

# Vanadium(V). Part XVI.\* Oxidation of D-Glucose and D-Mannose with Vanadium(V). A Comparative Kinetic Approach\*\*

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The kinetics of the oxidation of D-glucose and D-mannose with vanadium(V) were studied in aqueous perchloric acid solutions and the results compared with corresponding data for D-fructose. The reactions are of first order with respect to the carbohydrate concentration, but the values of the rate constant for fructose increase slightly, while those for mannose decrease slightly with increasing vanadium(V) concentration. At constant ionic strength the reaction for mannose like glucose is of second order but that for fructose of third order with respect to the hydrogen ion concentration. All the oxidations are subject to almost similar positive salt effects, but their susceptibilities to hydrogen sulfate ion catalysis are different. The enthalpies of activation are more or less similar and, thermodynamically, the rate differences arise mainly from different entropies of activation. At least a major part of the oxidations of the monosaccharides are believed to proceed through their open-chain forms. Possible mechanisms involving carbon-carbon bond fission for glucose and mannose to arabinose and carbon-hydrogen bond fission for fructose to dicarbonyl-compounds as the first reaction products have been suggested.

In Part XII<sup>2</sup> of this series we reported rate constants, salt and temperature effects as well as hydrogen ion and hydrogen sulfate ion catalysis for the oxidation of a ketohexose, D-fructose, with vanadium(V). Kumar & Mehrotra<sup>3</sup> have studied the kinetics of oxidation of some aldoses in sulfuric and perchloric acid solutions and Pati & Panda<sup>4</sup> in sulfuric acid solutions. However, not all the interesting effects have been studied in experimental conditions comparable to our experiments on fructose. Therefore, continuing our investigations on monosaccharides, we studied kinetically the oxidation of two epimeric aldohexoses, glucose and mannose, in order to find out how these three monosaccharides differ

in their kinetic features. The oxidation of monosaccharides is known to be subject to both hydrogen ion and hydrogen sulfate ion catalysis (e.g. Ref. 2, 3). As the reactions readily take place in the presence of perchloric acid, these solutions, as in our studies on fructose, were used throughout the present investigation to minimize the number of different catalyzing species. In this way more detailed information was expected to be obtained on the studied oxidations.

## Experimental

Ammonium metavanadate was a guaranteed *pro analysi* reagent from E. Merck AG, Darmstadt, FRG. D-glucose was an *Aristar* ultra-pure chemical from BDH Chemical Ltd., Poole, England and D-mannose a reagent for biochemistry and microbiology from E. Merck AG. They were used without further purification.

\*Part XV, See Ref. 1.

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The reaction took place in aqueous solutions of perchloric acid in the concentration range 0 to 2.9 M and (in most cases) at 50 °C. The extent was followed by analyzing for vanadium(V) as described in Ref. 5.

The reaction products were analyzed by GC-MS using chemical ionization by isobutane.<sup>6</sup> The compounds were analyzed as their O-methoxime trimethylsilyl derivatives.<sup>7</sup> They were separated at 40–250 °C on a 25-meter fused silica capillary with a diameter of 0.32 mm. The wall was coated with OV-1 methyl silicone 0.2 µm thick. The mass spectra were run with a Kratos MS80RF autoconsole mass spectrometer. The capillary of the gas chromatograph was coupled directly to the ion source of the mass spectrometer with a silica capillary.

Glucose and mannose were found to oxidize at first to arabinose, which then reacts further to

erythrose, which reacts to glyceraldehyde. No dicarbonyl compounds were detected. From the reaction products of fructose, erythrose, glyceraldehyde and dicarbonyl compounds were analyzed, but no arabinose was detected. A more comprehensive study of dicarbonyl compounds was not possible, as the reaction proceeded too far during the preparation of the samples.

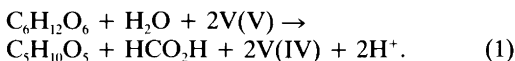
## Results

The kinetic results obtained in this study refer to the reactions in which glucose and mannose are oxidized to arabinose as the first reaction products and two equivalents of vanadium(V) are used per mole of formic acid produced.<sup>3,4</sup> Vanadium is reduced to V(IV), which is seen from the increase of the absorption at 765 nm.<sup>8</sup> All the rate constants were determined under pseudo first or-

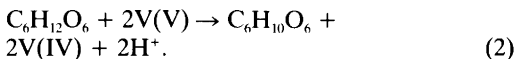
Table 1. Variation of the rate constant with the concentration of carbohydrate and vanadium(V) for the oxidations of D-glucose and D-mannose with vanadium(V) at 50 °C in water.  $[\text{HClO}_4] = 1.4561 \text{ M}$ .

$[\text{V(V)}]/\text{M}$	$[\text{C}_6\text{H}_{12}\text{O}_6]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$r$	$(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/\text{M}^{-1} \text{ s}^{-1}$
<b>Glucose</b>				
0.0198	0.1998	$(6.75 \pm 0.31) \times 10^{-5}$	0.9958	$(3.38 \pm 0.16) \times 10^{-4}$
0.0198	0.3903	$(1.04 \pm 0.02) \times 10^{-4}$	0.9993	$(2.65 \pm 0.05) \times 10^{-4}$
0.0198	0.5998	$(1.75 \pm 0.06) \times 10^{-4}$	0.9982	$(2.92 \pm 0.17) \times 10^{-4}$
0.0198	0.9898	$(2.86 \pm 0.06) \times 10^{-4}$	0.9991	$(2.89 \pm 0.06) \times 10^{-4}$
0.0020	0.3903	$(8.45 \pm 0.29) \times 10^{-5}$	0.9976	$(2.17 \pm 0.08) \times 10^{-4}$
0.0025	0.3903	$(8.42 \pm 0.35) \times 10^{-5}$	0.9962	$(2.16 \pm 0.09) \times 10^{-4}$
0.0033	0.3903	$(8.69 \pm 0.11) \times 10^{-5}$	0.9997	$(2.23 \pm 0.03) \times 10^{-4}$
0.0049	0.3903	$(9.00 \pm 0.49) \times 10^{-5}$	0.9940	$(2.31 \pm 0.13) \times 10^{-4}$
0.0099	0.3903	$(9.18 \pm 0.09) \times 10^{-5}$	0.9998	$(2.35 \pm 0.02) \times 10^{-4}$
0.0198	0.3903	$(1.04 \pm 0.02) \times 10^{-4}$	0.9993	$(2.65 \pm 0.05) \times 10^{-4}$
0.0396	0.3903	$(1.13 \pm 0.02) \times 10^{-4}$	0.9995	$(2.90 \pm 0.04) \times 10^{-4}$
0.0594	0.3903	$(1.26 \pm 0.03) \times 10^{-4}$	0.9991	$(3.22 \pm 0.07) \times 10^{-4}$
<b>Mannose</b>				
0.0198	0.2990	$(7.80 \pm 0.21) \times 10^{-5}$	0.9986	$(2.61 \pm 0.07) \times 10^{-4}$
0.0198	0.4945	$(1.32 \pm 0.01) \times 10^{-4}$	0.9999	$(2.68 \pm 0.03) \times 10^{-4}$
0.0198	0.6918	$(1.91 \pm 0.01) \times 10^{-4}$	0.9997	$(2.76 \pm 0.03) \times 10^{-4}$
0.0198	0.8968	$(2.47 \pm 0.03) \times 10^{-4}$	0.9996	$(2.75 \pm 0.04) \times 10^{-4}$
0.0020	0.4945	$(4.05 \pm 0.26) \times 10^{-4}$	0.9940	$(8.20 \pm 0.52) \times 10^{-4}$
0.0024	0.4945	$(3.72 \pm 0.37) \times 10^{-4}$	0.9900	$(7.52 \pm 0.76) \times 10^{-4}$
0.0026	0.4945	$(3.30 \pm 0.28) \times 10^{-4}$	0.9896	$(6.67 \pm 0.56) \times 10^{-4}$
0.0031	0.4945	$(2.85 \pm 0.22) \times 10^{-4}$	0.9915	$(5.76 \pm 0.44) \times 10^{-4}$
0.0040	0.4945	$(1.99 \pm 0.06) \times 10^{-4}$	0.9986	$(4.03 \pm 0.12) \times 10^{-4}$
0.0059	0.4945	$(1.65 \pm 0.02) \times 10^{-4}$	0.9998	$(3.33 \pm 0.04) \times 10^{-4}$
0.0099	0.4945	$(1.51 \pm 0.01) \times 10^{-4}$	1.0000	$(3.05 \pm 0.01) \times 10^{-4}$
0.0198	0.4945	$(1.32 \pm 0.01) \times 10^{-4}$	0.9999	$(2.68 \pm 0.03) \times 10^{-4}$

der conditions with carbohydrate in excess, and for glucose and mannose they refer to the reaction



For fructose the corresponding reaction is<sup>2</sup>



The observed rate constant  $k_{\text{obs}} = -\text{dln}[\text{V(V)}]/\text{dt}$  was found to vary linearly with the carbohydrate concentration (Table 1). Our results agree well with the values  $3.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  and  $2.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  obtained earlier using a different analytical method in 2 M perchloric acid at 50°C for glucose and mannose, respectively.<sup>3</sup>

In earlier experiments with fructose we noted that although in individual runs vanadium(V) disappears by first order kinetics, the rate constant increases slightly with increasing vanadium(V) concentration.<sup>2</sup> Moreover,  $(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])^{-1}$  is linearly correlated to  $[\text{V(V)}]^{-1}$  with a slope of  $19.2 \text{ M}^2 \text{ s}$ . For glucose it should be certain that there is no influence except at high vanadium concentration as shown in Fig. 1.

For mannose, in contrast to the above-mentioned saccharides, the rate constant decreases with increasing vanadium(V) concentration. This decrease in 0.4945 M mannose solution in the range 0.002 M to 0.020 M V(V) follows the equation

$$\begin{aligned} (k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1} = \\ (1.29 \pm 0.10) \times 10^{-6} \times [\text{V(V)}]^{-1}/M^{-1} + \\ (1.58 \pm 0.33) \times 10^{-4} \end{aligned} \quad (3)$$

with a correlation coefficient of 0.9807.

All the three oxidations show positive salt effects (Table 2). The addition of sodium perchlorate accelerates the rate of the oxidation of glucose in 0.9715 M perchloric acid in accordance with the equation

$$\begin{aligned} \log\{(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1}\} = \\ (1.46 \pm 0.05) \times 10^{-1} \times [\text{NaClO}_4]/M - \\ (3.69 \pm 0.01) \end{aligned} \quad (4)$$

with a correlation coefficient of 0.9986. This is very similar to the effect observed for fructose,

202

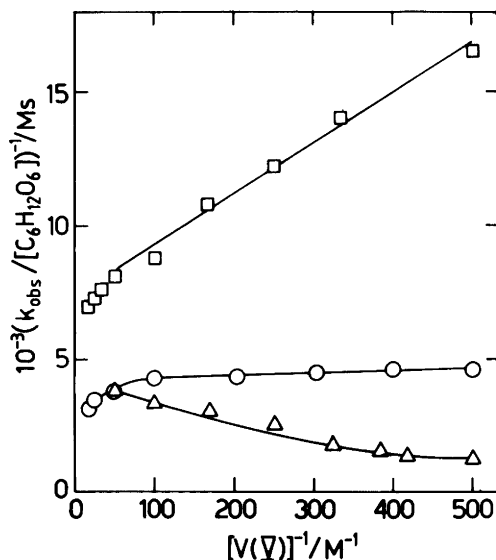


Fig. 1. Reciprocal plot for the reactions of D-glucose, D-mannose and D-fructose with vanadium(V).  $\circ$  D-glucose in 1.456 M perchloric acid at 50°C;  $\square$  D-fructose in 0.981 M perchloric acid at 25°C, ref. 2;  $\triangle$  D-mannose in 1.456 M perchloric acid at 50°C.

the corresponding slope being  $1.49 \times 10^{-1}$ .<sup>2</sup> For mannose in 0.4945 M perchloric acid the rate follows the equation

$$\begin{aligned} \log\{(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1}\} = \\ (9.91 \pm 0.32) \times 10^{-2} \times [\text{NaClO}_4]/M - \\ (3.78 \pm 0.01) \end{aligned} \quad (5)$$

with a correlation coefficient of 0.9984.

The oxidation of mannose, similar to that of fructose, is subject to hydrogen sulfate ion catalysis. At a constant ionic strength maintained by variation of the concentrations of sodium perchlorate and hydrogen sulfate, the increase of the rate constant is linearly proportional to the hydrogen sulfate concentration:

$$\begin{aligned} (k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1} = \\ (9.08 \pm 0.38) \times 10^{-5} \times [\text{HSO}_4^-]/M + \\ (4.27 \pm 0.09) \end{aligned} \quad (6)$$

with a correlation coefficient of 0.9974. For fructose the corresponding slope is  $1.60 \times 10^{-3}$ .<sup>2</sup> For glucose the values in Table 2 do not imply any such catalysis.

Table 2. Variation of the rate constant with the concentration of sodium perchlorate and hydrogen sulfate for the oxidations of D-glucose and D-mannose with vanadium(V) at 50°C in water.  $[V(V)] = 0.0198 \text{ M}$ .

$[\text{NaClO}_4]/\text{M}$	$[\text{NaHSO}_4]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$r$	$k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6]/\text{M}^{-1} \text{ s}^{-1}$
Glucose, $[\text{C}_6\text{H}_{12}\text{O}_6] = 0.3930 \text{ M}$ , $[\text{HClO}_4] = 0.9715 \text{ M}$				
–	–	$(8.19 \pm 0.13) \times 10^{-5}$	0.9995	$(2.08 \pm 0.03) \times 10^{-4}$
0.9898	–	$(1.13 \pm 0.02) \times 10^{-4}$	0.9991	$(2.88 \pm 0.06) \times 10^{-4}$
1.9796	–	$(1.50 \pm 0.01) \times 10^{-4}$	0.9998	$(3.81 \pm 0.04) \times 10^{-4}$
2.9694	–	$(2.16 \pm 0.04) \times 10^{-4}$	0.9994	$(5.49 \pm 0.10) \times 10^{-4}$
3.9592	–	$(3.13 \pm 0.01) \times 10^{-4}$	1.0000	$(7.97 \pm 0.03) \times 10^{-4}$
–	3.9595	$(3.29 \pm 0.06) \times 10^{-4}$	0.9994	$(8.38 \pm 0.15) \times 10^{-4}$
0.9898	2.9696	$(2.93 \pm 0.04) \times 10^{-4}$	0.9996	$(7.45 \pm 0.11) \times 10^{-4}$
1.9796	1.9796	$(2.83 \pm 0.06) \times 10^{-4}$	0.9990	$(7.20 \pm 0.16) \times 10^{-4}$
2.9695	0.9897	$(2.76 \pm 0.02) \times 10^{-4}$	0.9999	$(7.02 \pm 0.05) \times 10^{-4}$
3.9592	–	$(3.13 \pm 0.01) \times 10^{-4}$	1.0000	$(7.97 \pm 0.03) \times 10^{-4}$
Mannose, $[\text{C}_6\text{H}_{12}\text{O}_6] = 0.4945 \text{ M}$ , $[\text{HClO}_4] = 0.4854 \text{ M}$				
–	–	$(8.38 \pm 0.12) \times 10^{-5}$	0.9996	$(1.69 \pm 0.02) \times 10^{-4}$
0.9898	–	$(1.02 \pm 0.02) \times 10^{-4}$	0.9993	$(2.06 \pm 0.04) \times 10^{-4}$
1.9796	–	$(1.26 \pm 0.02) \times 10^{-4}$	0.9997	$(2.56 \pm 0.03) \times 10^{-4}$
2.9694	–	$(1.59 \pm 0.01) \times 10^{-4}$	0.9999	$(3.21 \pm 0.02) \times 10^{-4}$
3.9593	–	$(2.07 \pm 0.02) \times 10^{-4}$	0.9999	$(4.19 \pm 0.03) \times 10^{-4}$
–	3.9595	$(3.88 \pm 0.08) \times 10^{-4}$	0.9991	$(7.85 \pm 0.16) \times 10^{-4}$
0.9898	2.9696	$(3.40 \pm 0.03) \times 10^{-4}$	0.9999	$(6.88 \pm 0.05) \times 10^{-4}$
1.9796	1.9798	$(3.08 \pm 0.05) \times 10^{-4}$	0.9994	$(6.23 \pm 0.11) \times 10^{-4}$
2.9694	0.9898	$(2.58 \pm 0.04) \times 10^{-4}$	0.9994	$(5.21 \pm 0.09) \times 10^{-4}$
3.9593	–	$(2.07 \pm 0.02) \times 10^{-4}$	0.9999	$(4.19 \pm 0.03) \times 10^{-4}$

The effect of the acid concentration on the oxidation of mannose was studied by partially neutralizing the perchloric acid solution with sodium hydroxide solution to maintain a constant ionic strength. The results are presented in Table 3. The plot of the rate constant on different powers of the acid concentration is most linear at the second power and the dependence follows the equation

$$(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1} = (2.45 \pm 0.18) \times 10^{-5} \times [\text{HClO}_4]^2/M^2 + (4.29 \pm 0.09) \times 10^{-4} \quad (7)$$

with a correlation coefficient of 0.9920. According to equation (7) the reaction seems to proceed quite well even in the absence of perchloric acid as the acid-dependent term reaches the same level as the constant term at about 4 M perchloric

Table 3. Variation of the rate constant with the concentration of perchloric acid at a constant ionic strength for the oxidation of D-mannose with vanadium(V) at 50°C in water.  $[V(V)] = 0.0198 \text{ M}$ ,  $[\text{C}_6\text{H}_{12}\text{O}_6] = 0.3093 \text{ M}$ ,  $I = 2.91 \text{ M}$ .

$[\text{HClO}_4]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$r$	$(k_{\text{obs}}/[\text{C}_6\text{H}_{12}\text{O}_6])/M^{-1} \text{ s}^{-1}$
0.972	$(1.38 \pm 0.01) \times 10^{-4}$	0.9999	$(4.47 \pm 0.04) \times 10^{-4}$
1.734	$(1.56 \pm 0.02) \times 10^{-4}$	0.9996	$(5.04 \pm 0.07) \times 10^{-4}$
1.937	$(1.60 \pm 0.01) \times 10^{-4}$	0.9999	$(5.19 \pm 0.03) \times 10^{-4}$
2.379	$(1.80 \pm 0.02) \times 10^{-4}$	0.9997	$(5.82 \pm 0.08) \times 10^{-4}$
2.912	$(1.94 \pm 0.02) \times 10^{-4}$	0.9998	$(6.28 \pm 0.07) \times 10^{-4}$

Table 4. Effect of temperature on the rate constant of the oxidations of D-glucose and D-mannose with vanadium(V) in water.  $[V(V)] = 0.0200$  M,  $[HClO_4] = 1.471$  M at 25°C.

$t/^\circ\text{C}$	$[C_6H_{12}O_6]/\text{M}$	$k_{\text{obs}}/\text{s}^{-1}$	$r$	$(k_{\text{obs}}/[C_6H_{12}O_6])/\text{M}^{-1} \text{s}^{-1}$
Glucose				
25	1.0000	$(1.05 \pm 0.02) \times 10^{-5}$	0.9987	$(1.05 \pm 0.02) \times 10^{-5}$
35	0.9958	$(3.96 \pm 0.07) \times 10^{-5}$	0.9993	$(3.97 \pm 0.07) \times 10^{-5}$
45	0.9920	$(1.50 \pm 0.03) \times 10^{-4}$	0.9994	$(1.51 \pm 0.03) \times 10^{-4}$
50	0.9898	$(2.86 \pm 0.06) \times 10^{-4}$	0.9991	$(2.89 \pm 0.06) \times 10^{-4}$
Mannose				
25	0.4996	$(7.49 \pm 0.64) \times 10^{-6}$	0.9859	$(1.50 \pm 0.13) \times 10^{-5}$
35	0.4975	$(2.28 \pm 0.03) \times 10^{-5}$	0.9998	$(4.58 \pm 0.01) \times 10^{-5}$
45	0.4956	$(7.46 \pm 0.04) \times 10^{-5}$	0.9999	$(1.51 \pm 0.01) \times 10^{-4}$
50	0.4945	$(1.32 \pm 0.01) \times 10^{-4}$	0.9999	$(2.68 \pm 0.03) \times 10^{-4}$

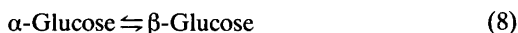
acid. Kumar and Mehrotra<sup>3</sup> have also reported linear correlation between the rate constant of glucose and mannose and the square of the hydrogen ion concentration in perchloric and sulfuric acid solutions. At higher ionic strength of 6 M we calculated from their data in perchloric acid solutions the values of  $1.7 \times 10^{-4}$  and  $1.8 \times 10^{-4}$  for the corresponding slope for glucose and mannose, respectively.

The effect of temperature on the rate of the oxidation of glucose and mannose is seen in Table 4. The values of  $103.7 \pm 1.4$  kJ mol<sup>-1</sup> and  $90.0 \pm 2.2$  kJ mol<sup>-1</sup> for the enthalpy of activation and the values of  $7.3 \pm 4.5$  J K<sup>-1</sup> mol<sup>-1</sup> and  $-35.8 \pm 7.1$  J K<sup>-1</sup> mol<sup>-1</sup> for the entropy of activation have been evaluated from  $k_{\text{obs}}/[C_6H_{12}O_6]$  for the oxidation of glucose and mannose, respectively. The corresponding values for fructose are  $104.5 \pm 0.2$  kJ mol<sup>-1</sup> and  $26.1 \pm 0.7$  J K<sup>-1</sup> mol<sup>-1</sup>.<sup>2</sup>

## Discussion

Glucose and mannose are polyhydroxyaldehydes and fructose a polyhydroxyketone which have the same configuration on C<sub>(3)</sub>, C<sub>(4)</sub> and C<sub>(5)</sub>. Glucose and mannose are identical except for the configuration at C<sub>(2)</sub>. On the basis of the different kinetic features presented in the results section, it is clear that the conversion *via* the enol form does not interfere in acidic solutions.

For the reversible pseudo first order process



the equilibrium constant  $K = k_d/K_p$  and the observed rate constant  $k_{\text{obs}} = k_\alpha + k_\beta = k_o + k_H \times [H^+] = 9.90 \times 10^{-4} + 3.28 \times 10^{-2} \times [H^+] = 3.38 \times 10^{-2} \text{ s}^{-1}$  in 1 M perchloric acid at 35.21°C.<sup>9</sup> Comparing this value with the values of  $k_{\text{obs}}$  for the oxidations in Tables 1–4, one can see that in our experimental conditions mutarotation is fast compared to the oxidation. The equilibrium also involves  $\gamma$ -glucose, the aldehyde form. The amount of this open-chain sugar has been estimated from polarographic studies to be 0.024% for D-glucose and 0.064% for D-mannose at pH 7.0 at 25°C.<sup>10</sup> The ratio of the  $\alpha$ - and  $\beta$ -pyranose forms has been estimated from NMR studies at 30°C to be 36:64 and 64:36 for glucose and mannose, respectively.<sup>11</sup>

Kinetically, monosaccharides can be considered polyols in which the reactivities of the alcohol groups have been affected by the carbonyl group. It can be approximated that under identical experimental conditions the ratio of the rate constants of hydroxyacetone and ethanol is about  $10^5$ .<sup>12,13</sup> The carbonyl group is thus of notable importance for both the reaction rate and the site.

It is interesting to compare the rate constant of  $2.89 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  for glucose and that of  $2.68 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  for mannose in 1.46 M perchloric acid at 50°C (Table 4) with the rate constants of  $1.8 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  for glycol and  $5.3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  for glycerol in similar experimental conditions<sup>14</sup> on the one hand and with the comparable rate constant for hydroxyacetone, which can be estimated to be  $1.5 \times 10^{-1} \text{ s}^{-1}$ , on the other hand.<sup>12</sup> A direct comparison would predict much higher

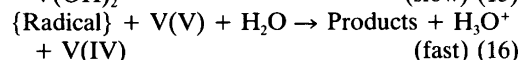
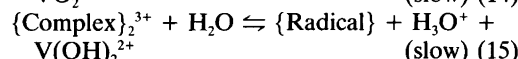
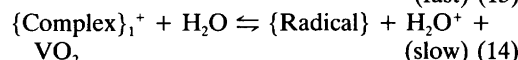
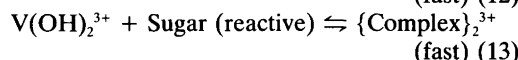
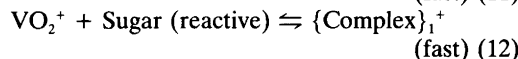
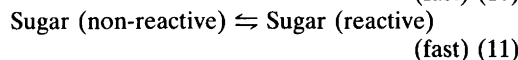
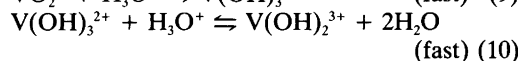
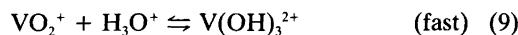
values of the rate constants for sugars than were observed. We consider the low apparent rates for monosaccharides to provide strong evidence suggesting that at least a major part, if not all, of the oxidations proceed through their open-chain forms. Taking the fastness of the mutarotation process into account, it is likely that the slow apparent rates arise from the fast pre-equilibria involving  $\gamma$ -forms. The ratios of the rate constants of sugars to that of hydroxyacetone approximate in simple form the values for the percentages of  $\gamma$ -forms 0.14 % for glucose and 0.13 % for mannose in these acidic solutions at 50 °C. These figures are surprisingly well in accordance with the above-mentioned numbers obtained from polarographic studies in neutral solutions at 25 °C.<sup>10</sup> For fructose the corresponding percentage can be calculated to be 2.2 % at 50 °C in accordance with the assumption that they represent the approximate relative amounts of the open-chain forms.<sup>2</sup>

All three monosaccharides show very similar salt effects, but their susceptibilities to the variation of the concentrations of vanadium(V) and hydrogen sulfate ion differ. This shows that complex formation is sensitive to configurational phenomena. Therefore, the kind of comparisons of these effects made for simpler alcohols<sup>15</sup> and deductions of reaction type are not suitable for carbohydrates.

The oxidation is acid-catalyzed and the dependence of the rate constant is on the square of the acid concentration. Although different correlations with acidity, both on  $H^+$ - and  $h_0$ -scales, have been presented, a linear dependence on the second power of the acid concentration has been found often, e.g. for butane-1,3-diol,<sup>16</sup> glycerol,<sup>17</sup> triethanolammonium ion<sup>18</sup> and some aldoses.<sup>3</sup> As vanadium(V) exists in slightly acidic solutions as  $VO_2^+$ ,  $pK_a = 3.70$  at 25 °C<sup>19</sup> and at higher acid concentrations as  $V(OH)_3^{2+}$  and  $V(OH)_2^{3+}$ ,<sup>20</sup> the observed dependencies (this work, Ref. 3) imply that for glucose and mannose in perchloric acid solutions the main oxidizing species is  $V(OH)_2^{3+}$ . It should also be pointed out that Madic *et al.*<sup>21</sup> recently reported having found the reaction  $2VO_2^+ + 2H^+ \rightleftharpoons V_2O_5^{4+} + H_2O$  to occur in concentrated perchloric acid.

Taking into consideration all the above-mentioned aspects, the following mechanism is assumed in a simplified form to describe the oxidation of glucose and mannose in perchloric acid solutions where the order of the reaction with re-

spect to the hydrogen ion concentration is two and uncatalyzed reactions also proceed:



This mechanism leads to the rate law

$$\text{rate} = (k_{14}K_{12}K_{11} + k_{15}K_{13}K_{11}K_{10}K_9) [H_3O^+]^2 [VO_2^+] [\text{Sugar}] \quad (17)$$

For mannose the rate constant decreases with increasing vanadium(V) concentration according to equation (3). One possible explanation for this correlation takes into account any pre-equilibrium which is independent of the concentration of vanadium(V) and slow enough to be rate-controlling. In the scheme (9)–(16), reaction (11) presents the reaction which competes with reaction (15). At a constant hydrogen ion concentration

$$\text{rate} = k_{11}[\text{Sugar}] + k_{app}[V(V)][\text{Sugar}] \quad (18)$$

$$= \left[ \frac{k_{11}}{[V(V)]} + k_{app} \right] [V(V)][\text{Sugar}] \quad (19)$$

in which  $k_{app}$  is the expression in parentheses in equation (17). In the equation (3) the slope =  $k_{11}/[\text{Sugar}] = 1.29 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  and therefore  $k_{11} = 6.0 \times 10^{-7} \text{ s}^{-1}$ . The formation of an open-chain form from cyclic mannoses can be assumed, on the basis of the mutarotation rates,<sup>22</sup> to be faster as are also both the hydration and the dehydration of the aldehyde group.<sup>23</sup> Therefore,  $k_{11}$ , if real, must include conformational rates and/or equilibria. The change of order from 0 to  $-1$  with decreasing vanadium(V) concentration is represented in Fig. 2.

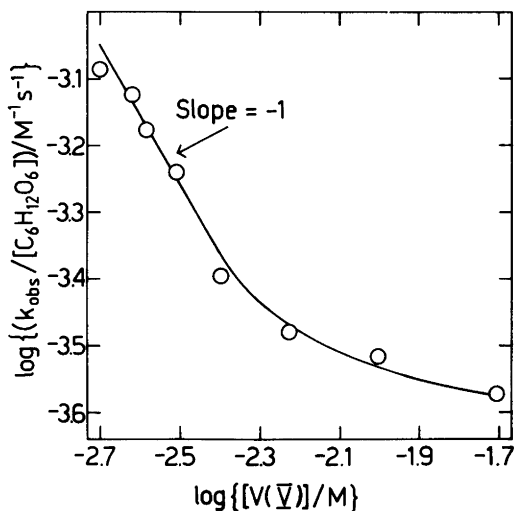


Fig. 2. Dependence of the logarithm of the second order rate constant of the oxidation of D-mannose with vanadium(V) on the logarithm of the concentration of vanadium(V) at constant perchloric acid and D-mannose concentrations.

The mechanism (9)–(16) is, in principle, also suitable for fructose.<sup>2</sup> This monosaccharide is, however, assumed to react in a protonated form with the assistance of an extra vanadium(V) species via carbon-hydrogen bond fission in the rate-determining stage.

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