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In vitro reducing abilities towards chromate of various hydroxy-containing compounds, including saccharides and their derivatives *

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ABSTRACT

The reduction of potassium chromate has been carried out with a variety of OH-containing compounds as reductants, which include pentoses, polyols, glycols, and sugar derivatives. The corresponding reactions were followed using UV-vis and EPR spectroscopies and electrochemistry. The progress of the chromate reduction reactions has been monitored by measuring UV-vis and EPR spectra as a function of time. The observed pseudo first-order reaction rate constants are derived based on the changes in the intensities of the Cr(VI), Cr(V), and Cr(III) signals. Cyclic voltammograms of the simple reductants and their final Cr(III) products formed from the reactions of chromate have also been measured. The reductive abilities of all these reductants have been derived from the spectral data and are discussed on a comparative basis. Based on the results, the aspects that makes a particular reductant more efficient has been addressed. The results obtained from UV-vis, EPR, and cyclic voltammetry are found to be mutually dependent and exhibit among themselves a linear correlation, suggesting that both the reducing and complexing nature of these molecules play important roles in the chromate reduction.

INTRODUCTION

Saccharides and their derivatives are very attractive molecules because of their multihydroxy functionalities. These substances do not only act as chelators, but they also can reduce certain metal ions under suitable conditions. Chromium(VI) salts are known to be mutagens and carcinogens[1,2]. Recent studies, including ours, have indicated that these salts are reduced by a variety of hydroxy- and thiol-containing molecules that mimic several components of the cell and soil[3]. These include various small molecular components such as amino acids and peptides, ascorbic acid, saccharides and their derivatives, nucleotides, humic and fulvic

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* This paper is dedicated to Professor Richard H. Holm on his 60th birthday.

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acids, and large molecular components such as proteins, nucleic acids, and other subcellular components. However, current interest also involves the isolation and characterisation of Cr(III) products formed in chromate reduction[3i,4b]. Reduction of chromate is known to proceed via a Cr(V) intermediate species, followed by formation of the final Cr(III) products where the coordination sphere possesses the reductant. The process has been followed monitoring with UV-vis and EPR spectroscopies.

Recently, we have demonstrated that the reduction of crown–chromate complexes with L-cysteine ethyl ester and several monosaccharides such as D-glucose, D-fructose, and D-galactose in methanol, and several monosaccharides (both D- and L- compounds) in water, gives a final Cr(III) species. Furthermore, the reactions were shown, using EPR and UV-vis spectroscopies to go via a Cr(V) intermediate species[4a–c]. Several saccharides[4,5], hydroxyacids[6], molecules related to humic and fulvic acids[7], milk components[8], and formaldehyde–H_2O_2 (ref 9) are known to reduce chromate at relatively slow rates compared to L-cysteine[10], penicillamine, glutathione, various thiol-containing molecules[11], and L-ascorbic acid[4a,12]. While several of the saccharides and related reactions were formulated to proceed via reactive and soluble Cr(V) intermediate species[4,13], the formaldehyde–H_2O_2 (ref 9) reaction was shown to go via a Cr(IV) species. Gould and co-workers have suggested certain mechanistic aspects for the electron-transfer reaction in chromium systems[14]. However, there are no systematic studies available in the literature addressing the relative reducing and complexing abilities of several potential small molecular components. While there are some studies depicting the in vitro reaction mechanism of these ligands with chromate, the influence of geometry and stereochemistry of the reductants, mainly hydroxy-containing ones, has not been explored. We have started a systematic study of the reduction of potassium chromate with different types of OH-containing molecules, including saccharides and their derivatives, to understand their abilities towards chromate reduction and the nature of their complexation. In order to achieve this we have studied the reduction of Cr(VI) by pentoses, polyols, glycols, and sugar derivatives using UV-vis, EPR, and electrochemistry and the relative reducing capabilities are reported in this paper.

EXPERIMENTAL

General.—All chromate reduction reactions were carried out at pH 0.35 using UV-vis {[CrO_4^{2-}], 5 mM} and EPR {[CrO_4^{2-}]: 50 mM} at ambient temperature.

Pentoses.—In vitro reduction of potassium chromate by pentoses, namely, D-ribose (D-Rib), D-lyxose (D-Lyx), D-arabinose (D-Ara), and D-xylose (D-Xyl) was followed using UV-vis spectroscopy at two different chromate concentrations (5 and 50 mM prepared in N HCl) and EPR spectroscopy at 50 mM chromate concentration. Both studies had a starting pH of 0.35. While the UV-vis studies were carried out using several pentose-to-chromate molar ratios in the range of

4 : 1 to 24 : 1, the EPR measurements were done only at 8 : 1, 16 : 1, and 24 : 1 molar ratios.

The disappearance of Cr(VI) and the increase of the Cr(III) species during the reaction were established by monitoring the intensities of the corresponding absorption bands [Cr(VI), 355 nm and Cr(III), 570 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 and Cr(III), $g = 1.968$, $\Delta\nu_{1/2} = 17$ mT, in the case of {[D-Rib]/[CrO_4^{2-}] in 24 : 1 molar ratios}, as a function of time during the reaction progress.

Electrochemical studies were performed with 25 mM solutions of all the pentoses in N_2-purged 0.1 N NaOH by measuring cyclic voltammograms in the range -0.9 to 0.5 V using Pt as the working electrode. The final Cr(III) species obtained from chromate reduction at pH 0.35 using all the pentoses (in the case of pentose-to-chromate molar ratio of 16 : 1) have also been subjected to cyclic voltammetric measurements using the hanging mercury drop (HMD) as the working electrode in the potential range -0.7 to -1.5 V. Peak potentials are given with respect to Ag/AgCl as the reference electrode. Also, proper care was taken in measuring the voltammograms of the systems in order to differentiate these from the background. Similar studies of absorption, EPR, and cyclic voltammetry have been carried out with polyols such as ethylene glycol (Etol), glycerol (Gro), threitol (Thr-ol), xylitol (Xyl-ol), and mannitol (Man-ol); glycols, such as, ethylene glycol (Etol), diethylene glycol (Digol), triethylene glycol (Trigol), tetraethylene glycol (Tetragol), and polyethlene glycol (Polygol, average molecular weight 380–420), where only the number of glycol units ($-O-CH_2-CH_2-$) differ, and these are 1, 2, 3, 4, and 8, respectively; and sugar derivatives such as sugar acids [D-glucuronic acid (D-GlcA), D-gluconic acid (D-Glc-onic), D-glucaric (D-Glc-aric), and D-galacturonic acid (D-GalA)]; sugar alcohols [D-glucitol (D-Glc-ol) and galacitol (Gal-ol)], and amino sugars [*N*-methylglucamine {D-Glc-(1 → N)-Me} and D-glucosamine · HCl (D-GlcN)].

Pseudo first-order rate constants (k_0')—The observed pseudo first-order reaction rate constants (k_0' values) were derived from the slopes of the straight lines obtained by plotting logarithmic peak decay or peak growth vs. time for bands corresponding to Cr(VI) and Cr(III) species in the UV-vis and Cr(V) and Cr(III) species in the EPR spectra. The rate for the Cr(V) species could not be calculated from the UV-vis spectra as only marginal changes were observed in the absorbance of the band at 750 nm. These observed k_0' values are derived for various ligand-to-chromate molar ratios in case of all the reductants studied and from all the bands.

"Reductive coefficient" $\{k_0'/([\text{ligand}]/[CrO_4^{2-}])\}$.—All the k_0' values derived as mentioned earlier exhibited linear relations with respect to ligand-to-chromate molar ratios in case of all the ligands studied. The slopes of these straight lines are different for different reductants. Hence, these are used to compare the relative

reductive abilities of these components towards Cr(VI). Thus the reductive coefficient has been defined as k_0' per unit ligand-to-chromate ratio, $k_0'/([\text{ligand}]/[\text{CrO}_4^{2-}])$, which can be derived from the slopes of these straight lines. Thus the reductive coefficients have been derived based on both UV-vis and EPR techniques.

RESULTS AND DISCUSSION

The reduction of chromate with the reductants such as pentoses, polyols, glycols, and sugar derivatives was studied by UV-vis spectroscopy [using Cr(VI) and Cr(III) bands] and EPR [using Cr(V) and Cr(III) signals] spectroscopy. The changes observed in the spectra during the progress of the reactions are essentially similar to those obtained with hexoses as reported in our recent papers[4b,c]. The plots of observed pseudo first-order rate constants (k_0') derived based on these bands (from logarithmic peak decays or peak growth vs. time plots) vs. reductant-to-chromate molar ratios gave straight lines in all cases. From our recent study the observed k_0' were found to be dependant upon the ligand-to-chromate molar ratio, the chromate concentration, and pH of the solution[4c]. However, as the main thrust of this paper is to determine the relative reductive abilities of variety of small molecules and also to understand the factors that influence the chromate reduction, we have treated the data in a quasi-kinetic manner. In order to make appropriate comparisions of the abilities, we have introduced a new term called the reductive coefficient. This is derived from the slope of the plots of k_0' vs. reductant-to-chromate molar ratios $\{k_0'/([\text{ligand}]/[\text{CrO}_4^{2-}])\}$ using both UV-vis and EPR data. The reductive coefficients thus derived from different species using both techniques are totaled, and the corresponding average values are used to compare the efficiency of the reducing agent employed and the factors that influences this. This parameter has already been used to interpret the results of chromate reduction with hexoses[4c].

Pentoses.—The pseudo first-order rate constants (k_0') derived from both absorption and EPR spectroscopy are plotted against [pentose]/$[\text{CrO}_4^{2-}]$ molar ratios as shown in Fig. 1. The reductive abilities, derived from these slopes (reductive coefficients) in the case of various pentoses using UV-vis spectra, for a given set of conditions, follow a trend, D-Xyl < D-Ara < D-Lyx < D-Rib. A similar trend is seen even from EPR studies. Taking the reductive coefficients obtained both from UV-vis and EPR studies into consideration, and assuming that the reductive ability of D-Xyl as unity (this being the least), the abilities of the other pentoses, D-Ara, D-Lyx, and D-Rib, were found to be ca. 2-, 4-, and 6-fold greater, respectively. In an attempt to correlate these results with the corresponding pentose structure of the pentoses, the following empirical rules have emerged: (*a*) A pentose having a furanose structure as the predominant species, with one primary hydroxyl group, dominates the reaction as observed with D-Rib, unlike its other pentose counterparts such as D-Ara, D-Xyl, or D-Lyx, which predominantly show pyranose rings in

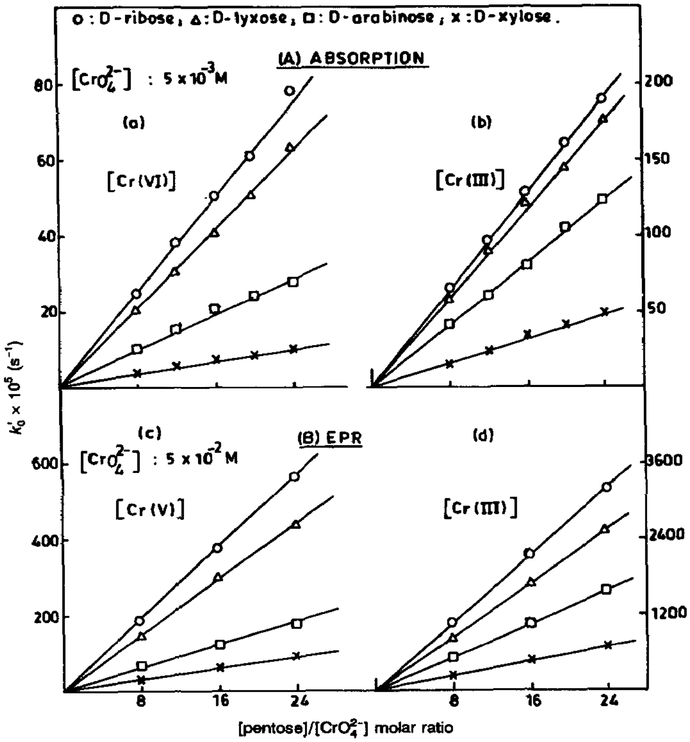

Fig. 1. Plots of observed pseudo first-order reaction rate constants (k_0') vs. pentose-to-chromate molar ratios for D-Rib, D-Lyx, D-Ara and D-Xyl: (A), from UV-vis data: (a) based on Cr(VI) band; (b) based on Cr(III) band; (B) from EPR data: (c) based on Cr(V) signal and (d) based on Cr(III) signal.

solution[15]. (*b*) Examination of the C-2, C-3, and C-4 OH groups of the open-chain form clearly indicates that the presence of *cis*-diol groups in D-Lyx and D-Ara may be responsible for their higher reactivity over D-Xyl. (*c*) The presence of OH groups in the C-2$_{ax}$ and C-3$_{eq}$ positions in the case of D-Lyx seem to be coordinatively more favoured over C-2$_{ax}$ and C-3$_{ax}$ as in D-Ara. Similar empirical correlations have been made, even in the case of studies with hexoses[4c].

Polyols.—The pseudo first-order rate constants (k_0') derived from both absorption and EPR spectroscopies are plotted against [polyol]/$[CrO_4^{2-}]$ molar ratios. The reductive abilities observed for the reaction of chromate with polyols was found to be: Etol < Gro < Thr-ol < Xyl-ol < Man-ol from both the UV-vis and EPR studies. Plots of reductive coefficients vs. number of OH groups gave linear relations from the UV-vis (Fig. 2a) and EPR data (Fig. 2b), showing that with increase in the number of hydroxyl groups, the reductive abilities increases linearly. Taking the reductive coefficients from both UV-vis and EPR studies into consideration, and assuming that the reductive coefficient of Etol is unity (this being the least), the abilities of the other polyols, namely, Gro, Thr-ol, Xyl-ol, and Man-ol were found to be 1.5-, 2.0-, 2.5-, and 3.0-fold, greater, respectively. Thus

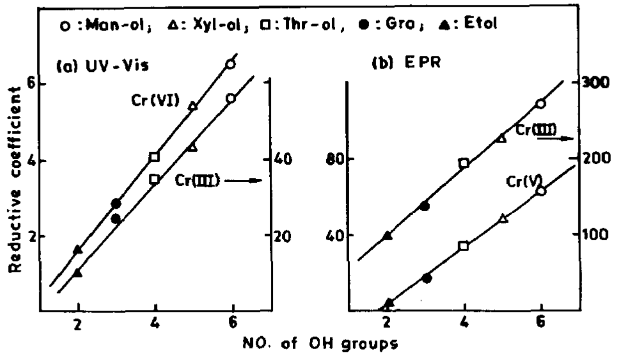

Fig. 2. Plot of reductive coefficients {$k_0'/([\text{polyol}]/[\text{CrO}_4^{2-}])$} vs. number of OH-groups for Etol, Gro, Thr-ol, Xyl-ol, and Man-ol: (a) from UV-vis data and (b) from EPR data.

the results show that for an increase of every two OH groups (carbon-attached), there seems to be a two-fold increase in the reductive ability. Though the present studies are limited to only six OH groups, intuitively, it may be expressed that molecules containing a large number of OH groups are definitely expected to be more efficient in their ability to reduce chromate.

Glycols.—The pseudo first-order rate constants (k_0') were derived as mentioned earlier. In contrast to the detection of both the Cr(V) and Cr(III) species in the previous cases, in the case of glycols, only the Cr(III) species was observed from the EPR spectra, although the UV-vis spectra show a 750-nm band corresponding to the Cr(V) species. This, however, can be interpreted based on the formation of an antiferromagnetically coupled chromium species. Sufficient evidence has been provided in the literature by Lay and Farrell[13]. From both the UV-vis and EPR studies, the reducing trends towards chromate were found to be Polygol < Tetragol < Trigol < Digol > Etol. As can be noted from this data, the reductive abilities increase from Etol to Digol, but, upon further addition of $-\text{O}-\text{CH}_2-\text{CH}_2$ (glycol) units, the ability decreases exponentially (Fig. 3). The reductive coefficient increases initially by ca. two times on going from Etol to Digol, but after this it decreases upon further addition of glycol units. Thus, the results show that the separation of the two OH groups by two intervening glycol units is found to be optimal for chromate reduction, as in the case of Digol. On increasing the number of glycol units, the flexibility of the chain increases through the possible free rotations, thereby reducing the binding nature of the glycols to chromium dramatically, which, in turn, is reflected in their reductive abilities towards chromate. This further indicates that the ligands not only reduce Cr(VI) but also bind to Cr(III). Thus the Digol shows the highest reducing power indicating that the geometry and the distance between the end OH groups are optimal in this case, followed by Etol, Trigol, Tetragol, and Polygol.

From the UV-vis and EPR studies, it can be concluded that the reducing ability increases with increase in the number of OH groups, which indicates that polysac-

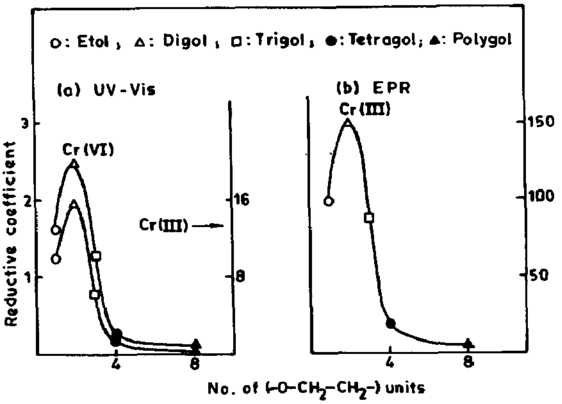

Fig. 3. Plot of reductive coefficients $\{k_0'/([\text{polyol}]/[CrO_4^{2-}])\}$ vs. number of $-O-CH_2-CH_2-$ units for Etol, Digol, Trigol, Tetragol, and Polygol: (a) from UV-vis data and (b) from EPR data.

charides and other molecules containing multihydroxy groups may act as potential reductants towards chromate. On the other hand, the reducing ability decreases with increase in glycol units, indicating that polyglycols are poor reductants.

Sugar derivatives.—The reduction of chromate with sugar derivatives of D-Glc and D-Gal gave the following results based on absorption spectroscopy. Taking the $k_0'/([\text{sugar derivative}]/[CrO_4^{2-}])$ from UV-vis and EPR studies into consideration and further assuming the reductive ability of D-Glc to be unity, the abilities of the other sugar derivatives were found, and the results are discussed below. In an exercise of a similar kind for derivatives of D-Gal, the ability of D-Gal was taken as unity.

In the case of acid derivatives of D-Glc, the reductive abilities were found to be 4-, 10-, and 16-times higher in the case of D-GlcA, D-Glc-onic, and D-Glc-aric, respectively, which fits with the trend, D-Glc < D-GlcA < D-Glc-onic < D-Glc-aric. Thus, the results are consistent with an increase of 2.5-times in the reductive ability in going from a cyclic to an open-chain acid derivative (D-GlcA to D-Glc-onic) and further with an almost two-fold increase in the ability in going from a derivative with a single carboxylate group to another containing two carboxylate groups (D-Glc-onic to D-Glc-aric). Similarly, for the acid derivative of D-Gal, i.e., D-GalA, the reductive ability was found to be ca. five times higher.

The alditols, namely, Glc-ol, Gal-ol, and Man-ol, reduce chromate about 6–8 times more efficiently than the corresponding saccharides. The reductive ability of D-Gal is almost twice that of D-Glc, and this reflects the orientation change of the 4-OH group from axial to equitorial, respectively[4c]. The effect of the 4-OH orientation on chromate reduction is preserved, even among their alcohol derivatives, i.e., Gal-ol and D-Glc-ol. In the case of Xyl-ol, the reductive ability is about 10 times higher than the corresponding pentose, namely, D-Xyl.

In the case of the amine derivatives of D-Glc, the reductive abilities were

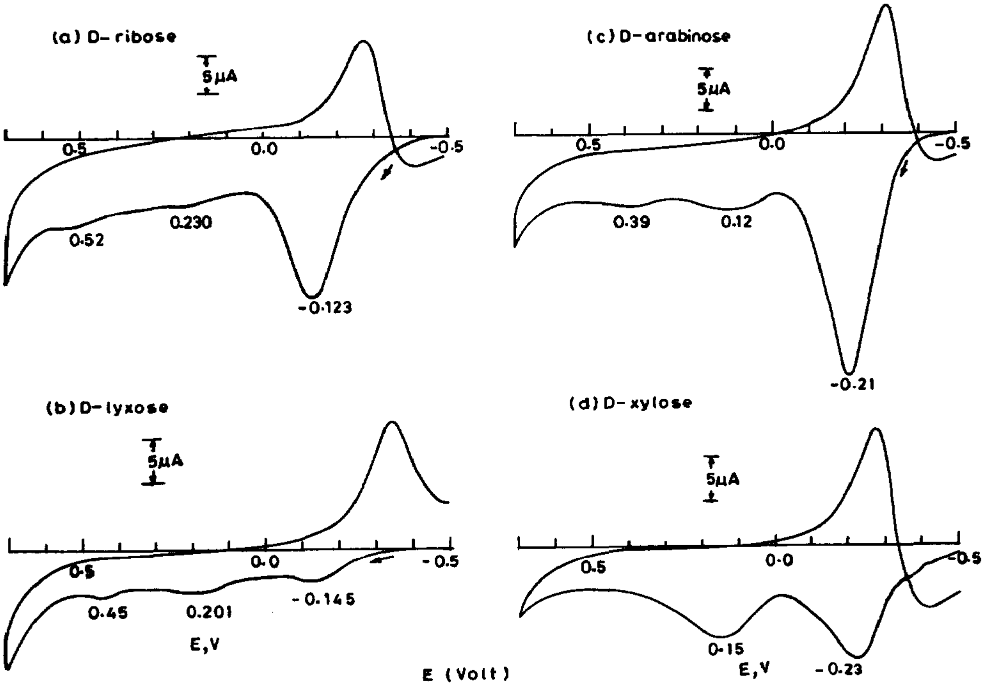

Fig. 4. Cyclic voltammograms of pentoses (25 mM): (a) D-Rib; (B) D-Lyx; (c) D-Ara; (d) D-Xyl; in N_2 purged 0.1 N NaOH; Pt working electrode; Ag/AgCl reference electrode; scan speed, 0.1 V/s.

derived based on the UV-vis absorption data alone and found to follow a trend, D-GlcN < D-Glc < D-Glc-(1 → *N*)-Me. In this, the D-Glc was found to reduce chromate twice as efficiently as the corresponding 2-amino derivative (D-GlcN), indicating that the 2-OH group is important for the reduction. On the other hand, the *N*-methyl derivative [D-Glc-(1 → *N*)-Me], is about 18 times more efficient than D-Glc.

Based on the spectroscopic studies, the overall reductive ability trend of the D-Glc derivatives has been found to be, D-GlcN < D-Glc < D-GlcA < D-Glc-(1 → N)-Me < D-Glc-ol < D-Glc-onic < D-Glc-aric, and the trend of D-Gal derivatives has been found to be, D-Gal < D-GalA < Gal-ol.

Electrochemistry.—Electrochemical studies were carried out both with simple reductants (i.e., the organic moieties) and also with the final Cr(III) species formed at the end of chromate reduction using cyclic voltammetry with Pt or HMDE as the working electrode.

Pentoses.—The anodic oxidation (E_p^a) of D-Rib in 0.1 M NaOH exhibited a more positive potential for its oxidation as compared to the other three as seen in Fig. 4. Further, the oxidation potentials follow a trend, D-Rib > D-Lyx > D-Ara > D-Xyl among the pentoses. Plots of $k_0'/([\text{pentose}]/[\text{CrO}_4^{2-}])$ vs. the first E_p^a gave a straight line, where the rate information is based on UV-vis data [fig. 5A(a)] and

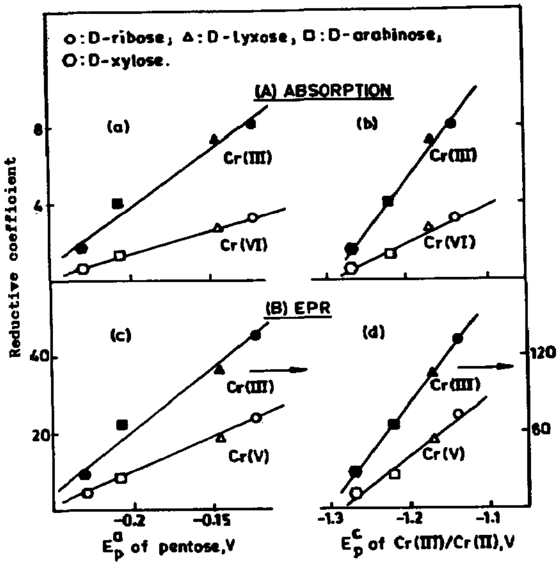

Fig. 5. Plot of reductive coefficient $k_0'/([\text{pentose}]/[\text{CrO}_4^{2-}])$ vs. potential: (A) from absorption, for (a) oxidation (E_p^a); (b) reduction (E_p^c); (B) from EPR spectra for (c) oxidation (E_p^a); (d) reduction (E_p^c).

EPR data [Fig. 5B(c)]. The results suggest that the pentose having the more positive (i.e., the less negative) E_p^a is a better reductant.

Cr(III)-pentose products.—Voltammograms obtained in all the cases exhibited one irreversible cathodic reduction peak in the range of -1.14 to -1.27 V as seen in Fig. 6. The reduction potentials for Cr(III) → Cr(II) (E_p^c) exhibited a trend: D-Rib > D-Lyx > D-Ara > D-Xyl, which is in accordance with the reductive abilities of various pentoses derived based on UV-vis and EPR spectroscopies. The plot of $k_0'/([\text{pentose}]/[\text{CrO}_4^{2-}])$ obtained from absorption and EPR spectra against E_p^c gave straight lines in all cases [Figs. 5A(b) and B(d)], indicating that the pentoses not only reduce Cr(VI) to Cr(III), but also form complexes with Cr(III) in the product.

Polyols.—The peak potentials of the oxidation processes (E_p^a) of the simple ligands exhibited a systematic trend among the four polyols, where D-Man-ol exhibits a more positive potential for its oxidation as compared to the other three and the oxidation potentials are in the order: Man-ol > Xyl-ol > Thr-ol > Gro. A plot of $k_0'/([\text{polyol}]/[\text{CrO}_4^{2-}])$ vs. the first E_p^a gave a straight line, where the rate information is based on both UV-vis and EPR data. The results suggest that the polyol having the more positive (less negative) E_p^a is a better reductant.

Cr(III)-polyol products.—The Cr(III) → Cr(II) reduction potentials (E_p^c) exhibited a trend, Man-ol > Xyl-ol > Thr-ol > Gro > Etol, which is in accordance with the reductive capabilities of various polyols. The plot of $k_0'/([\text{polyol}]/[\text{CrO}_4^{2-}])$ obtained from UV-vis and EPR spectra against E_p^c of Cr(III) → Cr(II) gave straight lines in all cases, suggesting the influence of the polyols in the reduction of

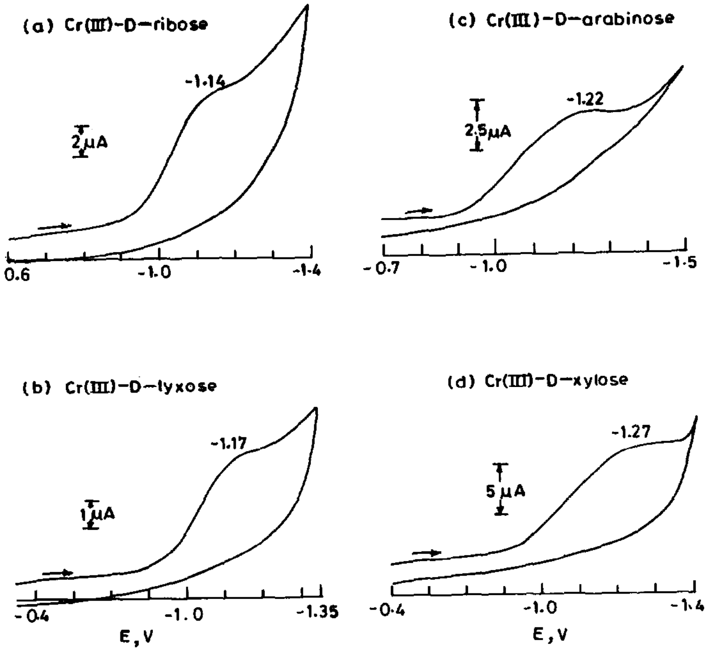

Fig. 6. Cyclic voltammograms of the final mixture of chromate and pentoses in 1:16 molar ratio at pH 0.35; HMD working electrode; Ag/AgCl reference electrode; scan speed, 0.1 V/s.

Cr(VI) as well as a role in the complexation of Cr(III). Thus, the increase of the E_p^a or E_p^c is found to be linear as a function of the number of OH groups, as expected.

Glycols.—The first E_p^a values of the simple ligands exhibited a systematic trend among all the four ligands where Digol exhibits a more positive potential and the overall trend is as follows: Digol > Trigol > Tetragol > Polygol.

Cr(III)-glycol products.—The E_p^c exhibited a trend, Digol > Etol > Trigol > Tetragol > Polygol, which is in accordance with that obtained for the reductive abilities of these ligands, as derived from the results of both UV-vis and EPR spectroscopies. The plot of $k_0'/([\mathrm{glycol}]/[\mathrm{CrO}_4^{2-}])$ obtained from absorption and EPR spectra against E_p^c gave straight lines as in the other cases. These results once again affirm that the glycols behave in the same way as the other examples. Thus, the plot of E_p^a or E_p^c vs. the number of glycol units is similar to that of rate vs. the number of glycol units (Fig. 3), as expected.

The trends observed in E_p^a values among the members of each set of reductants of pentoses, polyols, and glycols are in accordance with the trends observed in their reductive abilities based on the UV-vis and EPR data.

The results obtained from all the three techniques (UV-vis, EPR, and cyclic voltammetry) are mutually dependent and exhibit linear correlations among them (Fig. 5). These findings strongly suggest that the reductive nature of the ligands and their complexing behaviour with chromium are very important in chromate reduction.

CONCLUSIONS

In this paper we have demonstrated the role of various OH-containing molecules, including several saccharides and their derivatives, in the reduction of chromate using UV-vis and EPR spectroscopies and electrochemistry. In order to interpret the results, we have used a quasi-kinetic approach while introducing a parameter that can be used in comparing the relative reductive abilities of these molecules (reductants) towards Cr(VI). The parameter, reductive coefficient, is derived from the slope of linear relations obtained with observed pseudo first-order rate constants (k_0') vs. ligand–chromate molar ratios. All the molecules used in this study for reducing chromate are those arising from the following four categories, namely, pentoses, polyols, glycols, and sugar derivatives. The higher the value of $k_0'/(\text{ligand–CrO}_4^{2-})$, the better is the reductive ability. The following aspects are concluded based on these results. In the case of pentoses the reductive abilities are in the order, D-Rib > D-Lyx > D-Ara > D-Xyl. The empricial rules derived in this case are similar to those for hexoses[4c]. In the case of polyols, the trend is found to be Man-ol > Xyl-ol > Thr-ol > Gro > Etol, and the presence of a larger number of carbon-attached hydroxyl groups is responsible for the higher reactivity. The results show that, for an increase of two carbon-attached OH groups, there seems to be a two-fold increase in the reductive ability. In the case of glycols, the trend is found to be Digol > Etol > Trigol > Tetragol > Polyol. The OH groups separated by two glycol units, as in the case of Digol, is optimal for chromate reduction. The larger the number of glycol units separating the end OH groups, the lower is its reductive ability.

In the case of sugar derivatives, a carboxylic acid group at the C-1 or C-6 carbon atom enhances the ability of chromate reduction. The ability increases upon opening the ring structure. There is an increase in the ability on going from simple saccharides to their alcohol derivatives, i.e., from D-Glc to D-Glc-ol, and from D-Gal to Gal-ol. On replacing the 2-OH group by 2-NH_2, as in the case of D-Glc and D-GlcN, the ability is found to decrease, indicating that the presence of a 2-OH group is important for reduction.

As the results obtained from UV-vis, EPR, and cyclic voltammetry showed strong linear correlations, it is logical to suggest that the reducing and complexing nature of the molecules play important roles in chromate reduction.

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