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Reduction of potassium chromate by D-fructose, D-galactose, D-mannose, D-glucose, and L-sorbose

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ABSTRACT

Chromate is readily reduced by various saccharides under different experimental conditions, and its reduction has been followed using absorption and EPR spectroscopies and electrochemistry. The reduction of Cr(VI) was found to be characteristic of the saccharide used and the reductive capabilities follow a trend, D-fructose > L-sorbose > D-galactose > D-mannose > D-glucose at pH 1.65 and D-fructose > D-galactose > D-mannose > L-sorbose > D-glucose at pH 0.35. Similar trends were noticed from EPR and electrochemistry studies. As the reduction of chromate was found to go via soluble, reactive, and relatively long-lived Cr(V) intermediates having different life times, the biological toxicity and ecological hazard created in the presence of Cr(VI) salts by various molecules containing such saccharide moieties is expected to follow a reverse trend.

INTRODUCTION

Saccharides belong to an interesting class of chemical compounds that play important roles in humans, animals, and plants by being present as essential components of a variety of biological molecules, namely, polysaccharides, glycoproteins, glycolipids, nucleic acids, etc. They are further important due to their wide occurrence and multihydroxy functionality that allows coordination and chelation to many metal ions. As the saccharide moiety can be oxidized to a carboxylic acid group, it is interesting to look at its ability to reduce Cr(VI) to Cr(III), which may find relevance in the context of chromate reduction activity and also in the transport of metal ions through soil causing environmental pollution.

Recent studies[1,2], including ours[3], have indicated that Cr(VI) salts are reduced by a variety of mono- and di-saccharides. While the reduction of Cr(VI) by cellular components causes cancer, the same by soil components induces transport of chromium from chemical disposal sites to the environment via the formation of active soluble species, thereby causing environmental pollution. Oxidation of some

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sugars by Cr(VI) salts in a $HClO_4$ medium is reported in the literature[4]. However, the information regarding the mechanism of reduction and the reactive capabilities of monosaccharides towards Cr(VI) are not reported, though these are of paramount importance in view of the potential hazards posed by this element both in a biological and an ecological context. In order to establish these aspects, we have adopted a quasi-kinetic approach using absorption and EPR spectroscopies and electrochemistry techniques. Herein, we present our results regarding the reductive capabilities of five monosaccharides, namely, D-glucose (D-Glc), D-mannose (D-Man), D-galactose (D-Gal), D-fructose (D-Fru), and L-sorbose (L-Sor) towards potassium chromate.

EXPERIMENTAL

Absorption spectra were measured using a Shimadzu UV-260 spectrophotometer and EPR spectra were measured with a Varian ESR-112 spectrometer; Cyclic voltammetry was carried out with a BAS100B electrochemical analyser. All the saccharides used in this study were purchased from either Sigma Chemical Co. (USA) or Aldrich Chemical Co. (USA), and were used without further purification. Other chemicals were purchased from local commercial sources.

In vitro reduction of potassium chromate by D-Fru, D-Gal, D-Man, L-Sor, and D-Glc was studied using absorption spectroscopy at three different chromate concentrations (0.5, 5, and 50 mM) and at several starting pH values in the range of pH 0.35–1.65 (the solution pH was obtained by adjusting with an appropriate amount of HCl). EPR spectroscopy was carried out at a 50 mM chromate concentration and pH 0.35. While the absorption studies were carried out using several saccharide-to-chromate mole ratios in the range 2:1 to 24:1, the EPR measurements were done with 8:1, 16:1, and 24:1 molar ratios.

The disappearance of Cr(VI) and the appearance of Cr(III) species during the reaction were established by monitoring the intensities of the corresponding absorption bands [Cr(VI): 360 ± 10, 260 ± 10 nm; Cr(III): 570 ± 10 nm] as a function of time. The reactions were also monitored for the formation of Cr(V) species and its subsequent conversion to the final Cr(III) products by EPR spectroscopy [Cr(V): $g = 1.978$, $\Delta\nu_{1/2} = 0.35$ mT; Cr(III): $g = 1.968$, $\Delta\nu_{1/2} = 17$ mT] as a function of time during the reaction.

Electrochemical studies were performed with 25 mM monosaccharides in N_2-purged 0.1 N NaOH solutions by measuring the cyclic voltammograms in the range 0.5 to -0.9 V using Pt as the working electrode. The final mixtures obtained from chromate reduction at pH 0.35 using all these monosaccharides (saccharide-to-chromate mole ratio of 8:1) were subjected to cyclic voltammetric measurements using a hanging mercury drop (HMD) working electrode in the potential range -0.7 to -1.5 V. All the peak potentials are given with respect to Ag/AgCl as the reference system. Further, all the voltammograms were compared with their respective background ones.

RESULTS AND DISCUSSION

Absorption spectroscopy.—Conversion of Cr(VI) to Cr(III) by the interaction with saccharides was followed by absorption spectroscopy by monitoring the disappearance of Cr(VI) bands (360 ± 10 and 260 ± 10 nm) and the growth of the Cr(III) band (570 ± 10 nm) as a function of time, saccharide equivalents, chromate concentration, and acid strength. Representative spectra are shown in Fig. 1 in the case of the D-Fru reaction with chromate in 24:1 molar ratio at pH 0.35 (A, C) and

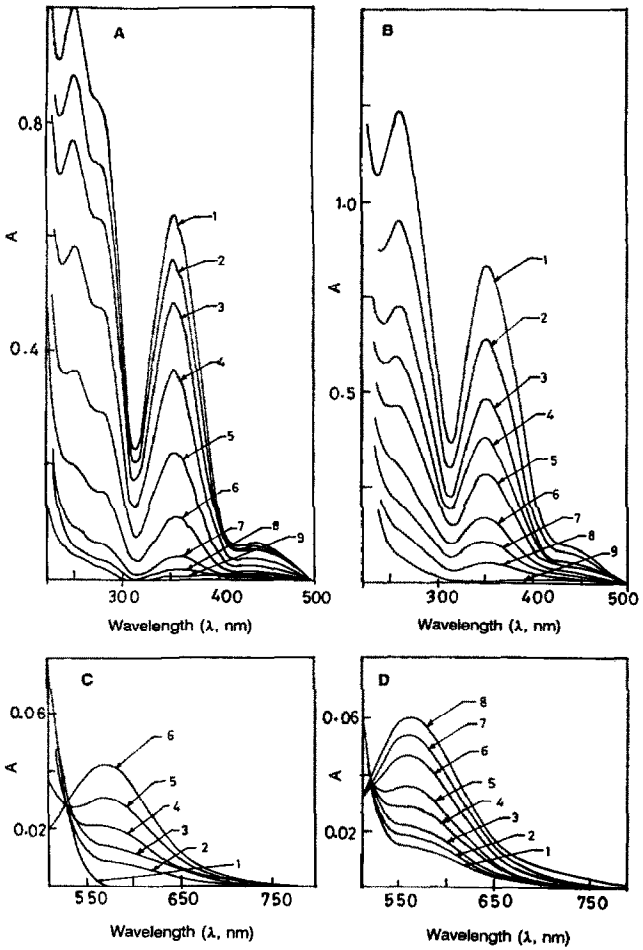

Fig. 1. Absorption spectra of the reaction between potassium chromate and D-fructose as a function of time. Molar ratio: CrO_4^{2-} (5 mM): D-Fru = 1:24. Panel A, pH 0.35: Scans (1) 0.02 h, (2) 0.38 h, (3) 0.63 h, (4) 1.08 h, (5) 1.75 h, (6) 2.52 h, (7) 3.53 h, (8) 4.17 h, and (9) 6.20 h. Panel B, pH 1.65: Scans (1) 0.02 h, (2) 17.25 h, (3) 31.32 h, (4) 48.37 h, (5) 63.00 h, (6) 89.00 h, (7) 113.33 h, (8) 138.67 h, and (9) 191.68 h. Panel C, pH 0.35: Scans (1) 0.02 h, (2) 0.25 h, (3) 0.52 h, (4) 1.03 h, (5) 3.03 h, and (6) 3.18 h. Panel D, pH 1.65: Scans (1) 18.03 h, (2) 24.93 h, (3) 31.00 h, (4) 42.42 h, (5) 63.83 h, (6) 114.00 h, (7) 191.00 h, and (8) 359.20 h.

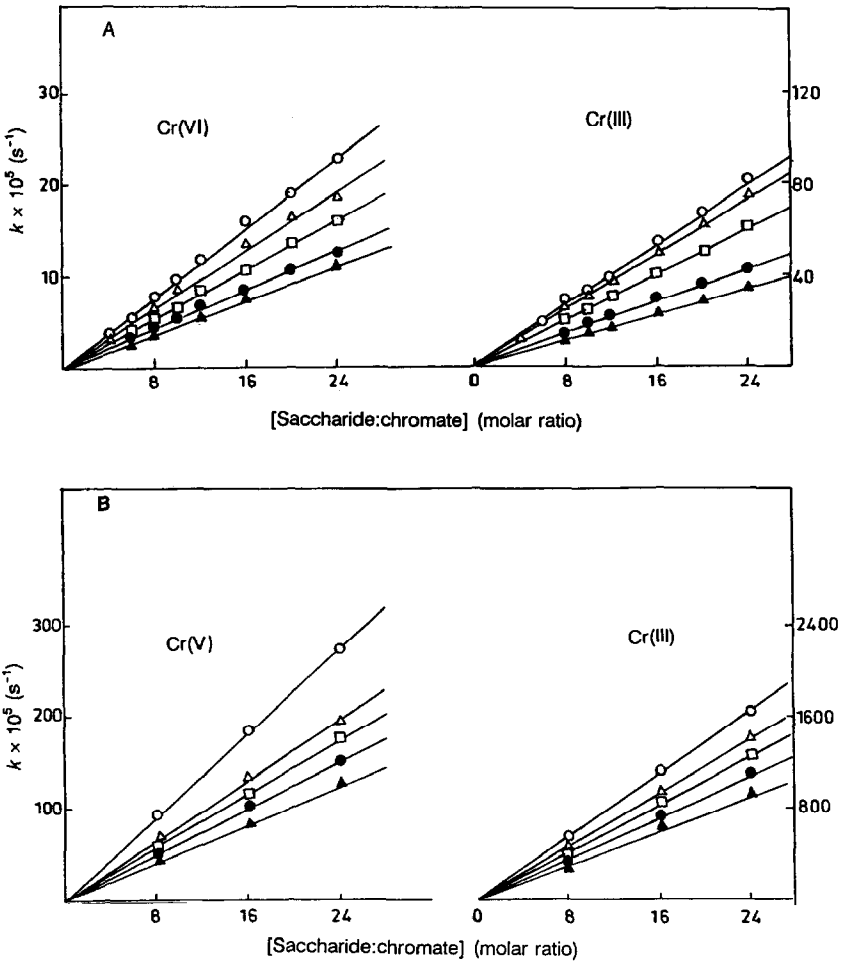

Fig. 2. Plots of first-order reaction rate constants vs. saccharide-to-chromate molar ratios for D-Fru (○), D-Gal (△), D-Man (□), D-Sor (●), and D-Glc (▲). Panel A: Absorption data for Cr(VI) at λ 570±10 nm. Panel B: EPR data for Cr(V) ($g = 1.978$) and Cr(III) ($g = 1.968$).

1.65 (B, D). The first-order reaction rates were derived from the slopes of the straight lines obtained by plotting absorbance vs. time for bands corresponding to Cr(VI) ($\lambda = 360 \pm 10$ nm) and Cr(III) ($\lambda = 570 \pm 10$ nm) species. These reaction rates of Cr(VI) and Cr(III) increase considerably with increase in the concentration of the chromate, the acid strength, and the number of saccharide equivalents. The reaction rate increases linearly with increase in saccharide-to-chromate mole ratio (Fig. 2A). On changing the pH from 1.65 to 0.35 with [CrO_4^{2-}] at 5 mM, the corresponding first-order rates for Cr(VI) band (360 ± 10 nm) and Cr(III) band (570 ± 10 nm) increases by about 30–60-fold among the five saccharides studied, showing a strong dependence on the nature of the saccharide. When the concentration of chromate was increased 10-fold from 0.5 to 5 mM and a pH of 0.35, the

corresponding Cr(VI) rate increases by 10.5-fold in D-Fru, D-Gal, D-Man, and L-Sor and 17.5 times in D-Glc. Under the same conditions, the increase in the first-order rate of Cr(III) band was found to be about 25-fold in all cases. Reaction rates were found to be linear with respect to pH in the pH range 0.35–1.65 for all these saccharides and for both Cr(VI) and Cr(III) species. Beyond pH > 2 the reactions proceeded extremely slowly and did not reach completion over several weeks to months, depending upon the actual pH of the solution. However, these are completed in shorter periods when the reactions were allowed to proceed under refluxing conditions[7b]. This can be explained due to the presence of very labile and protonated species of chromate and dichromate in the reaction mixture with pH < 2. Thus, the present study suggests a first-order involvement of chromate and saccharide in the rate expression and also the involvement of the pH term in the numerator.

For a given set of conditions (chromate concentration, pH, etc.), the plot of saccharide to metal ratio vs. first-order rate constants showed a linear relationship with varying slopes for different saccharides (Fig. 2A). Second-order rate constants of chromate reduction reaction were derived per unit of ligand concentration from the slopes of these straight lines. These were in fact different for different saccharides and provide good criteria to judge the relative reactivities of the saccharides towards Cr(VI) salts. Therefore, the reductive capacities, derived from the second-order rate constants of various monosaccharides from the absorption spectra, for a given set of conditions, follow the trend, D-Glc < L-Sor < D-Man < D-Gal < D-Fru up to about pH 1, and at pH 1.65, the trend is, D-Glc < D-Man < D-Gal < L-Sor < D-Fru. From the observed reaction rates, it is understandable that the rate decreases with an increase in pH for all saccharides; however, this trend is more pronounced with D-saccharides than with L-sorbose. Generalization of this result needs further study. Thus, the reaction trend was found to differ with pH. Further, comparison of the data revealed that D-Gal and D-Fru reduce Cr(VI) about 2–2.5-fold more efficiently than D-Glc at pH 0.35. Thus, our quasi-kinetic approach clearly demonstrates that at higher concentration of chromate, the reaction goes to completion at faster rates and precludes the step associated with the formation of the final Cr(III) species from being the rate-determining process.

EPR spectroscopy.—The reaction between saccharide and crown–chromate in methanol was found to proceed via soluble, reactive, and relatively long-lived Cr(V) intermediate species[3a]. The lability of the Cr(V) species has been recently reviewed by Farrel and Lay who were kind enough to provide us with their preprint[3b]. Both the Cr(V) intermediate, as well as the final Cr(III) species, were EPR active. In the EPR spectra measured at pH 8.5 in H_2O, we initially observed an increase in the intensity of Cr(V) signal, followed by its decay. On the other hand, in the strongly acidic (pH 0.35) solutions, only the decay of the Cr(V) species is noted in order to give the final Cr(III) products. This suggests that the rate of the reaction depends upon the protonated state of the chromate species. Typical plots of EPR spectra as a function of time are shown in Fig. 3 for both Cr(V) and

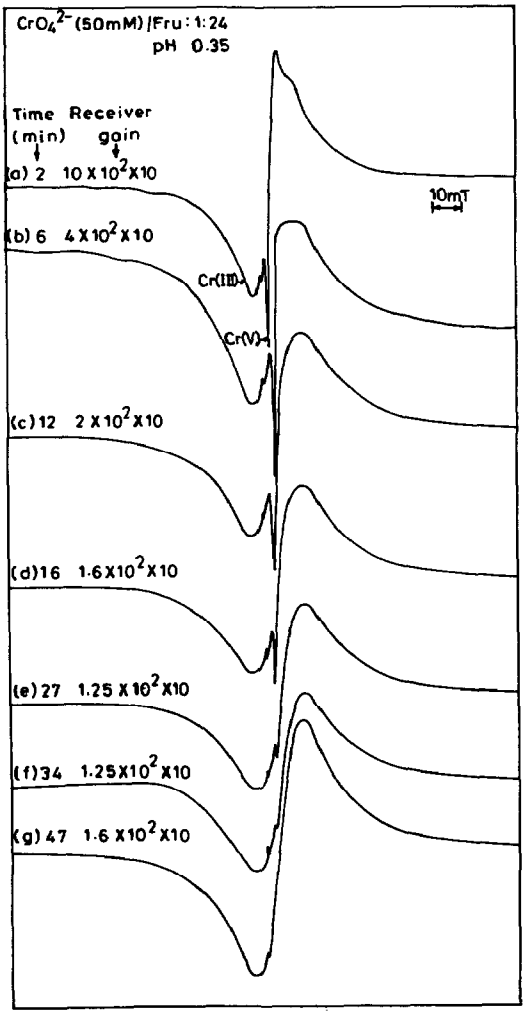

Fig. 3. EPR spectra measured as a function of time during the reaction progress of the D-fructose–chromate system at 24:1 molar ratio and pH 0.35. Presence of Cr(V) and Cr(III) species is indicated.

Cr(III) species for a reaction system where the chromate-to-fructose molar ratio was 1:24 and the initial chromate concentration was 50 mM at pH 0.35. The rate of decay of the Cr(V) species and the rate of formation of the Cr(III) species were derived from corresponding peak intensity vs. time plots. The rate of decay of the Cr(V) species is dependent both on the pH as well as the type of saccharide in a manner that the reactions with D-Fru converts Cr(V) species to the final Cr(III) products in a much shorter period than D-Glc, and the remaining saccharides exhibit intermediate behaviour. The trend in the decay of Cr(V) and formation of the Cr(III) species observed from EPR is in agreement with that derived from absorption data.

Plots of the first-order rate constants vs. saccharide-to-chromate molar ratios gave straight lines for all five monosaccharides, indicating a linear dependance of the rate with ligand ratio (Fig. 2B). The decay of Cr(V) and the formation of Cr(III) is about 2–2.5-fold faster in the case of D-Fru than D-Glc, and the rest are intermediate. The reduction of Cr(VI) to Cr(III) follows the trend, D-Fru > D-Gal > D-Man > L-Sor > D-Glc. Thus all the results obtained from EPR studies were in agreement with those obtained from absorption spectroscopy.

Electrochemistry.—Cyclic voltammograms measured in N_2-purged 0.1 N NaOH at the Pt electrode exhibited two anodic oxidations and one cathodic reduction for all five monosaccharides studied. The peak potentials of both the oxidation processes exhibited a systematic trend among all the five saccharides (Fig. 4). D-Fru exhibits a more positive (or less negative) potential for its oxidation as compared to the rest four. This trend is further noted for the series, D-Fru > L-Sor > D-Gal > D-Man > D-Glc. This trend is similar to that found from absorption studies for the chromate reduction by saccharides at pH 1.65. Though the reaction rate decreases dramatically with increase in pH, the relative trend among the four D-saccharides remains unaltered. The electrochemical behaviour of D-Glc was recently reported in the literature[5].

Reduction reactions were performed between various saccharides and potassium chromate in an 8:1 molar ratio at pH 0.35. Upon the completion of the reaction, the mixture was subjected to voltammetric studies using the HMD electrode. Voltammograms obtained in all the cases exhibited one irreversible cathodic peak in the range −1.175 to −1.285 V (Fig. 5). Comparison of this data with that obtained in case of $CrCl_3(THF)_3$, $CrCl_3$, and $Cr(NO_3)_3$ under similar conditions resulted in the assignment of the peak to Cr(III) to Cr(II) reduction. The reduction potentials exhibited the trend, D-Fru < D-Gal < D-Man < L-Sor < D-Glc, which is parallel to that obtained for the reducing capabilities of various saccharides obtained from both absorption and EPR spectroscopies.

Results obtained from all three techniques are mutually dependent and exhibit an almost linear correlation among them. In order to demonstrate this, we have plotted reaction rates derived from both absorption and EPR data with Cr(III) → Cr(II) reduction potentials (E_p^c) obtained from the final mixtures of saccharide–chromate systems and these are shown in Fig. 6. These data strongly suggest that the nature of the saccharides is very important in the chromate reduction.

Disaccharides.—When similar reactions were performed with dichromate (5 mM, pH 0.3) and disaccharides (disaccharide-to-chromate molar ratios were varied from 2:1 to 12:1), the reactivity was found to follow a trend, D-sucrose > D-lactose > D-maltose, where the first-order rates of these disaccharides turned out to be the sum of the rates of their constituent monosaccharides. If one extends this result further, it appears that the reactivity of an oligo- and/or poly-saccharide can be judged based on the type and number of its monomer units.

Saccharide influence.—The reduction of Cr(VI) by D-Fru, D-Gal, D-Man, D-Glc, and L-Sor seems to depend on the number of available primary hydroxyl groups,

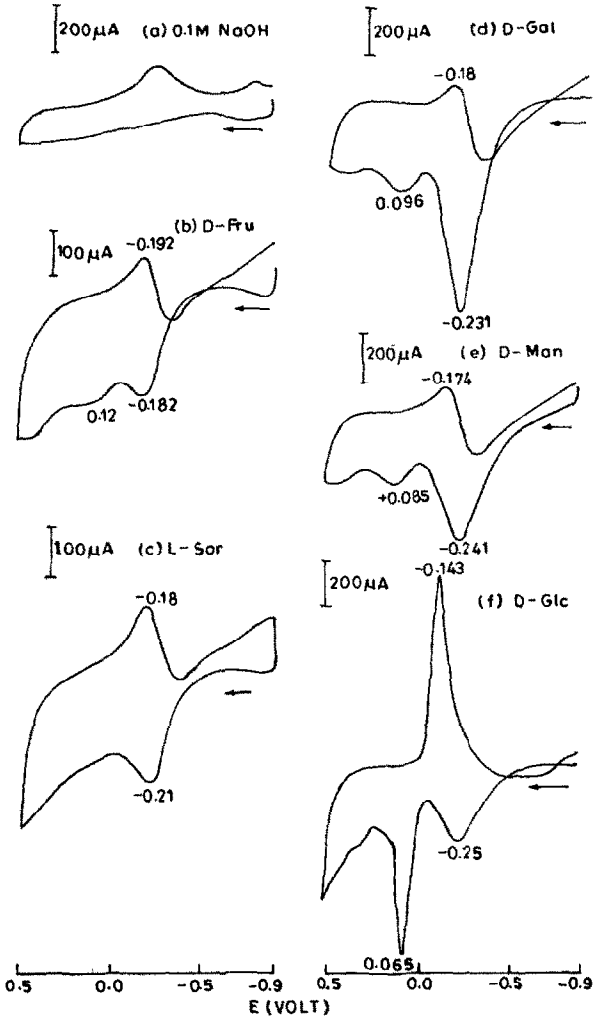

Fig. 4. Cyclic voltammograms of (a) 0.1 N NaOH; and 25 mM of saccharides: (b) D-Fru; (c) L-Sor; (d) D-Gal; (e) D-Man, and (f) D-Glc; all in N_2-purged 0.1 N NaOH; working electrode, Pt; reference electrode, Ag/AgCl; scan speed, 100 mV/s (arrow indicates the direction of scanning).

the stereochemistry, and the chelating ability of the saccharide. This is true as the saccharide acts as both reducing and complexing agent for chromium. The following empirical rules, derived based on the saccharide structures, play influential roles in explaining the relative reactivities of these saccharides on the Cr(VI) reduction process: (*1*) five-membered furanose structures possessing two primary hydroxyl groups dominate the reaction in D-Fru and L-Sor over its pyranose counterpart, i.e., D-Gal, D-Man, and D-Glc; (*2*) the presence of a *cis*-diol group in D-Fru provides favourable five-membered chelation with the metal, giving a rapid reactivity towards Cr(VI) as compared to L-Sor; (*3*) examination of the C-2, C-3,

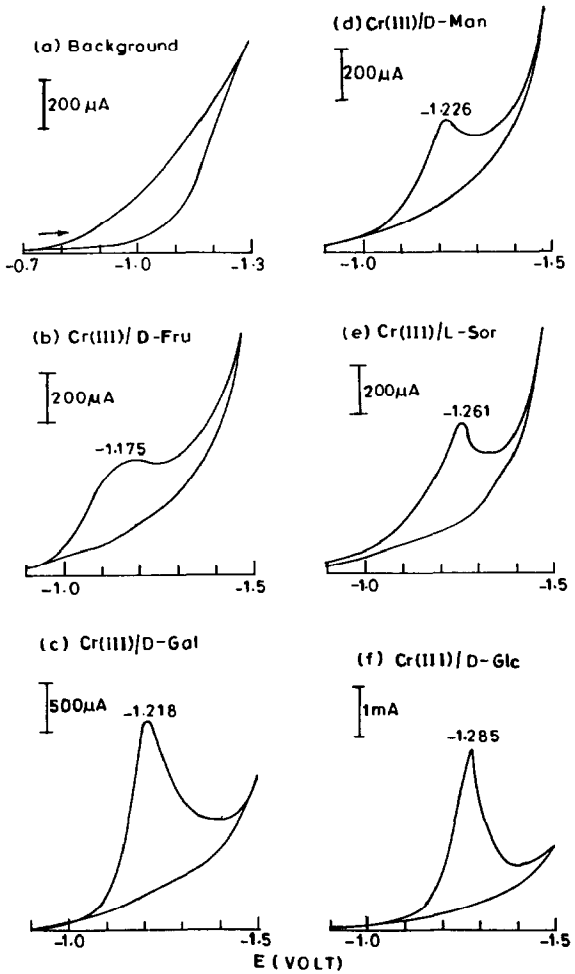

Fig. 5. Cyclic voltammograms of the final mixture of saccharides and chromate in 8:1 molar ratio at pH 0.35; working electrode, HMD; reference electrode, Ag/AgCl; scan speed, 100 mV/s.

and C-4 carbons of the open-chain form clearly indicates the presence of a *cis*-diol group in D-Man and D-Gal that is responsible for their higher reactivity over that of D-Glc; (*4*) presence of a C-4 axial OH group in the case of D-Gal is coordination-wise more favoured over an axial C-2 OH (as in D-Man), along with the OH of the C-6 carbon. ^{13}C NMR spectra of these monosaccharides measured in 1 N HCl did not provide any chemical shifts corresponding to C=O group, indicating that the cyclic structures are intact even in acidic conditions. ^{1}H NMR studies carried out with pure saccharides in D_2O and Me_2SO-d_6 clearly demonstrated the existence of α and β anomers in all the cases in the D-Fru in addition to both furanose and pyranose forms[6]. Saccharides used in the study not only reduce Cr(VI) to Cr(III) but also coordinate with the metal in the final product. In our laboratory we have recently isolated and characterized saccharide complexes of

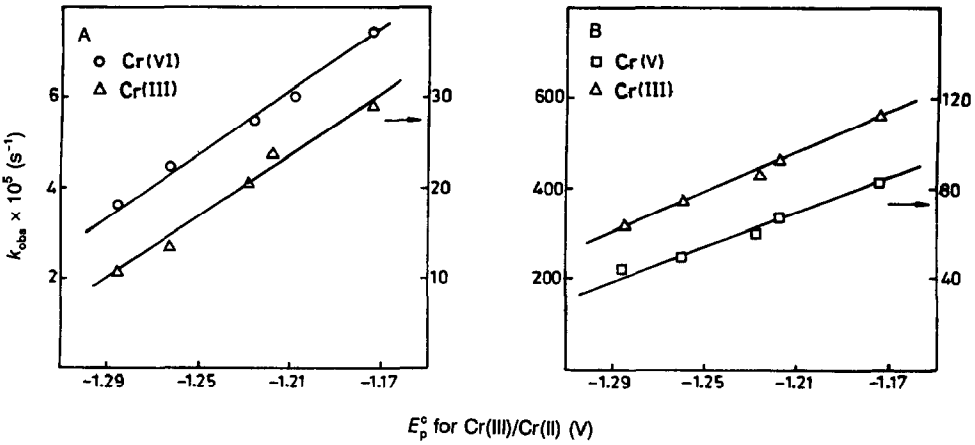

Fig. 6. Plot of first-order rate constants vs. reduction potentials. Panel A, from absorption spectral data, and Panel B, from EPR spectral data.

various transition metals[3a,7]. Binding of saccharides through deprotonated hydroxyl groups and the influence of stereochemistry and chelation on the complex formation have also been predicted in case of iron–saccharide complexes[8]. Similar factors may govern the interaction of various polysaccharides and other relevant biomolecules with chromate to induce cellular toxicity and environmental pollution.

During the reviewing process, a referee brought to our attention a very recent publication by Signorella et al.[9] regarding the detection of chromium intermediates formed in the oxidation of oxalic acid, gluconic acid, L-rhamnose, and 2-hydroxy-3-methylbutanoic acid by potassium dichromate. The mechanism suggested by these workers is essentially the same as that experimentally observed in our case. We detected the chromium(V) intermediate species both from EPR and also from absorption (750 nm) with an initial formation of Cr(VI)-ester species at 430 nm. The initial changes observed in these bands allowed us to further derive the rate of disappearance of Cr(VI) and Cr(V), and the formation of the Cr(III) species. Thus, the rate obtained for each saccharide provided a way to compare the relative reducing capabilities of these saccharides.

CONCLUSIONS

In this paper, we have presented information regarding the reduction of Cr(VI) by five monosaccharides using absorption and EPR spectroscopies, and cyclic voltammetric studies. These reactions were understood to proceed via soluble, reactive, and relatively long-lived Cr(V) intermediate species whose formation and decay to give final inert Cr(III) products are dependent upon the type of saccharide used — faster in the case of an easily oxidizable saccharide such as D-Fru and slower in the case of a poorly oxidizable saccharide such as D-Glc. From our

studies it has been possible to deduce that the relative reducing capabilities of the saccharides towards chromate follow a trend, D-Fru > D-Gal > D-Man > L-Sor > D-Glc at pH 0.35, and D-Fru > L-Sor > D-Gal > D-Man > D-Glc at pH 1.65. Hence, the ability for cross linking of cellular components and induction of transport of chromium through soil are expected to follow a reverse order, since such phenomena depend upon the lability of the intermediate Cr(V) species. Thus, the present study also predicts that molecules that possess more D-Glc units pose more danger to cells, or to the environment in general, than those containing D-Fru units.

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