Mechanism of Oxidation of Cyclohexanehexol (Inositol) by Quinquevalent Vanadium

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Abstract

The oxidation of inositol by quinquevalent vandadium in acid medium is a first-order reaction both in vanadium (V) and inositol. The stoichiometry of the reaction is consistent with the use of two equivalents of vanadium (V) per mole of inositol with the formation of one mole of inosose. The reaction is catalyzed both by sulfuric and perchloric acid, but the rate is faster in sulfuric acid than in perchloric acid. In $1M$–$6M$ perchloric acid solutions the reaction has shown a variable order in H^+, but in solutions of $2M$–$5M$ sulfuric and perchloric acid of constant ionic strength, the rate has a linear dependence on $[H^+]^2$. There is also a linear correlation between the rate and bisulfate ions in sulfuric acid at constant hydrogen ion concentration. The energy of activation is found to be 19 kcal/mole and a negative entropy value of -14 e.u. A suitable mechanism, consistent with the kinetics in $2M$–$5M$ acid solutions, is suggested and the values of various rate constants are evaluated.

Introduction

The oxidation kinetics of sorbitol by quinquevalent vanadium in $2M$ sulfuric acid has recently been reported by Saccubai and Santappa [1]. The reaction is reported to have a first-order dependence both in vanadium (V) and sorbitol. There is also a linear correlation between the rate and the first power of hydrogen ion concentration. Although no kinetic evidence could be obtained for the formation of an intermediate complex between vanadium (V) and sorbitol, its formation in the mechanism was supported by the visual deepening of the color of the vanadium (V) solution on mixing the sorbitol solution. We, therefore, thought it of interest to investigate another polyhydroxy alcohol, which is structurally different from sorbitol, in an attempt to know if the structural change has any bearing on the kinetics and mechanism of oxidation of a polyhydroxy alcohol. The present results, over a wide range of acid concentrations, indicate that the kinetics with respect to the hydrogen ion has a fairly good second-order dependence

15

on hydrogen ion concentrations between $2M$ and $5M$ at constant ionic strength; the first-order dependence below $2M$ acid [1] is also confirmed.

Experimental

Materials

Ammonium metavanadate, Hopkin and Williams' G.P.R. reagent, is dissolved in aqueous sulfuric or perchloric acid as required. The acid concentration of the stock vanadium (V) solution is taken as the difference between the amount initially added and the amount used by reaction (1):

$$(1) \qquad NH_4VO_3 + 2H^+ \rightarrow NH_4^+ + VO_2^+ + H_2O$$
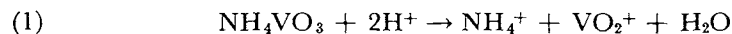
E. Merck's meso inositol has been used and its solutions were prepared by direct weighing of the sample. The freshly prepared solutions were always used. All other chemicals that have been used were either chemically pure grade reagents or reagents of AnalaR quality.

Stoichiometry and the oxidation product

The stoichiometry of the reaction has been determined under two different conditions. In one case the oxidant was taken in excess, the vanadium (V) concentration was four to five times the concentration of inositol present in the reaction mixture. In this series of experiments it was noted that the reduction rate of vanadium (V) had considerably slowed down after two equivalents of vanadium (V) were used. It indicated that any further oxidation of the oxidation product is a much slower process. The oxidation product, extracted with ether at this stage, yielded a hydrazone derivative (mp $196 \pm 2°C$) with 2,4-dinitrophenylhydrazine (DNP). This compares well with the melting point ($194 \pm 2°C$) of the corresponding hydrazone derivative obtained in the permanganate oxidation.

In the other case the stoichiometry was determined with the inositol concentration present in large excess of vanadium (V) such as that used in the study of the oxidation kinetics. The oxidation product was extracted with ether from the blue reaction mixture and treated with 2,4-DNP. The precipitated hydrazone was filtered after keeping it overnight. It was washed, dried, and weighed. However, it was noted that the various amounts of the hydrazone recovered from different sets of reaction mixtures corresponded to 65–70% of the yield calculated on the basis of the following reaction:

$$(2) \qquad C_6H_{12}O_6 + 2V(V) \rightarrow C_6H_{10}O_6 + 2V(IV) + 2H^+$$
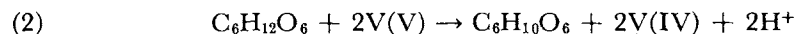
The carbonyl compound of the oxidation product is a ketone and not an aldehyde; this is borne out by the fact that the oxidation product did not give any coloration with the schiffs reagent and did not reduce the Fehling's solution. The deficit yield of the hydrazone could possibly be due to the steric hindrance that prevents the complete precipitation of the hydrazone derivative.

The formation of the inosose rather than an aldehyde as the oxidation product is consistent with the knowledge that the hydroxyl group of the primary and

secondary glycols is oxidized to the carbonyl group without any C–C fission [2]. It is interesting to note that the primary oxidation product of inositol, with strong oxidants such as permanganate and hot nitric acid, is a ketone [3]. It is only under drastic conditions that the ketone is further oxidized to the carboxylic acid stage [3]. This is consistent with our observation that the rate of reduction of vanadium (V) is considerably retarded after its two equivalents had been used.

Rate measurements

The rate measurements have been carried out in a thermostatted water bath maintained at the desired temperature; i.e., 50°C, unless stated otherwise. The kinetics have been studied under pseudo first-order conditions, the inositol was always present in large excess in the reaction mixtures. The progress of the reaction was followed by quenching a fixed volume of the reaction mixture in a known volume of a freshly prepared standard ferrous ammonium sulfate solution. The unreacted ferrous solution was titrated back with a standard vanadium (V) solution to a barium diphenylaminesulfonate endpoint in presence of phosphoric acid. Previously it had been made sure that the presence of inositol in ferrous solution did not affect the titer value at room temperature.

The reaction was followed to more than two half-lives, and the plots of log (titerchanges) versus time were found to be linear for the entire range. It indicated that the reaction has a first-order dependence in vanadium (V). The first-order rate constant k_1, with respect to vanadium (V), has been calculated from the slopes of these linear plots.

Results

The first-order dependence in vanadium (V) is further established by studying the effect of the vanadium (V) concentration on the rate constant k_1. The bisulfate ion concentration had been suitably adjusted to keep the ionic strength constant while varying the initial vanadium (V) concentration. The results in Table I indicate that the rate constant k_1 remains unaffected by the variation in initial vanadium (V) concentration.

TABLE I. Dependence of rate constant k_1 on initial vanadium (V) concentration.

[Vanadium (V)], M	$10^4 k_1$, sec^{-1}
0.01	1.60
0.03	1.64
0.05	1.61
0.07	1.60
0.08	1.65
0.10	1.66
Average $10^4 k_1 = 1.63 \pm 0.02$ sec^{-1}	

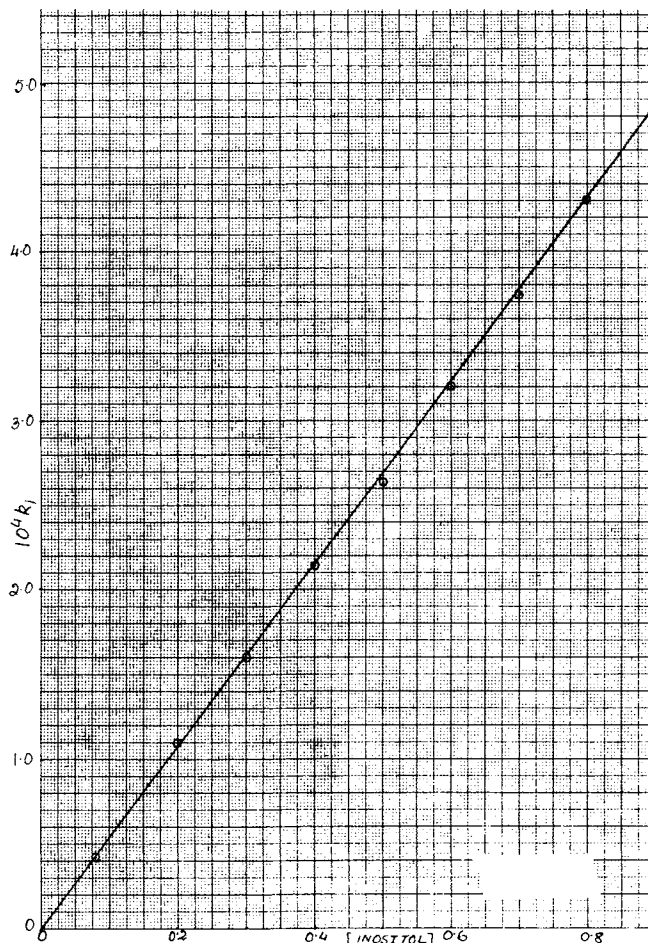[Inositol] = $0.3M$; [sulfuric acid] = $2M$; temperature 50°C.

Figure 1. Linear plot, passing through origin, of rate constant k_1 vs. respective concentrations of inositol.

    The proportional increase in the rate with the increase in inositol concentration (Table II) indicated the first-order dependence in inositol also. It is confirmed by the linear plot of the first-order rate constant k_1 against [inositol] (Fig. 1), which passes through the origin.

    The oxidation rate increased with the increase in sulfuric or perchloric acid. The variation was affected without keeping the ionic strength constant. The results in Table III indicate that the rate is faster in sulfuric acid than in perchloric acid of the same concentration.

TABLE II. Dependence of rate constant k_1 on initial inositol concentration.

[Inositol], M	$10^4 k_1$ sec^{-1}	$10^4 k_1$/[inositol]
0.08	0.42	5.25
0.20	1.10	5.50
0.35	1.90	5.40
0.50	2.63	5.26
0.70	3.74	5.34
0.80	4.30	5.37
0.90	4.82	5.35

Average $10^4 k_1$/[Inositol] = 5.35 ± 0.06 l./mole-sec

[Vanadium (V)] = 0.02M; [sulfuric acid] = 2M; temperature 50°C.

TABLE III. Dependence of rate constant k_1 on initial acid concentration.

[Sulfuric acid], M	$10^4 k_1$, sec^{-1}	[Perchloric acid], M	$10^5 k_1$, sec^{-1}
2.0	2.14	2.0	4.1
3.0	5.60	3.0	8.7
4.0	11.80	4.0	18.8
5.0	30.40	5.0	41.7
6.0	84.80	6.0	110.0

[Vanadium (V)] = 0.02M; [inositol] = 0.4M; temperature 50°C.

TABLE IV. Dependence of rate constant k_1 on [H$^+$] at constant perchlorate ion concentration.

[Inositol] = 0.2M; [ClO$_4^-$] = 6M			[Inositol] = 0.4M; [ClO$_4^-$] = 5M		
[H$^+$], M	$10^5 k_1$, sec^{-1}	$10^4 k_1$/[inositol]	[H$^+$], M	$10^4 k_1$, sec^{-1}	$10^4 k_1$/[inositol]
1.0	3.0	1.5	2.0	0.80	2.0
2.0	6.2	3.1	3.0	1.56	3.9
3.0	11.4	5.7	3.5	2.04	5.1
4.0	19.0	9.5	4.0	2.64	6.6
5.0	28.6	14.3	5.0	4.00	10.0
6.0	55.0	27.5			

[Vanadium (V)] = 0.02M; temperature = 50°C.

The order in the hydrogen ion was determined by plotting log k_1 versus log[HClO$_4$] ($\mu = 6M$). However, such a plot was found to have breaks in the linearity near about $2M$ and $5M$ acid. The slopes of the linear portions of the plot, 1.0, 2.0, and 3.6 below $2M$, between $2M$ and $5M$, and beyond $5M$, respectively, apparently indicate that the rate law of the reaction could be expressed by (3)

$$(3) \qquad \frac{-d[\text{V(V)}]}{dt} = (k^1[\text{H}^+] + k^2[\text{H}^+]^2 + k^3[\text{H}^+]^4) \, [\text{V(V)}] \, [\text{Inositol}]$$

In lower acid concentrations ($<5M$) the last term could be neglected and after dividing the rate law (3) by [H$^+$], it could be rewritten as (4)

$$(4) \qquad \frac{k_1}{[\text{H}^+]} = (k^1 + k^2[\text{H}]^+) \, [\text{Inositol}]$$

The rate law (4) indicates that the plot of $k_1/[\text{H}^+]$ versus [H$^+$] should be linear with a positive intercept on the $k_1/[\text{H}^+]$ axis. However, such a plot again showed a break near about $2M$ perchloric acid. This particular behavior is supposed to indicate that the hydrogen ion has no continuum effect on the reaction rate. It could be explained by assuming different reactive vanadium (V) species in different regions of hydrogen ion concentrations. The linear correlation between the second-order rate constant k_2 and the square power of the hydrogen ion (Fig. 2) is consistent with the second-order dependence of the reaction in the hydrogen ion.

The effect of the bisulfate ion on the reaction rate (Table V) was studied in mixtures of sulfuric and perchloric acid such that the hydrogen ion concentration was always $5M$. In computing the concentrations of either the hydrogen ion or the bisulfate ion it was assumed that sulfuric acid behaved like a strong monobasic acid in the range used. The first-order dependence in the bisulfate ion is also evident from the linear plot of k_2 against [HSO$_4^-$] (Fig. 3) at constant hydrogen ion concentration.

TABLE V. Dependence of rate constant k_1 on [HSO$_4^-$] at constant [H$^+$].

[HSO$_4^-$], M	$10^4 k_1$, sec^{-1}	$10^4 k_1$/[insoitol]
1.0	8.4	21.0
2.0	13.0	32.5
2.5	15.4	38.5
3.0	17.6	44.0
4.0	22.4	56.0
4.5	24.8	62.0
5.0	30.4	76.0

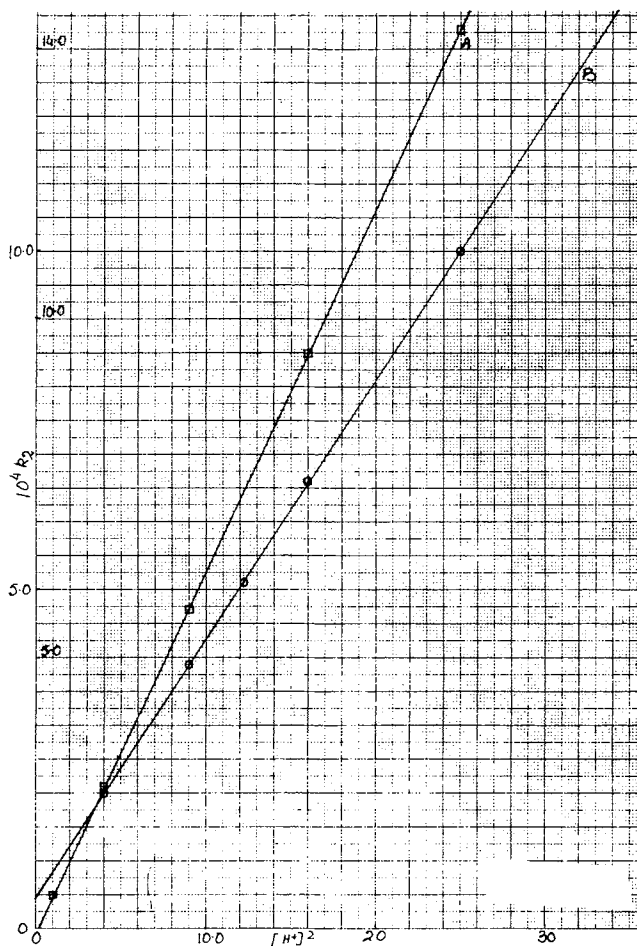[Vanadium (V)] = $0.02M$; [Inositol] = $0.4M$; [H$^+$] = $5M$; temperature = $50°C$.

Figure 2. Linear plot of second-order rate constant $k_2\{= -\langle d[\mathrm{V(V)}]/dt\rangle\ [\mathrm{V}]$ [inositol]} vs. square power of hydrogen ion concentration when ionic strength is kept constant by adjusting concentrations of perchlorate ion. Plot A: inner rate axis, —[●]—, ClO_4^- concentration constant at $6M$; Plot B: outer rate axis, —◉—, ClO_4^- concentration constant at $5M$.

The energy of activation of 19 kcal/mole and the entropy of activation of -14 e.u. were calculated by studying the reaction at different temperatures. The values of the rate constant k_1 at different temperatures are reported in Table VI.

Mechanism and Discussion

The kinetic data are equally satisfied by an initial inositol–vanadium (V) complex or a bimolecular reaction between these reactants exclusive of a complex.
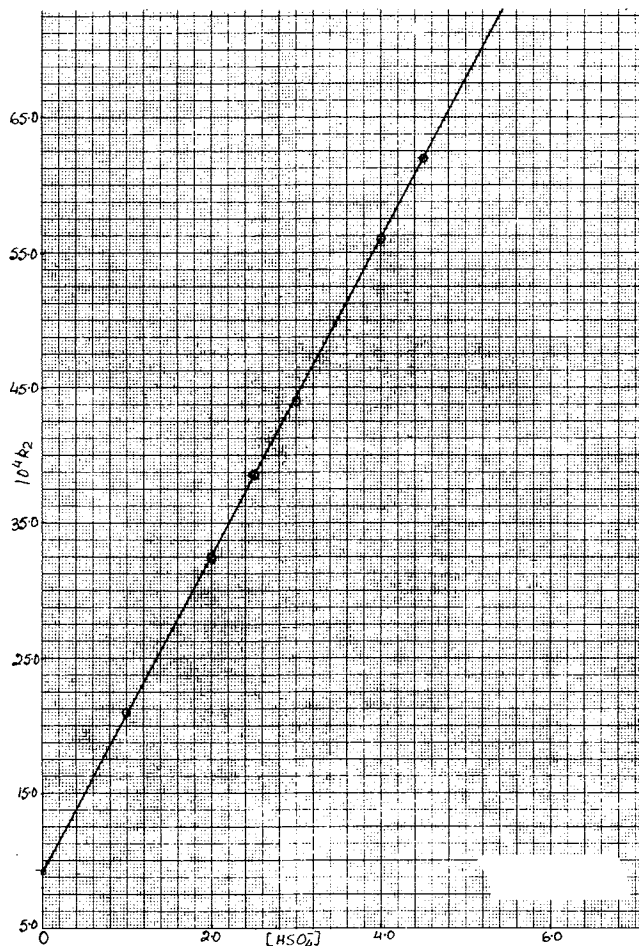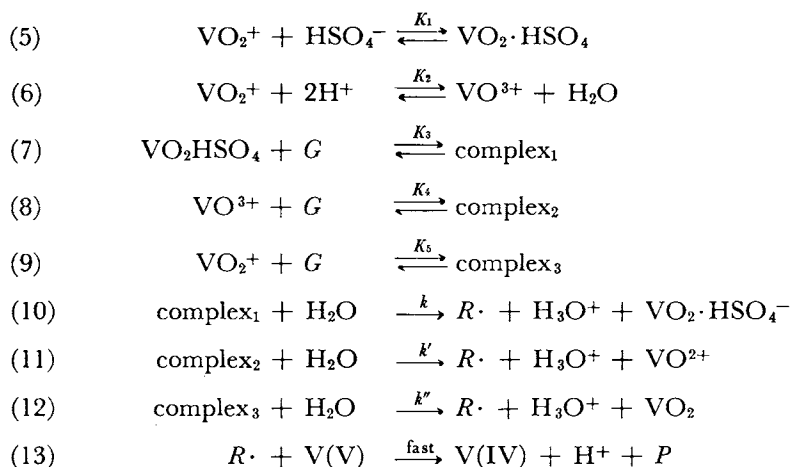
22   KUMAR AND MEHROTRA

Figure 3. Linear plot of second-order rate constant k_2 vs. [HSO$_4$$^-$] at constant concentration of hydrogen ion (= $5M$).

The first indication of the formation of the intermediate complex comes from the visual deepening of the color of the vanadium (V) solution on the addition of inositol solution to initiate the reaction. The formation of the complex is further supported by a distinct shift in the absorbance wavelength from 391 nm for vanadium (V) solution in $1M$ acid to an average value of 399 nm calculated from the flattened peak. The flattening of the absorbance peak is consistent with the general behavior of the complexes of the transition metals.
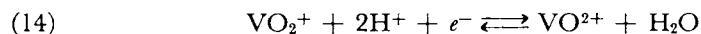
The following reactions are supposed to explain the redox kinetics between $2M$ and $5M$ acid concentration:

$$(5) \qquad VO_2^+ + HSO_4^- \overset{K_1}{\rightleftharpoons} VO_2 \cdot HSO_4$$

$$(6) \qquad VO_2^+ + 2H^+ \overset{K_2}{\rightleftharpoons} VO^{3+} + H_2O$$

$$(7) \qquad VO_2HSO_4 + G \overset{K_3}{\rightleftharpoons} complex_1$$

$$(8) \qquad VO^{3+} + G \overset{K_4}{\rightleftharpoons} complex_2$$

$$(9) \qquad VO_2^+ + G \overset{K_5}{\rightleftharpoons} complex_3$$

$$(10) \qquad complex_1 + H_2O \overset{k}{\longrightarrow} R \cdot + H_3O^+ + VO_2 \cdot HSO_4^-$$

$$(11) \qquad complex_2 + H_2O \overset{k'}{\longrightarrow} R \cdot + H_3O^+ + VO^{2+}$$

$$(12) \qquad complex_3 + H_2O \overset{k''}{\longrightarrow} R \cdot + H_3O^+ + VO_2$$

$$(13) \qquad R \cdot + V(V) \overset{fast}{\longrightarrow} V(IV) + H^+ + P$$

where VO_2^+ is the simplest of vanadium (V) cation that exists [4–6] in the acidity region pH < 1; the existence of the species VO^{3+} has been discussed by various authors [7–9] and has been considered to be the reactive species in the oxidation of glycerol (10, 11).

Foerster and Böttcher [12] have interpreted the redox system between vanadium (V) and vanadium (IV) in terms of an equilibrium between the respective species VO_2^+ and VO^{2+}, which could be represented as:

$$(14) \qquad VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$

The above equilibrium helps to explain the steep rise in the redox potential

TABLE VI. Effect of temperature on rate constant k_1 for calculations of energy and entropy of activation

Temperature, °C	$10^4 k_1$, sec^{-1}
35	0.64
40	1.03
45	1.66
50	2.63
55	4.13
60	6.30
65	9.60

Energy of activation = 19 kcal/mole
Entropy of activation $\Delta S^\dagger = -14$ cal/deg-mole
Free energy of activation = 24.5 kcal/mole

[Vanadium (V)] = $0.02M$; [sulfuric acid] = $2M$; [inositol] = $0.5M$.

of the vanadium (V)–vanadium (IV) couple at higher acidities [13] in terms of the activity of water which decreases with the increase in the acidity.

In the above mechanism G has been written for inositol and $R\cdot$ is the free radical the formation of which has been confirmed by the induced polymerization of acrylonitrile; P has been used for the inosose, the oxidation product.

The rate of disappearance of vanadium (V) concentration during the redox reaction is given by

$$(15) \quad \frac{-d[\mathrm{V(V)}]}{dt}$$

$$= \frac{2(kK_3K_1[\mathrm{HSO_4}^-] + k'K_4K_2[\mathrm{H^+}]^2 + k''K_5) \, [\mathrm{V(V)}] \, [G]}{1 + K_1[\mathrm{HSO_4}^-] + K_2[\mathrm{H^+}]^2 + (K_3K_1[\mathrm{HSO_4}^-] + K_4K_2[\mathrm{H^+}]^2 + K_5) \, [G]}$$

Since the order of the reaction with respect to inositol is strictly one and the order with respect to hydrogen and bisulfate ions is two and one, respectively, Eq. (15) is thus reduced to

$$(16) \quad \frac{-d[\mathrm{V(V)}]}{dt} = 2(kK_3K_1[\mathrm{HSO_4}^-] + k'K_4K_2[\mathrm{H^+}]^2 + k''K_5) \, [\mathrm{V(V)}] \, [G]$$

In the presence of perchloric acid, reactions (5), (7), and (10) are nonexistent, and therefore the rate of disappearance of vanadium (V) concentration in this medium could be expressed by Eq. (17), which could be deduced from Eq. (15) by neglecting all the terms involving $[\mathrm{HSO_4}^-]$ and, as explained earlier, by assuming that all the factors appearing in the denominator of Eq. (15) are much less than unity and as such these factors are negligible:

$$(17) \quad \frac{-d[\mathrm{V(V)}]}{dt} = 2(k'K_4K_2[\mathrm{H^+}]^2 + k''K_5) \, [\mathrm{V(V)}] \, [G]$$

Values of kK_3K_1, $k'K_4K_2$, and $k''K_5$

Equation (17) indicates a linear correlation between the second-order rate constant $k_2\{=(-d[\mathrm{V(V)}]/dt)/[\mathrm{V(V)}] \, [G]\}$ and the square power of the hydrogen ion. The required plot is shown in Figure 2. These correspond to the rates measured at constant perchlorate ion concentrations ($5M$ and $6M$) and constant ionic strength. The slope and intercept values of the linear plot corresponding to $[\mathrm{ClO_4}^-] = 5M$, calculated by using the method of least squares, are 3.8×10^{-5} and 4.6×10^{-5}, respectively. Thus the values of $k'K_4K_2$ is 1.9×10^{-5} l.^{2}/mole^2-sec and that of $k''K_5$ is 2.3×10^{-5} l./mole-sec. The corresponding values at $[\mathrm{ClO_4}^-] = 6M$ are 2.6×10^{-5} l.^{2}/mole^2-sec and 4.7×10^{-5} l./mole-sec. In the absence of any knowledge about the values of K_5, K_4, and K_2, the absolute values of the rate constants k' and k'' remain indeterminate.

Similarly the linear correlation between k_2 and $[\mathrm{HSO_4}^-]$, illustrated in Figure 3, is consistent with the rate law (16). The slope ($= 2kK_3K_1$) and intercept

$(= 2k'K_4K_2[H^+]^2 + 2k''K_5)$ values of the linear plot, calculated with the method of least squares, are 11.68×10^{-4} and 9.24×10^{-4}, respectively. Thus the value of kK_3K_1 is found to be $5.84 \times 10^{-4} \, 1.^2/\text{mole}^2\text{-sec}$.

Since the value of $k''K_5 \, (= 2.3 \times 10^{-5})$ is known, the value of $k'K_4K_2$ could be calculated from the intercept value $(= k'K_4K_2[H^+]^2 + k''K_5 = 4.62 \times 10^{-4})$. The value thus calculated is 1.76×10^{-5}, which compares well with the value of 1.9×10^{-5} calculated from the slope of the plot illustrated in Figure 2. The difference between the average value $(= 1.83 \times 10^{-5})$ and the two individual values of $k'K_4K_2$ is less than four percent.

Dependence on $[H^+]$

The plot of the second-order rate constant k_2 versus $[H^+]^2$, illustrated in Figure 2, is well fitted by the acid concentrations up to $5M$; the point corresponding to $6M$ perchloric acid is significantly off the linear plot and as such is not shown.

This together with the observation of Saccubai and Santappa [1] that the redox reaction between vanadium (V) and sorbitol has a first-order dependence in hydrogen ion led us to draw a plot of $\log k_1$ versus $\log [H^+]$ (Table IV, $[ClO_4^-] = 6M$) in an attempt to know if the order with respect to the hydrogen ion changed with the change in its concentration. The plot shows a curvature with an initial slope of about 1.0 (first two points) and a final slope of 3.6 (last two points) whereas the slope of the middle linear curve is 2.0 with a reasonably good fit.

This thus confirms the earlier observation of Saccubai and Santappa [1] about the first-order dependence of the hydrogen ion in the oxidation of sorbitol. These authors have used a maximum acid concentration of $2M$. As such the reactive vanadium (V) species, in this range of acid concentration, are VO_2^+ or $V(OH)_4^+$, the later being regarded as the correct representation [14] of the pervanadyl ion VO_2^+ in aqueous solution, $V(OH)_3^{2+}$, and $VO_2 \cdot HSO_4$ in sulfuric acid.

The higher order in the hydrogen ion at high acid concentration could be due to various reasons. There is a likelihood of a change in the reactive vanadium (V) species like one observed below and above $2M$ concentration. One is restricted from proposing any specific reactive species because of considerable uncertainty about the nature of vanadium (V) cation at high acid concentrations. There is also a possibility of the protonation of the substrate, and this possibility is seemingly supported by the linearity of the plot between $\log k_1$ versus $-H_0$, the Hammett acidity function [15] (Fig. 4). However, the slopes of these plots are near about 0.7, which is less than the ideal slope of unity expected in such plots. The H_0 values are taken from Paul and Long's review [16] on the acidity function.

There is also a linear correlation between the rate constant k_1 and the activity of the water. The linear correlation in terms of Bunnett's hypothesis [17] is shown in Figure 5. The slope of the linear plots in sulfuric and perchloric acid is 2.7 and 3.1, respectively. However, it has been felt desirable not to attach [18] any mechanistic significance to the slope values, which are generally called w values, except that a water molecule participates in the rate-limiting step.
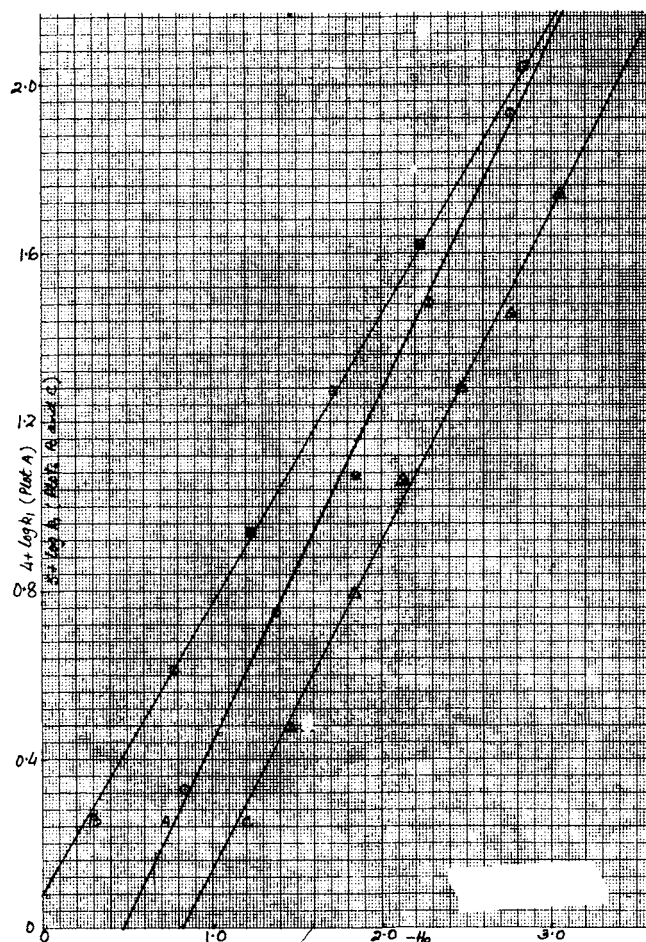
Figure 4. Linear plots of log k_1 vs. $-H_0$, the Hammetts acidity function. Plot A: Sulfuric acid, varying ionic strength, slope $= 0.83$; Plot B: Perchloric acid, varying ionic strength, slope $= 0.69$; Plot C: Perchloric acid, constant ionic strength, slope $= 0.76$.

The linear dependence of the rate, measured in an acid medium of constant ionic strength, on the Hammett acidity function is considered [19] to indicate the formation of a cyclic chelate complex and C–C fission in the rate-limiting disproportionation of the cyclic complex. The general applicability of this particular criterion of mechanism [19] has been doubted [18] previously. However, in the present case the formation of the five-membered ring complex is possible because of the presence of hydroxyl groups on the two adjacent carbon atoms, but the C–C fission is ruled out in the light of the extracted oxidation product, which is a ketone.
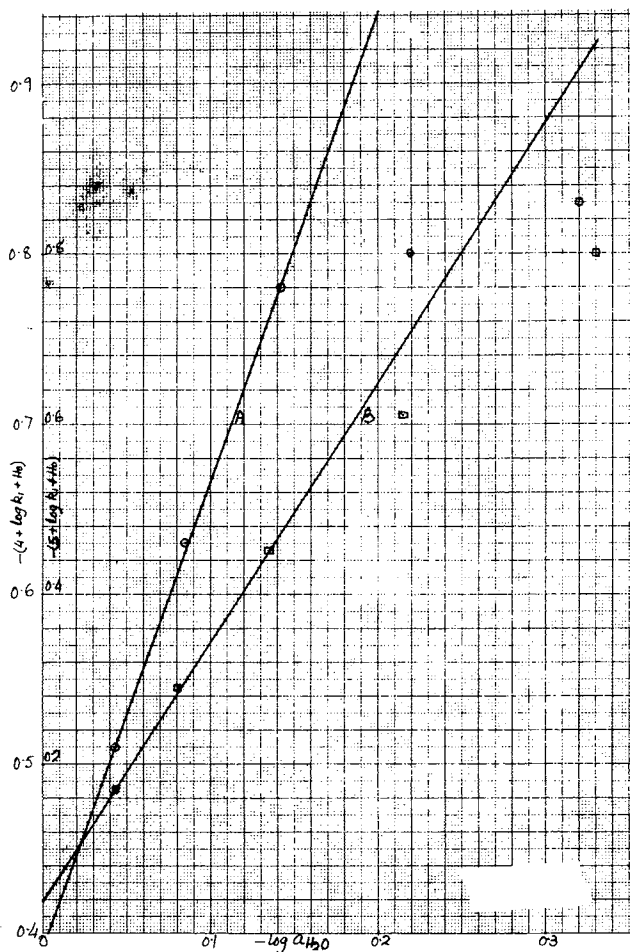
Figure 5. Linear plots of (log k_1 + H_0) vs. log (activity of water). Plot A: Sulfuric acid, outer rate axis, slope = 2.7; Plot B: Perchloric acid, inner rate axis, slope = 3.1.

Had there been any C–C fission the product would have been an aldehyde. The rate-limiting process is therefore considered to be C–H fission, and the ligand of the metal ion is considered to be involved in the electron transfer during the redox process. This thus explains the higher reactivity of the bisulfate complex of vanadium (V) in the redox reaction.

It is interesting to note that the w value in the present case resembles the w values in other oxidations [11] that are known to involve C–H fission in the rate-limiting step. However, it is not intended to propose that the w values could be a criterion to distinguish between C–H and C–C fission.

Acknowledgement

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