

On the Kinetics of the Oxidation of Formic Acid by Vanadium(IV) in Aqueous Solution

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Abstract

The oxidation of formic acid by oxovanadium(IV) ions in sulphuric acid medium has been investigated spectrophotometrically. Platinum dispersed on titanium dioxide was used as a catalyst. The kinetics indicated a set of consecutive reactions, where the product of the first reaction, vanadium(III), was further reduced to vanadium(II) by formic acid. The rate constants were determined and a mechanism is proposed for the oxidation. The rate constants of both reactions were found to decrease with increasing hydrogen concentration.

Introduction

The homogeneous oxidation of methanol and of formic acid by metal ions can be regarded as a close analogue to the electrochemical oxidation of methanol in a fuel cell and it is therefore of considerable technological interest.

The analogy is the more interesting the closer the redox potential of the oxidant is to that of the $\text{CH}_3\text{OH}/\text{CO}_2$ couple. For this and other reasons we have chosen to investigate the $\text{VO}^{2+}/\text{V}^{3+}$ couple. The qualitative results for oxidation of methanol, formaldehyde and formic acid with oxovanadium(IV) ions in acid solution have been given elsewhere [1].

In the present paper we wish to report on the quantitative aspects of the oxidation of formic acid.

As is well known, the catalysts used in the electrochemical oxidation of methanol and formic acid are likely to be poisoned by intermediates that are strongly adsorbed on the electrode surface. In order to reduce this effect one has attempted to partly cover the catalyst surface with non-noble metals such as tin or bismuth [2, 3].

In the present investigation we have used an analogue to this in the way that the platinum was deposited on titanium dioxide as a carrier. It is known from the chemistry of conventional heterogeneous catalysis that the Pt/TiO₂ system under

reducing conditions forms what is called SMSI, 'strong metal support interaction' [4]. Part of this effect is caused by the presence of titanium(III) ions in the oxide and on the surface of the platinum [5]. These ions may be considered as analogues to the tin or bismuth atoms on a platinum surface on the electrodes of a fuel cell.

Using such a Pt/TiO₂ catalyst we have measured the kinetics of the reaction between vanadium(IV) and formic acid.

Experimental

The Pt/TiO₂ catalyst used in the experiments was prepared as described in the previous work [1], closely following the prescriptions of Mills and Porter [6]. The measurements were made in the way that a solution of 0.2 M VO_2SO_4 in a $\text{H}_2\text{SO}_4/\text{Na}_2\text{SO}_4$ electrolyte solution and an excess (0.65 M) of pure formic acid was heated under effective reflux to the desired temperature (c. 85 °C) and the catalyst was added to start the reaction. Measurements were also performed with higher concentrations of VO_2SO_4 (cf. Table 1).

The course of reaction was followed by spectrophotometric measurements of the vanadium(III) concentration at 400 nm. Samples were extracted from the reaction vessel at regular intervals. The spectrophotometer used was a Hitachi EPS-3T model.

The actual value of the ionic strength and the hydrogen ion concentration for each experiment was estimated from a mean value of 10^{-1} M for the K_a of HSO_4^- [7] and the composition of the electrolyte solution. At the prevailing pH the dissociation of formic acid is negligible (cf. Table 1).

Results

In the previous investigation [1] we obtained a slight deviation from first order behaviour such as is reproduced in Fig. 1 here. Curiously enough, in the present investigation we obtain a much more

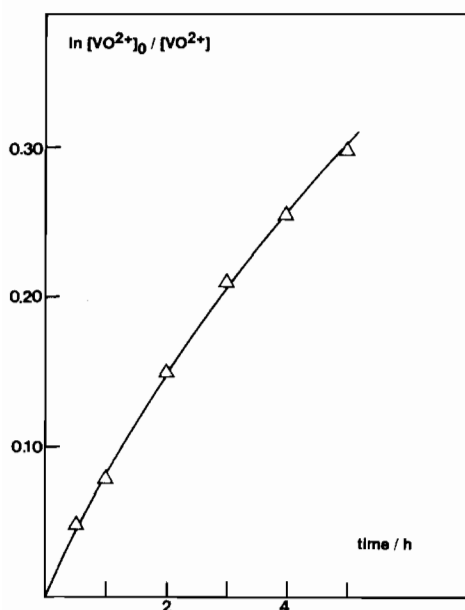


Fig. 1. A first order reaction plot of the reaction of formic acid with oxovanadium(IV) ions. Large excess of formic acid and presence of chloride ions in the electrolyte medium. (Reproduced from Fig. 2 in ref. 1.)

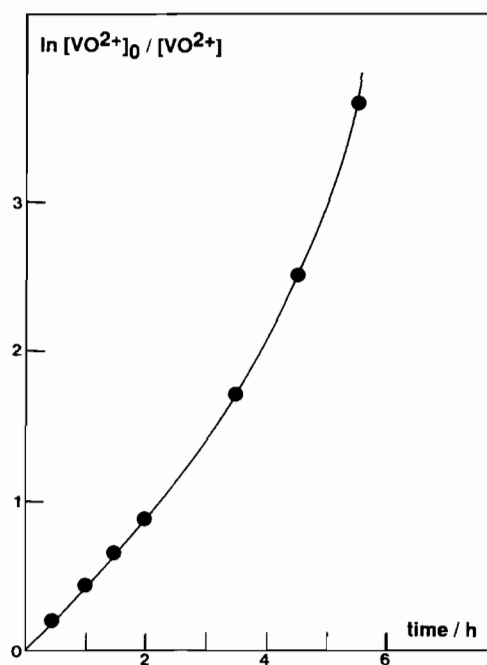


Fig. 2. A representative example from the present investigation of a first order reaction plot for the oxidation of formic acid with oxovanadium(IV) ions in complete absence of chloride ions in the electrolyte.

linear relation, or indeed, a slight curvature upwards. A representative example of our results is given in Fig. 2.

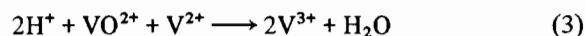
The difference between the two systems – that we know about – is that the solution of the first experiment contained a certain amount of hydrochloric acid, whereas the preparation of the solutions of the latter investigation was made with rigorous exclusion of chloride ions. The possible influence of the chloride ions on the kinetics will be treated below.

The curve of Fig. 2 can be interpreted as showing an autocatalytic effect, i.e. the vanadium(III) that is formed in the reaction affects the rate constant of the reaction. A much more reasonable explanation is, however, that the product formed, viz. V(III), is also participating in the oxidation of the formic acid.

This can be formulated as



followed by a rapid oxidation of V^{2+}



The following denotations are used: A = total concentration of vanadium species, a = concentration of vanadium(III), i.e. the experimentally determined quantity.

Thus

$$-d(A - a)/dt = k'(A - a) + k''a \quad (4)$$

resulting in

$$\ln k'A - \ln(k'A - (k' - k'')a) = (k' - k'')t \quad (5)$$

At low degrees of conversion, the rate of reaction (2) must be negligible and it is immediately realized

TABLE 1. Experimental values of the rate constants k' and k'' in various experiments with different electrolyte composition. The estimated error in k' is $\pm 0.02 \text{ h}^{-1}$ and in k'' it is $\pm 0.01 \text{ h}^{-1}$

Electrolyte	$C(\text{V})$ (M)	I (M)	$[\text{H}^+]$ (M)	k' (h^{-1})	k'' (h^{-1})
0.1 M H_2SO_4 0.9 M Na_2SO_4	0.1	3.0	0.02	0.37	0.07
0.25 M H_2SO_4 0.75 M Na_2SO_4	0.1	2.4	0.065	0.38	0.07
0.5 M H_2SO_4 0.5 M Na_2SO_4	0.1	1.8	0.15	0.42	0.10
0.75 M H_2SO_4 0.25 M Na_2SO_4	0.1	1.5	0.55	0.43	0.06
1.0 M H_2SO_4	0.1	1.4	1.0	0.36	0.08
1.0 M H_2SO_4	0.2	1.6	0.9	0.30	0.06
1.0 M H_2SO_4	0.3	1.8	0.8	0.28	0.04

that k' corresponds to the rate constant of the initial rate, determined by extrapolating the slope of the curve $\ln A/A - a$ versus t to the value $t = 0$.

The rate constant k' is reported in Table 1. Thereafter the rate constant k'' was determined in an iterative way so that the left hand side of eqn. (5) should be proportional to t and with the correct coefficient of proportionality. The results of these operations are also given in Table 1.

Discussion

At first we must consider if the steady increase of the curve of the kinetic plot is caused by other effects than those considered above. It might be, for example, that the influence of ionic strength and hydrogen concentration, varying because of the conversion of the reactants into products, could cause a change as observed.

First, in order to determine roughly the influence of the hydrogen concentration we compared the two experiments with one and the same ionic strength ($I = 1.8$ M) but with a considerable difference in hydrogen ion concentration, viz. $[H^+] = 0.15$ M and $[H^+] = 0.80$ M. From this one gets a relation as eqn. (6).

$$k' = k'_0 - 0.22[H^+] \quad (6)$$

(Nearly the same slope (0.25) is obtained from the mean value of the slopes from the three experiments at ionic strengths 1.8, 1.5–1.6 and 1.4–1.5 M, respectively.) By using eqn. (6), considered as most reliable as the ionic strength was constant, the proper value of k'_0 was calculated for each experiment.

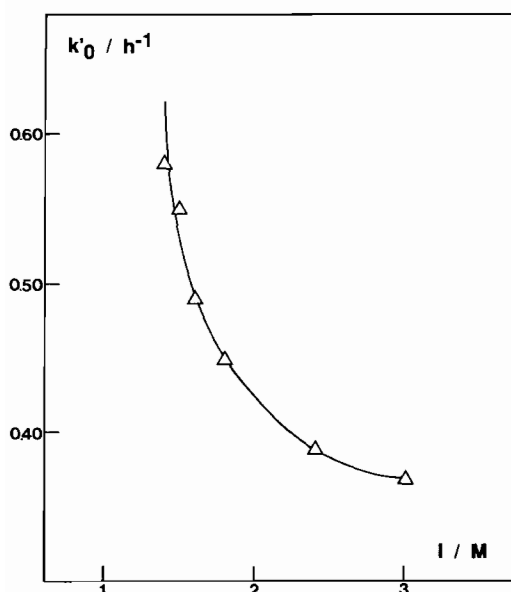


Fig. 3. k'_0 plotted against the ionic strength.

The thus obtained k'_0 was plotted against the ionic strength. The result is given in Fig. 3 and can be rationalized as the formula (7).

$$k'_0 = 1.15 - 0.56I + 0.10I^2 \quad (7)$$

This relation could in principle be used for deciding if the rate determining step involves differently charged or similarly charged ions. The range of the ionic strength is, however, so large that there is no realistic point in discussing any kind of ionic strength influence in such terms; we are far from the range of the limiting law.

The two formulae (6) and (7) can be added to one total relation (8)

$$k' = 1.15 - 0.56I + 0.10I^2 - 0.22[H^+] \quad (8)$$

In order to answer the question raised above we have calculated the rate constant at certain values of conversion for the different experiments using the thus obtained formula (8). If it were that the steady rise of the kinetic curve was caused by an influence of ionic strength and pH changes, this should be indicated by a steady rise of the value of k' thus calculated. The results (Table 2) are however, contrary to such an expectation. Rather, one finds a reasonably constant value of k' .

TABLE 2. Expected values of the rate constant k' at certain degrees of conversion. The constants are calculated from eqn. (8) from the actual values of the ionic strength and hydrogen ion concentration that follow from the reaction. For comparison, k' at zero conversion (from Table 1) is included

Electrolyte	C(V) (M)	[V(III)] (M)	Conversion (%)	k' (h ⁻¹)
0.1 M H ₂ SO ₄	0.1	0	0	0.37
0.9 M Na ₂ SO ₄		0.059	59	0.38
		0.092	92	0.38
0.25 M H ₂ SO ₄	0.1	0	0	0.38
0.75 M Na ₂ SO ₄		0.061	61	0.37
		0.091	91	0.37
0.5 M H ₂ SO ₄	0.1	0	0	0.42
0.5 M Na ₂ SO ₄		0.068	68	0.42
		0.093	93	0.43
0.75 M H ₂ SO ₄	0.1	0	0	0.43
0.25 M Na ₂ SO ₄		0.052	52	0.40
		0.085	85	0.40
1.0 M H ₂ SO ₄	0.1	0	0	0.36
		0.057	57	0.33
		0.091	91	0.31
1.0 M H ₂ SO ₄	0.2	0	0	0.30
		0.096	48	0.30
		0.182	91	0.29
1.0 M H ₂ SO ₄	0.3	0	0	0.28
		0.139	46	0.28
		0.283	94	0.27

Therefore we can conclude that the rise of the kinetic curve is caused by a consecutive set of reactions, the mechanisms of which are to be discussed shortly.

Before doing this, however, we must look for the origin of the rather strong variation of k'' that follows from the data given in Table 1. As a first step let us look for a dependence on the hydrogen ion concentration as we did for k' . The two points with the same ionic strength (1.8 M) give a relation that is analogous to eqn. (6)

$$k'' = k''_0 - 0.09[H^+] \quad (9)$$

Using this relation, k''_0 was calculated for all the experiments and plotted against the ionic strength (Fig. 4). The analytical expression for this relation was found to be

$$k''_0 = 0.52 - 0.33I + 0.06I^2 \quad (10)$$

It may be worthwhile to remark that eqn. (10) can be written as

$$k''_0 = 0.52 - 0.33I(1 - 0.18I) \quad (11)$$

whereas eqn. (7) can be reformulated as

$$k'_0 = 1.15 - 0.56I(1 - 0.18I) \quad (12)$$

Substituting the expression $I(1 - 0.18I)$ from (11) into (12) one gets a linear relation between k''_0 and k'_0 . The existence of such a relation is very well shown graphically, cf. Fig. 5. The reason for this effect is not quite clear but indicates anyway a close similarity of the ionic strength dependence of the two rate constants. Furthermore, the common factor makes it reasonable that our analysis is relevant, especially the $[H^+]$ dependence of k'' .

By adding eqns. (9) and (10) we get

$$k'' = 0.52 - 0.33I + 0.06I^2 - 0.09[H^+] \quad (13)$$

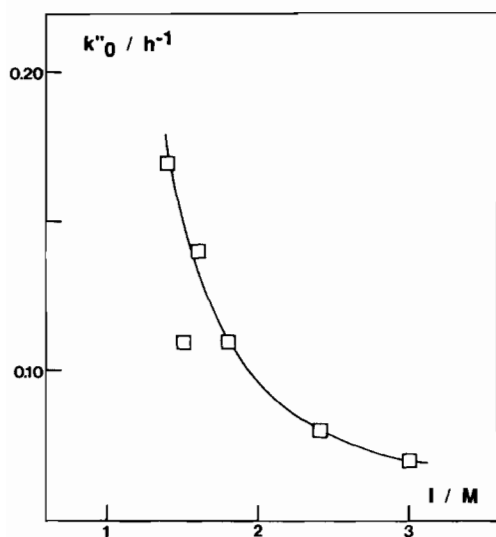


Fig. 4. k''_0 plotted against the ionic strength.

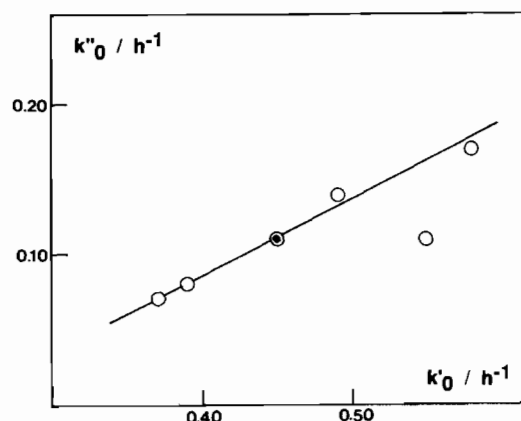
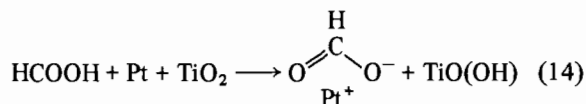


Fig. 5. Demonstration of a linear relation between k''_0 and k'_0 as a consequence of eqns. (11) and (12).

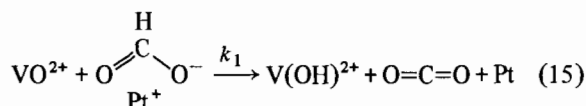
Mechanism

To rationalize the above-reported observations one may start by recalling the common knowledge on the decomposition mechanism of HCOOH on Pt and other catalysts. There is strong evidence that the rate-determining step in that reaction involves the formate ion, decomposing by a splitting of the hydrogen atom to give the product, CO_2 [8, 9].

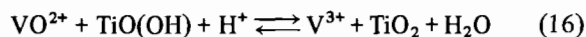
Hence one can suspect that also in this case the formation of a Pt^+ /formate $^-$ complex is the first step of the reaction. This implies a reduction of the titanium as in eqn. (14)



By a concerted action of the Pt(I) and the vanadium(IV) the hydrido-like H atom on the formate ion is oxidized as in eqn. (15)



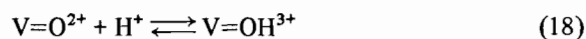
and



$$rate_1 = k_1[VO^{2+}] \quad (17)$$

where 'rate $_1$ ' means that part of the total rate that is caused by the action of oxovanadium(IV) ions.

However, in strongly acidic solutions there will occur a certain protonation of the vanadyl oxygen atom



This reaction was discovered by Rivkind using NMR [10].

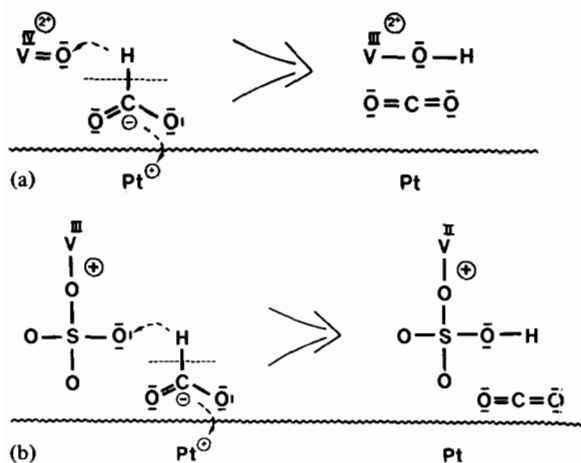


Fig. 6. A scheme of the probable reaction step of the redox process. (a) Oxovanadium(IV) as oxidant; (b) the sulphato complex of vanadium(III) as oxidant.

We now suggest that the rate determining step is the attack of the hydrogen atom on the formate ion on the oxo atom of the oxovanadium(IV) ion, cf. eqn. (15) and Fig. 6. If this atom is already blocked by a proton as in (18) this reaction must be hindered. Therefore the only vanadium(IV) species that can react is the free oxovanadium(IV) ion. The concentration of free oxovanadium(IV) ion is therefore the relevant term in the kinetic expression (4, 17). As we determine vanadium(IV) in the reaction by measuring the concentration of vanadium(III) we arrive at a quantity that contains the concentrations of both VO^{2+} and VOH^{3+} . Let us call this quantity $[\text{V(IV)}]$.

Hence

$$[\text{V(IV)}] = A - [\text{V(III)}] = [\text{VO}^{2+}] + [\text{VOH}^{3+}] \quad (19)$$

if A means the total concentration of vanadium

Thus

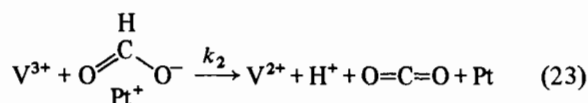
$$[\text{VO}^{2+}] = [\text{V(IV)}] - [\text{VOH}^{3+}] \quad (20)$$

$$\text{where } [\text{VOH}^{3+}] = K' [\text{VO}^{2+}] [\text{H}^+] \quad (21)$$

with K' designating the protonation constant of VO^{2+} , and

$$\begin{aligned} \text{rate}_1 &= k_1 [\text{VO}^{2+}] \\ &= k_1 ([\text{V(IV)}] - K' [\text{VO}^{2+}] [\text{H}^+]) \end{aligned} \quad (22)$$

In order to explain the appearance of the consecutive reaction (2) one must realize that the normal potential of the V(III)/V(II) couple is very close to that of the formic acid/carbon dioxide (-0.255 V compared to -0.196 V [11]). Therefore it is a fair route of continued reduction that the vanadium(III) that is formed reacts in its turn with the excess of formic acid. Thus, formally, one can write



As stated above the vanadium(II) probably reacts with vanadium(IV) to yield more vanadium(III) in a rapid equilibrium.

Therefore a certain part of the disappearance of vanadium(IV) is attributed to the presence of vanadium(III)

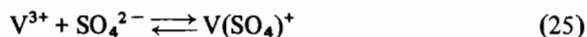
$$\text{rate}_2 = k_2 [\text{V(III)}] \quad (24)$$

where 'rate₂' has the analogous meaning to 'rate₁'.

However, we must also consider the dependence of k'' on the hydrogen ion concentration reported in eqn. (9).

The similarity between eqns. (6) and (9) might suggest that there is a common mechanism for the hydrogen ion dependence. It is, however not really possible to assume a protonization of the hexaquo vanadium(III) ion in direct analogy to the formation of $\text{V}=\text{OH}^{3+}$. Therefore a somewhat different reaction must be responsible for the $[\text{H}^+]$ dependence of k'' .

To find such a reaction one must realize that the highly charged $\text{V}(\text{OH})_2^{3+}$ is as strongly complexed by sulphate ions as other three valent ions.



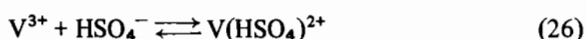
At ionic strengths between 1 and 3 M available literature data [7, 12] indicate that the equilibrium constant

$$K_1 = [\text{V}(\text{SO}_4)^+] [\text{SO}_4^{2-}]^{-1} [\text{V}^{3+}]^{-1} \quad (25a)$$

is

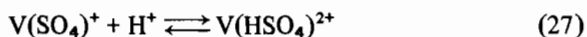
$$\log K_1 = 1.45 \pm 0.1 \quad (25b)$$

In sulphuric acid solutions there exists also, however, HSO_4^- ions to a considerable extent. Therefore a certain complexity with hydrogen sulphate ions must be considered.



$$K_2 = [\text{V}(\text{HSO}_4)^{2+}] [\text{HSO}_4^-]^{-1} [\text{V}^{3+}]^{-1} \quad (26a)$$

We now suggest that the hydrogen ion dependent reaction that we have traced concerns the equilibrium between the two sulphato complexes



with an equilibrium constant K''

$$K'' = [\text{V}(\text{HSO}_4)^{2+}] [\text{V}(\text{SO}_4)^+]^{-1} [\text{H}^+]^{-1} \quad (27a)$$

$$\text{It follows that } K'' = K_2 K_1^{-1} K_a^{-1} \quad (28)$$

where K_a is the acid constant of HSO_4^- .

K_a is of the order 10^{-1} M [7] and K_2 can be estimated from data on HSO_4^- and NO_3^- complexes

for comparable high valent ions in the collation on stability constants [7] to be around 1 M^{-1} for ionic strengths of the order of the present investigation. With the value of $K_1 = 10^{1.45} \text{ M}^{-1}$ already quoted this yields

$$K'' = 0.35 \text{ M}^{-1} \quad (29)$$

If we further assume that VSO_4^+ is the only vanadium(III) species that is active as oxidant, it follows that

$$\begin{aligned} \text{rate}_2 &= k_2[\text{VSO}_4^+] \\ &= k_2([\text{V(III)}] - K''[\text{H}^+][\text{VSO}_4^+]) \end{aligned} \quad (30)$$

Now adding eqns. (22) and (30) we arrive at

$$\begin{aligned} -d[\text{V(IV)}]/dt &= \text{rate}_1 + \text{rate}_2 \\ &= k_1([\text{V(IV)}] - K'[\text{VO}^{2+}][\text{H}^+]) \\ &\quad + k_2([\text{V(III)}] - K''[\text{H}^+][\text{VSO}_4^+]) \end{aligned} \quad (31)$$

which, supposing that $[\text{VO}^{2+}] \approx [\text{V(IV)}]$ and $[\text{VSO}_4^+] \approx [\text{V(III)}]$ is equal to

$$\begin{aligned} -d[\text{V(IV)}]/dt &= [\text{V(IV)}](k_1 - k_1K'[\text{H}^+]) \\ &\quad + [\text{V(III)}](k_2 - k_2K''[\text{H}^+]) \end{aligned} \quad (32)$$

Thus, by comparing with eqn. (4) we get

$$k' = k_1 - k_1K'[\text{H}^+] \quad (33)$$

$$k'' = k_2 - k_2K''[\text{H}^+] \quad (34)$$

Eqn. (33) expresses the experimental result that k' is slightly decreasing with increasing $[\text{H}^+]$ and eqn. (34) tells the same about k'' .

Combining eqns. (33) and (8) one can roughly estimate that at, for example, ionic strength $I = 1 \text{ M}$ the equilibrium constant of the protonation reaction (18) would be $K' = 0.3 \text{ M}^{-1}$. It is of interest to note that this value is the same as the equilibrium constant reported by Rivkind [10] for 'sulphuric acid medium', viz. $K' = 0.3_1 \text{ M}^{-1}$. This close similarity indicates that our interpretation is soundly based.

Similarly, combining eqns. (34) and (13) one can get an estimate of K'' at ionic strength $I = 1 \text{ M}$ from $k_2 = 0.25 \text{ h}^{-1}$ and $k_2K'' = 0.09 \text{ h}^{-1} \text{ M}^{-1}$. Hence $K'' = 0.36 \text{ M}^{-1}$ to be compared with $K'' = 0.35 \text{ M}^{-1}$ as given in eqn. (29).

It is also in this case of importance to note that the experimental quantity is of the same order of magnitude as the constant derived from the mechanistic model, eqn. (28). The complete agreement is of course fortuitous as it depends to a large degree on the estimation of K_2 .

The Redox Process

We suggested above that the detailed mechanism of the reaction when VO^{2+} was the oxidant involved a transfer of hydrogen towards the oxo atom and that the $\text{V}=\text{OH}^{3+}$ species was inactive. We can now add that it is possible to describe the kinetics for the vanadium(III) oxidation in the way that a low charged ion (VSO_4^+) is the reactive one also in the vanadium(III) case and a more highly charged ion (VHSO_4^{2+}) is not effective. If this observation has a deeper significance we cannot say, however. Perhaps the more extensive hydration around a highly charged ion makes it difficult for the reactive vanadium species to come close to the surface of the catalyst where the formate ion is situated. The hydrogen transfer towards the sulphato complex is depicted in Fig. 6b.

The Poisoning of the Catalyst by Chloride Ions

We now come to the difficult question on why the hydrochloride acid present in the first experiment [1] seemed to give a poisoning of the reaction that is not observed in its absence. First one must observe that the chloride complexity of oxovanadium(IV) as well as of vanadium(III) ions is not very pronounced [7]. Therefore any substantially shifts of the redox potentials cannot be expected.

One possibility would be that the Ti(IV)/Ti(III) system of the catalyst is influenced adversely by chloride ions. So, for example, substitution of O^{2-} for Cl^- in the titanium oxide structure, slowly taking place, would obstruct the continued reaction according to eqn. (14). For this suggestion speaks the fact that the poisoning does not seem to appear initially but grows slowly during the reaction. Indeed, from FT-IR spectra on the catalyst after use [13], we have observed sulphate ions incorporated in the TiO_2 structure so it is not unreasonable to expect also chloride ions to incorporate in the surface.

A second, and perhaps equally likely, possibility is a direct adsorption of chloride ions on the platinum surface. This would block the adsorption sites thus hindering the reaction of eqn. (14). This suggestion will be in agreement with the 'soft'-'soft' interaction expected between Cl and Pt. It does not, however, readily explain the slow increase of poisoning.

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