{2+} compounds were determined from the first-order kinetic build-up of the absorption band centred near 380 nm as a function of $[V^{2+}]$. Typically triplicate determinations for each of 3 concentrations [20–60 μmol dm^{-3} for e^-_{aq} rate; 30–90 μmol dm^{-3} for the $CO_2^{\cdot-}$ and $(CH_3)_2\dot{C}OH$ transfer rates] were made. The rate constants are presented in table 1.

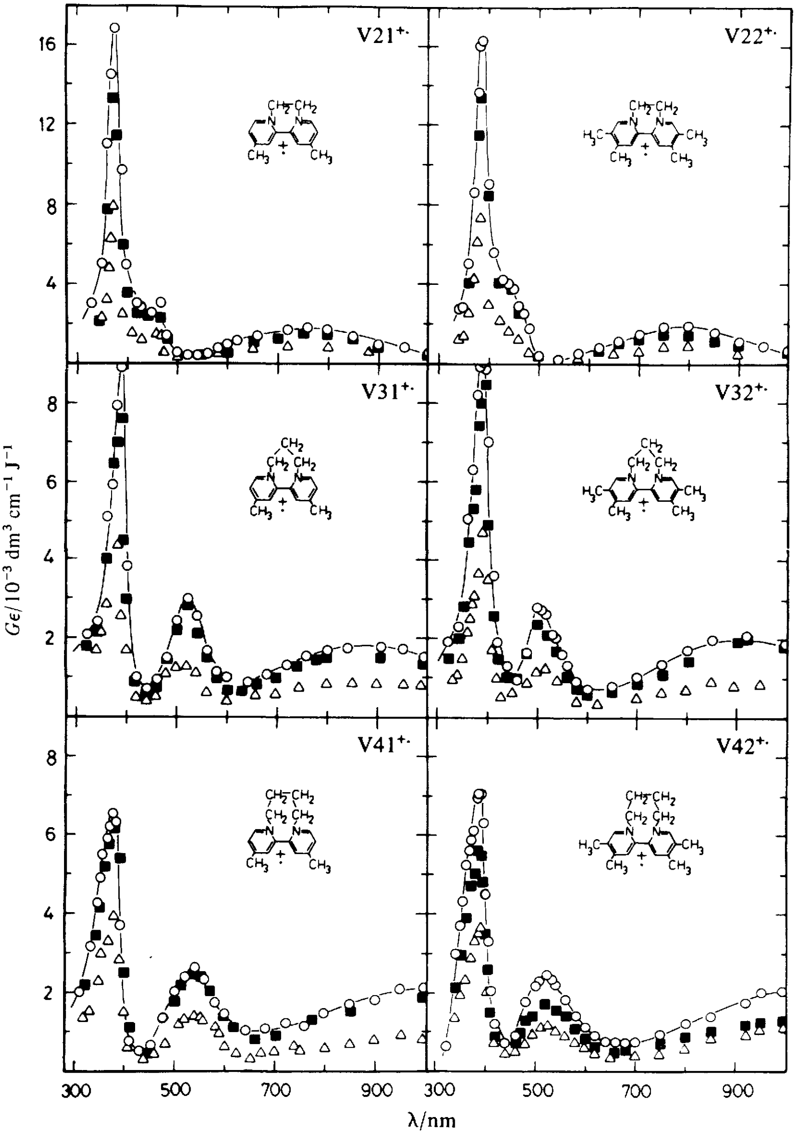


Fig. 1. Optical radical spectra of the viologens produced by pulse radiolysis (0.3 Gy in 0.1 μs) of the viologens (0.25 mmol dm^{-3}) in oxygen-free solutions containing: ○, sodium formate (0.1 mol dm^{-3}) and N_2O (25 mmol dm^{-3}) measured after *ca.* 10 μs; ■, propan-2-ol (0.2 mol dm^{-3}) and N_2O (25 mmol dm^{-3}) measured after *ca.* 50 μs; △, 2-methylpropan-2-ol (0.2 mol dm^{-3}) measured after *ca.* 2 μs.

ONE-ELECTRON REDUCTION POTENTIALS OF THE REFERENCE COMPOUNDS

The E^1 of the V^{2+} compounds were determined relative to $V30^{2+}$ (triquat) as the reference standard. The E^1 of $V30^{2+}$ has been well established by voltammetry[4, 13, 25] and we take $E^1 = -548 \pm 5$ mV as the mean of these values. Because of the exceptionally low potential of the V^{2+} compounds two intermediary low-potential

Table 1. Structures, one-electron reduction potentials (E^1) and rate constants with e^-_{aq} (k_{10}), CO_2^- (k_{11}) and $(CH_3)_2\dot{C}HOH$ (k_{12}) for V^{2+} compounds

designation	structure (see p. 2694)						
	n	R_1	R_2	E^1/mV[a]	$k_{10}/10^{10}$ dm^3 mol^{-1} s^{-1}[b]	$k_{11}/10^9$ dm^3 mol^{-1} s^{-1}[b]	$k_{12}/10^9$ dm^3 mol^{-1} s^{-1}[b]
$V20^{2+}$	2	H	H	-356 ± 5[c]	5.0[d]	12[e]	4.0
$V21^{2+}$	2	CH_3	H	-491 ± 6	5.0	11	2.8
$V30^{2+}$	3	CH_3	H	-548 ± 5[f]	6.2[d]	11[e]	3.9
$V22^{2+}$	2	CH_3	CH_3	-613 ± 5	5.5	9	2.6
$V40^{2+}$	3	H	H	-635 ± 5[g]	5.5[d]	9[e]	3.0
$V31^{2+}$	3	CH_3	H	-690 ± 6	5.5	5.8	3.2
$V41^{2+}$	4	CH_3	H	-740 ± 6	5.0	4.2	0.55
$V32^{2+}$	3	CH_3	CH_3	-777 ± 6	5.5	6.3	0.90
$V42^{2+}$	4	CH_3	CH_3	-832 ± 11	5.0	4.2	0.17

[a] Data from table 3; [b] error < 10%; [c] ref. (3); [d] revised from ref. (23); [e] in agreement with ref. (24); [f] ref. (4), (13) and (25); [g] ref. (4) and (23).

Table 3. Equilibrium data (K) and one-electron reduction potentials (E^1) of V^{2+} compounds relative to reference compounds (R)

reference, R,	AM-1[a]			$V22^{2+a}$				$E^1(V^{2+}/V^{\cdot+})$/mV	
V^{2+} compound	K[b]	$59 \log f_r$[c]	ΔE/mV	K[b]	ΔE/mV	k_1[d]	k_{-1}[e]	*vs* AM-1	*vs* $V22^{2+}$
$V21^{2+}$	0.032 ± 0.003	-4	-96 ± 2	—	—	—	—	-491 ± 6	—
$V22^{2+}$	5.72 ± 0.74	-10	45 ± 3	—	—	—	—	-618 ± 6	—
$V31^{2+}$	150 ± 16	-16	128 ± 3	16.2 ± 7	71 ± 1	2.4	15	-695 ± 6	-686 ± 5
$V32^{2+}$	3400 ± 300	-15	208 ± 3	632 ± 33	165 ± 2	6.0	1.0	-775 ± 6	-778 ± 6
$V41^{2+}$	432 ± 19	-8	155 ± 3	175 ± 16	132 ± 3	2.8	1.6	-735 ± 6	-745 ± 6
$V42^{2+}$	—	—	—	515 ± 800	219 ± 8	6.3	0.13	—	-832 ± 11

[a] $E^1(AM\text{-}1/AM\text{-}1^{\cdot-}) = -583\pm5$ mV; $E^1(V22^{2+}/V22^{\cdot+}) = -613\pm5$ mV (see table 2); [b] observed equilibrium constant; [c] calculated using eqn (9); [d] units 10^8 dm^3 mol^{-1} s^{-1}; [e] units 10^6 dm^3 mol^{-1} s^{-1}.

Table 2. Equilibrium data (K^1) and one-electron reduction potentials (E^1) of reference compounds (R) relative to $V30^{2+}$ (triquat)[a]

$$R^{\cdot -} + V30^{2+} \overset{K^b}{\rightleftharpoons} R + V30^{\cdot +}$$

reference, R	K^b	ΔE/mV	$59 \log f_r^c$/mV	$E^1(R/R^{\cdot})$/mV
AM-1	2.75 ± 0.13	25 ± 1	10	-583 ± 5
$V22^{2+}$	12.40 ± 0.32	65 ± 1	0	-613 ± 5

[a] E^1 ($V30^{2+}/V30^{\cdot +}$) taken as -548 ± 5 mV, ref. (4), (13) and (25); [b] observed equilibrium constant; [c] calculated using eqn (9).

compounds (AM-1 and $V22^{2+}$) were used as reference compounds. The use of $V22^{2+}$ to establish equilibria with lower-potential V^{2+} compounds was possible by making use of the radical absorption band centred near 530 nm seen for the propano- and butano-bridged V^{2+} compounds which is shifted to lower wavelengths in the ethano-bridged V^{2+} compounds (see fig. 1). Possible errors in the application of eqn (9) are avoided when $V22^{2+}$ is used to determine K^1 values as the forward and reverse reactions [equilibrium (1)] are symmetric in charge.

Equilibria between $V30^{2+}$ (100–600 μmol dm^{-3}) and both AM-1 (0.5–1.0 mmol dm^{-3}) and $V22^{2+}$ (0.75–1.5 mmol dm^{-3}) in solutions containing propan-2-ol (0.2 mol dm^{-3}) was observed at 530 nm. The data obtained from 5 mixtures of each pair of solutions ($I < 0.012$) together with the determined E^1 values are presented in table 2.

ONE-ELECTRON REDUCTION POTENTIALS OF V^{2+} COMPOUNDS

The E^1 of all V^{2+} compounds were determined against AM-1 and/or $V22^{2+}$. The $V^{\cdot +}$, AM-1$^{\cdot -}$ and $V22^{\cdot +}$ species were produced in solutions containing propan-2-ol, except for $V42^{\cdot +}$ where 2-methylpropan-2-ol was used.

Four mixtures of both V^{2+} (50–100 μmol dm^{-3}) + AM-1 (2.5–5.0 mmol dm^{-3}) and $V22^{2+}$ (100–300 μmol dm^{-3}) + AM-1 (50–100 μmol dm^{-3}) were used to study the position of equilibrium (1). Measurements were made at 400 nm within a few tens of microseconds of the pulse where $V21^{\cdot +}$ and $V22^{\cdot +}$ absorb and AM-1$^{\cdot -}$ does so only minimally.

Two sets of equilibria between $V31^{2+}$, $V32^{2+}$ and $V41^{2+}$ with both AM-1 and $V22^{2+}$ were established. In all cases [$V31^{2+}$], [$V32^{2+}$] and [$V41^{2+}$] were in excess of [AM-1] and [$V22^{2+}$]. Measurements were made at 530 nm in every case of 4 mixtures of AM-1 (15–80 μmol dm^{-3}) + V^{2+} (1–4 mmol dm^{-3}) within 200 μs of the pulse.

Equilibria between four mixtures of $V42^{2+}$ (1–5 mmol dm^{-3}) + $V22^{2+}$ (10–25 μmol dm^{-3}) were also observed some 250 μs after the pulse.

The rate of approach to equilibrium was also studied. Since in every case [$V^{\cdot +}$], [$V22^{\cdot +}$] < [V^{2+}], [$V22^{2+}$] the first-order rate constant for the approach to equilibrium (1), k_{obs}, is given by

$$k_{\text{obs}}/\text{s}^{-1} = k_1[V22^{2+}] + k_{-1}[V^{2+}]. \qquad (14)$$

Plots of $k_{\text{obs}}/[V^{2+}]$ against $[V22^{2+}]/[V^{2+}]$ yield k_1 from the slope and k_{-1} from the intercept. These rate constants are presented in tables 2 and 3.

Table 4. Absorption bands and extinction coefficient[a] of one-electron reduced methyl-substituted viologens ($V^{\cdot +}$).

	band I		band II		band III	
radical species	λ_{max} /nm	ε /dm^3 mol^{-1} cm^{-1}	λ_{max} /nm	ε /dm^3 mol^{-1} cm^{-1}	λ_{max} /nm	ε /dm^3 mol^{-1} cm^{-1}
$V21^{\cdot +}$	380	26250	450[b]	5000	790	3125
$V22^{\cdot +}$	390	25000	450[b]	4700	790	3125
$V31^{\cdot +}$	380	13900	520	4400	900	3000
$V32^{\cdot +}$	390	13900	520	4200	900	3125
$V41^{\cdot +}$	380	10625	540	3750	990	3275
$V42^{\cdot +}$	390	10625	535	3750	990	3275

[a] Calculated from fig. 1 assuming $G(CO_2^{\cdot -}) = 0.66$ μmol J^{-1}; [b] shoulder.

ONE-ELECTRON REDUCTION POTENTIAL OF 1-METHYLNICOTINAMIDE (MN^+)

In a previous study $V41^{2+}$ was used as the reference standard to determine E^1 for the $NAD^+/NAD^{\cdot}$ and $MN^+/MN^{\cdot}$ couples.[10] These potentials were checked using the lower-potential compound $V42^{2+}$ where K^1 should be smaller. Whereas a mixture of NAD^+ (5 mmol dm^{-3}) + $V42^{2+}$ (35 μmol dm^{-3}) gave an expected $K^1 = 23$ [$\Delta E^1 = 80$ mV and on correction $E^1(NAD^+/NAD^{\cdot}) = -0.92$ V] a similar mixture of $MN^+ + V42^{2+}$ gave a much greater K^1. Furthermore no equilibrium could be obtained with mixtures of $MN^+ + V32^{2+}$.

Equilibria between 4 mixtures of MN^+ (15 mmol dm^{-3}) + $V42^{2+}$ (25–40 μmol dm^{-3}) were observed some 30 μs after the pulse. Measurements yielded $K^1 = 800 \pm 60$ and after correction $E^1(MN^+/MN^{\cdot}) = -1.01 \pm 0.01$ V. In these experiments 2-methylpropan-2-ol was used and not propan-2-ol as in the previous work. The use of 2-methylpropan-2-ol resulted in a smaller conversion into $V42^{\cdot +}$ at equilibrium than with propan-2-ol and hence the necessary correction to the low [$V42^{2+}$] in the calculation of K^1 and in the determination of the rates of electron transfer (see above) is kept to a minimum. These experiments caution against the use of propan-2-ol in experiments with very-low-potential compounds where slow rates of electron transfer might give rise to a false equilibrium being measured.

DISCUSSION

The radical spectra of all the methyl-substituted viologens ($V^{\cdot +}$) show similar features to the radical spectra of unsubstituted viologens[23, 24] in having 3 absorption bands: I(380–390 nm), II(450–535 nm) and III(790–990 nm) (see table 4). Only band I decreases in intensity upon increasing length of the methylene bridge. This effect might be related to a progressive loss in the probability of transition with departure from coplanarity. Methyl substitution slightly decreases the intensity of band I by *ca.* 10–15% [*cf.* ref. (23) and (24)] but the position of this band and the position and intensities of bands II and III are unaffected.

The measured E^1 value for $V21^{2+}$ agrees well with the original value obtained by potentiometric titration[13] and also with a recent value obtained by cyclic voltammetry.[26] A range of E^1 values for $V31^{2+}$ has been published[27] but our value agrees with the

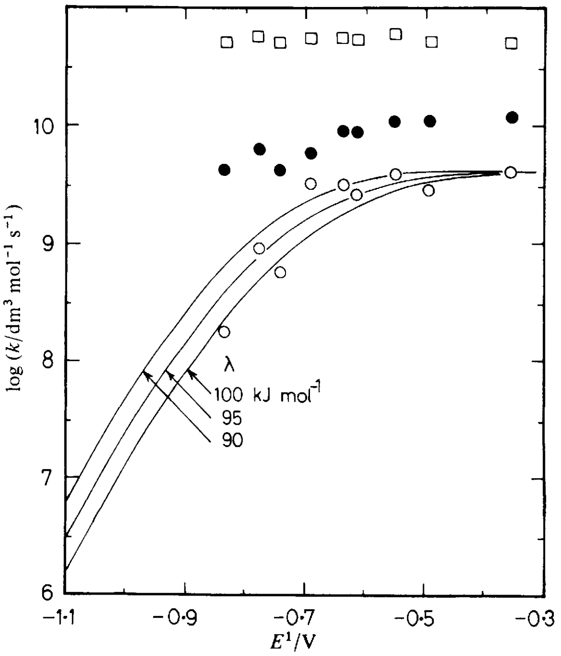


Fig. 2. Dependence of the rate constants of e_{aq}^- scavenging, □, and electron transfer from $(CH_3)_2\dot{C}OH$, ○, and $CO_2^{\cdot -}$, ●, to V^{2+} compounds on $E^1(V^{2+}/V^{\cdot +})$. The lines are calculated using the equations of Marcus as described in the text for the free-energy dependence of electron transfer from $(CH_3)_2\dot{C}OH$.

recent measurements[26] whereas our value of E^1 for V41^{2+} is 40 mV higher. A recent value for V32^{2+} determined in acetonitrile and corrected to the aqueous phase[17] is also in agreement with our direct measurements.

According to the Marcus theory[28] an observed rate constant, k_{obs}, can be related to the diffusion-controlled rate constant, k_{diff}, and the activation controlled rate constant, k_{act}, by

$$k_{obs} = k_{diff}k_{act}/(k_{act}+k_{diff}). \qquad (15)$$

The invariance of $k_{10}(e_{aq}^- + V^{2+})$ with E^1 is understood by $k_{obs} \approx k_{diff}$ when $k_{act} \gg k_{diff}$. The rate constants for electron transfer from $CO_2^{\cdot -}$ and $(CH_3)_2\dot{C}OH$ to V^{2+} compounds are constant for V^{2+} compounds possessing $E^1 >$ *ca.* −0.6 and −0.7 V, respectively, and can be taken as their k_{diff}. At lower potentials k_{obs} decreases with decreasing E^1 of the V^{2+} compounds (see table 1 and fig. 2).

The data for $k_{12}[(CH_3)_2\dot{C}OH + V^{2+}]$ *vs* E^1 $(V^{2+}/V^{\cdot +})$ can be fitted to the Marcus theory, which describes k_{act} as

$$k_{act} = Z \exp(-\Delta G^*/RT) \qquad (16)$$

where the free energy of activation, ΔG^*, when one of the reactants and products are uncharged, is related to the reorientation parameter, λ, and the standard free energy of the reaction, $\Delta G^{\ominus}$, by

$$\Delta G^* = (\lambda/4)(1+\Delta G^{\ominus}\lambda)^2. \qquad (17)$$

Several reports have substantiated this theoretical relationship which predicts a parabolic relationship between $\log k_{\text{obs}}$ and $\Delta G^{\ominus}$, or near linear over a limited range in $\Delta G^{\ominus}$.[29, 30]

$\Delta G^{\ominus}$ values for the electron transfer from propan-2-oxyl radicals to V^{2+} compounds can be calculated from the ΔE^1 between $E^1[(CH_3)_2CO/(CH_3)_2\dot{C}OH]$ and $E^1(V^{2+}/V^{\cdot+})$ since $\Delta G^{\ominus} = nF\Delta E^1$. $E^1[(CH_3)_2CO/(CH_3)_2\dot{C}OH]$ is not known but is probably in the region of -1.2 to -1.0 V *vs* NHE.[31] When $\Delta G^{\ominus} = 0$ the interpolated value of k is in the range $(2\text{–}6) \times 10^6$ dm^3 mol^{-1} s^{-1} for $E^1[(CH_3)_2CO/(CH_3)_2\dot{C}OH] = -1.1$ V and $\lambda = 90\text{–}100$ kJ mol^{-1}, (see fig. 2). These rate constants are similar to the value of *ca.* 1.0×10^7 dm^3 mol^{-1} s^{-1} found by e.s.r. for electron exchange between the propan-2-oxyl radical anion $[(CH_3)_2CO^{\cdot-}]$ and acetone in basic solution.[29]

The rate constants for the forward and reverse electron-transfer reactions between the $V22^{2+}/V22^{\cdot+}$ couple and other $V^{2+}/V^{\cdot+}$ couples can also be plotted against the $\Delta G^{\ominus}$ of the reaction to yield the rate constant for electron exchange between $V22^{\cdot+}$ and $V22^{2+}$ as 5×10^7 dm^3 mol^{-1} s^{-1}, (when $\Delta G^{\ominus} = 0$) (see fig. 3). This rate constant is the same as that predicted and found for many electron-exchange reactions of organic systems occurring in aqueous solution[29] and has been assumed in the free-energy correlation for catalysis of outer-sphere electron-transfer reactions by non-coordinated pyridine derivatives.[32]

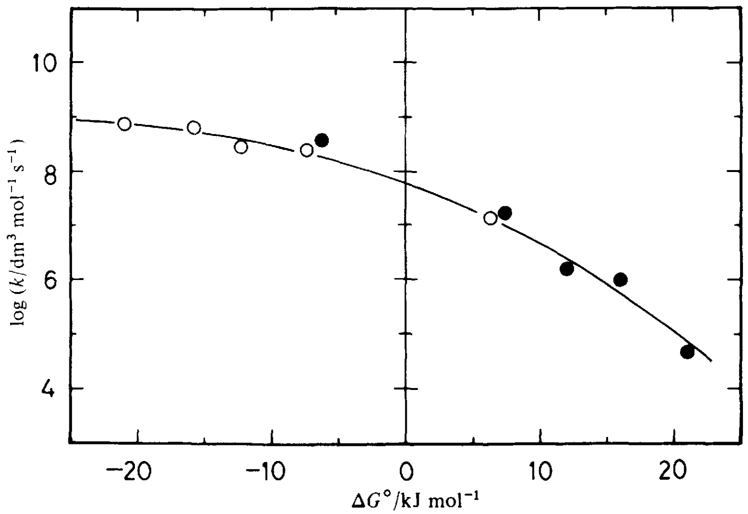


Fig. 3. Free-energy correlation of rate constants of electron exchange between one-electron reduced forms of $V22^{2+}$ and other V^{2+} compounds. ○, Forward reaction and ●, reverse reaction of equilibrium (1).

The use of low-potential V^{2+} compounds and MN^+ as reference standards may enable the possible influence of E^1 in structure–activity relationships[33] to be investigated for compounds of low electron affinity. Preliminary investigations show that certain uncouplers of oxidative phosphorylation have E^1 values in the now accessible range.[34]

Also it has been found that the tetramethyl-substituted compound $V32^{2+}$ is much more resistant to hydrogenation than its unsubstituted derivative $(V30^{2+})$,[17] but its E^1 value is lower than that required for optimum hydrogen formation when acting as an electron-transfer agent. Our data suggest that compound $V22^{2+}$, which is also tetramethyl-substituted but possessing a higher E^1 than $V32^{2+}$, might well be a good candidate as a practical electron-transfer agent for the production of hydrogen.

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