Short Communication

Comparison of the Kinetics of Oxidation of Monosaccharides by Ce(IV), Cr(VI) and V(V)

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In earlier studies on the oxidation of hydroxylic compounds, we have measured the rates of the oxidation of three aldohexoses, two ketohexoses and three aldopentones by V(V)[1-4] and Ce(IV).[5] Continuing this work, we investigated the kinetics of the oxidation of the same monosaccharides by Cr(VI) and here compare the kinetic parameters for the oxidation by all three metal ions.

Experimental

Chemicals were reagent grade. The reactions were carried out in the temperature-controlled cell attachment of a Hitachi Perkin-Elmer 139 spectrophotometer. [Cr(VI)] was determined on the basis of the absorbance at 349 nm, where it is free of interference from Cr(III).[6] The rate constants $k_{obs} = -\mathrm{d}\ln[\mathrm{Cr(VI)}]/\mathrm{d}t$ were determined under pseudo first-order conditions with monosaccharide in excess, and they refer to the oxidation of the first alcohol group (C-2 for aldo sugars, C-1/C-3 for keto sugars). The rate law is of first order with respect to [Sugar].

Results and discussion

The rate constants $k_2 = k_{obs}/[\mathrm{Sugar}]$ were mea-

Table 1. Kinetic data for the oxidation of monosaccharides by Ce(IV), Cr(IV) and V(V).

Sugar	Ce(IV)[a]		Cr(VI)[b] $k_2/M^{-1} s^{-1}$	V(V)[c] $k_2 M^{-1} s^{-1}$
	k_{diss}/s^{-1}	K_{ass}/M^{-1}		
D-Galactose	2.0	100	5.29×10^{-3}	2.52×10^{-5}
D-Glucose	0.72	34	1.79×10^{-3}	1.05×10^{-5}
D-Mannose	0.35	38	3.05×10^{-3}	1.50×10^{-5}
L-Arabinose	3.3	67	4.40×10^{-3}	6.76×10^{-5}
D-Ribose	1.4	1000	1.38×10^{-2}	9.52×10^{-5}
D-Xylose	2.4	42	2.11×10^{-3}	9.28×10^{-5}
D-Fructose	3.0	140	3.88×10^{-3}	2.70×10^{-4}
L-Sorbose	2.5	120	1.70×10^{-3}	3.52×10^{-4}

[a]From Ref. 5. $[\mathrm{HClO_4}] = I = 1.00$ M, $t = 25\,°C$, $[\mathrm{Ce(IV)}] = 3.0 \times 10^{-3}$M. [b]This work. $[\mathrm{HClO_4}] = I = 0.50$ M, $t = 30\,°C$, $[\mathrm{Cr(VI)}] = 4.0 \times 10^{-4}$M. [c]From Ref. 4. $[\mathrm{HClO_4}] = I = 1.47$ M, $t = 25\,°C$, $[\mathrm{V(V)}] = 2.0 \times 10^{-2}$M.
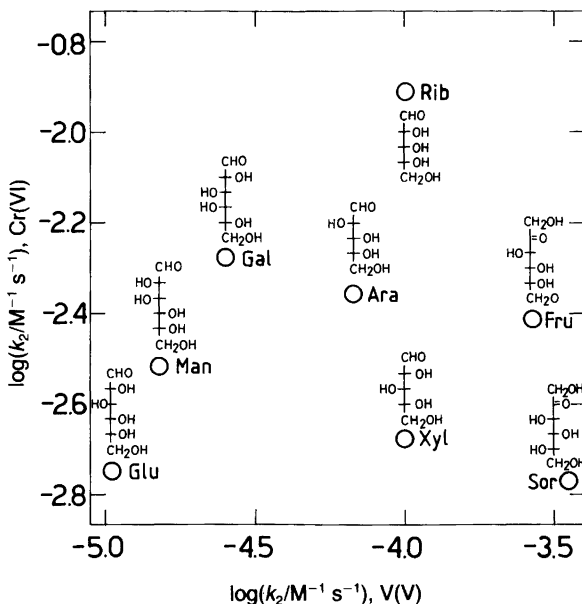
Fig. 1. Comparison of the rate constants of the oxidation of monosaccharides with Cr(VI) and V(V). For experimental details, see Table 1.

sured for 4×10^{-3} M and 4×10^{-2} M monosaccharide, and the mean values of k_2, together with the same data for Ce(IV) and V(V), are shown in Table 1.

Using the stopped-flow technique, we found that the oxidation of monosaccharides by Ce(IV) proceeds via two consecutive complexes.[5] The first complex is rapidly formed in a pre-equilibrium reaction (K_{ass}) and then dissociates rapidly (k_{diss}) in accordance with Michaelis-Menten kinetics. We suggested that the fast-forming complex is that between a Ce(IV) species and the *open-chain* form of the monosaccharide.

V(V) oxidation is kinetically a simple second-order reaction, first order with respect to [Sugar].[1-4] A mechanism involving formation of a radical by hydrogen atom transfer in the rate-determining decomposition of an *open-chain* monosaccharide-V(V) comples was suggested.

In studies on the kinetics of the oxidation of monosaccharides by Cr(VI), Sen Gupta *et al.*[7,8] found no indication of intermediate complex formation. They suggest that in the rate-determining step, protonated chromic acid, $H_3CrO_4^+$, reacts with a preponderant *ring* form of the sugar.

The values of the quantities in Table 1 show no trends. The plot in Fig. 1 of the values of log (k_2/M^{-1} s^{-1}) for Cr(VI) oxidation versus the values of log (k_2/M^{-1} s^{-1}) for V(V) oxidation is

clearly a scatter diagram, and similar diagrams are obtained for the plots of the log(k_{diss}/s^{-1}) and log($k_{diss}K_{ass}$/M^{-1} s^{-1}) values for Ce(IV) oxidation versus the values of log(k/M^{-1} s^{-1}) for V(V) oxidation.

The amounts of the open-chain aldo and keto sugars have been estimated from polarographic data[9,10] and from circular dichroism spectra.[11] The relative amounts of the open-chain forms decrease in the order D-galactose > D-mannose > D-glucose for aldohexoses, in the order D-ribose > L-arabinose > D-xylose for aldopentoses and in the order of D-fructose > L-sorbose for ketohexoses. Interestingly, the values of k_2 for Cr(VI) oxidation decrease in the same order (Fig. 1). We have earlier[5] suggested that it may be of general importance that the properties mentioned decrease in the order described in Scheme 1. The same order has now been confirmed for the relative amounts of the *open-chain* forms of the sugars,[9-11] for the complex constant K_{ass} of Ce(IV)

Scheme 1.

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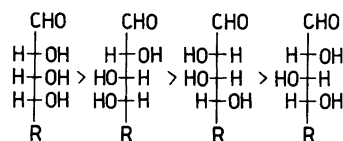
Table 2. Effect of temperature on the rate constant of the oxidation of L-arabinose by Cr(VI) in water. [Cr(VI)] = 4.0×10^{-4} M, [HClO$_4$] = 0.500 M at 25 °C.

$t/°C$	[C$_5$H$_{10}$O$_5$]/10^{-3} M	$k_{ob2}/10^{-5}$ s^{-1}	r	$k_2/10^{-3}$ M^{-1} s^{-1}
30	3.90	1.77(3)	0.9991	4.54(8)
35	4.02	2.37(7)	0.9986	5.9(2)
40	3.95	3.41(7)	0.9933	8.6(2)
45	3.95	4.7(1)	0.9991	1.18(2)
50	3.92	6.7(1)	0.9994	1.70(3)

$$\log(k_2/\text{M}^{-1}\,\text{s}^{-1}) = 2.50(6) \times 10^{-1}[\text{NaClO}_4]/\text{M} - 2.5(4) \tag{1}$$

$$k_2/\text{M}^{-1}\,\text{s}^{-1} = 4.2(2) \times 10^{-2}[\text{HClO}_4]^2/\text{M}^2 + -10(7) \times 10^{-3} \tag{2}$$

oxidation (Table 1) and for the rate constant k_2 of Cr(VI) oxidation (Table 1, Fig. 1).

For L-arabinose, we investigated the dependence of the rate constant upon the temperature, the ionic strength and the concentration of HClO$_4$.

The effect of temperature on the rate is shown in Table 2. The value of 51(3) kJ mol^{-1} for the enthalpy of activation and the value of $-129(9)$ J K^{-1} mol^{-1} for the entropy of activation were evaluated from k_2. The high negative value of the entropy of activation is in agreement with a bimolecular rate-determining reaction.

The addition of NaClO$_4$ accelerates the rate in 0.50 M HClO$_4$ at 30 °C in accordance with eqn. (1), with a correlation coefficient of 0.9986. The positive slope with a value of less than unity indicates a rate-determining reaction of a neutral substrate with a positive oxidant.

The effect of [HClO$_4$] was studied by partially neutralizing 2.5 M HClO$_4$ with NaOH to maintain a constant ionic strength. At 30 °C the correlation is given by eqn. (2), with a correlation coefficient of 0.9961. This result, like the results of Sen Gupta *et al.*,[7,8] implies that the oxidant may well be H$_3$CrO$_4^+$.

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