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

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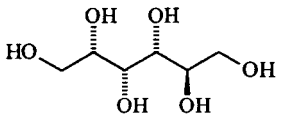
The oxidation of D-glucitol and D-mannitol by $Cr^{VI}$ yields the aldonic acid (and/or the aldonolactone) and $Cr^{III}$ as final products when an excess of alditol over $Cr^{VI}$ is used. The redox reaction occurs through a $Cr^{VI} \rightarrow Cr^{V} \rightarrow Cr^{III}$ path, the $Cr^{VI} \rightarrow Cr^{V}$ reduction being the slow redox step. The complete rate laws for the redox reactions are expressed by: *a*) $-d[Cr^{VI}]/dt = \{k_{M2H}[H^+]^2 + k_{MH}[H^+]\}[\text{mannitol}][Cr^{VI}]$, where $k_{M2H} = (6.7 \pm 0.3) \cdot 10^{-2}$ M$^{-3}$ s$^{-1}$ and $k_{MH} = (9 \pm 2) \cdot 10^{-3}$ M$^{-2}$ s$^{-1}$; *b*) $-d[Cr^{VI}]/dt = \{k_{G2H}[H^+]^2 + k_{GH}[H^+]\}[\text{glucitol}][Cr^{VI}]$, where $k_{G2H} = (8.5 \pm 0.2) \cdot 10^{-2}$ M$^{-3}$ s$^{-1}$ and $k_{GH} = (1.8 \pm 0.1) \cdot 10^{-2}$ M$^{-2}$ s$^{-1}$, at 33°. The slow redox steps are preceded by the formation of a $Cr^{VI}$ oxy ester with $\lambda_{max}$ 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.

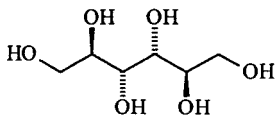
**1. Introduction.** – Chromium(VI) ($Cr^{VI}$) is a potential hazard both in a biological and an ecological context [1]. The observation of $Cr^{V}$ and $Cr^{IV}$ intermediates in the selective oxidation of organic substrates by $Cr^{VI}$ and their implication in the mechanism of Cr-induced cancers [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 $\alpha$-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 OH–C(1), and in methyl glycosides, where the anomeric position is blocked, the oxidation takes place at OH–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].




Glc-ol




Man-ol

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 $\lambda_{max}$ 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 In(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 $[H^+]$ 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 $[H^+]$ (*Table 1*). 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(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.* [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 $[HClO_4]$, which may be expressed by *Eqn. 1*, where $k_{G2H} = (8.5 \pm 0.2) \cdot 10^{-2}$ м$^{-3}$ s$^{-1}$ and $k_{GH} = (1.8 \pm 0.1) \cdot 10^{-2}$ м$^{-2}$ s$^{-1}$ for Glc-ol, and $k_{M2H} = (6.7 \pm 0.3) \cdot 10^{-2}$ м$^{-3}$ s$^{-1}$ and $k_{MH}$ $(9 \pm 2) \cdot 10^{-3}$ м$^{-2}$ 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*.

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

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

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 $\lambda_{max}$ 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°; $[Cr^{VI}]_0 = 6 \cdot 10^{-4}$ м; $I$ = 1м.

| $[HClO_4]$/м | $10^4\,k_6/s^{-1}$ for [Glc-ol] | | | | | | | $10^3\,k_G$/м$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | 0.06м | 0.12м | 0.18м | 0.21м | 0.24м | 0.3м | | |
| | | | | | | 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) |
| $[HClO_4]$/м | $10^4\,k_6/s^{-1}$ for [Man-ol] | | | | | | | $10^3\,k_M$/м$^{-1}$ s$^{-1}$ |
| | 0.06м | 0.12м | 0.18м | 0.24м | | 0.30м | | |
| | | | | 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]) $[Cr^{VI}] = 6 \cdot 10^{-3}$ м.

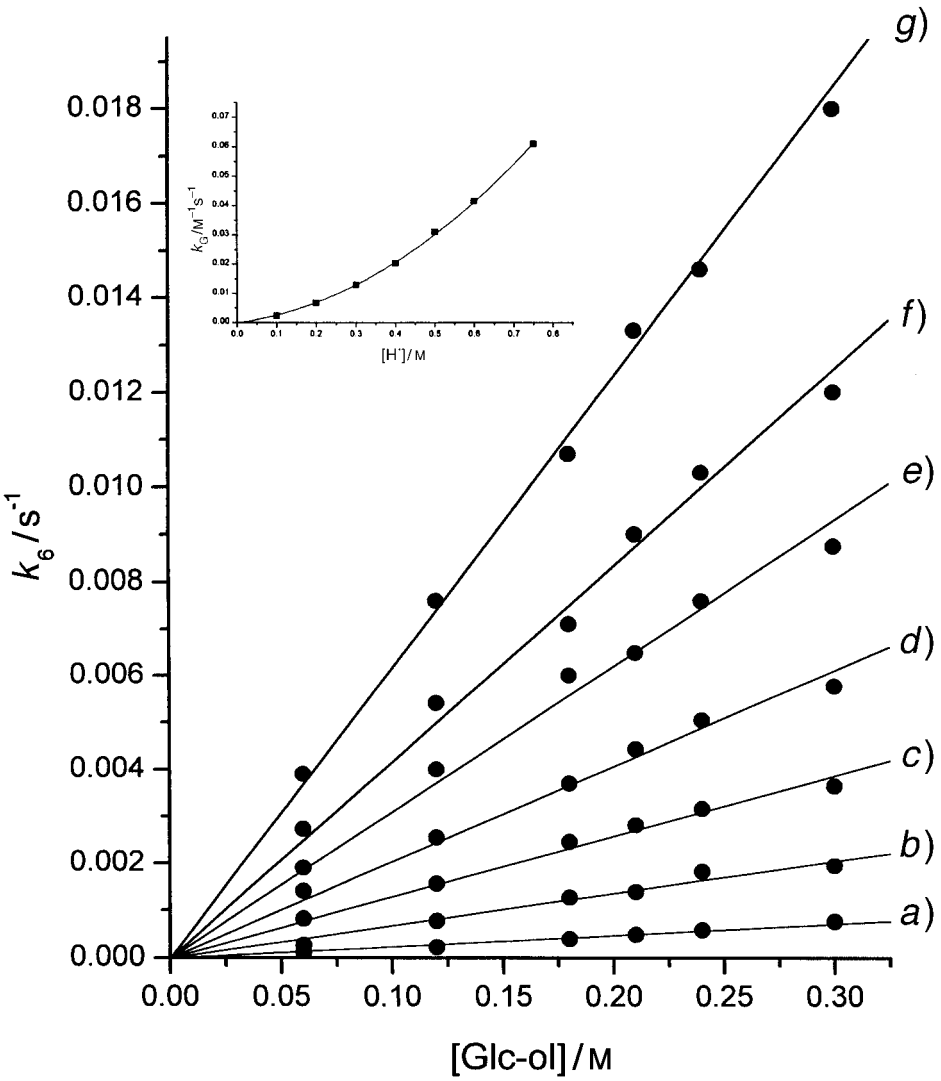



Fig. 1. *Effect of [Glc-ol] on* $k_6$ *at 33°*, I = *1.00*M, *and [H$^+$]/*M: a) *0.10*, b) *0.20*, c) *0.30*, d) *0.40*, e) *0.50*, f) *0.60, and* g) *0.75*. Inset: Effect of acidity on $k_G$.

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 [H$^+$] range, the EPR spectra consist of a minor signal at $g_{iso} = 1.9793$ – which is a composite of

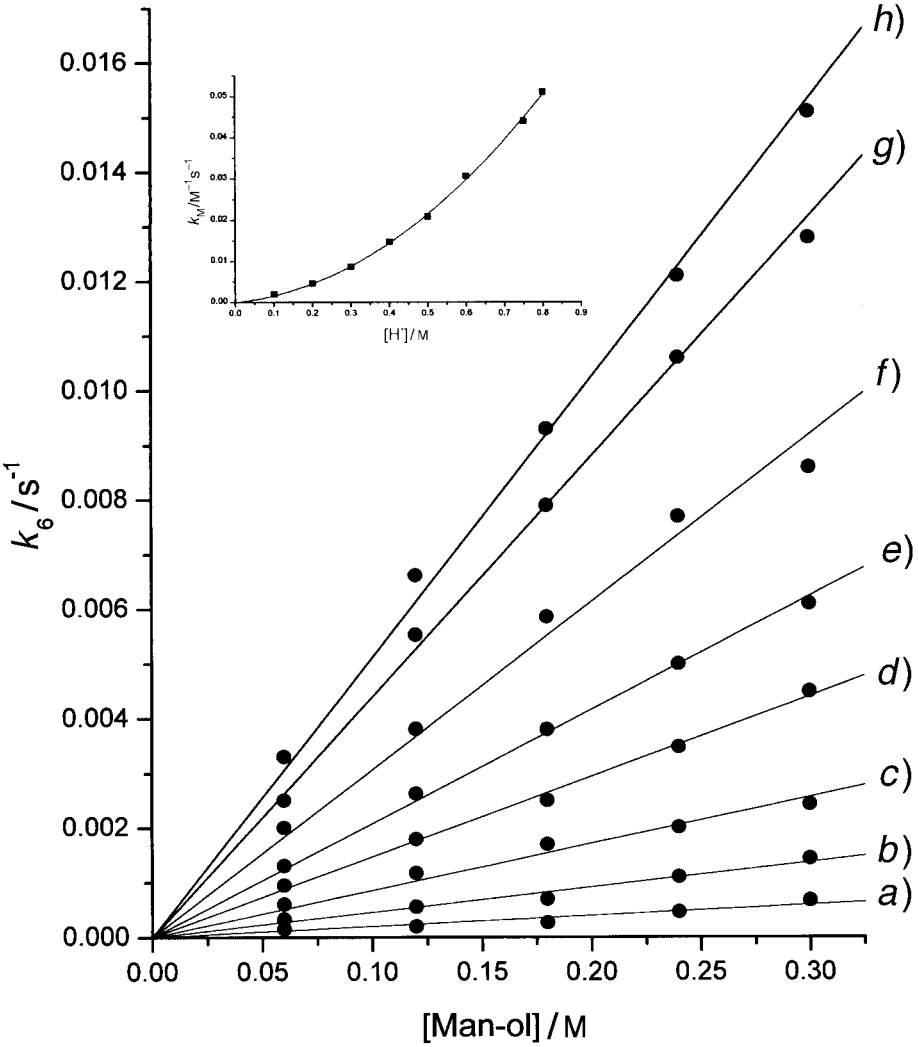



Fig. 2. *Effect of [Man-ol] on* $k_6$ *at 33°,* I = *1.00*M *and [H$^+$]/*M: a) *0.10,* b) *0.20,* c) *0.30,* d) *0.40,* e) *0.50,* f) *0.60,* g) *0.75, and* h) *0.80.* Inset: Effect of acidity on $k_M$.

several $Cr^V$ species, as discussed below – and a major signal at $g_{iso} = 1.9718$ (or 1.9719, resp.). The signal at lower $g_{iso}$ is not observed at pH > 1 where the electron-transfer reaction becomes extremely slow and the $Cr^V$ species with $g_{iso} = 1.9793$ remain a long time in solution. By contrast, in the $[H^+]$ 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 $\varepsilon^V$ refers to the $Cr^V$ molar absorptivity at this wavelength

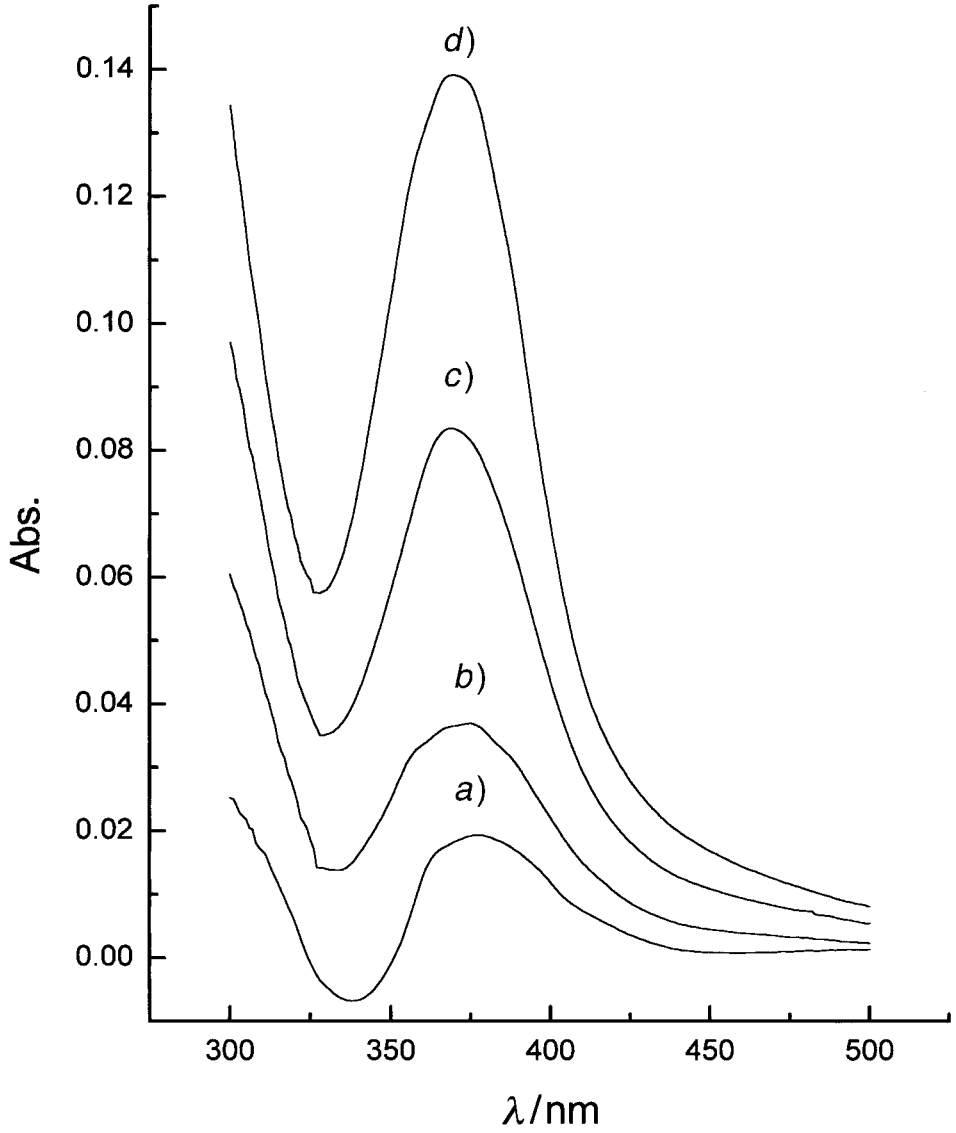



Fig. 3. *UV/VIS Difference spectra of* $Cr^{VI}$*/Glc-ol solutions at pH 4.5, showing the increasing band at 371 nm with increasing [Glc-ol]:* a) *0.12,* b) *0.18,* c) *0.24, and* d) *0.30*м. $[Cr^{VI}] = 6 \cdot 10^{-4}$ м, *T* 33°, *I* = 1м. Spectra taken after 20 min.

and is assumed to be the same as for the complex $[Cr^{V}(O)(ehba)_2]^-$ ($\varepsilon = 38$ м$^{-1}$ 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 $[H^+]$ are listed in *Table 2*. The $k_6$ values obtained agree perfectly with values calculated from data at 350 and 570 nm.

$$Abs^{750} = k_6\, \varepsilon^{V}\, [Cr^{VI}]_0\, (e^{-k_5 t} - e^{-k_6 t})/(k_6 - k_5) \qquad (3)$$

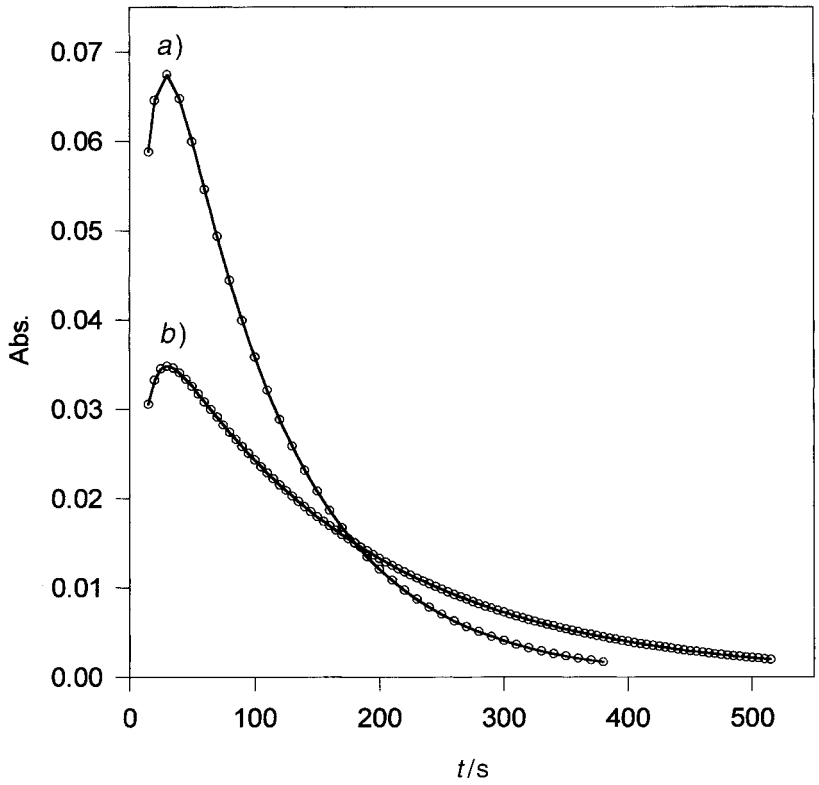



Fig. 4. *Absorbance* vs. *time curves for the chromic oxidation of* a) *Glc-ol and* b) *Man-ol.* $[Cr^{VI}] = 1.8 \cdot 10^{-2}$ M, [Ald-ol] = 0.9M, $[H^+] = 0.30$M, $I = 1$M, $T = 33°$, $\lambda$ 750 nm.

Table 2. *Observed Pseudo-First-Order Rate Constants*[a]) $k_5$ *and* $k_6$ *for Different [$HClO_4$] Obtained at $\lambda$ 750 nm.* $[Cr^{VI}] = 0.018$M; [alditol] = 0.9M; $I = 1$M; $T$ 33°.

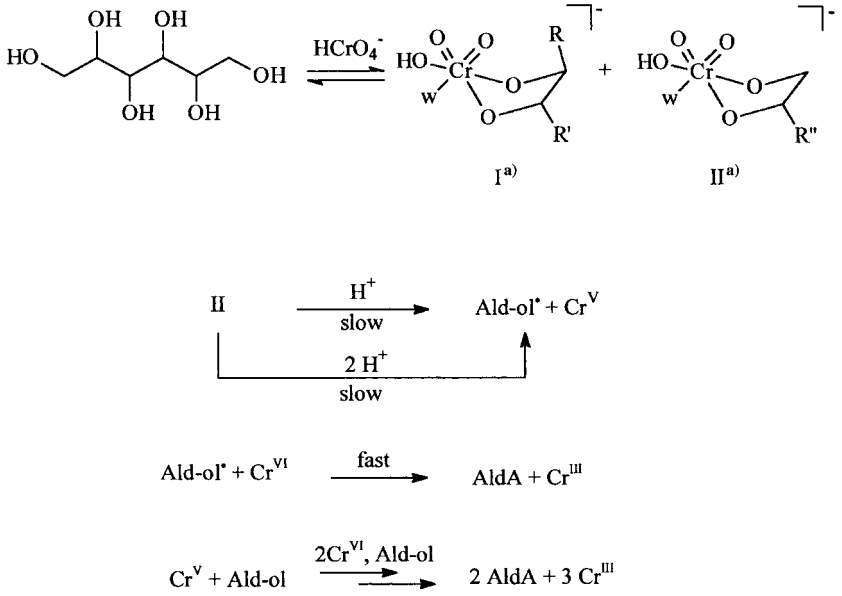
| $[HClO_4]$/M | Man-ol | | |
|---|---|---|---|
| | $10^3\ k_{6(calc.)}$[b])/$s^{-1}$ | $10^3\ k_6/s^{-1}$ | $10^2\ k_5/s^{-1}$ |
| 0.1 | 1.3 | 1.0(2) | 4.4(1) |
| 0.2 | 4.0 | 3.8(1) | 6.6(1) |
| 0.3 | 8.0 | 6.1(1) | 9.9(1) |
| 0.4 | 13 | 12(1) | 11(1) |
| 0.5 | 20 | 18(2) | 13(1) |
| $[HClO_4]$/M | Glc-ol | | |
| | $10^3\ k_{6(calc.)}$[b])/$s^{-1}$ | $10^3\ k_6/s^{-1}$ | $10^2\ k_5/s^{-1}$ |
| 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 ($[Cr^{V}]_{max}$) 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 $[Cr^{VI}]$.

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 $[Cr(H_2O)_6]^{3+}$ 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.

*Scheme*




a) R,R′,R″ = polyhydroxy-substituted residues; w = water.

In the $[H^+]$ 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 $[Cr^{VI}]$. 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 $Cr^{VI} \rightarrow Cr^{V} \rightarrow Cr^{III}$ redox pathway, indicating that the slow redox step in these reactions corresponds to a one-electron-transfer process ($Cr^{VI} \rightarrow Cr^{V}$). 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$^{\cdot}$ radical and $Cr^{V}$ through two parallel acid-catalysed paths. Polymerization after addition of acrylonitrile supports the formation of the Ald-ol$^{\cdot}$ radical. This Ald-ol$^{\cdot}$ 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.

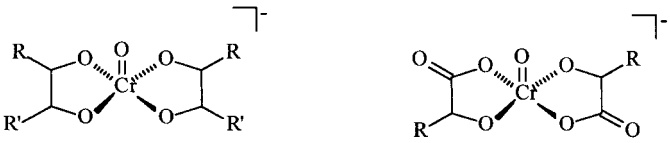
In contrast to monohydric alcohols [28][46][47], the alditols under study are not oxidized to the aldehyde, but directly to the carboxylic acid. For monohydric alcohols, it has been shown that the aldehyde oxidation rates are of the same order of magnitude than those of the corresponding alcohols [48][49]; 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: $k_{Glc\text{-}ol}/k_{Glc} = 9.4$; $k_{Man\text{-}ol}/k_{Man} = 2.2$ [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 $H_2O$ 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 $CrO^{3+}$ 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 $A_{iso} = 16.5(3) \cdot 10^{-4}\ cm^{-1}$. 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 ($Cr^V$/Glc-$ol_2$). The different shf coupling constants indicate that the different species are linkage isomers of the $Cr^V$ bis-chelate $[Cr(O)(O^{2(3)},O^{3(4)}\text{-Glc-ol})_2]^-$ (type **A**), with $O^{2(3)},O^{3(4)}$-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 $[Cr(O)(O^2,O^3,O^4\text{-Glc-ol})(OH_2)]$ ($g_{calc} = 1.9783$) or $[Cr(O)(O^2,O^3,O^4\text{-Glc-ol})(OH_2)_2]$ ($g_{calc} = 1.9735$) monochelates and $[Cr(O)(O^2,O^3,O^4\text{-Glc-ol})(O^2,O^3\text{-Glc-ol})]^{2-}$ ($g_{calc} = 1.9759$) 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.

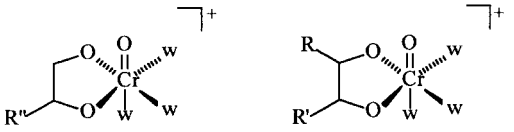
At pH 2 and ligand-to-metal ratios up to 10 : 1, and at pH 4–5 and ligand-to-metal ratios $\geq 20$, the spectra show the three signals attributed to the linkage isomers $[Cr(O)(O^{2(3)},O^{3(4)}\text{-Glc-ol})_2]^-$, besides an additional signal at $g_4 = 1.9787$ (*Fig. 5,b*). The $g_{iso}$ value of 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



Type A[a])



Type B[a])



Type C[a])

[a]) R,R′,R″ = polyhydroxy-substituted residues; w = water.

Table 3. *EPR-Spectral Parameters*

| $Cr^V$ species | $g_{iso}$ | $A_{iso}/10^4$ cm$^{-1}$ | $a_H/10^4$ cm$^{-1}$ ($N$)[a]) |
|---|---|---|---|
| $[Cr(O)(O^{2(3)},O^{3(4)}\text{-Glc-ol})_2]^-$ | 1.9800 | $16.5 \pm 0.3$ | 0.78 (4) |
| | 1.9798 | | 0.68 (4) |
| | 1.9797 | | 0.60 (4) |
| $[Cr(O)(O^1,O^2\text{-GlcA})_2]^-$ | 1.9787 | [b]) | 0.68 (2) |
| $[Cr(O)(O^{1(2,3)},O^{2(3,4)}\text{-Glc-ol})(H_2O)_3]^+$ | 1.9719 | $20 \pm 1$ | [b]) |
| $[Cr(O)(O^3,O^4\text{-Man-ol})_2]^-$ | 1.9799 | $16.5 \pm 0.3$ | 0.90 (4) |
| | 1.9798 | | 0.88 (4) |
| $[Cr(O)(O^1,O^2\text{-ManA})_2]^-$ | 1.9787 | [b]) | [b]) |
| $[Cr(O)(O^{1(3)},O^{2(4)}\text{-Man-ol})(H_2O)_3]^+$ | 1.9718 | [b]) | [b]) |
| $[Cr(O)(O^2,O^3\text{-Gal-ol})_2]^-$ | 1.9799 | $16.3 \pm 0.2$ | 0.88 (4) |
| | 1.9798 | | 0.80 (4) |
| | 1.9795 | | 0.85 (4) |
| $[Cr(O)(O^{1(2)},O^{2(3)}\text{-Gal-ol})(H_2O)_3]^+$ | 1.9720 | $20 \pm 1$ | [b]) |

[a]) $N$ = number of equivalent protons. [b]) Not determined.

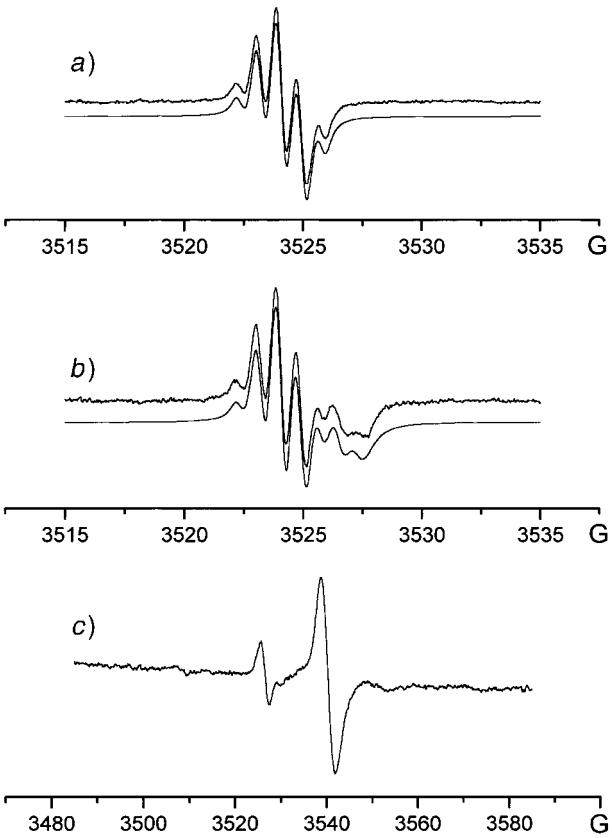



Fig. 5. *Experimental and simulated X-band EPR spectra of solutions of Glc-ol and $Cr^{VI}$:* a) *Glc-ol/$Cr^{VI}$ 10 : 1, pH 5* (mod. ampl. 0.4 G); b) *Glc-ol/$Cr^{VI}$ 20 : 1, pH 5* (mod. ampl. 0.4 g); c) *Glc-ol/$Cr^{VI}$ 10 : 1, [$H^+$] = 0.1*M (mod. ampl. 1.01 G). *T* 25°, frequency 9.7815 GHz.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

bis-chelate $[Cr(O)(O^{2(3)},O^{3(4)}\text{-Glc-ol})_2]^-$, 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 $[Cr(O)(O^1,O^2\text{-GlcA})_2]^-$ (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 $[Cr(O)(O^{1(2,3)},O^{2(3,4)}\text{-Glc-ol})(H_2O)_3]^+$ (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 $[H^+]$. This $Cr^V$ mono-chelate is possibly responsible for the higher rates observed for the $Cr^V$-Ald-ol redox reactions at 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 $A_{iso} = 16.5(3) \cdot 10^{-4}\ cm^{-1}$. 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 $[Cr(O)(O^3,O^4\text{-Man-ol})_2]^-$ (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 $[Cr(O)(O^3,O^4\text{-Man-ol})_2]^-$, 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-$Cr^V$ $[Cr(O)(O^1,O^2\text{-ManA})_2]^-$ (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 $[Cr(O)(O^{1(3)},O^{2(4)}\text{-Man-ol})(H_2O)_3]^+$ (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 $[Cr(O)(O^2,O^3\text{-Gal-ol})_2]^-$ (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.

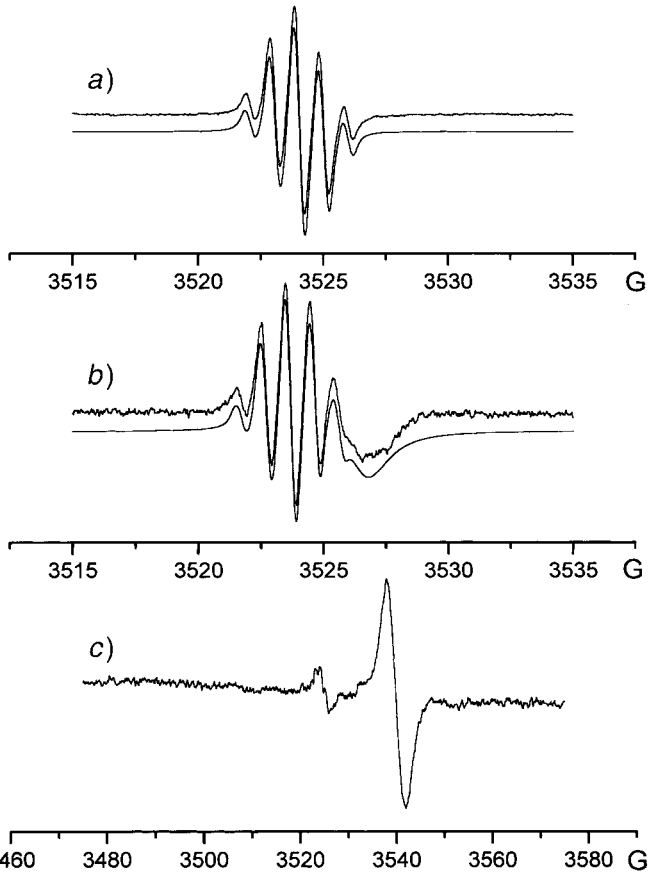



Fig. 6. *Experimental and simulated X-band EPR spectra of solutions of Man-ol and* $Cr^{VI}$*:* a) *pH 5* (mod. ampl. 0.4 G, frequency 9.7819 GHz); b) *pH 2* (mod. ampl. 0.4 G, frequency 9.7808 GHz); c) $[H^+] = 0.1$ M (mod. ampl. 1.01 G, frequency 9.7788 GHz). *T* 25°, $[Cr^{VI}] = 2.5 \cdot 10^{-3}$ 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 $[Cr(O)(O^{1(2)},O^{2(3)}\text{-Gal-ol})(H_2O)_3]^+$ (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 $Cr^{VI} \rightarrow Cr^V \rightarrow Cr^{III}$ reduction path, with the $Cr^{VI} \rightarrow Cr^V$ step being the rate-determining one.

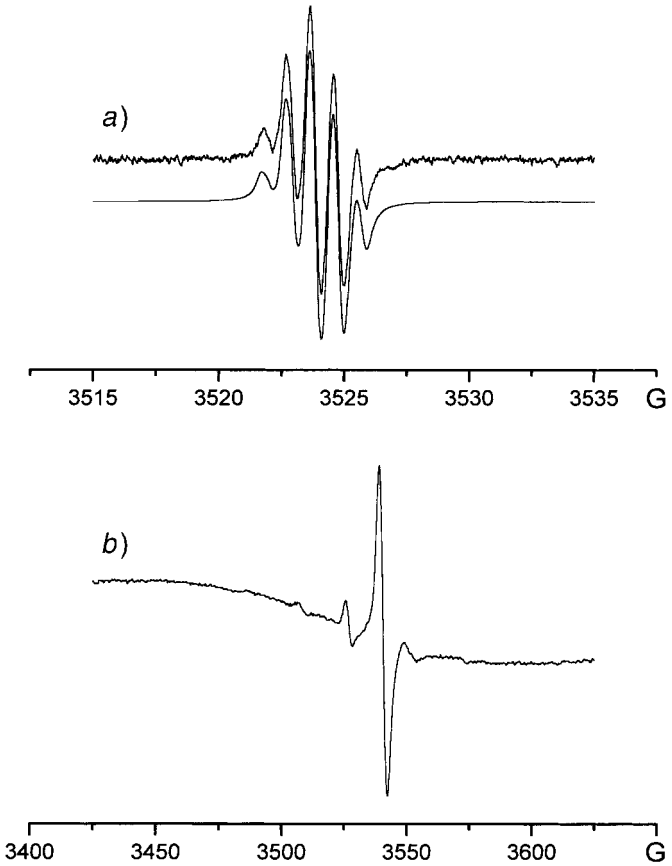



Fig. 7. *Experimental and simulated X-band EPR spectra of solutions of Gal-ol and $Cr^{VI}$.* a) *Gal-ol/$Cr^{VI}$ 20 : 1, pH 5* (mod. ampl. 0.4 G, frequency 9.7814 GHz); b) *Gal-ol/$Cr^{VI}$ 10 : 1, $[H^+] = 0.5$*M (mod. ampl. 2.0 G, frequency 9.7827 GHz). *T* 25°, $[Cr^{VI}] = 2.5 \cdot 10^{-3}$ M.

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 $[H^+]$. At $[H^+] \geq 0.1$M, positively charged hexacoordinate $Cr^V$ monochelates are formed, and are believed to be responsible for the fast electron-transfer process in the $[H^+]$ 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*), $K_2Cr_2O_7$ (*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 ($I = 1.0$M) and different $[H^+]$, 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 $[H^+]$ 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 $\ln(Abs^{350})$ *vs.* time, were deduced from multiple determinations and were within ±5% of each other. The first-order dependence of the rate upon $[Cr^{VI}]$ was verified by calculating the pseudo-first-order rate constants at various $[Cr^{VI}]_o$, but at constant temperature, $[alditol]_o$, $[H^+]$, and $I$. As expected from a $-d(\ln[Cr^{VI}])/dt = k_6$ rate law, where $k_6 = f([alditol][H^+])$, $k_6$ was found to be essentially constant with increasing $[Cr^{VI}]_o$.

The formation of $Cr^{III}$ was monitored at 570 nm ($[Cr^{VI}] = 6 \cdot 10^{-3}$ M) in the presence of excess alditol and $[HClO_4]$ in the 0.10–0.80M range. Under these conditions, the first-order dependence of the rate upon $[Cr^{VI}]$ 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 $-r_i/(A_o - A_f)$, with average values of the initial rate and calculated estimates of $(A_o - A_f)$. 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 $\lambda_{max}$ 409 nm ($\varepsilon$ 16.2 $dm^3\,mol^{-1}\,cm^{-1}$) and $\lambda_{max}$ 574 nm ($\varepsilon$ 13.6 $dm^3\,mol^{-1}\,cm^{-1}$). Both VIS and UV spectral maxima and intensities were in close agreement with those observed for the $[Cr(H_2O)_6]^{3+}$ 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 $[HClO_4]$. At this wavelength, kinetic traces were evaluated from a nonlinear iterative computer fit of the rate expression derived from two consecutive first-order reactions $Cr^{VI} \rightarrow Cr^V \rightarrow Cr^{III}$. 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, $I = 1.0$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 ($300 \times 7.8$ mm, *Bio-Rad Laboratories*), $3 \cdot 10^{-3}$ M $H_2SO_4$ 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 $HClO_4$ and chromatographed separately to determine the $t_R$ of each sample.

Under all experimental conditions (large to moderate excess of alditol over $Cr^{VI}$), $CO_2$ 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 $8 \cdot 10^{-4}$ M $Cr^{VI}$ and 0.04M Glc-ol in 0.5M $HClO_4$ 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 $t_R$s 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 aldonolactone produced was qualitatively identified by PC with BuOH/AcOH/$H_2O$ 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/$H_2O$ 5:1:4 as eluent, a solvent separating $\gamma$-lactones from $\delta$-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 $7.3 \cdot 10^{-3}$ M $Cr^{VI}$ and 0.36M Man-ol in 0.5M $HClO_4$ 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 $K_2Cr_2O_7$ ($2 \cdot 10^{-3}$ mmol) and alditol (0.02 mmol) in 2 ml of 0.50M $HClO_4$, acrylonitrile (0.5 ml) was added at 33°. After a few minutes, a white precipitate appeared. Control experiments (without $K_2Cr_2O_7$ 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 $[Cr^VO(ehba)_2]K$ 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-1*H*-pyrrole 1-oxide (DMPO) to the reaction mixture resulted in the appearance of an EPR signal at $g = 2.003$ with splitting constants of $7.48 \cdot 10^{-4}$ $cm^{-1}$ and $3.65 \cdot 10^{-4}$ $cm^{-1}$ ($\times 2$), corresponding to the oxidized spin trap, and the signal of the DMPO-OH$^\bullet$ spin adduct [64]. The EPR signal of the DMPO-sorbitol$^\bullet$ 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$^\bullet$ spin adduct was detected. Similarly, 5-(diethoxyphosphoryl)-4,5-dihydro-5-methyl-1*H*-pyrrole 1-oxide (DEPMPO) and (4-pyridyl-1-oxide)-*N*-(*tert*-butyl)nitrone (=1,1-dimethyl-*N*-[(1-oxidopyridin-4-yl)methylidene]ethanamine *N*-oxide; POBN) trapped only OH$^\bullet$. 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$^\bullet$ spin adduct [30][31].

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