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COMMUNICATION

VANADIUM(V). PART XXI.¹ A COMPARISON OF THE RATES OF OXIDATION OF MONOSACCHARIDES AND SELECTED MODEL COMPOUNDS WITH VANADIUM(V)²

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In earlier studies on the oxidation of hydroxylic compounds with vanadium(V), we have measured the rates of the oxidation of some aldohexoses,³ a ketohexose⁴ and aldopentoses⁵ and of the model compounds acetoin⁶ and hydroxyacetone.⁷ Continuing this work, we investigated the kinetics of the oxidation of D-galactose, L-sorbose, D-gluconic acid and 1,3-dihydroxyacetone, and now in the present communication report the rate constants for all the monosaccharides and model compounds we have studied, for the same experimental conditions. The data allow both a comparison of the reactivities and an estimation of the amounts of the open-chain forms of the compounds.

The details of the kinetic experiments have been described earlier.^{3,4} The kinetic data for the compounds in all cases include the dependence of the rate constant upon the concentration of perchloric acid, the ionic strength and temperature. Therefore, despite the great differences in reactivity of the compounds the rate constants can be interpolated to the same experimental conditions. The results are shown in Table 1.

The rate constants in Table 1 refer to reactions in which the compounds are oxidized to their first oxidation products. Accordingly, the results reflect the structural features that influence the reactivity

Table 1. The Rate Constants for the Oxidation of Monosaccharides and Selected Model Compounds with Vanadium(V) in Water. $[\text{HClO}_4] = I = 1.471 \text{ M}$ at 25°C .

Compound	$k_2^{25} / \text{M}^{-1} \text{s}^{-1}$ a	k_{rel}^{25} b	$k_2^{50} / \text{M}^{-1} \text{s}^{-1}$ a	k_{rel}^{50} b	Ref.
D-Galactose	2.52×10^{-5}	2.40	6.29×10^{-4}	2.18	This work
D-Glucose	1.05×10^{-5}	1.00	2.89×10^{-4}	1.00	3
D-Mannose	1.50×10^{-5}	1.43	2.68×10^{-4}	0.93	3
D-Fructose	2.70×10^{-4}	25.7	7.63×10^{-3}	26.4	4
L-Sorbose	3.52×10^{-4}	33.5	1.09×10^{-2}	37.7	This work
L-Arabinose	6.76×10^{-5}	6.44	1.68×10^{-3}	5.81	5
D-Ribose	9.52×10^{-5}	9.09	1.88×10^{-3}	6.51	5
D-Xylose	9.28×10^{-5}	8.84	2.25×10^{-3}	7.79	5
D-Gluconic acid	2.13×10^{-3}	203	2.85×10^{-2}	98.6	This work
Hydroxyacetone	1.93×10^{-2}	1840	1.52×10^{-1}	526	7
Dihydroxyacetone	1.53×10^{-2}	1460	1.61×10^{-1}	557	This work
Acetoin	2.61×10^{-2}	2490	2.02×10^{-1}	699	6
D-Glucitol	6.00×10^{-6}	0.57	1.12×10^{-4}	0.39	8

a. The second order rate constant at 25°C and at 50°C .

b. The relative rate constant $k_2(\text{compd})/k_2(\text{glucose})$ at 25°C and at 50°C .

of the compounds, features such as their existence in solution in ring or open-chain forms.

In our acidic experimental conditions, mutarotation is much faster than oxidation,^{3,9} so that the solutions of monosaccharides being oxidized will contain, in equilibrium, the open-chain form as well as the pyranose and furanose forms. Table 1 shows the reactivity of a compound like hydroxyacetone to be more than three thousand times as great as that of glucitol. In the oxidation of alcohols by vanadium(V), the carbon radical is formed by hydrogen atom transfer in the

rate-determining step.³⁻⁷ The carbonyl group encourages the formation of this radical by resonance, and so facilitates the oxidation of monosaccharides and oxoalcohols. Likewise allylic alcohols oxidizes also much more easily than their saturated analogues.¹⁰

We have earlier suggested that at least a major part, if not all, of the oxidations of the monosaccharides proceed through their open-chain forms and involve a C-H bond fission.³ The same conclusion has been drawn earlier by Kumar and Mehrotra¹¹ and Haldorsen.¹² From Table 1, the reactivity order is ketohexoses aldopentoses aldohexoses. In the case of the three model compounds and gluconic acid, the values of k_{rel} are markedly different at 25 °C and 50 °C. Because these compounds exist in solution solely as open-chain forms (gluconic acid at least for the most part), temperature affects only the rate of oxidation. The monosaccharides, on the other hand, also exist in ring forms and temperature affects the equilibrium concentration of the different forms as well as the rate of oxidation.

The structure and conformation of monosaccharides in solution have been studied by NMR.¹³ The amounts of aldo- and ketosugars have been estimated from polarographic data^{14,15} and from circular dichroism spectra.¹⁶ The relative amounts of the open-chain forms are very small, however, and the results differ from each other considerably.

Acetoin, MeCOCH(OH)Me , which has a secondary alcohol group, can be considered a model compound for aldo- and ketosugars ($\text{C}_{(2)}-\text{C}_{(3)}$ complexation) while hydroxyacetone, MeCOCH_2OH , which has a primary alcohol group, can be considered a model compound for ketosugars ($\text{C}_{(2)}-\text{C}_{(1)}$ complexation). From the values of the rate constants of the monosaccharides and model compounds in Table 1, we estimated the amounts of the open-chain forms, assuming that the rates of oxidation of the open-chain forms dominate the overall rate. If this assumption is true the formation constants of the bidentate complexes formed from the monosaccharides and from the model compounds can be assumed to be equal. On the same basis the relative reactivities of the complexes may also be assumed equal. The results are shown in Table 2.

The data in Table 2 show, except for ribose, a relatively good correlation between the kinetic and polarographic results. It is also noteworthy that the amounts of the open-chain forms calculated from kinetic studies increase with temperature, as one would expect.

Table 2. The Estimated Proportions of the Open-chain Forms of Mono-saccharides in Water. $[\text{HClO}_4] = 1.471 \text{ M}$ at 25°C .

Compound	Proportion of the open-chain sugar		
	from kinetics ^a at $25^\circ\text{C}/\%$	from kinetics ^a at $50^\circ\text{C}/\%$	from polarography ^b at $25^\circ\text{C}/\%$
Galactose	0.097	0.31	0.082
Glucose	0.040	0.14	0.024
Mannose	0.057	0.13	0.064
Fructose	0.57	2.2	-
Sorbose	0.77	3.1	-
Arabinose	0.26	0.83	0.28
Ribose	0.37	0.93	(8.5) ^c
Xylose	0.36	1.1	-
Gluconic acid	(8.2)	(19)	-

a. This work.

b. Ref. 14, at pH 7.0.

c. The parentheses are from Ref. 14.

The estimated amounts of the open-chain forms obtained from circular dichroism spectra are lower than the values in Table 2, for example 0.002 % for glucose at 20°C at pH 5.2 - 7.0¹⁶ The difference may be due to the different experimental conditions, to the considerable reactivities of the ring forms etc. The low reactivity of the open-chain glucitol (Table 1) and of the other polyhydric alcohols⁸ (without the carbonyl group) as compared with that of the mono-saccharides suggests that the ring forms of the glycoses are not stereochemically suitable for the formation of bidentate complexes with vanadium(V) species and therefore are only weakly reactive.

The estimated proportion of D-glucono- δ -lactone in buffered D-gluconic acid solutions at 25°C has been found to be 10 % by polarimetry¹⁷ and 21 % by pH-static method.¹⁸ In comparison with these

Table 3. The Relative Amounts of the Open-chain Forms of the Mono-saccharides Estimated by Different Methods.

Compound	Relative amount of the open-chain form		
	kinetics ^a	polarography ^b	circular dichroism ^c
Galactose	2.4	3.4	10
Glucose	<u>1.0</u>	<u>1.0</u>	<u>1.0</u>
Mannose	1.4	2.7	2.5
Fructose	14	-	350
Sorbose	19	-	100
Arabinose	6.5	12	15
Ribose	9.3	(350) ^d	25
Xylose	9.0	7.1	10

a. This work, 25 °C at pH -0.17.

b. Ref. 14, 25 °C at pH 7.0.

c. Ref. 16, 20 °C at pH 5.2 - 7.0.

d. The parentheses from Ref. 14.

values, the value 92 % (Table 2) in 1.471 M HClO₄ is much too high. 2-Hydroxycarboxylic acids have been reported to undergo a C-C bond fission.¹⁹ Since this likely holds for gluconic acid too, acetoin, which undergoes a C-H bond fission, is not a proper model compound for it.

The relative proportions of the open-chain forms of the mono-saccharides, estimated by different methods, are shown in Table 3. Through widely ranging, they are at least useful in considering the sequence of the amounts of the open-chain forms.

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