

Kinetics and Mechanism of the Reduction of Chromium(VI) and Chromium(V) by D-Glucitol and D-Mannitol

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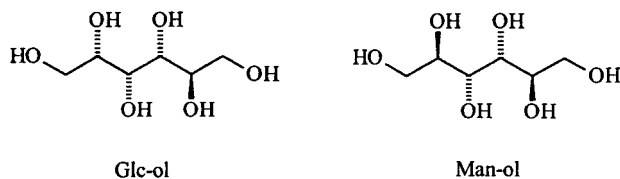
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The oxidation of D-glucitol and D-mannitol by Cr^{VI} yields the aldonic acid (and/or the aldonolactone) and Cr^{III} as final products when an excess of alditol over Cr^{VI} is used. The redox reaction occurs through a Cr^{VI} → Cr^V → Cr^{III} path, the Cr^{VI} → Cr^V reduction being the slow redox step. The complete rate laws for the redox reactions are expressed by: *a*) $-d[\text{Cr}^{\text{VI}}]/dt = \{k_{\text{M2H}} [\text{H}^+]^2 + k_{\text{MH}} [\text{H}^+]\}[\text{mannitol}][\text{Cr}^{\text{VI}}]$, where $k_{\text{M2H}} = (6.7 \pm 0.3) \cdot 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$ and $k_{\text{MH}} = (9 \pm 2) \cdot 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$; *b*) $-d[\text{Cr}^{\text{VI}}]/dt = \{k_{\text{G2H}} [\text{H}^+]^2 + k_{\text{GH}} [\text{H}^+]\}[\text{glucitol}][\text{Cr}^{\text{VI}}]$, where $k_{\text{G2H}} = (8.5 \pm 0.2) \cdot 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$ and $k_{\text{GH}} = (1.8 \pm 0.1) \cdot 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$, at 33°. The slow redox steps are preceded by the formation of a Cr^{VI} oxy ester with λ_{max} 371 nm, at pH 4.5. In acid medium, intermediate Cr^V reacts with the substrate faster than Cr^{VI} does. The EPR spectra show that five- and six-coordinate oxo-Cr^V intermediates are formed, with the alditol or the aldonic acid acting as bidentate ligands. Pentacoordinate oxo-Cr^V species are present at any [H⁺], whereas hexacoordinate ones are observed only at pH < 2 and become the dominant species under stronger acidic conditions where rapid decomposition to the redox products occurs. At higher pH, where hexacoordinate oxo-Cr^V species are not observed, Cr^V complexes are stable enough to remain in solution for several days to months.

1. Introduction. – Chromium(VI) (Cr^{VI}) is a potential hazard both in a biological and an ecological context [1]. The observation of Cr^V and Cr^{IV} intermediates in the selective oxidation of organic substrates by Cr^{VI} and their implication in the mechanism of Cr-induced cancers [2–3] has generated a considerable amount of interest in their chemistry and biochemistry [4–7]. The biological reduction of Cr^{VI} to lower states has been observed with a wide variety of naturally occurring cellular reductants [8–12]. Ligands that possess two O-atoms able to form five-membered rings about the metal ion, such as 1,2-diols and α -hydroxy acids, are effective as nonenzymatic reductants and complexation agents towards hypervalent chromium and can stabilize the labile oxidation states of chromium [13–19]. For this reason, it is interesting to look at the ability of polyhydroxy compounds to reduce Cr^{VI} to Cr^{III}, in order to know the role they may play in the chemistry of Cr^{VI}.

We are studying the possible fate of Cr^{VI} and Cr^V in biological systems by examining reactions of Cr^{VI} with low-molecular molecules [20–34]. Our studies on the reduction of Cr^{VI} and intermediate Cr^V by aldoses [20][30][31][33], deoxyaldoses [20][23][25][30][31], sugar acids [22][27][29], and methyl glycosides [34] showed that the relative redox reactivities of these saccharides toward chromate is based on the relative rates of the oxidation *vs.* complexation processes [31][32]. Under conditions of

excess reductant over Cr^{VI} , aldoses, deoxyaldoses, and sugar acids are selectively oxidized at $\text{OH}-\text{C}(1)$, and in methyl glycosides, where the anomeric position is blocked, the oxidation takes place at $\text{OH}-\text{C}(6)$. These results reflect the inertness of the secondary OH groups of saccharides to be oxidized by Cr^{VI} , as compared to the hemiacetal and primary OH groups. We decided to evaluate the oxidation of alditols (=sugar alcohols), in order to determine whether the selectivity of the oxidation of cyclic polyhydroxy compounds by Cr^{VI} (inertness of the secondary OH group) is retained in open-chain polyols. Alditols constitute a group of compounds closely related to sugars and widely distributed in microorganisms, fungi, animals, and plants [35]. Among the physiological functions attributed to alditols are structural functions, energy storage, coenzyme regulation, and sugar interconversion [36]. Hexitols are the most common alditols, with mannitol being the most abundant sugar found in over 100 different species of higher plants [37]. D-Glucitol is a normal metabolite in mammals and is used frequently in the industrial manufacture of food ingredients [38][39].



In this work, we study the Cr^{VI} oxidation of D-glucitol (Glc-ol) and D-mannitol (Man-ol), and provide information on the mechanism as well as on the structure of the intermediate Cr^{V} species.

2. Results and Discussion. – 2.1. Rate Studies: Cr^{VI} Oxidation of Glc-ol and Man-ol.

Over the whole range of perchloric acid concentrations used in the kinetic measurements, UV/VIS studies show that the reaction of alditols with Cr^{VI} result in an absorbance band with λ_{max} 350 nm, and the rate constants are calculated from the absorbance changes at this wavelength. The kinetic traces show an initial deviation from first-order decay over very short time periods, probably due to Cr^{V} species that also absorb at 350 nm and may superimpose the Cr^{VI} absorbance [40]. However, it is known that when Cr^{V} reacts faster than Cr^{VI} and exists in solution in a sufficiently small concentration, changes in absorbance at 350 nm essentially reflect changes in Cr^{VI} concentration – except for the short initial period – and the rate constants can be calculated from the linear part of the $\ln(\text{Abs})$ vs. time curves. To avoid a wrong interpretation of spectrophotometric absorbance decay values due to superimposition of Cr^{V} absorbance, we determined the relative values of the Cr^{VI} vs. Cr^{V} reduction rate constants (k_6 vs. k_5) from spectrophotometric data at 750 nm (see below), and we found that $k_5 \gg k_6$, in the range of $[\text{H}^+]$ used in the kinetic measurements. Besides, we followed the formation of Cr^{III} at 570 nm in the HClO_4 concentration range 0.1–0.8M to determine the rate of Cr^{III} formation relative to that of the Cr^{VI} consumption. The pseudo-first-order rate constants obtained at this wavelength are coincident with those obtained from the Cr^{VI} decay at 350 nm, with the same dependence on $[\text{H}^+]$ (Table I). This means that Cr^{III} forms as fast as Cr^{VI} is consumed, and that the slow redox path effectively implies the reduction of Cr^{VI} , which should react slower than Cr^{V} does. Thus,

pseudo-first-order rate constants (k_6) calculated from the slopes of the linear part of the $\ln(\text{Abs})$ vs. time curves correspond to the Cr^{VI} consumption. *Table 1* summarizes values of k_6 for various concentrations of Glc-ol and Man-ol at different concentrations of HClO_4 . For both alditols, plots of k_6 vs. $[\text{Ald-ol}]$ (*Figs. 1* and *2*) give good straight lines from which values of k_G and k_M can be determined (*Table 1*). Insets in *Fig. 1* and *2* show the dependence of k_G and k_M on $[\text{HClO}_4]$, which may be expressed by *Eqn. 1*, where $k_{\text{G2H}} = (8.5 \pm 0.2) \cdot 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$ and $k_{\text{GH}} = (1.8 \pm 0.1) \cdot 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$ for Glc-ol, and $k_{\text{M2H}} = (6.7 \pm 0.3) \cdot 10^{-2} \text{ M}^{-3} \text{ s}^{-1}$ and $k_{\text{MH}} = (9 \pm 2) \cdot 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$ for Man-ol. The complete rate law for the reaction of Glc-ol and Man-ol with Cr^{VI} is then given by *Eqn. 2*.

$$k_{\text{G(M)}} = k_{\text{G2H(M2H)}} [\text{H}^+]^2 + k_{\text{GH(MH)}} [\text{H}^+] \quad (1)$$

$$-d[\text{Cr}^{\text{VI}}]/dt = k_6 [\text{Cr}^{\text{VI}}]_T = \{k_{\text{A2H}} [\text{H}^+]^2 + k_{\text{AH}} [\text{H}^+]\} [\text{Ald-ol}] [\text{Cr}^{\text{VI}}] \quad (2)$$

2.2. Detection of the Intermediate Cr^{VI} Ester. Differential UV/Vis spectra of mixtures of Cr^{VI} and Glc-ol or Man-ol exhibit an absorption band at λ_{max} 371 nm (*Fig. 3*) consistent with that ascribed to Cr^{VI} oxy esters [41][42]. At pH 4.5, the redox reaction of Cr^{VI} with the alditols studied proceeds very slowly, with negligible reduction of Cr^{VI} within the first hour. Thus, at this pH, the ester-formation step can be distinguished clearly from the electron-transfer reaction. Spectra obtained within 20 s

Table 1. Observed Pseudo-First-Order Rate Constants (k_6)^a for Different Concentrations of HClO_4 and Alditol. T 33°; $[\text{Cr}^{\text{VI}}]_0 = 6 \cdot 10^{-4} \text{ M}$; $I = 1\text{M}$.

[HClO_4]/M	$10^4 k_6/\text{s}^{-1}$ for [Glc-ol]							$10^3 k_G/\text{M}^{-1} \text{ s}^{-1}$
	0.06M	0.12M	0.18M	0.21M	0.24M	0.3M		
						λ 350 nm	λ 570 nm ^b)	
0.10	1.3(1)	2.25(5)	4.0(1)	4.9(1)	5.8(1)	7.7(1)	7.2(2)	2.4(1)
0.20	2.7(1)	7.75(5)	12.7(1)	13.9(1)	18.2(1)	19.4(1)	20.3(6)	6.8(2)
0.30	8.2(1)	15.6(1)	24.6(7)	28.1(5)	31.6(7)	36.4(1)	34.6(5)	12.9(3)
0.40	14.1(1)	25.5(2)	37.0(3)	44.3(7)	50.4(6)	57.6(5)	51(2)	20.3(4)
0.50	19.0(1)	40.0(2)	60.0(8)	64.8(7)	75.9(8)	87.5(5)	82(2)	31.0(7)
0.60	27.3(4)	54.1(9)	71(2)	90(2)	103(1)	120(2)	–	41.6(9)
0.75	39.1(5)	76(2)	107(1)	133(3)	146(1)	180(2)	–	61(1)
[HClO_4]/M	$10^4 k_6/\text{s}^{-1}$ for [Man-ol]							$10^3 k_M/\text{M}^{-1} \text{ s}^{-1}$
	0.06M	0.12M	0.18M	0.24M		0.30M		
				λ 350 nm	λ 570 nm ^b)	λ 350 nm	λ 570 nm ^b)	
0.10	1.55(1)	1.95(5)	2.65(5)	4.65(5)	5.1(8)	6.7(1)	6.9(3)	2.0(1)
0.20	3.30(1)	5.55(5)	6.95(5)	11.0(2)	10.8(9)	14.4(3)	13.7(1)	4.6(2)
0.30	6.01(2)	11.7(1)	17.0(1)	20.1(1)	20.1(9)	24.3(2)	24.6(9)	8.6(3)
0.40	9.50(1)	17.9(2)	25.0(6)	34.8(9)	33.4(2)	45(1)	40.5(9)	14.7(2)
0.50	13.1(1)	26.3(4)	38.0(9)	50(1)	50.3(3)	61(2)	60.4(6)	20.8(4)
0.60	20.0(2)	38.1(3)	58.6(5)	77(2)	71.0(2)	86(2)	85(2)	30.7(9)
0.75	25.2(3)	55.3(3)	79(1)	106(2)	110(2)	128(2)	129(3)	44(1)
0.80	33.1(2)	66.2(4)	93(2)	121(2)	124(1)	151(4)	149(5)	51(1)

^a) Mean values from multiple determinations. ^b) $[\text{Cr}^{\text{VI}}] = 6 \cdot 10^{-3} \text{ M}$.

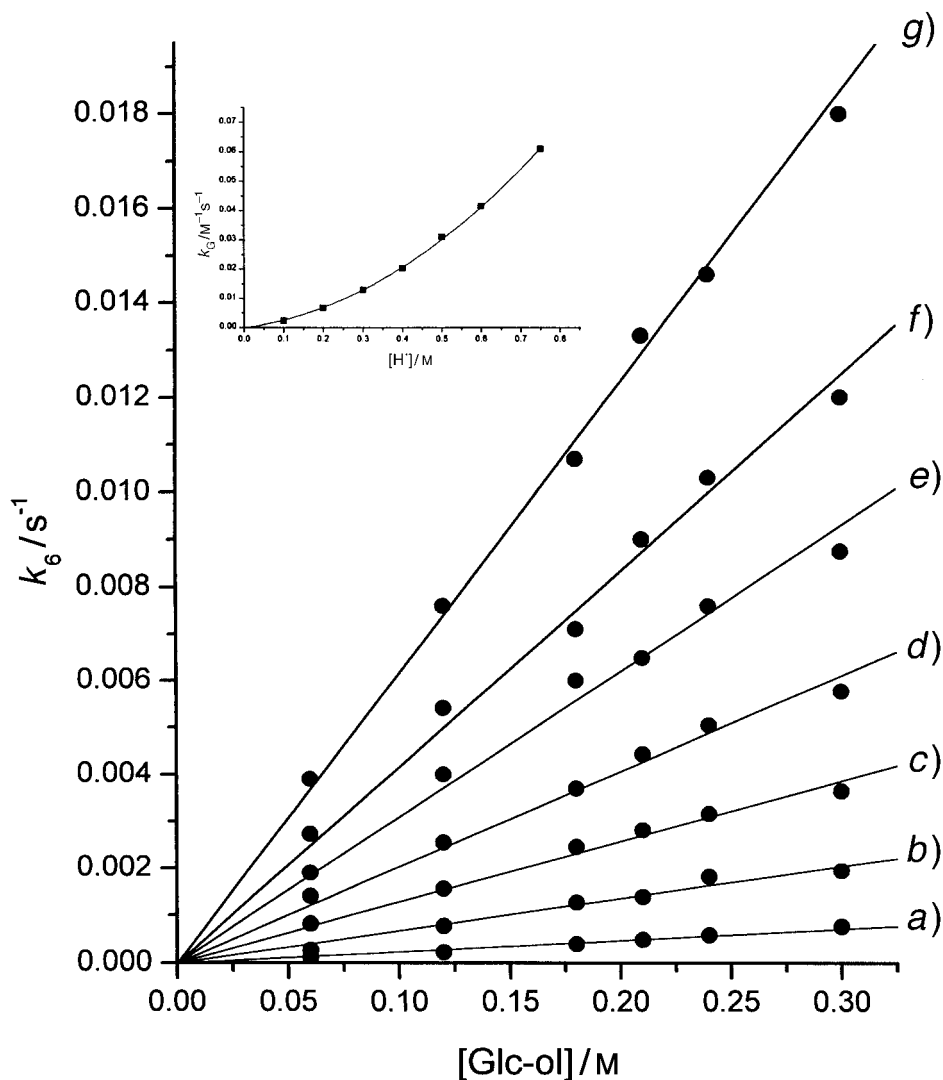


Fig. 1. Effect of $[\text{Glc-ol}]$ on k_6 at 33° , $I = 1.00\text{M}$, and $[\text{H}^+]/\text{M}$: a) 0.10, b) 0.20, c) 0.30, d) 0.40, e) 0.50, f) 0.60, and g) 0.75. Inset: Effect of acidity on k_G .

after mixing show a distinctive absorption band at 371 nm. Continued scanning for 30 min reveals no further change in the spectra. Varying the excess concentration of Glc-ol or Man-ol at pH 4.5 shows that the absorbance at 371 nm increases with increasing concentration of alditol, probably as a result of a shift toward the ester in the esterification equilibrium.

2.3. *Intermediacy of Cr^V* . The EPR spectra of mixtures of Man-ol or Glc-ol and Cr^{VI} in 0.1–0.8M HClO_4 show the formation of several intermediate Cr^{V} species. In this $[\text{H}^+]$ range, the EPR spectra consist of a minor signal at $g_{\text{iso}} = 1.9793$ – which is a composite of

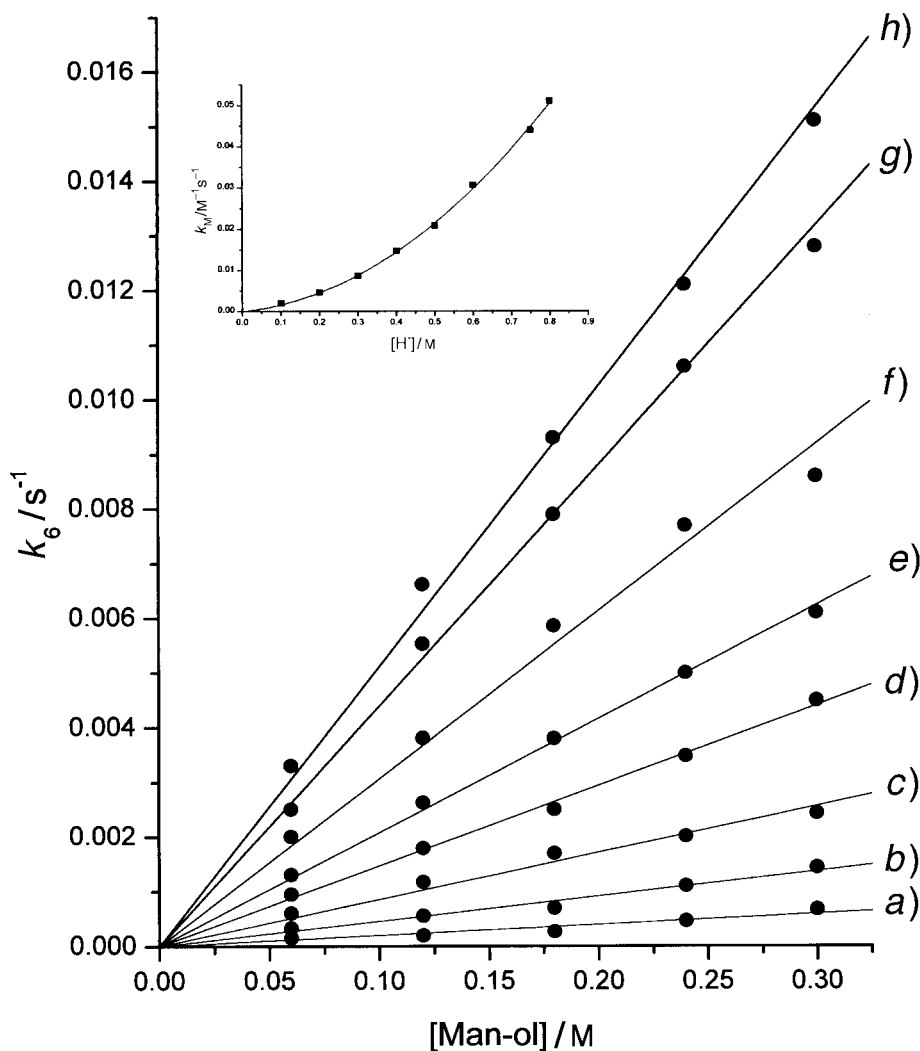


Fig. 2. Effect of $[\text{Man-ol}]$ on k_6 at 33° , $I = 1.00\text{M}$ and $[\text{H}^+]/\text{M}$: a) 0.10, b) 0.20, c) 0.30, d) 0.40, e) 0.50, f) 0.60, g) 0.75, and h) 0.80. Inset: Effect of acidity on k_M .

several Cr^{V} species, as discussed below – and a major signal at $g_{\text{iso}} = 1.9718$ (or 1.9719, resp.). The signal at lower g_{iso} is not observed at $\text{pH} > 1$ where the electron-transfer reaction becomes extremely slow and the Cr^{V} species with $g_{\text{iso}} = 1.9793$ remain a long time in solution. By contrast, in the $[\text{H}^+]$ range used in the kinetics measurements, the Cr^{V} EPR signal intensities grow and decay rapidly.

We investigated the kinetics of the formation and disappearance of Cr^{V} spectrophotometrically, at 750 nm, in 0.1–0.5M HClO_4 . At this wavelength, only Cr^{V} absorbs, and the experimentally observed intermediate Cr^{V} growth and decay curves can be fitted to Eqn. 3, where ε^{V} refers to the Cr^{V} molar absorptivity at this wavelength

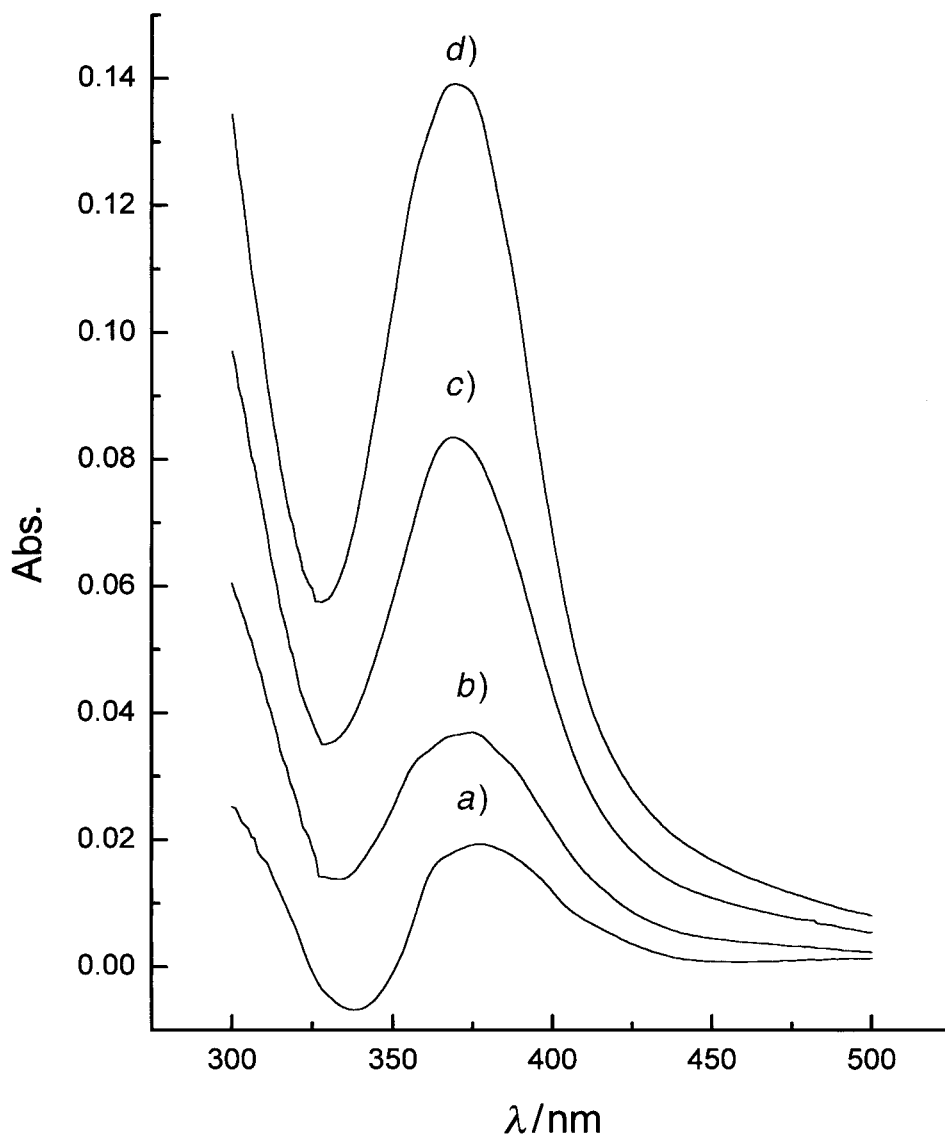


Fig. 3. UV/VIS Difference spectra of $\text{Cr}^{\text{VI}}/\text{Glc-ol}$ solutions at pH 4.5, showing the increasing band at 371 nm with increasing $[\text{Glc-ol}]$: a) 0.12, b) 0.18, c) 0.24, and d) 0.30 M. $[\text{Cr}^{\text{VI}}] = 6 \cdot 10^{-4}$ M, $T 33^\circ$, $I = 1$ M. Spectra taken after 20 min.

and is assumed to be the same as for the complex $[\text{Cr}^{\text{V}}(\text{O})(\text{ehba})_2]^-$ ($\epsilon = 38 \text{ M}^{-1} \text{ cm}^{-1}$; ehba = 2-ethyl-2-hydroxybutanoato(2-)) [43]. Fig. 4 shows typical curves for runs at 750 nm and the curve fit according to Eqn. 3. Values of k_5 and k_6 determined from these fits for a 50:1 alditol/ Cr^{VI} ratio and different $[\text{H}^+]$ are listed in Table 2. The k_6 values obtained agree perfectly with values calculated from data at 350 and 570 nm.

$$\text{Abs}^{750} = k_6 \epsilon^{\text{V}} [\text{Cr}^{\text{VI}}]_0 (e^{-k_5 t} - e^{-k_6 t}) / (k_6 - k_5) \quad (3)$$

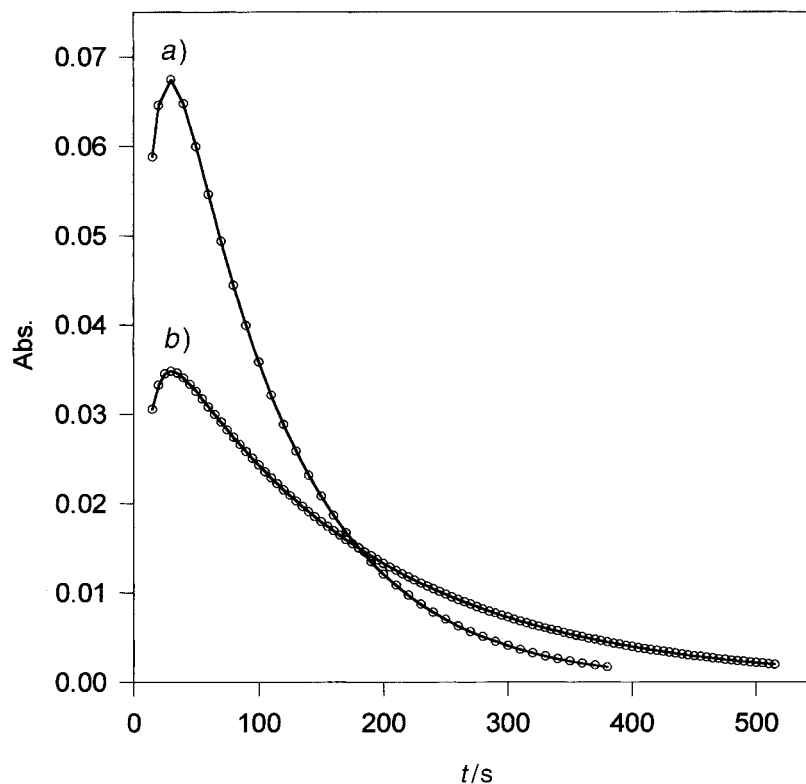


Fig. 4. Absorbance vs. time curves for the chromic oxidation of a) Glc-ol and b) Man-ol. $[\text{Cr}^{\text{VI}}] = 1.8 \cdot 10^{-2} \text{ M}$, $[\text{Ald-ol}] = 0.9 \text{ M}$, $[\text{H}^+] = 0.30 \text{ M}$, $I = 1 \text{ M}$, $T = 33^\circ$, $\lambda = 750 \text{ nm}$.

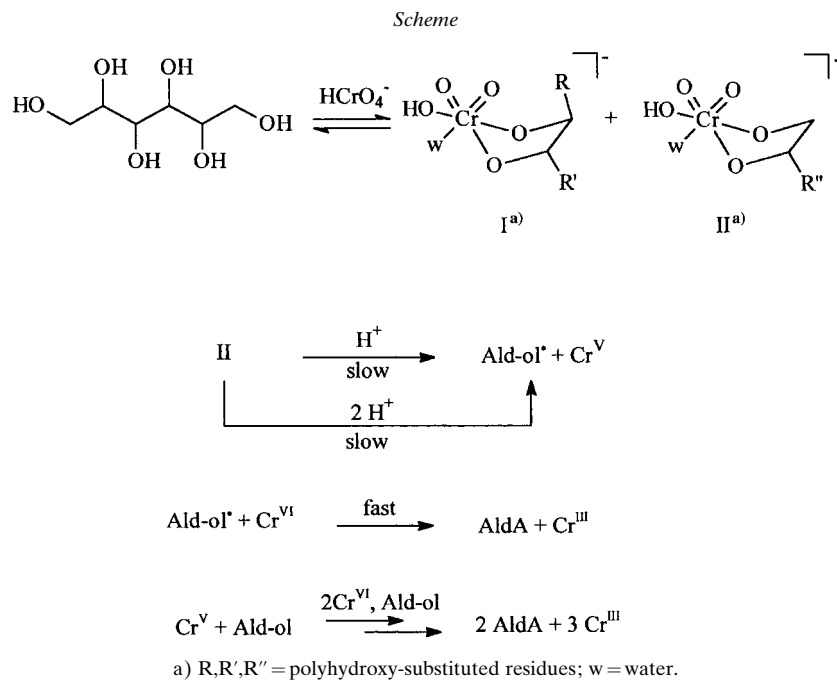
Table 2. Observed Pseudo-First-Order Rate Constants^{a)} k_5 and k_6 for Different $[\text{HClO}_4]$ Obtained at $\lambda = 750 \text{ nm}$. $[\text{Cr}^{\text{VI}}] = 0.018 \text{ M}$; $[\text{alditol}] = 0.9 \text{ M}$; $I = 1 \text{ M}$; $T = 33^\circ$.

$[\text{HClO}_4]/\text{M}$	Man-ol		
	$10^3 k_{6(\text{calc.})}^{\text{b)}/\text{s}^{-1}$	$10^3 k_6/\text{s}^{-1}$	$10^2 k_5/\text{s}^{-1}$
0.1	1.3	1.0(2)	4.4(1)
0.2	4.0	3.8(1)	6.6(1)
0.3	8.0	6.1(1)	9.9(1)
0.4	13	12(1)	11(1)
0.5	20	18(2)	13(1)
$[\text{HClO}_4]/\text{M}$	Glc-ol		
	$10^3 k_{6(\text{calc.})}^{\text{b)}/\text{s}^{-1}$	$10^3 k_6/\text{s}^{-1}$	$10^2 k_5/\text{s}^{-1}$
0.2	6.3	6.2(2)	7.4(1)
0.3	12	11(1)	8.1(2)

^{a)} Mean values from multiple determinations. ^{b)} Values calculated with Eqn. 2.

For alditol and Cr^{VI} concentrations used in the kinetic measurements, the calculated maximum Cr^{V} concentrations ($[\text{Cr}^{\text{V}}]_{\text{max}}$) represent up to 17% of the total Cr concentration, and the t_{max} values are very short compared to the total redox-reaction time, thus confirming that absorbance at 350 nm should essentially reflect changes in $[\text{Cr}^{\text{VI}}]$.

2.4. *Mechanism of the Oxidation of Alditols by Cr^{VI}* . In the range of substrate and acid concentration used in this work, the oxidation of Glc-ol and Man-ol by Cr^{VI} is a complex multistep reaction yielding $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and the aldonic acid (AldA) – in equilibrium with its lactone – as the final redox products. In the *Scheme*, we propose a mechanism that takes into account *a)* the kinetic results, *b)* the polymerization of acrylonitrile added to the reaction mixture, *c)* the detection of an intermediate Cr^{VI} ester, and *d)* the detection of intermediate oxochromate(V) species.



In the $[\text{H}^+]$ range under study, Cr^{VI} may exist as HCrO_4^- [44], and this species is proposed as the reactive form of Cr^{VI} , in agreement with the first-order dependence of the reaction rate on $[\text{Cr}^{\text{VI}}]$. It is known that the chromic oxidations of alcohols and glycols are preceded by the formation of a chromate ester [41][42]. The observation of the absorbance band characteristic of chromate esters around 371 nm a few seconds after mixing alditols and Cr^{VI} , under conditions where the redox reaction is extremely slow, reveals that such an intermediate Cr^{VI} complex is rapidly formed prior to the redox steps. Thus, the first step of the mechanism proposed in the *Scheme* may be interpreted as the formation of several linkage isomers **I** and **II** of the Cr^{VI} -Ald-ol monochelate [18] with the alditol acting as a bidentate ligand bound to Cr^{VI} via any pair of properly disposed OH groups. Taking into account that in the redox reaction only the

primary alcohol is oxidized, it seems reasonable to think that the complex **II** with the primary OH group bound to Cr^{VI} should be the precursor of the slow redox steps.

The slow redox step in the mechanism might take place by either a one-electron or a two-electron transfer [45]. The fit of absorbance data at 750 nm reveals that all of the Cr^{VI} reaches Cr^{III} through the intermediate Cr^V following the consecutive first-order Cr^{VI} → Cr^V → Cr^{III} redox pathway, indicating that the slow redox step in these reactions corresponds to a one-electron-transfer process (Cr^{VI} → Cr^V). This result differs from that observed for the oxidation of aldoses and methyl glycosides, in which the rate-determining step involves a two-electron-transfer process and only one-half of the Cr^{VI} reaches Cr^{III} through the intermediate Cr^V [20][23][25][30–34]. The two terms in the rate law (*Eqn. 2*) indicate that there are at least two transition states, differing in the protonation degree but similar in energy, through which the reduction of Cr^{VI} can proceed. Thus, in the slow redox step of the mechanism in the *Scheme*, complex **II** yields the Ald-ol[•] radical and Cr^V through two parallel acid-catalysed paths. Polymerization after addition of acrylonitrile supports the formation of the Ald-ol[•] radical. This Ald-ol[•] radical formed in the slow redox steps may react with Cr^{VI} to afford the final oxidized product (AldA) and Cr^{III}. For either Glc-ol or Man-ol, Cr^V formed in the slow step reacts with excess Ald-ol to yield the oxochromate(V) complex precursor of the electron-transfer steps, which then yields the redox products.

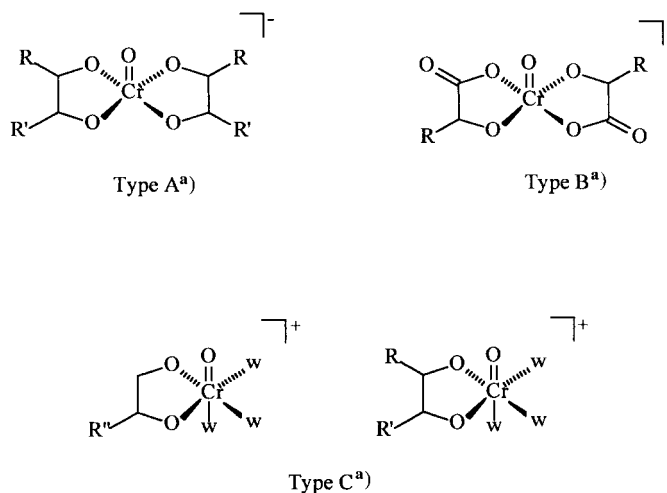
In contrast to monohydric alcohols [28][46][47], the alditols under study are not oxidized to the aldehyde, but directly to the carboxylic acid. For monohydric alcohols, it has been shown that the aldehyde oxidation rates are of the same order of magnitude than those of the corresponding alcohols [48][49]; so when a large excess of alcohol over Cr^{VI} is used, the [aldehyde] is not high enough to compete with the alcohol to reduce Cr^{VI}. In the case of the polyols under study, the rate of Cr^{VI} oxidation of aldoses, *i.e.* of the hemiacetal form of the aldehyde formed by oxidation of the corresponding alditol – is slower than that of alditols: $k_{\text{Glc-ol}}/k_{\text{Glc}} = 9.4$; $k_{\text{Man-ol}}/k_{\text{Man}} = 2.2$ [20][26][31]. Thus, if formed, the aldose should not be oxidized by Cr^{VI} to the aldonic acid when a large excess of alditol over Cr^{VI} is used. The non-observation of the aldose in the reaction mixture means that the aldose is not formed in these redox reactions, and that the alditols are directly oxidized to the corresponding aldonic acid. Consequently, the redox path shown in the *Scheme* takes into account the direct oxidation of the primary OH group to the carboxylate group with no formation of the aldehyde.

2.5. Characterization of Intermediate Cr^V Species by EPR Spectroscopy. 2.5.1. Preamble. The EPR spectral parameters, *i.e.* the g_{iso} and A_{iso} values, together with the proton superhyperfine (shf) coupling, have been shown to be useful in determining the binding modes of polyhydroxy compounds to the Cr^V center [20][25][30][31][50]. Polyols usually form weak complexes with metal cations. However, to compete with H₂O molecules for the occupancy of the first coordination sphere of a metal cation, these acyclic ligands must possess some pre-organization and contain particular spatial arrangements of the ligating groups [51]. The *threo* arrangement of two vicinal OH groups is particularly suitable for the complexation of hypervalent metal cations, which reinforces the CrO³⁺ preference to form five-membered Cr^V chelate rings [52–54]. Since the g_{iso} and A_{iso} values of the EPR signal of Cr^V complexes depend on the Cr^V coordination number and the nature of the donor groups bound to Cr^V [55–57], an estimation of the Cr^V species in solution may be made according to the shf pattern

together with the isotropic EPR parameters (g_{iso} and A_{iso} values) based on the empirical method developed by *Lay* and co-workers [55]. In the discussion that follows, we will use this approach to assign the coordination sphere of the intermediate Cr^{V} species formed in the reaction of Cr^{VI} with Glc-ol, Man-ol, and *meso*-galactitol (Gal-ol).

2.5.2. (*D*-Glucitol)chromium(V). In the reaction of Cr^{VI} with Glc-ol, at pH 4–5 and ligand-to-metal ratios < 20 (Fig. 5, a, Table 3), the EPR spectra of the intermediate Cr^{V} species show three *quint.* at $g_1 = 1.9800$, $g_2 = 1.9798$, and $g_3 = 1.9797$ and $A_{\text{iso}} = 16.5(3) \cdot 10^{-4} \text{ cm}^{-1}$. The g_{iso} and A_{iso} values correspond to those calculated for five-coordinate oxo- Cr^{V} complexes with four alcoholato donors [55], and the shf pattern is that expected for four equivalent CH–O protons – belonging to the diolate donor site of two bidentate Glc-ol bound to Cr^{V} – coupled to the Cr^{V} electronic spin. The independence of the spectra on [Glc-ol] confirms that all the species have a Cr^{V} coordination sphere saturated with respect to the alditol ($\text{Cr}^{\text{V}}/\text{Glc-ol}_2$). The different shf coupling constants indicate that the different species are linkage isomers of the Cr^{V} bis-chelate $[\text{Cr}(\text{O})(\text{O}^{2(3)}, \text{O}^{3(4)}\text{-Glc-ol})_2]^-$ (type A), with $\text{O}^{2(3)}, \text{O}^{3(4)}$ -Glc-ol corresponding to the ligand bound to Cr^{V} at any *threo*-diolate group (O^2, O^3 or O^3, O^4). The formation of $[\text{Cr}(\text{O})(\text{O}^2, \text{O}^3, \text{O}^4\text{-Glc-ol})(\text{OH}_2)]$ ($g_{\text{calc}} = 1.9783$) or $[\text{Cr}(\text{O})(\text{O}^2, \text{O}^3, \text{O}^4\text{-Glc-ol})(\text{OH}_2)_2]$ ($g_{\text{calc}} = 1.9735$) monochelates and $[\text{Cr}(\text{O})(\text{O}^2, \text{O}^3, \text{O}^4\text{-Glc-ol})(\text{O}^2, \text{O}^3\text{-Glc-ol})]^{2-}$ ($g_{\text{calc}} = 1.9759$) bis-chelate with one Glc-ol acting as a tridentate ligand *via* the 2,3,4-*xylo*-triolate (*threo-threo*) moiety is disregarded because no signal with the shf pattern and spectral parameters (g_{iso} and A_{iso} values) corresponding to such species are observed.

At pH 2 and ligand-to-metal ratios up to 10:1, and at pH 4–5 and ligand-to-metal ratios ≥ 20 , the spectra show the three signals attributed to the linkage isomers $[\text{Cr}(\text{O})(\text{O}^{2(3)}, \text{O}^{3(4)}\text{-Glc-ol})_2]^-$, besides an additional signal at $g_4 = 1.9787$ (Fig. 5, b). The g_{iso} value of the new signal corresponds to that calculated for a five-coordinate oxo- Cr^{V} complex, and the formation of this additional species is opposed to the formation of the



^{a)} R, R', R'' = polyhydroxy-substituted residues; w = water.

Table 3. EPR-Spectral Parameters

Cr ^V species	g_{iso}	$A_{\text{iso}}/10^4 \text{ cm}^{-1}$	$a_{\text{H}}/10^4 \text{ cm}^{-1} (N)^{\text{a}}$
[Cr(O)(O ²⁽³⁾ ,O ³⁽⁴⁾ -Glc-ol) ₂] ⁻	1.9800	16.5 ± 0.3	0.78 (4)
	1.9798		0.68 (4)
	1.9797		0.60 (4)
[Cr(O)(O ¹ ,O ² -GlcA) ₂] ⁻	1.9787	b)	0.68 (2)
[Cr(O)(O ^{1(2,3)} ,O ^{2(3,4)} -Glc-ol)(H ₂ O) ₃] ⁺	1.9719	20 ± 1	b)
[Cr(O)(O ³ ,O ⁴ -Man-ol) ₂] ⁻	1.9799	16.5 ± 0.3	0.90 (4)
	1.9798		0.88 (4)
[Cr(O)(O ¹ ,O ² -ManA) ₂] ⁻	1.9787	b)	b)
[Cr(O)(O ¹⁽³⁾ ,O ²⁽⁴⁾ -Man-ol)(H ₂ O) ₃] ⁺	1.9718	b)	b)
[Cr(O)(O ² ,O ³ -Gal-ol) ₂] ⁻	1.9799	16.3 ± 0.2	0.88 (4)
	1.9798		0.80 (4)
	1.9795		0.85 (4)
[Cr(O)(O ¹⁽²⁾ ,O ²⁽³⁾ -Gal-ol)(H ₂ O) ₃] ⁺	1.9720	20 ± 1	b)

^a) N = number of equivalent protons. ^b) Not determined.

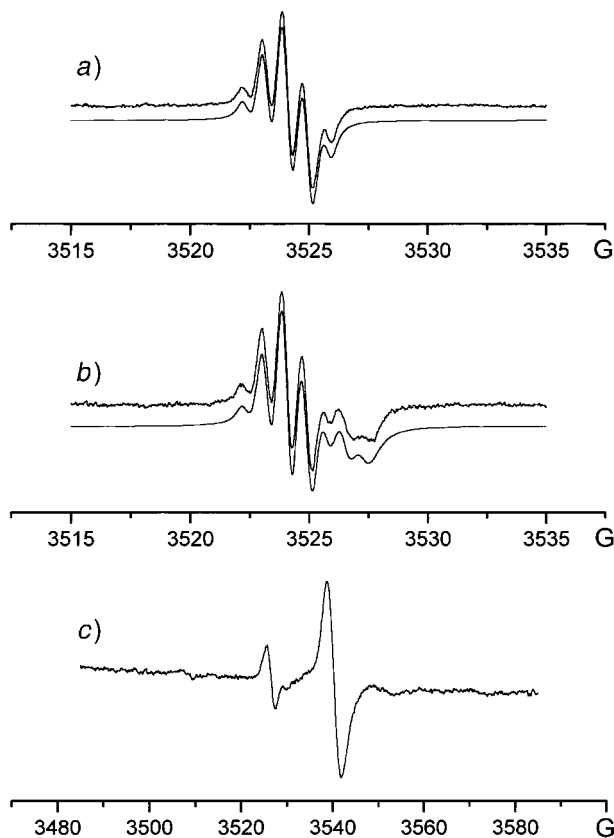


Fig. 5. Experimental and simulated X-band EPR spectra of solutions of Glc-ol and Cr^{VI}: a) Glc-ol/Cr^{VI} 10:1, pH 5 (mod. ampl. 0.4 G); b) Glc-ol/Cr^{VI} 20:1, pH 5 (mod. ampl. 0.4 G); c) Glc-ol/Cr^{VI} 10:1, [H⁺] = 0.1M (mod. ampl. 1.01 G). T 25°, frequency 9.7815 GHz. [Cr^{VI}] = $2.5 \cdot 10^{-3}$ M.

bis-chelate $[\text{Cr}(\text{O})(\text{O}^{2(3)}, \text{O}^{3(4)}\text{-Glc-ol})_2]^-$, which is independent of pH and [ligand]. The dependence of the signal at $g_4 = 1.9787$ on both the pH and the [ligand] is consistent with an oxo- Cr^{V} species formed with the oxidation product GlcA, coordination occurring *via* the 1-carboxylate and 2-hydroxy donor groups. The calculated g_{iso} (1.9783) for $[\text{Cr}(\text{O})(\text{O}^1, \text{O}^2\text{-GlcA})_2]^-$ (type **B**) is in reasonable agreement with the observed g_{iso} value. Besides, coordination to the oxidized ligand is consistent with the fact that Cr^{VI} is a stronger oxidant in more acidic medium.

At pH 1 and ligand-to-metal ratio 10 : 1, one additional signal at $g_5 = 1.9719$ appears, together with signals at $g_1 = 1.9800$, $g_2 = 1.9798$, $g_3 = 1.9797$ and $g_4 = 1.9787$. The shf pattern of this new signal is not resolved. However, its pH dependency and the g_{iso} value reveal some information on its nature. The formation of the species at g_5 is favored at higher acid concentrations, where it is the dominant one (*Fig. 5, c*). The low g_{iso} value of this signal suggests the presence of six-coordinate oxo- Cr^{V} species, possibly $[\text{Cr}(\text{O})(\text{O}^{1(2,3)}, \text{O}^{2(3,4)}\text{-Glc-ol})(\text{H}_2\text{O})_3]^+$ (type **C**). The calculated g_{iso} value for a six-coordinate oxo- Cr^{V} species with two alcoholato donor sites and three H_2O molecules (1.9724) is in agreement with the observed g_{iso} value. The positive charge of this species is also consistent with its appearance at high $[\text{H}^+]$. This Cr^{V} mono-chelate is possibly responsible for the higher rates observed for the Cr^{V} -Ald-ol redox reactions at $\text{pH} < 1$. At higher pH, where this Cr^{V} mono-chelate is not observed, Cr^{V} complexes are stable enough to remain in solution for several days to months.

2.5.3. (*D*-Mannitol)chromium(V). Intermediate Cr^{V} -Man-ol species formed in the reaction of Cr^{VI} with Man-ol, at pH 4–5 and ligand-to-metal ratios up to 25, have EPR spectra (*Fig. 6, a, Table 3*) consisting of two *quint.* at $g_1 = 1.9799$ and $g_2 = 1.9798$ with $A_{\text{iso}} = 16.5(3) \cdot 10^{-4} \text{ cm}^{-1}$. The g_{iso} and A_{iso} values and the shf pattern indicate these signals may be attributed to two geometric isomers of the five-coordinate oxo- Cr^{V} complex $[\text{Cr}(\text{O})(\text{O}^3, \text{O}^4\text{-Man-ol})_2]^-$ (type **A**), with Man-ol bound to Cr^{V} *via* the 3,4-*threo*-diolate moiety.

At pH 2 and ligand-to-metal ratios up to 10 : 1, the spectra show the two signals attributed to the geometric isomers $[\text{Cr}(\text{O})(\text{O}^3, \text{O}^4\text{-Man-ol})_2]^-$, together with an additional non-resolved signal at $g_3 = 1.9787$ (*Fig. 6, b*). As in the case of Glc-ol, this signal may be attributed to the five-coordinate oxo- Cr^{V} $[\text{Cr}(\text{O})(\text{O}^1, \text{O}^2\text{-ManA})_2]^-$ (type **B**), with ManA acting as a bidentate ligand *via* the 2-hydroxy acid moiety.

At pH 1 and ligand-to-metal ratio 10 : 1, Man-ol behaves similarly to Glc-ol. The EPR spectrum is now dominated by a non-resolved signal at $g_4 = 1.9718$ (85%), besides minor signals at $g_1 = 1.9799$, $g_2 = 1.9798$, and $g_3 = 1.9787$ (*Fig. 6, c*). The g_{iso} value of the signal at g_4 corresponds to a six-coordinate oxo- Cr^{V} species and may be assigned to $[\text{Cr}(\text{O})(\text{O}^{1(3)}, \text{O}^{2(4)}\text{-Man-ol})(\text{H}_2\text{O})_3]^+$ (type **C**).

2.5.4. (*meso*-Galactitol)chromium(V). To evaluate whether the pattern observed for Glc-ol and Man-ol may be generalized to other alditols, the reaction of Cr^{VI} with Gal-ol was also studied. At pH 4–5 and ligand-to-metal ratios up to 25 (*Fig. 7, a, Table 3*), the EPR spectra of intermediate Cr^{V} consist of three *quint.* at $g_1 = 1.9799$, $g_2 = 1.9798$, and $g_3 = 1.9795$, which may be attributed to three geometric isomers of the Cr^{V} bis-chelate $[\text{Cr}(\text{O})(\text{O}^2, \text{O}^3\text{-Gal-ol})_2]^-$ (type **A**), with O^2, O^3 -Gal-ol corresponding to the ligand bound to Cr^{V} at any *threo*-diolate group (coordination to O^2, O^3 and O^4, O^5 are equivalent). Here again, the independence of the signals on [Gal-ol] indicates that all three species have a Cr^{V} coordination sphere saturated with respect to the alditol.

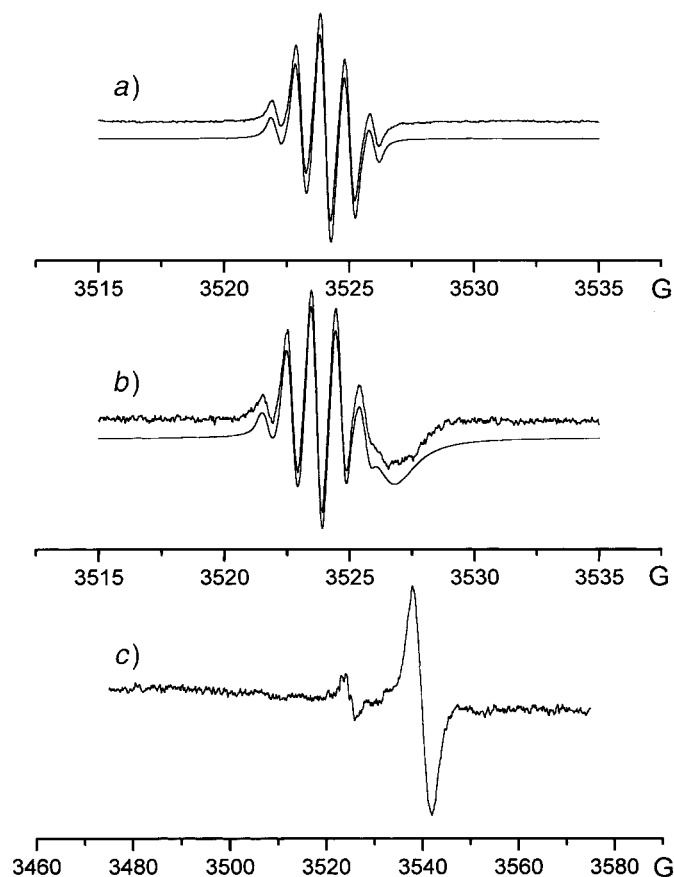


Fig. 6. Experimental and simulated X-band EPR spectra of solutions of Man-ol and Cr^{VI} : a) pH 5 (mod. ampl. 0.4 G, frequency 9.7819 GHz); b) pH 2 (mod. ampl. 0.4 G, frequency 9.7808 GHz); c) $[\text{H}^+] = 0.1\text{M}$ (mod. ampl. 1.01 G, frequency 9.7788 GHz). T 25°, $[\text{Cr}^{\text{VI}}] = 2.5 \cdot 10^{-3}$ M, Man-ol/ Cr^{VI} 10:1.

In 0.5M HClO_4 and ligand-to-metal ratio 10:1, the EPR spectrum is dominated (84%) by a new signal at $g_4 = 1.9720$, with non-resolved shf pattern (Fig. 7, b). The species at g_1 , g_2 , and g_3 are still present under these conditions, but the signal is now badly resolved, probably due to their very low concentration in the reaction mixture. Also in this case, the signal at g_4 may be assigned to the six-coordinate oxo- Cr^{V} complex $[\text{Cr}(\text{O})(\text{O}^{1(2)}, \text{O}^{2(3)}\text{-Gal-ol})(\text{H}_2\text{O})_3]^+$ (type C).

The ultimate fate of the Cr-atom in all of these reactions (*i.e.* also in 2.5.2 and 2.5.3) is a Cr^{III} species, and a typical broad Cr^{III} EPR signal centered at $g \approx 1.98$ is always observed at a later time.

3. Conclusions. – Alditols are selectively oxidized by Cr^{VI} at the primary OH group to yield the aldonic acid as the only oxidation product. The reaction involves a $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{III}}$ reduction path, with the $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}}$ step being the rate-determining one.

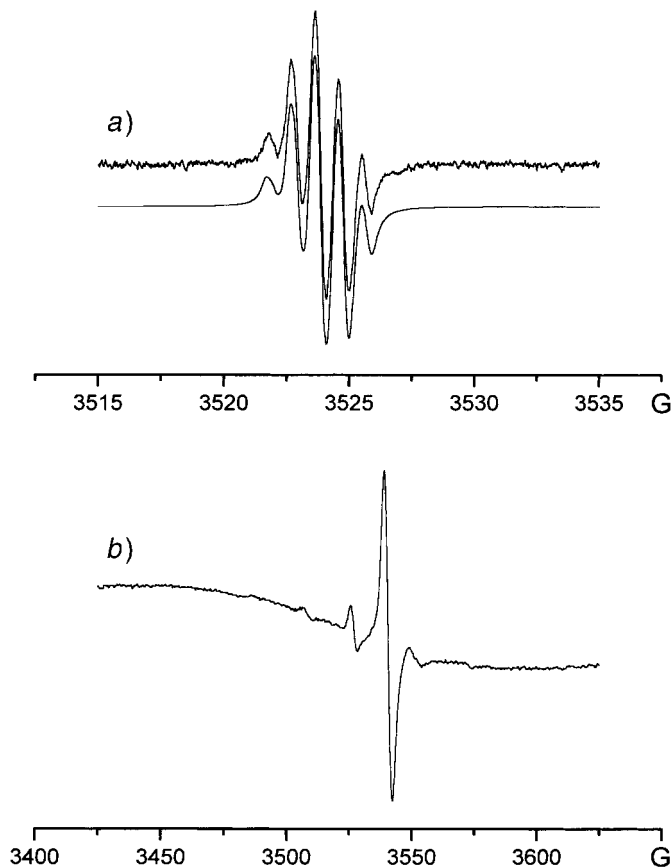


Fig. 7. Experimental and simulated X-band EPR spectra of solutions of Gal-ol and Cr^{VI} . a) Gal-ol/ Cr^{VI} 20:1, pH 5 (mod. ampl. 0.4 G, frequency 9.7814 GHz); b) Gal-ol/ Cr^{VI} 10:1, $[\text{H}^+] = 0.5\text{M}$ (mod. ampl. 2.0 G, frequency 9.7827 GHz). T 25°, $[\text{Cr}^{\text{VI}}] = 2.5 \cdot 10^{-3}\text{M}$.

The reaction requires protons to be present, and, at low acidity, the redox rate is negligible. The same mechanism is found for the oxidation of the two alditols Glc-ol and Man-ol, and the rate constants are very similar, meaning that the configuration at C(2) affects only slightly the redox rate. Glc-ol and Man-ol are oxidized 10 and 20 times faster than the respective methyl glycosides, for which the primary OH is also oxidized to the carboxylate. This different reactivity is consistent with the ability of alditols to form five-membered Cr^{V} chelate rings involving the primary OH, which is not possible in methyl glycosides with the vicinal OH group involved in the acetal bond. As in the case of sugars and their derivatives, the secondary OH groups are inert to oxidation when an excess of reductant over oxidant is used. Alditols stabilize Cr^{V} , yielding penta- and hexacoordinate oxo-chromate(V) complexes depending on the $[\text{H}^+]$. At $[\text{H}^+] \geq 0.1\text{M}$, positively charged hexacoordinate Cr^{V} monochelates are formed, and are believed to be responsible for the fast electron-transfer process in the $[\text{H}^+]$ range 0.1 – 0.8M. At pH > 1, only pentacoordinate Cr^{V} species are present, intramolecular redox

reactions are very slow, and the Cr^{V} complexes remain in solution for several days to weeks. The EPR parameters together with the shf pattern indicate that the five-coordinate oxo- Cr^{V} complexes formed with excess alditol involve metal binding to four secondary alcoholato donors, belonging to the diolate donor site of two bidentate Aldol bound to Cr^{V} . Thus, the more stable oxo- Cr^{V} complexes do not involve Cr^{V} coordinated to the primary OH group, similar to what has been observed for sugars and their derivatives [20][23][25][30][31][33][34].

Experimental Part

1. *Materials.* D-Sorbitol (*Sigma grade*), D-mannitol (*Sigma grade*), meso-galactitol (*Sigma grade*), $\text{K}_2\text{Cr}_2\text{O}_7$ (*Cicarelli c.a.*), acrylonitrile (*Aldrich grade*), perchloric acid (*Merck p.a.*), and sulfuric acid (*Merck p.a.*) were used without further purification. H_2O was purified by deionization, followed by double distillation from a KMnO_4 soln. For experiments performed in the pH range 1–5, the pH of the solns. was adjusted by addition of 0.5M HClO_4 . In experiments performed at constant ionic strength ($I = 1.0\text{M}$) and different $[\text{H}^+]$, mixtures of NaClO_4 solns. and HClO_4 solns. were used. NaClO_4 solns. were prepared from NaOH and HClO_4 solns. The concentration of stock solns. of HClO_4 was determined by titration by standard anal. methods [58].

The stability of the org. substrate under conditions used in the kinetic studies was tested by paper chromatography (PC) at a given $[\text{H}^+]$ and by HPLC.

2. *Spectrophotometry.* Spectrophotometric measurements were made by monitoring absorbance changes at 350, 570, and 750 nm on a *Jasco-V-530-UV/VIS* spectrophotometer with fully thermostated cell compartments. Reactant solns. were previously equilibrated and transferred into a cell of 1-cm path length immediately after mixing, and the reaction was followed until at least 80% conversion. Experiments were performed at 33° unless otherwise mentioned.

The Cr^{VI} consumption was followed spectrophotometrically at 350 nm. In all experiments, the concentration of Cr^{VI} was kept constant at $6 \cdot 10^{-4}$ M, while the alditol concentration was varied from 0.06 to 0.30M. The observed pseudo-first-order rate constants (k_6), determined from the slopes of the linear part of plots of $\ln(\text{Abs}^{350})$ vs. time, were deduced from multiple determinations and were within $\pm 5\%$ of each other. The first-order dependence of the rate upon $[\text{Cr}^{\text{VI}}]$ was verified by calculating the pseudo-first-order rate constants at various $[\text{Cr}^{\text{VI}}]_0$, but at constant temperature, [alditol], $[\text{H}^+]$, and I . As expected from a $-\text{d}(\ln[\text{Cr}^{\text{VI}}])/dt = k_6$ rate law, where $k_6 = f([\text{alditol}][\text{H}^+])$, k_6 was found to be essentially constant with increasing $[\text{Cr}^{\text{VI}}]_0$.

The formation of Cr^{III} was monitored at 570 nm ($[\text{Cr}^{\text{VI}}] = 6 \cdot 10^{-3}$ M) in the presence of excess alditol and $[\text{HClO}_4]$ in the 0.10–0.80M range. Under these conditions, the first-order dependence of the rate upon $[\text{Cr}^{\text{VI}}]$ was verified, and k_6 were obtained following the Cr^{III} growth at 570 nm. Initial reaction rates were obtained by fitting the absorbance at 570 nm/time data to a polynomial expression [59] and calculating the slope of the tangent at time zero (r_i). First-order rate constants were obtained from these initial rates by means of the equation $-r_i/(A_0 - A_t)$, with average values of the initial rate and calculated estimates of $(A_0 - A_t)$. The results at 570 nm were in total agreement with those obtained at 350 nm (*Table 1*). At the end of the reaction, the two $d-d$ bands ascribed to Cr^{III} were observed at λ_{max} 409 nm (ϵ 16.2 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) and λ_{max} 574 nm (ϵ 13.6 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$). Both VIS and UV spectral maxima and intensities were in close agreement with those observed for the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ion.

Cr^{V} was monitored by following the absorbance growth and decay at 750 nm of mixtures of Cr^{VI} (0.018M) and excess alditol (0.9M) at different $[\text{HClO}_4]$. At this wavelength, kinetic traces were evaluated from a nonlinear iterative computer fit of the rate expression derived from two consecutive first-order reactions $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{V}} \rightarrow \text{Cr}^{\text{III}}$. Values of k_6 obtained at this wavelength were coincident with those calculated from data at 350 and 570 nm. In multiple measurements, the reproducibility of the two rate constants was better than 10%.

Chromate esters were investigated by UV/VIS spectrophotometry in the 350–400 nm region in which these esters show characteristic absorption bands. Reactions were performed at pH 4.5, a pH where the redox reaction is slow enough to enable the observation of ester formation. The instrument was zeroed to an arrangement of the reference and sample beams passing through matched cuvettes, both containing Cr^{VI} in H_2O at pH 4.5. The soln. in the sample cell was replaced with the reaction soln. containing $6 \cdot 10^{-4}$ M Cr^{VI} and 0.12–0.30M alditol at pH 4.5, $I = 1.0\text{M}$ and 33°. Spectra obtained within 30 min after mixing revealed a distinctive absorption at 371 nm.

3. *Product Analysis*. 3.1. *General*. HPLC was employed to detect the reaction products under the conditions used in the kinetic measurements (excess of alditol over Cr^{VI}): *KNK-500A* chromatograph, *7125* HPLC pump; *Aminex-HPX-87 H* HPLC column (300 × 7.8 mm, *Bio-Rad Laboratories*), 3 · 10⁻³ M H₂SO₄ as eluent, flow rate 0.6 ml/min, at 35°; refractive-index detector (*ERC-7522, Erma Inc.*). The pH of the standard and the reaction-mixture samples was adjusted to 3 by addition of NaOH (to avoid precipitation inside the column), and then the samples were filtered through a 0.2-μm membrane prior to the injection into the chromatographic system.

Standard solns. of the Glc-ol, Man-ol, D-glucose, D-mannose, D-glucono-1,5-lactone, D-gulono-1,4-lactone, D-mannono-1,4-lactone, D-glucuronic acid, and D-mannofuranurono-6,3-lactone were prepared individually in 0.5M HClO₄ and chromatographed separately to determine the *t_R* of each sample.

Under all experimental conditions (large to moderate excess of alditol over Cr^{VI}), CO₂ was never observed as a reaction product, indicating that no degradation to the lower homologues occurred.

Alternatively, the possible formation of the aldose as the reaction product was tested by addition of (2,4-dinitrophenyl)hydrazine to the Cr^{VI}/alditol reaction mixtures. The 2,4-dinitrophenylhydrazone derivative was never observed.

3.2. *Glc-ol/Cr^{VI} System*. A reaction mixture obtained from 8 · 10⁻⁴ M Cr^{VI} and 0.04M Glc-ol in 0.5M HClO₄ was submitted to HPLC: only 1 product at *t_R* 8 min, 26 s. Co-HPLC with D-glucono-1,5-lactone resulted in an increased product peak; no D-glucuronic acid (*t_R* 7 min 25 s) was observed, however, the presence of D-glucose (*t_R* 8 min 20 s) and D-gulono-1,4-lactone (*t_R* 8 min 22 s) with *t_Rs* very close to that of D-glucono-1,5-lactone, could not be excluded. For this reason, and in the presence of an excess of alditol over Cr^{VI}, the aldono-lactone produced was qualitatively identified by PC with BuOH/AcOH/H₂O 4:1:5 as eluent and visualization by aniline hydrogenphthalate [60], a reagent specific for the detection of aldoses and uronic acids, and by ferric hydroxamate [61], a reagent specific for lactones. No colored spots appeared in the PC developed with aniline hydrogenphthalate, whereas with ferric hydroxamate, a violet compound was detected. An additional PC with BuOH/EtOH/H₂O 5:1:4 as eluent, a solvent separating γ-lactones from δ-lactones, revealed only D-glucono-1,5-lactone in the reaction mixture [62]; however, the presence of a small amount of D-gulono-1,4-lactone can not be excluded.

3.3. *Man-ol/Cr^{VI} System*. A reaction mixture obtained from 7.3 · 10⁻³ M Cr^{VI} and 0.36M Man-ol in 0.5M HClO₄ was chromatographed: only 1 product at *t_R* 10 min 13 s, corresponding to D-mannono-1,4-lactone. D-Mannose (*t_R* 8 min 55 s) and D-mannofuranurono-6,3-lactone (*t_R* 11 min 30 s) were not observed.

4. *EPR Measurements*. All of the EPR experiments were carried out at r.t. with a *Bruker ESP-300 E* spectrometer. The microwave frequency was generated with a *Bruker 04-ER* (9–10 GHz) and measured with a *Racal-Dana* frequency meter. The magnetic field was measured with a *Bruker* NMR-probe gaussmeter. EPR Spectra were simulated by means of the program PEST WinSIM [63], with 100% *Lorentzian* lineshapes.

5. *Free-Radicals Test*. The presence of free radicals was tested for the reaction of the alditols with Cr^{VI}. In a typical experiment, to a soln. of K₂Cr₂O₇ (2 · 10⁻³ mmol) and alditol (0.02 mmol) in 2 ml of 0.50M HClO₄, acrylonitrile (0.5 ml) was added at 33°. After a few minutes, a white precipitate appeared. Control experiments (without K₂Cr₂O₇ or reductant present) did not show the formation of a precipitate. The possible reaction of Cr^V with acrylonitrile was excluded based on the absence of a precipitate one day after mixing [Cr^VO(chba)₂]K and acrylonitrile under the same reaction conditions than before.

We tried several spin traps with the intention of detecting by EPR the intermediate radical formed during the redox reaction. The addition of 4,5-dihydro-5,5-dimethyl-1H-pyrrole 1-oxide (DMPO) to the reaction mixture resulted in the appearance of an EPR signal at *g* = 2.003 with splitting constants of 7.48 · 10⁻⁴ cm⁻¹ and 3.65 · 10⁻⁴ cm⁻¹ (× 2), corresponding to the oxidized spin trap, and the signal of the DMPO-OH· spin adduct [64]. The EPR signal of the DMPO-sorbitol· spin adduct has been reported and has a distinctive well defined hyperfine pattern [65]. However, in the present case, no signal attributable to the DMPO-alditol· spin adduct was detected. Similarly, 5-(diethoxyphosphoryl)-4,5-dihydro-5-methyl-1H-pyrrole 1-oxide (DEPMPO) and (4-pyridyl-1-oxide)-*N*-(*tert*-butyl)nitron (= 1,1-dimethyl-*N*-[(1-oxidopyridin-4-yl)methylidene]ethanamine *N*-oxide; POBN) trapped only OH·. Probably the intermediate radical could not be trapped because the spin trap preferred the redox reaction with Cr^V, which yields the paramagnetic products observed by EPR [66]. In previous works, the EPR *m* at *g* = 2.003 had been erroneously attributed to a DMPO-sugar· spin adduct [30][31].

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