

Kinetics and mechanism of oxidation of oxovanadium(IV) by $[\text{Mn}(\text{cydta})]^-$ complex ion: Application of the Marcus relationship in support of an outer-sphere mechanism

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The rapid scan and the stopped-flow traces of the reaction mixture containing oxovanadium (IV) and $[\text{Mn}(\text{cydta})]^-$ indicate the formation of intermediate complex(es). The inverse dependence of the rate on $[\text{H}^+]$ is attributed to the acidic dissociation of aquovanadium (IV) ion. Hence the intermediate complexes are formed between $[\text{VO}(\text{OH}_2)_5]^{2+}$ and $[\text{VO}(\text{OH})(\text{OH}_2)_4]^+$ with $[\text{Mn}(\text{cydta})(\text{OH}_2)]^-$ and they decay in the rate limiting steps with rate constants $k_{\text{H}_2\text{O}}$ and k_{OH} respectively. The higher ratio of $k_{\text{OH}}/k_{\text{H}_2\text{O}} \approx 30$ at 25°C , which previous workers considered to be indicative of an inner-sphere complex, perhaps, reflects the non-adiabaticity of the reaction with aquovanadium (IV) ion. The ratio is consistent with similar observations in several outer-sphere oxidations of $\text{V}^{\text{IV}}(\text{aq})$ by metal complexes. The application of the Marcus relationship indicates that the reaction is better grouped with outer-sphere reactions of vanadium (IV) studied with well known outer-sphere oxidants. The values of the rate constants for the formation of the complex, and $k_{\text{H}_2\text{O}}$ and k_{OH} the respective rate constants for the decay of the $[\text{Mn}(\text{cydta})(\text{OH}_2)\cdot\text{VO}(\text{OH}_2)_5]^+$ and $[\text{Mn}(\text{cydta})(\text{OH}_2)\cdot\text{VO}(\text{OH})(\text{OH}_2)_4]$ are reported.

The solid ethylenediaminetetraacetic acid (EDTA) complex of manganese (III) was first prepared and characterised by Yoshino and coworkers¹. Subsequently, complexes with *trans*-1,2-cyclohexanediaminetetraacetic acid (cydta) and hydroxyethyl-ethylenediaminetetraacetic acid (hedta) were prepared and characterised². Cydta is a hexadentate ligand. Manganese (III) is, therefore, coordinated to four of its carboxylato-arms and two diamino-nitrogens and the seventh coordination site is occupied by a water molecule^{2,3}. A number of studies on kinetics of oxidations by cydta-complex including those of dithionite⁴, aquovanadium (IV)⁵ and sulphite ions⁶ were reported. Nelson and Shepherd⁷ reinvestigated the oxidation of $[\text{VO}(\text{OH}_2)_5]^{2+}$ by $[\text{Mn}(\text{cydta})(\text{OH}_2)]^-$ (hereafter water molecules are deleted from the formulae unless needed to emphasise its presence) and found no evidence from spectral data to support the formation of a precursor or successor complexes in the oxidation.

The dithionite oxidation was considered outer-sphere because the bond rupture between one of

the carboxylato-arms and the metal centre is considered less rapid than the rate of electron-transfer⁴. We recently suggested⁸ that the oxidation of sulphite ion is better placed with outer-sphere reactions rather than treating it as an inner-sphere reaction⁶. We, therefore, re-examined the oxidation of aquovanadium (IV) ion and provide spectral and kinetic evidences for the formation of a precursor complex which was suggested by previous workers⁵. We have also compared the results with the known outer-sphere oxidations by substitution inert complexes such as tris(2,2'-pipyridyl)-iron (III)⁹, hexachloroiridate (IV)¹⁰, nickel (III)-macrocyclic¹¹ and metal-tris(polypyridine) complexes¹². It is felt that this reaction, in the light of Marcus theory¹³, is better placed with outer-sphere reactions.

Materials and Methods

Approximate solution of VOSO_4 (BDH) was treated with a stoichiometric amount of $\text{Ba}(\text{ClO}_4)_2$ (Fluka). The precipitated BaSO_4 was removed by decantation and filtration. The concentration of $\text{VO}(\text{aq})^{2+}$ was estimated titrimetrically against a standard solution of cerium (IV) ammonium nitrate.

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ate (Fisher) in acetic acid using ferroin as indicator.

The $[\text{Mn}(\text{cydt})(\text{OH}_2)]^-$ complex was prepared by the oxidation of $[\text{Mn}(\text{cydt})]^{2-}$ by PbO_2 in dilute sulphuric acid medium¹⁴. To a known solution of $\text{Mn}(\text{ClO}_4)_2$ was added a little more than one equivalent amount of H_4cydt followed by slow addition of NaHCO_3 until the solution became clear and the pH was approximately 4.0. A few ml of dilute H_2SO_4 was added followed by addition of small amounts of PbO_2 in several steps avoiding excess of PbO_2 because its excess causes the oxidation of H_4cydt to formaldehyde. The formation of the latter is easily recognised by its characteristic smell. The PbSO_4 and PbO_2 were removed by filtration through a sintered crucible and the pH of the filtrate was adjusted to 4.

NaClO_4 was prepared by neutralising Na_2CO_3 (BDH, AnalaR) with HClO_4 (E. Merck, GR) to a pH 7 and standardised gravimetrically. A stock buffer solution of the desired pH was prepared by mixing required volume of equimolar solutions of acetic acid and sodium acetate¹⁵. The pH of the buffer solution and the reaction mixture was checked with an Agronic pH meter. The solution of lithium perchlorate was prepared from $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (G.F Smith).

Kinetic measurements

The kinetics were studied under pseudo-first order conditions i.e. $[\text{VO}(\text{aq})^{2+}] \gg [\text{Mn}(\text{cydt})^-]$ by following the disappearance of $[\text{Mn}(\text{cydt})^-]$ at 510 nm². The temperature of the reactant solutions and the reaction cell was maintained ($\pm 0.1^\circ\text{C}$) by circulating water at the desired temperature from a Haake D8G refrigerated circulatory water bath. The progress of the reaction was monitored by following the disappearance of the later at 510 nm using an Union-Giken RA 401 stopped-flow spectrophotometer interfaced with a microcomputer which accepts analog output signals from the RA 401 and stores them in its memory after analog/digital conversion and performs various calculations including the calculation of the pseudo-first-order rate constant. However, this kind of capability is restricted to monophasic reactions (because of the limitation of the programs supplied with the instrument). Another limitation of the instrument was that the true absorbance-time data could not be accessed from the computer's memory though the same could be read out from the exponential curve reproduced on the oscilloscope screen. It was known from the experience that the method did not work satisfactorily for the fast reactions.

At least 10-12 measurements on a single run were made and good stopped-flow traces were stored in computer memory. An interesting observation was that the stopped-flow trace, Fig. 1, had a short lived ascending portion indicative of the complex formation followed by a long lived descending part representing the decay of the complex to the products of the reaction. The initial part of the curve, unfortunately, could not be analysed for k_{com} , the pseudo-first order rate constant for the formation of the complex (because of the limitations stated earlier). Hence, the kinetics of the decomposition of the complex was studied in detail. The descending curves were averaged for evaluating the k_{obs} , the pseudo-first order rate constants for the decay of the complex. The standard deviation for k_{obs} values were 5% and the values at different $[\text{V(IV)}]$ and temperatures are in Table 1.

The rapid scan of the reaction mixture and the Michaelis-Menten kinetics¹⁶, with respect to $\text{V}^{\text{IV}}(\text{aq})$ ion, confirm the formation of a complex.

Rapid scanning of the reaction mixture

The rapid scan spectrum, recorded with a Union-Giken RA-415 stopped-flow spectrophotometer, covered 48 nm on either side of the central wave length. In all 16 spectra could be recorded starting from few ms to a maximum period of 17s after mixing. The scans in Fig. 2, ($10^4[\text{Mn}(\text{cydt})^-] = 4.0$, $10^3[\text{VO}^{2+}] = 4.0 \text{ mol dm}^{-3}$, pH 4.27 at 25°C), were recorded at 3, 5, 7, 9, 13 and

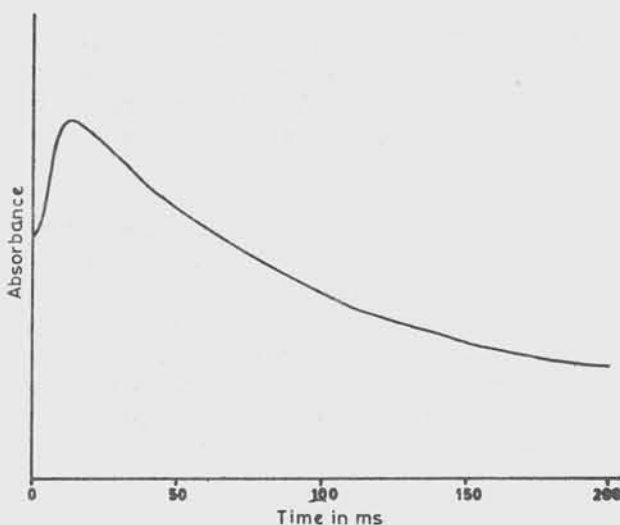


Fig. 1—The stopped-flow trace showing an initial fast ascending portion, indicative of the formation of an intermediate, and the relatively slow descending portion representing the rate determining redox reaction.

Table 1—The dependence of k_{obs} on the initial $[\text{VO}^{2+}]$ at different temperatures
 $10^4[\text{Mn}(\text{cydta})^-] = 4.0$, $[\text{CH}_3\text{COO}^-] = 0.06$, $I = 0.4 \text{ mol dm}^{-3}$ and $\text{pH } 4.27$
 $10^3 [\text{VO}^{2+}] (\text{mol dm}^{-3})$

T ($^{\circ}\text{C}$)	3.3	4.98	6.64	9.96	13.3	16.6	19.9	24.9	33.2
	$k_{\text{obs}} (\text{s}^{-1})$								
6.5	4.8	6.96	8.94	12.5	15.1	18.2	20.6	23.7	27.8
11.2	6.6	8.2	11.2	17.0	22.0	26.0	28.0	32.9	—
16.1	9.5	13.9	18.2	26.1	33.3	39.8	46.0	54.5	66.4
21.6	10.8	15.5	21.3	31.2	38.4	47.7	52.8	70.5	—
25.0	13.3	19.7	25.9	37.9	49.3	60.0	70.1	84.6	107

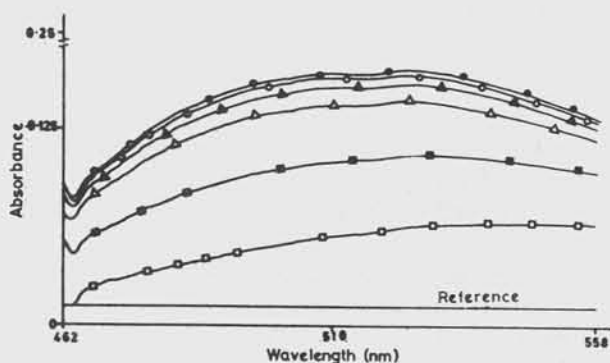
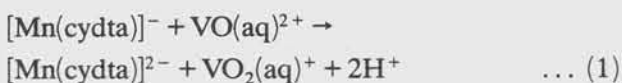


Fig. 2—The rapid scan of the reaction mixture, ($10^4[\text{Mn}(\text{cydta})^-] = 4.0$, $10^3[\text{VO}^{2+}] = 4.0 \text{ mol dm}^{-3}$, $\text{pH } 4.27$ at 24.9°C), carried out with gate time 1 ms and interval 0 ms. The spectrum (moving up) were recorded at 3 (\square), 5 (\blacksquare), 7 (\triangle), 9 (\blacktriangle), 13 (\diamond) and 17 (\bullet) ms after mixing. The increase in the absorbance indicates the formation of a complex between $[\text{Mn}(\text{cydta})^-]$ and $[\text{VO}^{2+}]$.

17 ms after mixing and show continuous increase in the absorbance which was saturated in about 17 ms indicating the complex formation equilibrium is established rapidly prior to the oxidation.

Stoichiometry

The stoichiometry of the reaction was determined using excess $[\text{Mn}(\text{cydta})^-]$ over a known $[\text{VO}(\text{aq})^{2+}]$ by noting the absorbance of the unreacted $[\text{Mn}(\text{cydta})^-]$ at 510 nm until it acquired a constant value. The results indicated that $\Delta[\text{Mn}(\text{cydta})^-]/\Delta[\text{VO}(\text{aq})^{2+}] = 1 \pm 0.04$ which was independent of the pH . Hence, the stoichiometry of the reaction is expressed by Eq. (1).



Results and Discussion

The complex formation between $[\text{Mn}(\text{cydta})^-]$

and oxovanadium (IV) is suggested by the (i) kinetics, (ii) rapid scans and (iii) the stopped-flow traces. The formation of the complex, probably, escaped detection by Boone, Hamm and Hunt⁵ because equimolar concentrations of the reactants were used. The same is confirmed at present with the help of the more sophisticated instruments available now. The stopped flow trace, Fig. 1, is indicative of the mechanism represented in Eq. (2) where B is in excess.



An examination of Fig. 1 indicates that the complex formation (short lived ascending portion reaching saturation absorbance in a much shorter period) is at least an order of magnitude greater than the redox process (the descending part).

Hence, the rate equation for the reaction in terms of disappearance of A (B is in excess) is expressed by Eq. (3).

$$-\frac{d[\text{A}]}{dt} = \frac{k_1 k_2 [\text{A}][\text{B}]}{(k_{-1} + k_2) + k_1 [\text{B}]} \quad \dots (3)$$

where $[\text{A}]$ and $[\text{B}]$ are the initial analytical concentrations. Now, if as a measure of approximation it is assumed that $1 + K_1[\text{B}] \gg k_2/k_{-1}$ ($K_1 = k_1/k_{-1}$), Eq. (3) is reduced to Eq. (4) which is the empirical rate law for the reaction.

$$-\frac{d[\text{A}]}{dt} = k_{\text{obs}}[\text{A}] = \frac{k_2 K_1 [\text{B}][\text{A}]}{1 + K_1 [\text{B}]} \quad \dots (4)$$

The Eq. (4) is consistent with the plots of k_{obs}^{-1} against $[\text{V(IV)}]^{-1}$, Fig. 3, at $\text{pH } 4.27$ and different temperatures. The fractional order, with respect to $[\text{V}^{\text{IV}}(\text{aq})]$, is in contrast to the first order de-

Table 2—The dependence of k_{obs} on pH at different temperatures

pH	$10^4[\text{Mn}(\text{cydtA})^-] = 4.0, 10^3[\text{VO}^{2+}] = 3.32, [\text{CH}_3\text{COO}^-] = 0.06$ and $I = 0.4 \text{ mol dm}^{-3}$				
	3.43	3.72	4.05	4.45	4.81
$T(^{\circ}\text{C})$			$k_{\text{obs}} (\text{s}^{-1})$		
6.5	2.94	3.38	3.75	5.65	9.59
11.2	4.32	4.80	5.25	7.50	12.1
16.1	5.88	6.51	7.04	9.2	14.1
21.6	9.40	10.0	10.7	13.3	17.8
25.0	11.7	12.6	12.8	15.2	20.5

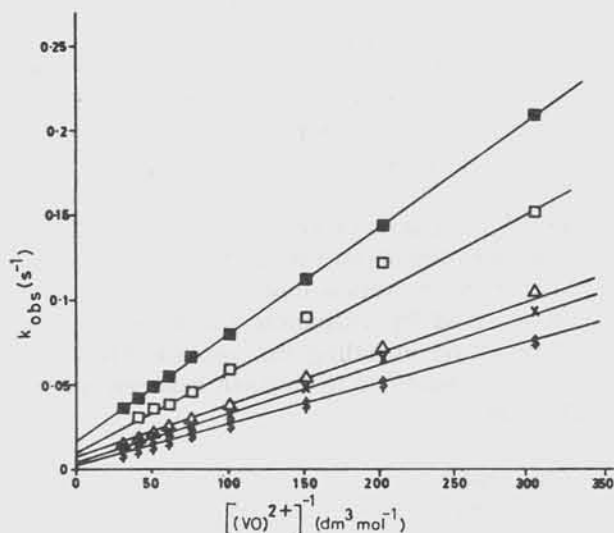


Fig. 3—The plots of k_{obs}^{-1} against $[\text{VO}^{2+}]^{-1}$ having intercepts on the rate ordinate at temperatures 6.5° (■), 11.2° (□), 16.1° (△), 21.6° (×) and 25°C (●).
 $[10^4[\text{Mn}(\text{cydtA})^-] = 4.0, [\text{CH}_3\text{COO}^-] = 0.06, I = 0.4 \text{ mol dm}^{-3}$ and pH 4.27

pendence in $[\text{V}^{\text{IV}}(\text{aq})]$ reported by previous workers⁵.

Proposed mechanism of the reaction

The dependence of k_{obs} on $[\text{H}^+]^{-1}$ (Table 2) at all the temperatures investigated, Fig. 4, strongly suggests the participation of hydroxo species in reactions involving aqua redox partners. The equilibria (5) and (6) for the Mn(III) and oxovanadium (IV) species are reported. The respective values of K_2 (ref. 5) and K_a (ref. 17a) are 7.9×10^{-9} and $4 \times 10^{-7} \text{ mol dm}^{-3}$. The associated value of ΔH_a is 48 kJ mol^{-1} (ref. 17b).

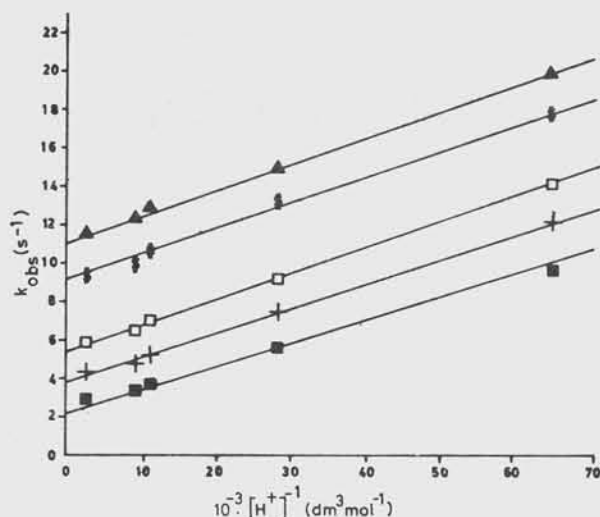
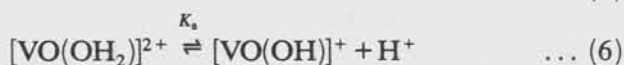
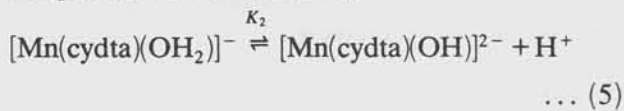


Fig. 4—The linear plots of k_{obs} against $[\text{H}^+]^{-1}$ with intercepts on the rate ordinate at temperatures 6.5° (■), 11.2° (+), 16.1° (□), 21.6° (\$) and 25°C (△).
 $10^4[\text{Mn}(\text{cydtA})^-] = 4.0, 10^3[\text{VO}^{2+}] = 3.32, [\text{CH}_3\text{COO}^-] = 0.06$ and $I = 0.4 \text{ mol dm}^{-3}$.

The value of K_2 , which is somewhat two order of magnitude smaller than the value of K_a , suggested that equilibrium (5) will play an insignificant role in the mechanism compared to equilibrium (6). Further, the oxidising power of $[\text{Mn}(\text{cydtA})(\text{OH})]^{2-}$, associated with a reduced potential¹⁸, is too weak as an oxidant and therefore the observed H^+ ion dependence derives from the deprotonation of $\text{V}^{\text{IV}}(\text{aq})$ as shown in equilibrium (6). Further, the interaction of $[\text{VO}(\text{OH})]^+$ species cannot be neglected in a study done in the pH range 3.4–4.8. The effect of the ionic strength (Table 3) and the slope value of the Davies plot¹⁹, $(\log k_{\text{obs}}$ against $\sqrt{I}/(1+\sqrt{I})$), -0.81 ± 0.06 , is also consistent with the unit charges on $[\text{Mn}(\text{cydtA})(\text{OH}_2)]^-$ and $[\text{VO}(\text{OH})]^+$.

The effect of lithium and sodium ions at constant ionic strength (Table 3) suggested that alkali metal ions did not act as a bridge in the ion-pair formation between oppositely charged $[\text{Mn}(\text{cydtA})]^-$ and V(IV) ions. Some sodium ions, present in the buffer as CH_3COONa , were invariably present even when LiCl was used.

The mechanism in Scheme 1, a refinement of the general mechanism discussed earlier, is proposed to account for the kinetics observations.

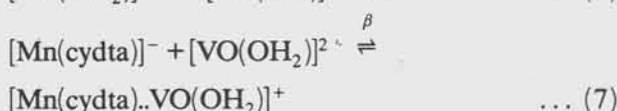
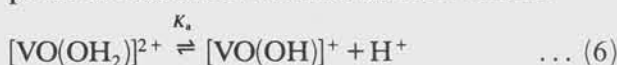
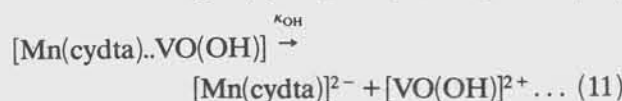
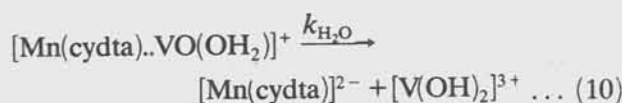
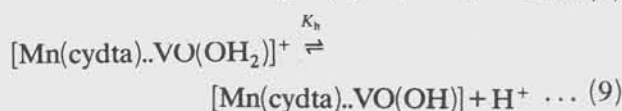
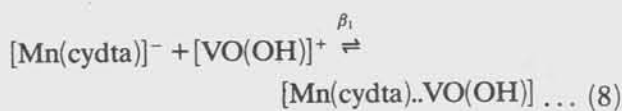


Table 3—The dependence of k_{obs} on the ionic strength adjusted with NaClO_4 at 25°C

$10^4[\text{Mn}(\text{cydta})^-] = 4.0$, $10^3[\text{VO}^{2+}] = 3.3$,
 $[\text{CH}_3\text{COO}^-] = 0.06 \text{ mol dm}^{-3}$ at pH 4.27

I (mol dm ⁻³)	0.2	0.3	0.4	0.5
$10^3 [\text{VO}^{2+}]$ (mol dm ⁻³)		k_{obs} (s ⁻¹)		
4.98	14.6	13.4	12.7	12.1
6.64	19.6	17.8	16.7	15.8



Scheme 1

The rate equation derived on the consideration of the reactions in Scheme 1 is given in Eq. (12).

$$-\frac{d[\text{Mn}(\text{cydta})^-]_0}{dt} = \frac{(k_{\text{H}_2\text{O}}\beta + k_{\text{OH}}\beta_1 K_h [\text{H}^+]^{-1})[\text{V}(\text{IV})]_0 [\text{Mn}(\text{cydta})^-]_0}{1 + K_h [\text{H}^+]^{-1} + (\beta + \beta_1 K_h [\text{H}^+]^{-1})[\text{V}(\text{IV})]_0} \dots (12)$$

where $[\text{V}(\text{IV})]_0$ and $[\text{Mn}(\text{cydta})^-]_0$ are the analytical concentrations. Equation (12) changes to Eq. (13) since $\beta_1 K_a = \beta K_h$ and assuming that $K_a \approx K_h$, because $[\text{Mn}(\text{cydta})\cdot\text{VO}(\text{OH}_2)]^+$ is considered a loose ion pair, and $1 \gg K_4 [\text{H}^+]^{-1}$ (K_4 and $[\text{H}^+]$ are of the orders of 10^{-6} and $10^{-5} \text{ mol dm}^{-3}$ respectively). The Eqs (14) and (15) (consistent with Figs 3 and 4 respectively) are obtained from Eq. (13).

$$k_{\text{obs}} = \frac{\beta(k_{\text{H}_2\text{O}} + k_{\text{OH}}K_4[\text{H}^+]^{-1})[\text{V}(\text{IV})]_0}{1 + \beta[\text{V}(\text{IV})]_0} \dots (13)$$

$$\frac{1}{k_{\text{obs}}} = \frac{1}{\beta(k_{\text{H}_2\text{O}} + k_{\text{OH}}K_h[\text{H}^+]^{-1})[\text{V}(\text{IV})]_0}$$

$$+ \frac{1}{(k_{\text{H}_2\text{O}} + k_{\text{OH}}K_h[\text{H}^+]^{-1})} \dots (14)$$

$$k_{\text{obs}} = \frac{\beta k_{\text{H}_2\text{O}}[\text{V}(\text{IV})]}{1 + \beta[\text{V}(\text{IV})]_0} + \frac{\beta k_{\text{OH}}K_h[\text{V}(\text{IV})][\text{H}^+]^{-1}}{1 + \beta[\text{V}(\text{IV})]_0} \dots (15)$$

The estimated values of $k_{\text{H}_2\text{O}}$, k_{OH} and β are in Table 4. The species $[\text{VO}(\text{OH})]^+$ is highly reactive and its reactivity has been observed in dimerisation²⁰, substitution and redox reactions²¹. The present value of $k_{\text{OH}}/k_{\text{H}_2\text{O}} = 108$ at 6.5°C and 31 at 25°C is in fair agreement with the value 72 at 1.7°C and pH 2.10 reported by Boone, Hamm and Hunt⁵. The small value for β is closer to that expected for an encounter complex than for a coordination complex.

Outer-sphere vis a vis inner-sphere mechanism

A definite idea about the nature of the mechanism, outer-sphere versus inner-sphere, is intended to be resolved by examining the results against various criteria including the applicability of the Marcus treatment¹³ to distinguish between the two mechanisms.

 $k_{\text{OH}}/k_{\text{H}_2\text{O}}$ ratio

The reaction was considered inner-sphere⁵ on the criterion that the ratio $k_{\text{OH}}/k_{\text{H}_2\text{O}} \approx 72$ (at 1.7°C and pH 2.10) happened to be in the range 10^2 - 10^4 observed in inner-sphere electron-transfer reactions²². The criterion is not absolute for the ratio $k_{\text{OH}}/k_{\text{H}_2\text{O}} \approx 10^3$ - 10^6 has been also observed in several outer-sphere oxidations of $\text{V}(\text{IV})$ ^{11,12,23}. The large difference in k_{OH} and $k_{\text{H}_2\text{O}}$ might be due to the differences in adiabaticity; the reactions of the hydroxo-complexes are relatively more adiabatic compared to considerably nonadiabatic reactions of aquo-complexes²³.

General consideration

On the basis of the present reactions having a great resemblance with the oxidations of sulphite⁸ and dithionite ions⁴, it might not be erroneous to assume that the rate of bond rupture between one of the carboxylato-arms and the metal centre to accommodate $\text{V}(\text{IV})$ is slower than the rate of electron-transfer. The plausibility of an inner-sphere is, therefore, unlikely.

Exchange rates

The rates of ¹⁸O exchange with water molecules in aquovanadium (IV) ion are: $< 20 \text{ s}^{-1}$ for axial

Table 4—The values of $k_{\text{H}_2\text{O}}$ (s^{-1}), k_{OH} (s^{-1}) and β at different temperatures and the related activation and thermodynamic parameters

Temp. ($^{\circ}\text{C}$)	6.5	11.2	16.1	21.6	25.0
β (mol dm^{-3})	27.1 ± 0.6	23.5 ± 0.3	15.5 ± 0.3	10.3 ± 0.2	8.80 ± 0.2
$k_{\text{H}_2\text{O}}$ (s^{-1})	30.6 ± 1.0	52.8 ± 2.0	111 ± 2	274 ± 6	398 ± 4
$10^{-3} k_{\text{OH}}$	3.30	4.42	6.84	10.4	12.5

$\Delta H^{\circ} = 45 \pm 4 \text{ kJ mol}^{-1}$; $\Delta S^{\circ} = -134 \pm 13 \text{ J K}^{-1} \text{ mol}^{-1}$;
 $\Delta H_{\text{H}_2\text{O}}^{\ddagger} = 97 \pm 4 \text{ kJ mol}^{-1}$; $\Delta S_{\text{H}_2\text{O}}^{\ddagger} = 147 \pm 14 \text{ JK}^{-1} \text{ mol}^{-1}$;
 $\Delta H_{\text{OH}}^{\ddagger} = 49 \pm 2 \text{ kJ mol}^{-1}$; $\Delta S_{\text{OH}}^{\ddagger} = 15 \pm 7 \text{ JK}^{-1} \text{ mol}^{-1}$.

O, 500 s^{-1} for the four equatorial H_2O and $5 \times 10^8 \text{ s}^{-1}$ for the axial H_2O (ref. 24). Similarly, the rate of exchange of the water molecule present in $[\text{Mn}(\text{cydtA})(\text{OH}_2)]^-$ is $8 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (ref. 25). No reaction is contemplated at the axial site since the rates of exchange of H_2O at this site both in $[\text{Mn}(\text{cydtA})]^-$ and $[\text{VO}_2(\text{OH}_2)_5]^+$ are nearly the same. Similarly no reaction is considered possible at double bonded oxygen because of its very strong bond²¹. The equatorial site is therefore the seat of reaction. The most accessible unpaired electron in the d_{xy} orbital for oxidant substitution is shown to be present in the equatorial plane by the molecular orbital treatment²⁶. The value of k_{OH} exceeds by one order from the rate of water exchange at equatorial position and thereby strongly suggests an outer-sphere mechanism.

Activation parameters

The activation parameters for the k_{OH} and $k_{\text{H}_2\text{O}}$ are given in Table 4. It is interesting to note that $\Delta H_{\text{OH}}^{\ddagger}$ is almost the same whereas $\Delta H_{\text{H}_2\text{O}}^{\ddagger}$ is almost twice as much as reported by the previous workers⁵. However, the activation entropy in the present case is positive for the two rate parameters against the negative entropy reported earlier. Nevertheless, the values of the activation parameters are more consistent with outer-sphere mechanism.

Inverse dependence of rate on $[\text{H}^+]$

An $[\text{H}^+]^{-1}$ term in the rate law for reactions involving aqua redox partners strongly suggests the participation of hydroxo species. A similar dependence was observed by the previous workers⁵ who interpreted it to indicate the inner-sphere mechanism. It is unique that the dependence of the rate on $[\text{H}^+]^{-1}$ is observed in several outer-sphere oxidations⁹⁻¹². If similar rates amongst different reactions are a valid criterion for prediction of the mechanism, the similarity of the mechanisms ought to be a still stronger criterion. Thus

the present reaction, it is felt, is better grouped amongst outer-sphere reactions. However, any distinction between outer-sphere and inner-sphere on certain similarities might be options of convenience. A better criterion is the application of Marcus theory¹³.

Marcus theory

The outer-sphere nature of the reaction is examined in the light of Marcus theory¹³, given by Eqs (16-19).

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} W_{12} \quad \dots (16)$$

$$\ln f_{12} = \frac{(\ln K_{12} + (w_{12} - w_{21})/RT)^2}{4(\ln(k_{11} k_{22}/Z^2) + (w_{11} + w_{22})/RT)} \quad \dots (17)$$

$$W_{12} = \exp[(w_{11} + w_{22} - w_{12} - w_{21})/2RT] \quad \dots (18)$$

$$w_{ij} = \frac{z_i z_j e^2}{D \sigma_{ij} (1 + \beta \sigma_{ij} \sqrt{\mu})} \quad \dots (19)$$

where k_{12} is the rate constant for electron transfer from V(IV) to the oxidant, k_{11} is the self-exchange rate constant for the $\text{VO}^{2+}/\text{VO}_2^+$ couple, k_{22} is the self-exchange rate constant for the various complexes (used as oxidants), K_{12} is the equilibrium constant for the various electron-transfer reaction, W_{12} is the electrostatic work term, w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (equal to the sum of the radii of the ions), D is the static dielectric constant of the medium, $\beta = (8\pi N e^2 / 1000 D k T)^{1/2}$, Z is the collision rate, a value 1×10^{25} is used for Z^2 (ref. 27), R is the gas constant ($\text{kcal mol}^{-1} \text{ K}^{-1}$) and a is the center to center distance when the species are touching. The radius of VO^{2+} is taken as 3.3 \AA and $E^0 = 0.76 \text{ V}$ for the $\text{VO}(\text{OH})^{2+/+}$ couple (6). Assuming adiabatic nature of the self-exchange reactions, Eq. (16) could be rearranged to Eq. (20).

$$2 \ln k_{12} - \ln f_{12} - 2 \ln W_{12} - \ln k_{22} = \ln k_{11} + \ln K_{12} \quad \dots (20)$$

Table 5—Data for Marcus cross relation for established outer-sphere oxidants for the oxidation of aquavanadium (IV) ion at 25°C and $I=1 \text{ mol dm}^{-3}$. The values of r_2 , E , $\ln k_{12}$ and $\ln k_{22}$ for the complexes 1-9 are taken from ref. 11

No.	Complex	r_2	$\ln k_{12}$ (Å)	$\ln k_{22}$	$\ln K_{12}$	E^V	$\ln k_{11}$	$\ln f_{12}$	Left hand Side of Eq. (20)
1	[Ni(cyclam)] ³⁺	6.0	11.4	7.6	9.35	1.0	6.54	-0.61	15.9
2	[Ni(Me ₂ cyclam)] ³⁺	6.0	11.5	8.4	10.5	0.97	4.93	-0.74	15.5
3	[Ni(tet-c)] ³⁺	6.0	14.0	3.4	19.5	1.26	7.45	-2.26	26.9
4	[Ni(tet-d)] ³⁺	6.0	14.5	4.1	18.7	1.24	8.51	-2.17	27.2
5	[Ni(Me ₂ diene)] ³⁺	6.0	10.0	8.0	9.8	1.01	3.06	-0.61	12.8
6	[Ni(Me ₆ diene)] ³⁺	6.0	12.9	1.8	22.6	1.34	4.24	-2.72	26.8
7	[Ni(non) ₂] ³⁺	6.0	9.1	8.7	7.4	0.95	2.63	-0.37	10.0
8	[Ni(dec) ₂] ³⁺	6.0	11.2	10.3	9.0	0.99	3.74	-0.56	12.7
9	[Ir(Cl) ₆] ²⁻	4.4	11.6 ²	12.3 ²⁷	5.1	0.89 ⁸	2.16	-0.14	7.2
10	[Mn(cydtA)] ⁻	6.0	6.0 ^a	1.0 ⁴	3.1	0.84 ²	6.21	-0.05	9.3

abbreviations: cyclam = 1,4,8,11-tetraazacyclotetradecane; Me₂cyclam = C-meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane; tet-c = rac-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tet-d = meso-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; Me₂diene = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; Me₆diene = 5,7,7,12,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; non = 1,4,7-triazacyclononane; dec = 1,4,7-triazacyclodecane; bpy = 2,2'-bipyridine, 4,4'-Me₂bpy = 4,4'-dimethyl-2,2'-bipyridine.
a = rate constant for path k.

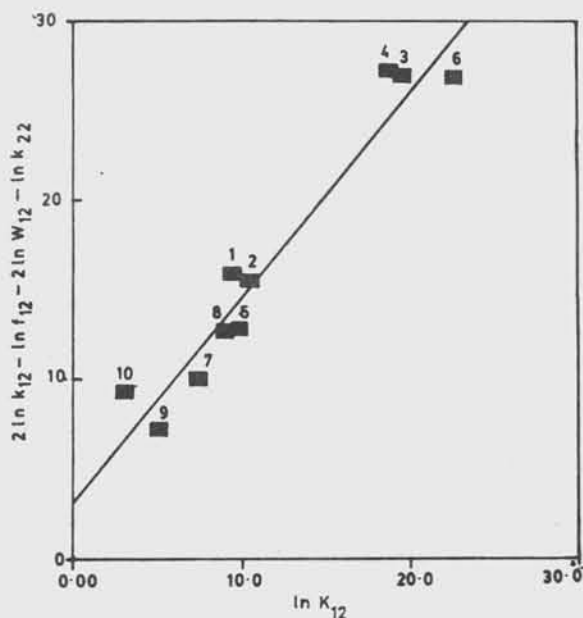


Fig. 5—The plot of $2 \ln k_{12} - \ln f_{12} - 2 \ln W_{12} - \ln k_{22}$ against $\ln K_{12}$. The points correspond to: [Ni(cyclam)]³⁺ (1), [Ni(Me₂cyclam)]³⁺ (2), [Ni(tet-c)]³⁺ (3), [Ni(tet-d)]³⁺ (4), [Ni(Me₂diene)]³⁺ (5), [Ni(Me₆diene)]³⁺ (6), [Ni(non)₂]³⁺ (7), [Ni(dec)₂]³⁺ (8), [Ir(Cl)₆]²⁻ (9) [Mn(cydtA)]⁻ (10). The abbreviations are explained in Table 5.

The plot of the data in Table 5, for known outer-sphere reactions⁹⁻¹¹, Fig. 5, is linear in accordance with Eq. (20) and has a least squares slope

value 1.15 ± 0.10 which is in fair agreement with a theoretical value of unity. The intercept gives the value of self-exchange rate between VO(OH)⁺/VO(OH)²⁺ couple = $24 \pm 8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This exchange rate is in the region $10^0-10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ derived from cross-reactions using nickel(III) polyaza macrocycle complexes¹¹. The closeness of the point corresponding to [Mn(cydtA)]⁻ to the straight line indicated that it is more similar to these complexes in its properties compared to the tris-(polypyridine) metal-complexes (not shown) which constituted a different straight line¹². It might be mentioned that in the sulphite oxidation by [Mn(cydtA)]⁻ a strong deviation from tris-(polypyridine) complexes was noted⁸ not because the S(IV) oxidation happened to be inner-sphere but because the manganese (III) complex behaves differently from these complexes. In conclusion, the oxidation of aquovanadium (IV) by [Mn(cydtA)]⁻ is better placed in the company of outer-sphere reactions.

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