EFFECT OF PRESSURE ON THE RATES OF OXIDATION OF MONO-SACCHARIDES WITH VANADIUM(V)* †

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ABSTRACT

The effect of pressure on the rates of the oxidation of D-galactose, D-glucose, D-mannose, D-fructose, L-sorbose, L-arabinose, D-ribose, and D-xylose with vanadium(V) in perchloric acid was studied. The activation volumes for the mono-saccharides were positive and approximately equal $(7.5 \pm 1.3 \text{ mL} \text{ mol}^{-1})$, with negligible dependence on pressure up to 200 MPa at least. These observations indicate the same mechanism for the formation of the activated complexes. A mechanism involving formation of a radical by hydrogen atom transfer in the rate-determining decomposition of a monosaccharide–vanadium(V) complex is proposed.

INTRODUCTION

Although the kinetics of the oxidation of monosaccharides with vanadium(V) in aqueous acidic media have been studied in detail²⁻⁹, there is no consensus about the reaction mechanism. The reaction has been proposed to proceed by unimolecular decomposition of a sugar-V(V) complex by C-C bond fission²⁻⁴, or, for fructose, by C-H bond fission^{5.6}, by bimolecular formation of radicals involving either C-H bond⁷ or C-C bond⁸ fission, and by a bimolecular mechanism in which the transition state decomposes in the rate-determined manner by C-H bond fission⁹.

Kinetic studies of reactions at high pressures provide a useful tool for the elucidation of reaction mechanisms¹⁰. In view of the lack of agreement over the reaction mechanism, we have measured the rates of oxidation of three aldohexoses, two ketohexoses, and three aldopentoses over a wide range of pressures. To our knowledge, this is the first time that this high pressure method has been applied to the oxidation of carbohydrates.

RESULTS AND DISCUSSION

The kinetic results refer to the reactions in which the monosaccharides are

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Fig. 1. Pressure dependence of $\ln k_{obs}$ for the oxidation of monosaccharides with V(V) in aqueous HClO₄ (for experimental conditions, see Table I): \bigcirc , D-Galactose; \triangle , D-glucose; \Box , D-mannose; \otimes , D-fructose; \boxtimes , L-sorbose; \bigoplus , L-arabinose, \blacktriangle , D-ribose; \blacksquare , D-xylose.

oxidized to their first reaction products and 2 mol of V(IV) are formed for every mol of sugar oxidized. For example, glucose is oxidized to arabinose^{2,4} as shown in eq. 1.

$$C_6H_{12}O_6 + H_2O + 2 V(V) \rightarrow C_5H_{10}O_5 + HCO_2H + 2 V(IV) + 2 H^+$$
 (1)

All of the rate constants were determined under pseudo-first-order conditions with carbohydrate in excess. As the reactions readily take place in the presence of $HClO_4$, solutions of $HClO_4$ were used to minimize the number of different catalyzing V(V) species¹¹.

The activation volumes ΔV_{obs}^* , defined by

$$\Delta V_{\rm obs}^* = V^* - V \,(\text{reactants}),\tag{2}$$

were determined from the observed rate constants,

$$k_{\rm obs} = -\mathrm{dln}[\mathrm{V}(\mathrm{V})]/\mathrm{d}t,\tag{3}$$

measured at five pressures. The activation volumes were calculated from the eq.¹⁰ (4).

$$\Delta V_{\rm obs}^* = -RT \partial \ln k_{\rm obs} / \partial P \tag{4}$$

Fig. 1 illustrates the pressure variation of $\ln k_{obs}$ for the eight monosaccharides.

The evaluated activation volumes are shown in Table I. In order to ensure that the oxidizing V(V) species were the same in each oxidation, the concentration

TABLE I

Monosaccharide	Temp. (degrees)	[<i>HClO</i> ₄] ^a (м)	$k_{obs}/[Sugar]^a$ ($M^{-1}.s^{-1}$) (× 10 ⁴)	ΔV^*_{obs} (mL.mol ⁻¹)
D-Galactose	50	1.485	5.30 ±0.20	6.7 ±0.3
D-Glucose	50	1.485	2.64 ± 0.03	7.3 ± 0.4
D-Mannose	55	1.481	5.62 ± 0.12	6.5 ± 0.4
D-Fructose	30	1.496	4.10 ± 0.04	7.9 ± 0.5
L-Sorbose	30	1.496	3.84 ±0.06	8.6 ± 0.4
L-Arabinose	40	1.491	5.23 ± 0.15	8.0 ± 0.4
D-Ribose	40	1.491	5.64 ± 0.15	6.2 ± 0.2
D-Xylose	40	1.491	6.73 ± 0.31	8.8 ± 0.3

ACTIVATION VOLUMES OF THE OXIDATION OF MONOSACCHARIDES WITH VANADIUM(V) IN AQUEOUS PERCHLORIC ACID

^aAt 0.1 MPa.

of perchloric acid was kept approximately constant. In order to obtain reasonable reaction times, the temperature was varied for different monosaccharides. The temperature effects on the activation volume are known to be small¹⁰. The reactivity order under identical conditions in 1.5M HClO₄ at 50° is L-sorbose \approx D-fructose > D-xylose \approx D-ribose > L-arabinose > D-galactose > D-mannose \approx D-glucose¹².

Three observations are relevant to the discussion of mechanism: (a) the activation volumes are positive; (b) the activation volumes are approximately equal, the mean value being $7.5 \pm 1.3 \text{ mL} \cdot \text{mol}^{-1}$; and (c) each of the plots shows a high degree of linearity^{*}.

The activation volume ΔV_{obs}^* is the sum of two terms, ΔV_{bond}^* and ΔV_{solv}^* . The ΔV_{solv}^* term is the volume change due to the changing interaction of the reacting molecules and activated complex with the solvent. In the reactions studied, the number of ionic charges remains constant and independent of the mechanism. Therefore, only minor changes in electrostriction are expected and ΔV_{solv}^* has been omitted from the examination.

The ΔV_{bond}^* term is the volume change due to the changing interactions of the reacting molecules during the formation of the activated complex, *e.g.*, changes in bond length and in electron densities around nuclei.

As ano and le Noble¹⁰ have estimated the contribution of bond cleavage to ΔV_{bond}^* to be ~+10 mL.mol⁻¹ and that of bond formation to be ~-10 mL.mol⁻¹. Since our values of ΔV_{obs}^* are positive, bimolecular mechanisms, which would give negative values of ΔV_{bond}^* , are unlikely. Therefore, it is concluded that a homolytic unimolecular decomposition occurs in the rate-determining step. This conclusion is supported by the observation (c) that the compressibility coefficient of activation $\Delta \beta^* = -(\partial \Delta V_{obs}^*/\partial P)_T$ is zero within experimental error. The same zero value has

^{*}By using the parabolic equation¹⁰ ln $k_{obs}^* = a + bP + cP^2$, then $\Delta V_{obs}^* = -bRT$ gives poorer correlation and both positive and negative values for c, although they should be positive since b is negative here.

been found for unimolecular homolytic dissociations, *e.g.*, for di-*tert*-butyl peroxide¹³, substituted benzenediazonium cations¹⁴, and a ketenimine¹⁵, and for homolytic fission of metal-ligand bonds¹⁶.

The following, simplified mechanism explains the present data:

$$S + V(V) \rightleftharpoons C$$
 (fast) (5)

$$C \qquad \rightleftharpoons \mathbf{R}^{\cdot} + \mathbf{V}(\mathbf{IV}) + \mathbf{H}^{+} \quad (\text{slow}) \tag{6}$$

$$\mathbf{R}^{*} + \mathbf{V}(\mathbf{V}) \rightleftharpoons \mathbf{P} + \mathbf{V}(\mathbf{IV}) + \mathbf{H}^{+} \quad \text{(fast)}$$

$$\tag{7}$$

In this mechanism, a co-ordination complex C is formed in a pre-equilibrium step 5 and disproportionates in a rate-determining step 6 to form a free radical \mathbf{R}^{\cdot} , which is then oxidized rapidly in 7 to give products P by either C–C or C–H bond fission. V(V) denotes the preponderant oxidizing species, which is^{4,6,12} probably V(OH)₂³⁺.

 ΔV_{obs}^* also includes the volume changes ΔV of any fast pre-equilibrium reactions. Since one molecule is formed from two molecules in reaction 5, ΔV for 5 is probably negative and ΔV_{bond}^* may be more positive than ΔV_{obs}^* .

Vanadium(V) exists in slightly acidic solutions as VO₂⁺, $pK_a = 3.70$ at 25°¹⁷, and in more acidic solutions as V(OH)₃²⁺ and V(OH)₂³⁺, for which the pK_a values are not known. Therefore, V(OH)₂³⁺ may be formed in a pre-equilibrium reaction.

The present experiments provide no information about the fast reactions following the rate-determining step, or about the formation of the products by either C-C or C-H bond fission. Glucose and mannose are oxidized *via* C-C bond fission to arabinose, which then reacts further to give erythrose and glyceraldehyde^{2,4}. The products from fructose are dicarbonyl compounds, erythrose, and glyceraldehyde⁴. It is possible, however, that C-C bond fission takes place simultaneously with C-H bond fission. Acetoin [MeCH(OH)COMe] oxidizes to biacetyl (MeCOCOMe) *via* C-H bond fission of a co-ordination complex¹⁸.

EXPERIMENTAL

Ammonium metavanadate was a guaranteed reagent from Merck, and Dgalatose, D-glucose, D-mannose, D-fructose, L-sorbose, L-arabinose, D-ribose, and D-xylose were analytical-grade products from Fluka AG. All were used without further purification.

The apparatus used for reactions at high pressures was that used earlier¹⁹. Samples were withdrawn at suitable intervals and analyzed²⁰ for V(V).

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