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Kinetics and mechanism of the oxidation of D-fructose by vanadium(V) in H_2SO_4 medium

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Abstract—The oxidative degradation of D-fructose by vanadium(V) in the presence of H_2SO_4 has an induction period followed by autoacceleration. The kinetics and mechanism of the induction period have been studied at constant ionic strength. The reaction was followed spectrophotometrically by measuring the changes in absorbance at 350 nm. Evidence of induced polymerization of acrylonitrile and of reduction of mercuric chloride indicates that a free-radical mechanism operates during the course of reaction. Vanadium(V) is only reduced to vanadium(IV). The reaction is first and fractional order in [V(V)] and [D-fructose], respectively; but dependence on $[H^+]$ is complex, that is,

$$-\frac{d[V(V)]}{dt} = \frac{k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}][V(V)]_T}{\{(1/K_{a1}[H^+][HSO_4^-]) + 1 + K_{es1}[\text{D-fructose}]\}}$$

At constant $[H_2SO_4]$, sodium hydrogensulfate accelerates the reaction. The effect of added sodium sulfate on the H_2SO_4 and HSO_4^--catalyzed reaction is also reported.

The activation parameters $E_a = 118\,kJ\,mol^{-1}$, $\Delta H^{\#} = 116\,kJ\,mol^{-1}$, $\Delta S^{\#} = -301\,J\,K^{-1}\,mol^{-1}$, and $\Delta G^{\#} = 213\,kJ\,mol^{-1}$ are calculated and discussed. Reaction products are also examined, and it is concluded that oxidation of D-fructose by vanadium(V) involves consecutive one-electron abstraction steps.

Keywords: Kinetics; Oxidation; D-Fructose; Vanadium(V); H_2SO_4

1. Introduction

The reduction of vanadium(V) by various organic and inorganic compounds has been reviewed.[1–9] Waters and Littler[1] have shown that most of these reactions proceed via a free-radical mechanism, wherein vanadium(V) undergoes a one-electron reduction. The study of mechanisms of oxidation of organic compounds by vanadium(V)[9] has implications about the behavior of vanadium oxide catalysts and is of value in problems concerning possible action of transient ions of chromium and manganese that may be concerned in certain oxidations by both chromic acid and potassium permanganate.[10] The oxidation of catechol[7] by vanadium(V) has been studied in detail because of its relevance in bioinorganic chemistry. It has been reported that NADPH is another biologically important vanadium(V) reductant.[11]

Carbohydrates are biologically important substances whose microbiological and physiological activities depend largely in their redox behavior. Oxidations of monosaccharides by different oxidizing agents are of special importance due to their biological relevance.[12–15] The kinetics of vanadium(V) oxidation of different monosaccharides in sulfuric, perchloric, and hydrochloric acid solutions have been the subject of large number of researchers.[16–20] However, their studies are not conclusive and need reinvestigation, as the reports contain no evidence of the autoacceleration path. In this paper,

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we propose a complete mechanism to explain the kinetic behavior of vanadium(V) oxidation of D-fructose.

2. Experimental

2.1. Materials

All reagents, D-fructose, ammonium monovanadate, sulfuric acid, sodium hydrogensulfate, sodium sulfate, were of analytical grade (E. Merck) and were used as provided. Doubly distilled water from an all-glass apparatus was used to prepare standard solutions. The D-fructose solution was freshly prepared by direct weighing of the sample. To prepare the vanadium(V) solution, ammonium monovanadate was dissolved or suspended in distilled water and calculated quantity of H_2SO_4 was added.

2.2. Kinetic measurements

Kinetic studies were performed using a Bausch & Lomb Spectronic-20D spectrophotometer. Known concentrations of both D-fructose and vanadium(V) were placed in separate reaction vessels, which were placed in a thermostat at desired temperature for a sufficient time to attain the temperature (±0.1). The two solutions were then mixed, and zero time was taken when half of the fructose solution had been added. The progress of the reaction was followed at 350 nm by monitoring the absorbance changes of vanadium(V). For this purpose, aliquots of the reaction mixture were taken out at definite time intervals and cooled in an ice bath to quench the reaction before each measurement. The pseudo-first-order rate constants (k_{obs}, s^{-1}) were determined from the linear part of the plots of log(absorbance) versus time by carrying out the reaction up to 80% completion. Other details of the kinetic procedure are described elsewhere.[20–22]

2.3. Test for free radicals

A solution of vanadium(V) ($0.1\,mol\,dm^{-3}$) in $1.12\,mol\,dm^{-3}$ H_2SO_4 was added to a mixture of D-fructose ($0.1\,mol\,dm^{-3}$) and 20% (v/v) acrylonitrile at 50 °C. Gel formation was observed after 20 min. Polymerization did not take place when the monomer was added to separate solutions of D-fructose or vanadium(V). The formation of white precipitate suggests the involvement of free radicals in the oxidation of D-fructose by vanadium(V).

2.4. Product identification

2.4.1. Vanadium(IV). Over the whole range of $[H_2SO_4]$ used in the kinetic measurements, UV–vis studies showed that the absorbance of vanadium(V) solution (pale yellow) decreased uniformly with increasing wavelength (Fig. 1A). In order to characterize the nature of vanadium species [i.e., the reduction product of vanadium(V)], in a typical experiment, D-fructose ($=50.0\times10^{-3}\,mol\,dm^{-3}$), vanadium(V) ($=20.0\times10^{-3}\,mol\,dm^{-3}$), and H_2SO_4 ($=3.8\,mol\,dm^{-3}$) were mixed at 50 °C. Although visual observation indicated that the reaction was over in 100 min, the reaction mixture was left for about 2 h at the same temperature. A single d–d band, ascribable to vanadium(IV),[23] was observed with $\lambda_{max}=760$ nm (Fig. 1B). Thus, vanadium(IV) (blue color) ion is confirmed as the product under conditions of this work. Blank experiments, without D-fructose, did not show formation of such a blue color.

2.4.2. Lactone and aldonic acid. Qualitative analysis of the oxidized reaction mixture with the excess [D-fructose] over [vanadium(V)] (the kinetic conditions) in presence of H_2SO_4 was performed. After the kinetic experiment was over, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution, and the presence of lactone in the reaction mixture was tested by $FeCl_3$–HCl blue test.[24]

To the other part of the reaction mixture, barium carbonate was added to make the solution neutral.[16] $FeCl_3$ solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration,[25] indicating the presence of aldonic acid. Thus, we conclude that lactone which is formed in the rate-determining step is hydrolyzed to form the aldonic acid in neutral medium in a fast step. At higher pH, the [lactone] is reduced because of the formation of aldonic acid anion that shifts the equilibrium away from lactone.[26]

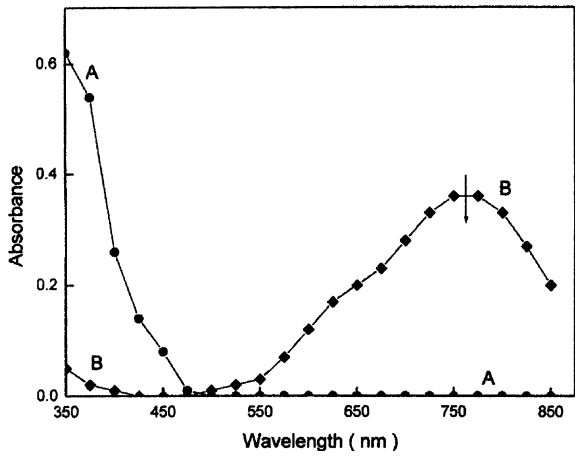


Figure 1. Absorption spectra of the reaction mixture containing [vanadium(V)] = $20.0\times10^{-3}\,mol\,dm^{-3}$, $[H_2SO_4]=3.8\,mol\,dm^{-3}$, and [D-fructose] = $50.0\times10^{-3}\,mol\,dm^{-3}$ just after mixing (A) and after completion of the reaction (B) at 50 °C.

2.4.3. Formaldehyde. In a typical experiment, D-fructose (20.0 cm^3, 0.1 mol dm^{-3}), vanadium(V) (10 cm^3, 0.01 mol dm^{-3}), H_2SO_4 (2.0 cm^3, 18 mol dm^{-3}), and distilled water (18.0 cm^3) were mixed at room temperature in a reaction flask. After completion of the reaction, the resultant mixture was transferred to a round-bottom flask and distilled. The distillate was collected in a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl. The precipitated 2,4-dinitrophenylhydrazone was filtered, washed, and dried. The procedure was repeated with known concentrations of formaldehyde under the same conditions. The most useful method of identification of 2,4-dinitrophenylhydrazone was by IR spectral comparison with authentic samples.[27]

3. Results and discussion

3.1. General considerations

In the present study it is necessary to point out that the oxidation of D-fructose by vanadium(V) showed an induction period, which was entirely eliminated at higher $[H^+]$ (Fig. 2). Another interesting feature, that is, autocatalysis, is due to the catalytic role of one of the oxidation products of the monosaccharide produced during the kinetic runs. It was noticed that the extent of induction period depended not only on $[H^+]$ but also on the concentrations of D-fructose and vanadium(V) as well as on temperature. Under such type of reaction, the choice of the best experimental conditions had been a crucial problem. Taking into consideration their effects on the induction period, a compromise was made to perform the reactions with $[H_2SO_4] = 2.2$ mol dm^{-3} and [D-fructose] $= 50.0 \times 10^{-3}$ mol dm^{-3}. The rates of the initial stage noncatalytic pathway were determined from the slopes of the plots of log(absorbance) versus time (Fig. 2).

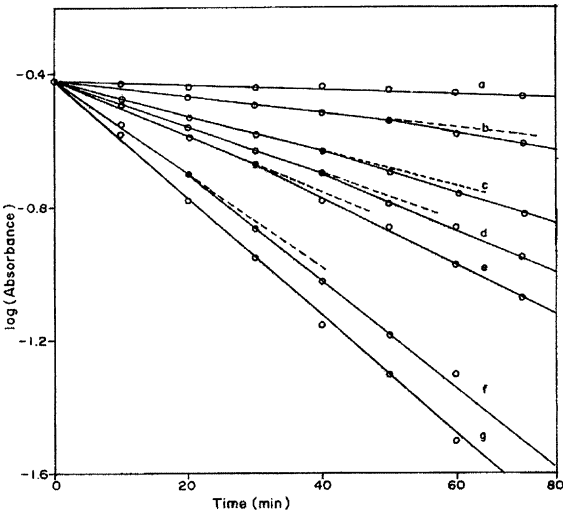


Figure 2. Plots of log(absorbance) versus time showing the induction and autoacceleration periods during the oxidation of D-fructose ($= 50.0 \times 10^{-3}$ mol dm^{-3}) by vanadium(V) ($= 4.0 \times 10^{-3}$ mol dm^{-3}) at 50 °C. Reaction conditions: $[H_2SO_4] = 0.04$ (a); 0.76 (b); 1.48 (c); 1.84 (d); 2.20 (e); 2.92 (f); and 3.28 mol dm^{-3} (g).

3.2. Vanadium(V) dependence

The order with respect to the [oxidant] was determined by carrying out the reaction at different initial concentrations where [D-fructose] $= 50.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 2.2$ mol dm^{-3}, and temperature = 50 °C. The vanadium(V) concentration was varied in the range 1.0×10^{-3}–5.0×10^{-3} mol dm^{-3}. Under these conditions where [D-fructose] $\gg$ [vanadium(V)], the plots of log(absorbance) versus time were linear, indicating the first-order dependence of rate on [vanadium(V)]; this was also confirmed near constancy of the pseudo-first-order rate constant values (Table 1).

3.3. D-Fructose dependence

D-Fructose concentration was varied from 10.0×10^{-3} to 70.0×10^{-3} mol dm^{-3} at [vanadium(V)] $= 1.0 \times 10^{-3}$, $[H_2SO_4] = 2.2$ mol dm^{-3}, and temperature = 50 °C. The k_{obs} values, summarized in Table 1, initially increase and

Table 1. Dependence of *pseudo*-first-order rate constants on [V(V)], [D-fructose], and $[H_2SO_4]$ for the oxidation of D-fructose by vanadium(V) at 50 °C

10^3 [V(V)] (mol dm^{-3})	10^3 [Fructose] (mol dm^{-3})	$[H_2SO_4]$ (mol dm^{-3})	$k_{obs} \times 10^5$ (s^{-1})
1.0	50.0	2.20	32.4
2.0			32.6
3.0			32.6
4.0			31.9
5.0			30.7
1.0	10.0	2.20	6.5
	20.0		13.4
	30.0		21.1
	40.0		26.8
	50.0		32.4
	60.0		36.4
	70.0		40.3
4.0	50.0	0.04	3.8 (11.1)[a]
		0.40	5.7 (15.3)
		0.76	9.5 (21.1)
		1.12	13.4 (30.0)
		1.48	21.1 (38.3)
		1.84	26.8 (61.4)
		2.20	31.9 (65.2)
		2.56	42.2 (79.3)
		2.92	53.7 (84.4)
		3.28	69.0 (98.2)

[a] The k_{obs} values obtained in the presence of $HSO_4^- = 0.73$ mol dm^{-3} are given in parentheses.

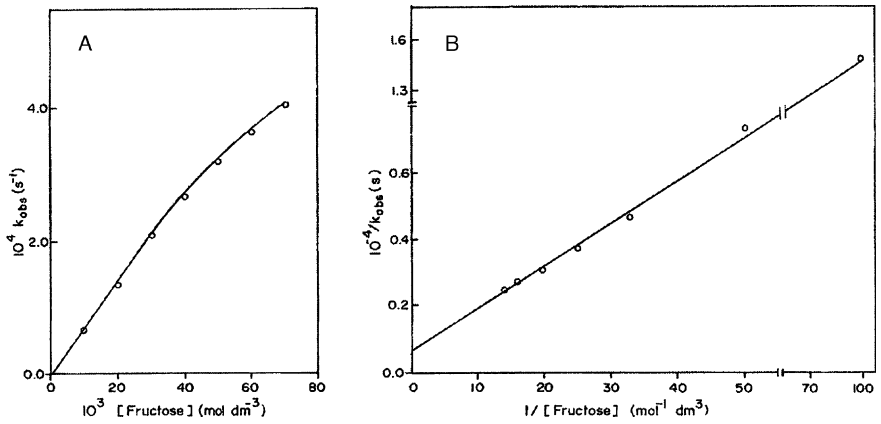


Figure 3. Plot of k_{obs} versus [D-fructose] (A) and $1/k_{obs}$ versus 1/[D-fructose] (B) for the oxidation of D-fructose by vanadium(V). Reaction conditions: [vanadium(V)] $= 4.0 \times 10^{-3}$ mol dm^{-3} and [H_2SO_4] $= 2.2$ mol dm^{-3} at 50 °C.

then tend toward a limiting value with increasing [D-fructose] (Fig. 3A). The plot of k_{obs} against [D-fructose] (Fig. 3A) indicates that the first-order kinetics at low concentrations ($\leqslant 40 \times 10^{-3}$ mol dm^{-3}) tends to become zero order in [D-fructose] at higher concentrations. Further, the plot yields a curve (Fig. 3A) concave in nature (facing down). The plot of k_{obs}^{-1} versus [D-fructose]$^{-1}$ is also linear with a positive intercept and slope (Fig. 3B). Such a plot is indicative of Michaelis–Menten behavior, which is a kinetic proof for complex formation between the reactants.

3.4. HSO_4^- dependence

To explain the dependence of k_{obs} on [HSO_4^-] (range: 0.03–1.10 mol dm^{-3}) at fixed [D-fructose] ($= 50.0 \times 10^{-3}$ mol dm^{-3}), [vanadium(V)] ($= 4.0 \times 10^{-3}$ mol dm^{-3}), and temperature ($= 50$ °C), the composition of the mixture, [H_2SO_4] $=$ [H^+] $= 2.2$ mol dm^{-3} (ignoring the dissociation of HSO_4^-) was varied.[28] The k_{obs} increased with increase in [HSO_4^-] at constant [H_2SO_4] (Table 2). This indicates that the reaction is of the ion–dipole type. The plot of log k_{obs} versus log[HSO_4^-] is linear. The reaction is, therefore, first order with respect to [HSO_4^-]. The effect of Na_2SO_4 (Table 2) was also investigated. The k_{obs} increased with increase in [SO_4^{2-}], indicating that sulfate complex of vanadium(V), that is, ($VO{\cdot}H_2O{\cdot}SO_4^+$) is the active species (vide infra).

3.5. H_2SO_4 dependence

At different [H_2SO_4] (assuming [H_2SO_4] $=$ [H^+]) in the range 0.04–3.28 mol dm^{-3} and at fixed [HSO_4^-] ($= 0.73$ mol dm^{-3}), [D-fructose] ($= 50.0 \times 10^{-3}$ mol dm^{-3}), [vanadium(V)] ($= 4.0 \times 10^{-3}$ mol dm^{-3}), and temperature ($= 50$ °C), the rate increased with increase in [H_2SO_4]. The results are represented graphically as Figure 4A. It has been found that the reaction is

Table 2. Dependence of *pseudo*-first-order rate constants on [HSO_4^-] and [SO_4^{2-}] for the oxidation of D-fructose ($= 50.0 \times 10^{-3}$ mol dm^{-3}) by vanadium(V) ($= 4.0 \times 10^{-3}$ mol dm^{-3}) in the presence of H_2SO_4 ($= 2.2$ mol dm^{-3}) at 50 °C

10 [HSO_4^-] (mol dm^{-3})	10^2 [SO_4^{2-}] (mol dm^{-3})	$k_{obs} \times 10^5$ (s^{-1})
0.0	0.0	31.9
0.3		40.3
1.8		46.0
3.6		51.2
5.5		57.5
7.3		61.4
9.1		72.9
11.0		76.7
0.0	0.0	31.9
	1.5	42.2
	3.0	49.8
	4.5	52.7
	6.0	53.4
	8.0	53.6
	10.0	52.9

catalyzed by [H^+] (cf. Table 1). Plot of log k_{obs} versus log[H_2SO_4] (Fig. 5A) resulted in two linear portions with slopes $= 0.92$ and 1.5, indicating the order with respect to [H_2SO_4] to be one and higher than one, respectively, in the lower and higher H_2SO_4 ranges. Figure 4A also indicates that the reaction has both acid-independent and acid-dependent paths. The intercept on the *y*-axis is due to the presence of some amount of H_2SO_4 in the stock solution of vanadium(V). In addition, the effect of [H_2SO_4] on the reaction rate was also studied over a fixed [HSO_4^-] ($= 0.73$ mol dm^{-3}). The results (Table 1) show that the k_{obs} increases with increasing [H_2SO_4]. The nonlinear plot between k_{obs} and [H_2SO_4] (Fig. 4B) and the double-logarithmic plot (Fig. 5B) are similarly interpreted. It may, therefore, be concluded that the redox reaction between vanadium(V) and D-fructose proceeds through the H_2SO_4-dependent path only.

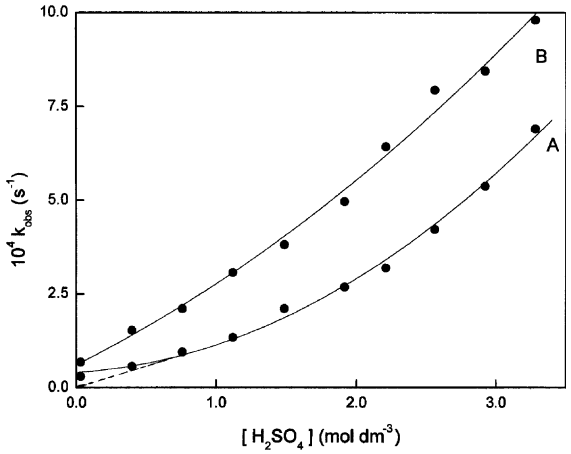


Figure 4. Dependence of the pseudo-first-order rate constants on $[H_2SO_4]$ in the absence (A) and presence (B) of $[HSO_4^-]$ for the oxidation of D-fructose by vanadium(V). Reaction conditions: [vanadium(V)] $= 4.0\times10^{-3}$ mol dm^{-3} and [D-fructose] $= 50.0\times10^{-3}$ mol dm^{-3} at 50 °C.

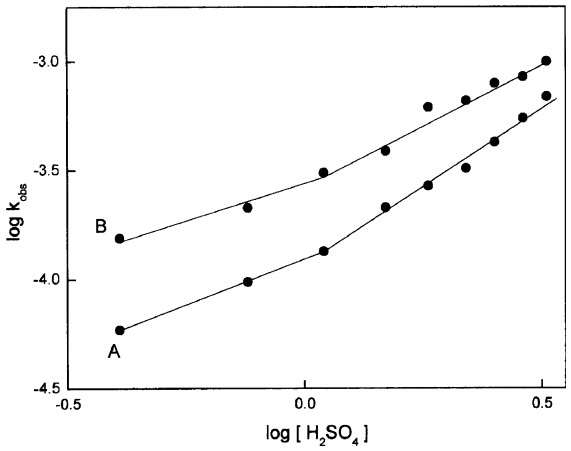


Figure 5. Double-logarithmic plot between k_{obs} and $[H_2SO_4]$ in the absence (A) and presence (B) of $[HSO_4^-]$ for the oxidation of D-fructose by vanadium(V). Reaction conditions were the same as in Figure 4.

Because of the existence of so many proton-dependent equilibria among vanadium(V) species, the exact computation of $[H^+]$ and interpretation of $[H^+]$ dependence get very much complicated at higher $[H_2SO_4]$. The observation is in agreement with the fact that the vanadium oxidation reaction in aqueous H_2SO_4 media gets catalyzed by $[H^+]$. On protonation, the positive charge on the vanadium(V)-sulfato species increases, and it facilitates the electron transfer toward the vanadium(V) center. The observed acid catalysis is not due to the acid-catalyzed mutarotation of the D-fructose, as the mutarotation process is much faster[16,29] than the present redox reaction under the experimental conditions. The mutarotation equilibrium is almost immediately attained[16] and, in all probability, the rate of D-fructose oxidation is not affected by the process of its mutarotation.

Table 3. The rate constants (k_{obs}) and activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$) for the oxidation of D-fructose ($=50.0\times10^{-3}$ mol dm^{-3}) by vanadium(V) ($=4.0\times10^{-3}$ mol dm^{-3}) in $H_2SO_4 = 2.2$ mol dm^{-3} at 50 °C

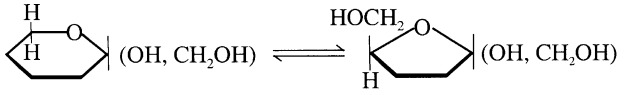
Temperature (°C)	$k_{obs}\times10^5$ (s^{-1})
30	1.9
40	7.6
50	31.9
60	84.4
Parameters	
E_a (kJ mol^{-1})	112
$\Delta H^{\#}$ (kJ mol^{-1})	116
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−301
$\Delta G^{\#}$ (kJ mol^{-1})	213

3.6. Temperature dependence

The kinetic studies were also carried out at different temperatures in the range of 30–60 °C (Table 3). Different activation parameters (E_a, $\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$) were calculated using both the Arrhenius and Eyring equations.

3.7. Mechanism

D-Fructose is known to exist in two forms in solution, for example, pyranoid and furanoid forms.[30] Out of these, only the pyranoid form is claimed to be involved in oxidation reactions.[31] As far as the conformation is concerned, the anomeric-OH in α- and β-fructose are present in axial and equatorial positions, respectively.



α– or β–D–fructopyranose (58%) ⇌ α– or β–D–fructopyranose (42%)

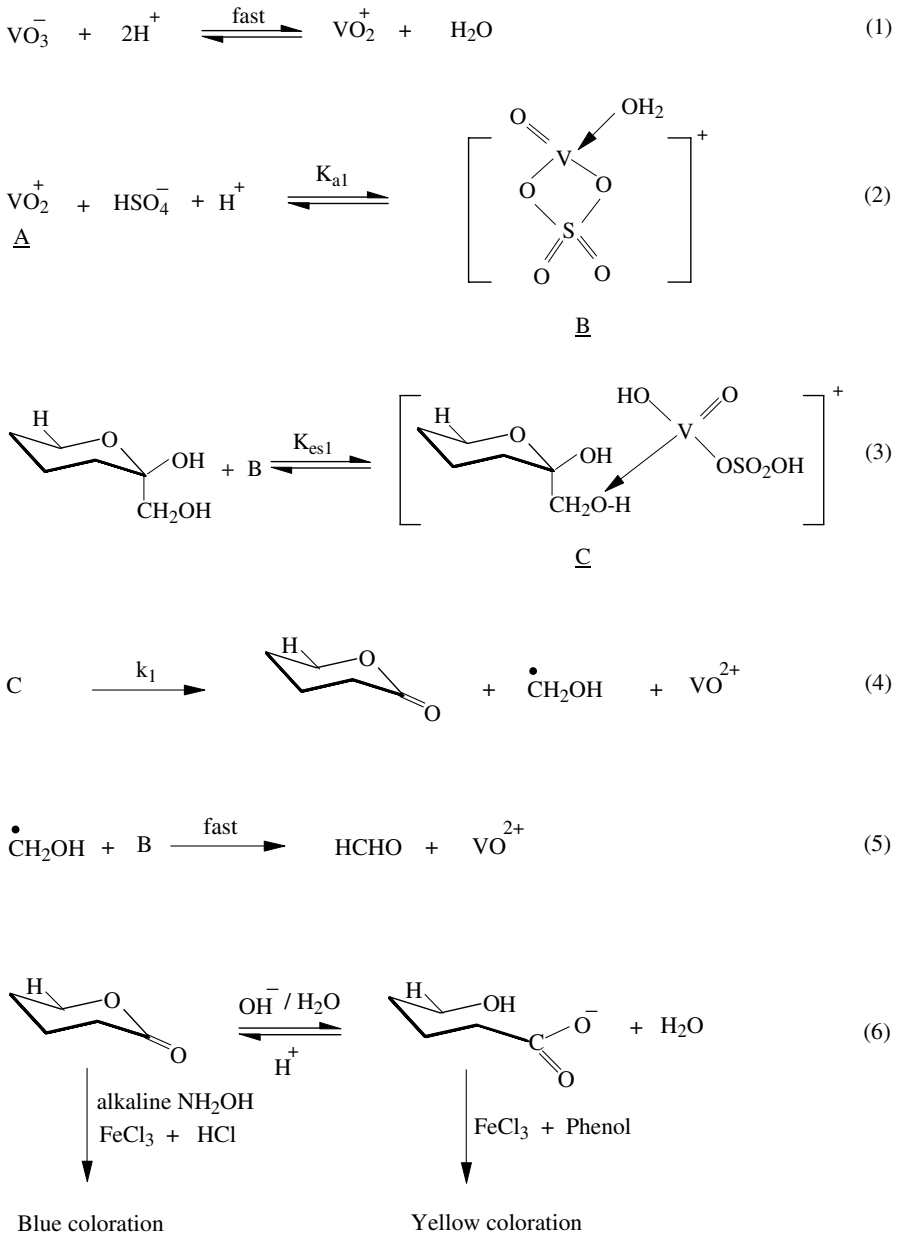
It has also been confirmed that the β-anomer should be more reactive than α-anomer.[31] On the other hand, different types of vanadium(V) species exist in acid–base equilibria,[32,33] which are designated as $(VO{\cdot}H_2O{\cdot}SO_4)^+$, $V(OSO_3H)_3^{2+}$, $V(OH)_3HSO_4^+$ or $VO(OSO_3H)^{2+}$, $(VO_2{\cdot}H_2O{\cdot}H_2SO_4)^+$, and $(VO_2{\cdot}2H_2SO_4)^+$ in the presence of H_2SO_4. As the $[H_2SO_4]$ increases, order with respect to $[H_2SO_4]$ increases, and the percentage of these species may increase. The rate increases steadily with increase in $[H_2SO_4]$; this may be due to the increased formation of the oxidant species with increase in acidity of the reaction mixture. The $(VO_2{\cdot}H_2O{\cdot}H_2SO_4)^+$ and $(VO_2{\cdot}2H_2SO_4)^+$ species do not participate in the redox reaction because we have not observed any rate retardation with increase

in $[SO_4^{2-}]$ at higher acidities (Table 2). Thus, we can assume $(VO{\cdot}H_2O{\cdot}SO_4)^+$ to be the active oxidizing species in the H_2SO_4-catalyzed reaction by vanadium(V). The presence of Michaelis–Menten type of kinetics suggests the possibility of the formation of an intermediate complex between the reactive species of vanadium(V) and D-fructose. Based on the observation recorded above, a probable mechanism may be proposed for the low-acidity region, that is, $[H_2SO_4] = 0.40$–$1.12\,mol\,dm^{-3}$ (Scheme 1).

Vanadium(V) is amphoteric[34] and under our experimental conditions (pH $\leqslant$ 1.0) exists as the bright-yellow pervanadyl ion, VO_2^+. The ion, VO_2^+, which is probably not linear, may be weakly hydrated in the presence of H_2SO_4 as in B. As Michaelis–Menten kinetics is observed, it is assumed that a complex (C) is formed between D-fructose and vanadium(V) (Eq. 3), which may break down unimolecularly in the slow step (Eq. 4). According to Scheme 1, the overall reaction rate is given by Eq. 7.

$$-\frac{d[V(V)]}{dt} = \frac{k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}][V(V)]_T}{\{(1/K_{a1}[H^+][HSO_4^-]) + 1 + K_{es1}[\text{D-fructose}]\}} \quad (7)$$

and



Scheme 1.

$$k_{obs} = \frac{k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}]}{\{(1/K_{a1}[H^+][HSO_4^-]) + 1 + K_{es1}[\text{D-fructose}]\}} \quad (8)$$

The equilibrium in step 2 lies well to the right; hence, the inequality $1 \gg 1/K_{a1}[H^+][HSO_4^-]$ will evidently exist and the rate equation 8 is reduced to Eq. 9, which explains the experimental results, that is, first-order dependence each on $[HSO_4^-]$ and $[H^+]$ and fractional-order dependence on [D-fructose].

$$k_{obs} = \frac{k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}]}{(1 + K_{es1}[\text{D-fructose}])} \quad (9)$$

The inequality $1 \gg K_{es1}$ [D-fructose] is evident at low [D-fructose], and the rate law, Eq. 9, then reduces to Eq. 10, which explains the experimental results obtained at these low concentrations (Fig. 3A). The value of $k_1 K_{es1} K_{a1}$ calculated from the slope of the plot is $3.4 \times 10^{-3}\,\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$.

$$k_{obs} = k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}] \quad (10)$$

The above inequality will be valid in the reverse direction at higher [D-fructose], that is, K_{es1} [D-fructose] $\gg 1$ will hold, and Eq. 9 is reduced to Eq. 11, which

$$k_{obs} = k_1 K_{a1} [H^+][HSO_4^-] \quad (11)$$

clearly explains the zero-order dependence of the reaction on [D-fructose] at higher concentrations. On the other hand, if $[H^+] = 0$, then $k_{obs} = 0$ at low as well as high concentrations of D-fructose.[†] Thus, Eqs. 10 and 11 correspond to two extreme conditions between which the reaction order should vary between unity and zero. The rate law, Eq. 9, which is consistent between the extreme conditions of Eqs. 10 and 11, has been verified by rewriting it as Eq. 12.

$$\frac{1}{k_{obs}} = \frac{1}{k_1 K_{es1} K_{a1} [H^+][HSO_4^-][\text{D-fructose}]} + \frac{1}{k_1 K_{a1} [H^+][HSO_4^-]} \quad (12)$$

According to Eq. 12, the plot of $1/k_{obs}$ versus 1/[D-fructose] should be linear with a positive intercept on the y-axis, and this was found to be so (Fig. 3B). From the slope of such plot, the value of $k_1 K_{es1} K_{a1}$ has been calculated to be $3.37 \times 10^{-3}\,\text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$ at constant $[H^+]$ ($= 2.2\,\text{mol}\,\text{dm}^{-3}$). The value of K_{es1} ($= 2.96\,\text{mol}^{-1}\,\text{dm}^3$) was also calculated using the values of slope and intercept of Figure 3B. In turn, using K_{es1} the value of $k_1 K_{a1}$ has been calculated as $1.14 \times 10^{-3}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$. Also, the value of $k_1 K_{a1} = 1.13 \times 10^{-3}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$ obtained from Eq. 10 is quite close to the above value. This agreement confirms the validity of the rate law, Eq. 9. On the other hand, Eqs. 10 and 11 indicate that k_{obs} becomes zero at $[H^+] = 0.0\,\text{mol}\,\text{dm}^{-3}$—this is confirmed by extrapolation of lower $[H_2SO_4]$ results (Fig. 4) as per the previous observation of first-order dependence in the lower acidity range.

Substituting the values of $k_1 K_{a1}$, K_{es1}, $[H^+]$, and [D-fructose] in Eq. 9, rate constants, k_{cal} have been calculated in various kinetic runs. For providing supporting evidence of the proposed mechanism and confirming the Michaelis–Menten reciprocal relationship (vide supra) these values compare well with those determined experimentally (Table 4).

In the entire range of $[H_2SO_4]$, the oxidation reaction of D-fructose by vanadium(V) ion occurs in two kinetically distinguishable steps. The first one is a fairly rapid vanadium(V)–D-fructose complex (C), and the second step is a slower rate-determining reaction to form the product. In solutions of high $[H_2SO_4]$, however, the oxidation is not so simple as Eqs. 3 and 4 indicate. As Table 1 and Figure 4 show, the rate of reaction markedly increases at high acidities. The most widely used way of explaining the change in the rate with acidities has been the Zucker–Hammett hypothesis,[35] where $\log k_{obs}$ is related to either $-H_0$, the Hammett acidity, or log[HX]. Sulfuric acid can be assumed to be a strong and monobasic acid throughout the range employed. The total rate constant, k_{obs}, can be divided into two portions, k_0, a hydrogen-independent value obtained by extrapolating the measured rate at $[H^+] = 0.0\,\text{mol}\,\text{dm}^{-3}$, and k_1, an acid-dependent path, such that $k_{obs} = k_0 + k_1$. To our knowledge, such dependence has not been hitherto reported in the oxidation of carbohydrates by vanadium(V).

As deviations from linearity in the plots of log(absorbance) versus time (Fig. 2) became evident at increased $[H_2SO_4]$ (0.76–2.92 $\text{mol}\,\text{dm}^{-3}$), one possibility is that the oxidation rate of one of the oxidation products of D-fructose becomes perceptible and shows up at higher $[H_2SO_4]$. A rate constant assigned to the second step oxidation (autoacceleration) cannot be a true value of the oxidation of D-fructose. It may be a mixture of the rates of D-fructose and its oxidation products (lactone and corresponding aldonic acid). Under this type of situation, the final oxidation of D-fructose has the following sequence

$$\delta\text{- or } \gamma\text{-lactone} + V(V) \rightarrow \cdots \rightarrow V(IV) + RCOCOOH$$
$$RCOCOOH + V(V) \rightarrow \cdots \rightarrow V(IV) + CO_2 + \text{other products}$$

Finally, we can state that when an excess of vanadium(V) over D-fructose is used, further oxidation of the intermediate(s) occurs to yield carbon dioxide and formic acid[36,37] as the final products.

The large negative value of $\Delta S^{\#}$ indicates the existence of compact activated state stabilized by a strong

[†] We are thankful to one of the referees for suggesting this point.

Table 4. Comparison of k_{obs} and k_{cal} values for the oxidation of D-fructose by vanadium(V)[a]

10^3 [D-Fructose] (mol dm^{-3})	[H_2SO_4] (mol dm^{-3})	$k_{obs} \times 10^5$ (s^{-1})	$k_{cal} \times 10^5$ [b] (s^{-1})	$(k_{obs} - k_{cal})/k_{obs}$
10.0	2.20	6.5	7.2	−0.10
20.0		13.4	14.0	−0.04
30.0		21.1	20.4	+0.03
40.0		26.8	26.5	+0.01
50.0		31.9	32.3	−0.01
60.0		36.4	37.8	−0.03
70.0		40.3	43.0	−0.06
50.0	0.40	5.7	5.5	+0.03
	0.76	9.5	10.5	−0.10
	1.12	13.4	15.5	−0.15
	1.48	21.1	20.5	+0.02
	1.84	26.8	25.5	+0.04
	2.20	31.9	30.5	+0.04

[a] Conditions were same as given in Table 1.
[b] Calculated by using Eq. 9.

hydrogen bonding and large solvation in the electron-transfer step. Although negative entropy of activation is a characteristic of rate limiting formation of an intermediate complex, fairly high positive value of enthalpy of activation ($\Delta H^{\#}$) also indicates that the transition state is highly solvated.

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