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Relative reducing abilities in vitro of some hydroxy-containing compounds, including monosaccharides, towards vanadium(V) and molybdenum(VI)

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Abstract

The reduction of vanadium(V) and molybdenum(VI) has been carried out in aqueous HCl by various hydroxy-containing compounds such as hexoses (D-glucose, D-fructose, and D-galactose), pentoses (D-ribose and D-xylose), glycols [ethylene glycol, di(ethylene glycol), tri(ethylene glycol), tetra(ethylene glycol), and poly(ethylene glycol)], and mono-, di-, and tri-ethanolamines. The relative reducing abilities of these compounds are compared with those of L-ascorbic acid and L-cysteine. The trend is similar to that reported earlier for chromium(VI) reduction. Based on this study it is concluded that hydroxy-containing compounds play important roles in complexation and reduction of metal ions.

Keywords: Monosaccharides; Polyols; Reduction; Metal ions

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1. Introduction

Hydroxy compounds, especially sugars and their derivatives, form a class of polymeric compounds that occur in nature either freely or as constituents of other biomolecules. The saccharides are known to have important roles in biological systems, not only in carbohydrate metabolism, but also to some extent in the reduction and complexation of various toxic and non-toxic metal ions [1]. These reactions occur under

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different conditions and at different rates and give rise to a variety of products, and, therefore, can have an overall effect on the bioavailability of the metal ions and hence on the constitution of the inorganic biosphere. The reduction of metal ions by polyhydroxy compounds in an acidic medium is an important aspect in soil chemistry. In the past two decades intensive investigations have been carried out on the kinetics of oxidation of sugars by metal ions such as V(V), Cr(VI), Ce(IV), Ir(IV), Fe(III) and Au(III). The oxidations were found to be catalysed by acid [2,3]. Vanadium(V) and Cr(VI) are closely related in their chemical properties, but the reduction of V(V) is difficult compared with that of Cr(VI) because of its lower redox potential, namely V(V)/V(IV) = 1.00 V, Cr(VI)/Cr(III) = 1.20 V. However, an increase in acid strength increases the redox potential and makes the reduction easier.

Vanadate acts as a phosphate analogue in biological systems [4]. The hydroxyl groups are readily esterified by vanadate, as demonstrated by ^{51}V NMR studies, [5], and are then accepted as enzyme substrates where phosphorylated substrates are normally required. Glucose, in the presence of vanadate, produces gluconic acid during the dehydrogenase activity of glucose-6-phosphate dehydrogenase [6]. We have studied extensively the reduction of Cr(VI) in HCl by a variety of saccharides and related compounds, namely sugar alcohols, sugar acids, sugar amines, nucleotides and their components, etc., and have reported the relative reducing abilities of these compounds in order to explain the chromate reductase activity [3]. We now report the relative reducing abilities of monosaccharides: namely, hexoses, D-glucose (D-Glc), D-fructose (D-Fru), and D-galactose (D-Gal); pentoses, D-ribose (D-Rib) and D-xylose (D-Xyl); ethanolamines: monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA); glycols: ethylene glycol (Etol), di(ethylene glycol) (Digol), tri(ethylene glycol) (Trigol), tetra(ethylene glycol) (Tetragol), and poly(ethylene glycol) (Polygol), towards V(V) and Mo(VI). A qualitative comparison of the relative reducing abilities of these compounds was carried out with L-ascorbic acid and a thiol, L-cysteine (L-Cys). Furthermore, the results are discussed in the light of similar studies already performed with Cr(VI) reduction by these compounds. The results were derived from absorption data under identical conditions and are purely relative. The scope of the present work does not include measurements of thermodynamic parameters and/or mechanistic aspects.

2. Experimental

All chemicals used were from commercial sources (Aldrich Chemical Co., Sigma Chemical Co., or SRL, India) and were used without further purification. All solutions were prepared using doubly distilled water. The reactions were carried out at ambient temperature and under identical conditions to determine relative reducing abilities of various compounds under such conditions. The V(V) reductions were carried out using 0.01 M V_2O_5 in 4 N HCl, and those of Mo(VI) were carried out using 0.1 M $Na_2MoO_4 \cdot 2H_2O$ in 5.5 N HCl. These concentrations were found to be satisfactory for measuring the absorbances in the 400–900 nm range because of lower extinction coefficients in the visible region. Only hexoses, glycols, L-ascorbic acid and L-cysteine were used for Mo(VI) reduction. The reductants were used in the concentrations, 8-, 12-, 16-, and 20-fold molar excess to that of the metal concentration. The reductions by L-Cys were carried out at 1:1, 1:2, 1:3, and 1:4 ratios for V(V) and 1:4, 1:6, and 1:8 for Mo(VI) reduction. The use of L-ascorbic acid at ratios as low as 1:1 produced an instantaneous reduction. The required amount of the reductant was freshly dissolved in the appropriate HCl solution prior to reaction. Experiments were performed with a Shimadzu UV-260 spectrophotometer using 5.0 cm cells in the visible region (400–900 nm). Progress of the reactions was monitored by recording the spectra at various times and observing the increase of the V(IV) band at ~ 760 nm and the Mo(V) band at ~ 700 nm. The faster reactions were monitored at their respective λ_{max} positions using the time-scan mode. The formation of V(IV) and Mo(V) were confirmed from EPR measurements of the reaction mixtures at room temperature on a Varian ESR 112 spectrometer. The linear best fits of the plots were obtained by using the GRAPHER software package.

3. Results and discussion

Reduction of V(V).—Vanadium(V) reductions were initially carried out at same acid strength (1.0 M) as used earlier with chromium(VI) reduction, but were found to be extremely slow and hence unsuitable for relative studies. In order to obtain optimum conditions for comparing the reducing abilities of various reductants, the concentration of HCl that gave a satisfactory result with the slowest reductant was chosen. A 4 N HCl solution was selected for carrying out these studies at a V(V) concentration of 0.02 M ($[V_2O_5] = 0.01$ M) at which VO_2^+ exists in solution [7a]. On addition of reductant, a band at 760 nm is formed and increases with time, and after a certain period absorbance

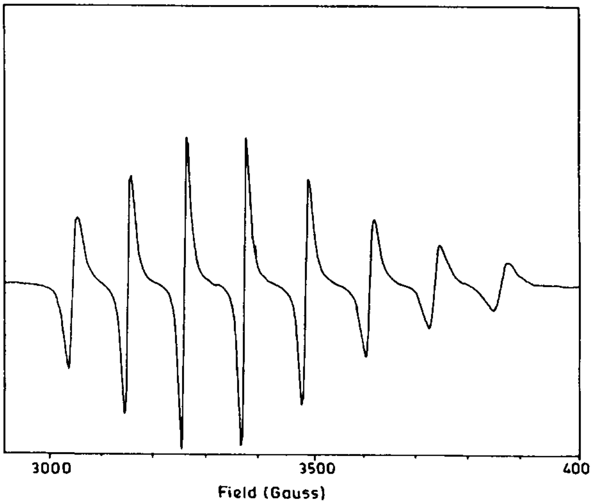

Fig. 1. X-Band EPR spectrum of final reaction mixture indicating the presence of VO^{2+} in 4 N HCl. Field marker = TCNE ($g = 2.00277$).

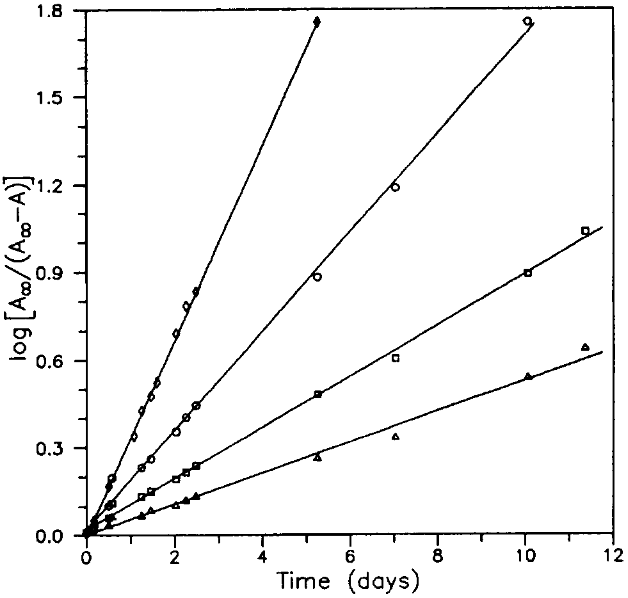

Fig. 2. Plot of log $[A_\infty/(A_\infty - A)]$ vs. time for V(V) reduction by D-Glc in 4 N HCl. $[V_2O_5] = 0.01$ M {[V(V)] = 0.02 M}, [D-Glc] = (◇) 0.4 M, (○) 0.32 M, (□) 0.24 M, (△) 0.16 M.

becomes constant, indicating all V(V) is converted to V(IV). The rate of increase of the 760-nm band [from V(IV) species] with time in the presence of different reductants was used as a criterion to determine the relative reducing abilities of various reductants. The faster the formation of V(IV), the faster the reducing ability. In an earlier paper we reported the relative reducing ability of saccharides and related compounds towards chromate [3] in a similar manner by monitoring the increase of a band at ~ 570 nm for the formation of Cr(III). The formation of final V(IV) (as VO^{2+}) was confirmed by the presence of an eight-line EPR spectrum ($I = 7/2$) with $g = 1.965 \pm 0.001$ and the corresponding hyperfine coupling constant A of ~ 115 Gauss (Fig. 1).

(a) Hexoses. The plots of absorbance vs. time give exponential curves suggesting that the reactions are pseudo first order. On plotting log $[A_\infty/(A_\infty - A)]$ versus time, straight lines were obtained, the slopes of which were used to get the k'_{obs} values for the formation of V(IV) (Fig. 2). The plot of k'_{obs} against reductant concentration (Fig. 3) exhibited linear behaviour with different slopes for different reductants. The slopes (min^{-1} M^{-1}) indicate relative reducing abilities of the compounds towards V(V). The k'_{obs} [reductant] values for D-Glc, D-Fru, and D-Gal were calculated to be 18.53×10^{-4}, 19.28×10^{-2}, and 28.35×10^{-4} min^{-1} M^{-1}, respectively. Based on the k'_{obs}/[reductant] values, the reducing abilities of these hexoses follow a trend: D-Fru ≫ D-Gal > D-Glc. The relative magnitudes of the reducing abilities of D-Fru and D-Gal with respect to D-Glc were 104 and 1.5 times, respectively. In turn, the reducing ability of D-Fru is 68 times greater than that of D-Gal. The faster reduction by D-Fru compared with D-Glc and D-Gal may be due to the formation of a reducing enediol from its

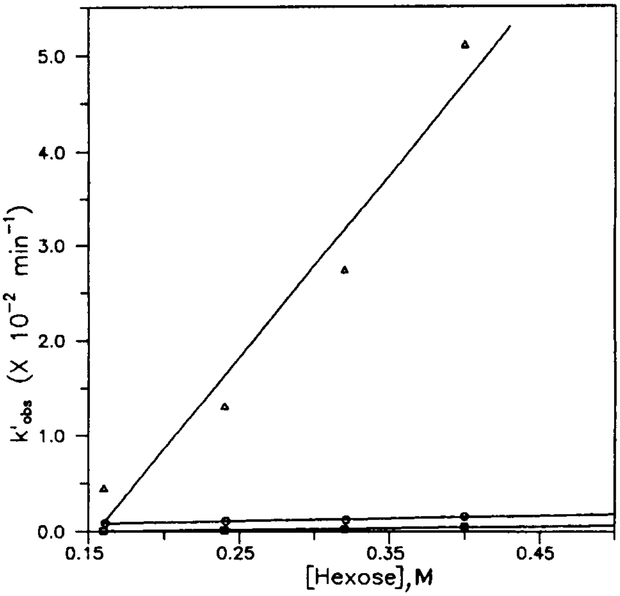

Fig. 3. Plot of k'_{obs} /[reductant] for V(V) reduction by hexoses; (△) D-Fru, (○) D-Gal, (□) D-Glc.

furanose form. This implies that in polysaccharides the reduction is expected to be mainly from the D-Fru units, and the contribution made by D-Glc and D-Gal is extremely small.

(b) Pentoses. Both pentoses, D-Rib and D-Xyl, exhibited behaviour similar to that of the hexoses. The k'_{obs}/[reductant] values were calculated to be 11.47×10^{-3} and 8.39×10^{-3} min^{-1} M^{-1} for D-Rib and D-Xyl, respectively. Thus, it is clear that the reduction by D-Rib is only marginally (1.4 times) faster than that by D-Xyl. Compared with the hexoses, the reducing abilities of these two pentoses is greater than that of D-Glc and D-Gal, and less than that of D-Fru. Thus, in general, keto sugars have better reducing ability towards V(V) than aldoses; however, aldopentoses are better reductants than aldohexoses.

(c) Glycols. Based on the k'_{obs}/[reductant] values obtained in a similar manner to that described earlier for hexoses, the reducing abilities (min^{-1} M^{-1}) of glycols towards V(V) follow a trend, Etol (7.16×10^{-4}) > Polygol (3.49×10^{-4}) > Trigol (2.75×10^{-4}) ≥ Tetragol (2.63×10^{-4}) ≥ Digol (2.34×10^{-4}). The relative reducing abilities between various glycols compared with Digol are Etol (3.1 times), Polygol (1.5 times), Trigol (1.2 times), Tetragol (1.1 times). A plot of k'_{obs}/[reductant] values as a function of number of glycol units ($-O-CH_2-CH_2-$) is shown in Fig. 4. From this plot it can be seen that, from Etol to Digol, the reducing ability decreases by one-third, and further addition of glycol units does not show any appreciable change in reducing abilities. Based on the above discussion, it can be deduced that one glycol unit separating H and OH is the most favourable for V(V) reduction, suggesting that Etol is an effective reductant as a result of its better chelation ability in forming a five-membered ring.

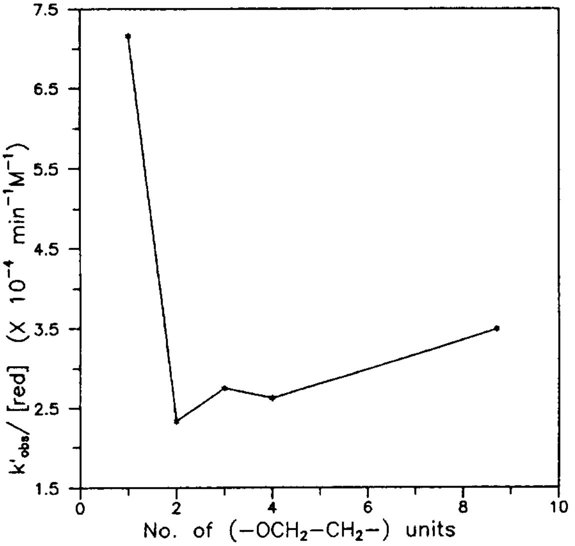

Fig. 4. Plot of k'_{obs} /[reductant] vs. number of $-OCH_2CH_2-$units for V(V) reduction by glycols.

(d) Ethanolamines. The k'_{obs}/[reductant] values obtained similarly were 3.40×10^{-5}, 11.40×10^{-5}, and 30.06×10^{-5} min^{-1} M^{-1}, respectively, for MEA, DEA, and TEA. Compared with MEA, the reduction by DEA is 3.4 times faster, and that by TEA is 8.8 times faster. This can be clearly attributed to the increase of the CH_2CH_2OH groups on N. A plot of k'_{obs}/[reductant] as a function of number of $-CH_2CH_2OH$ groups is shown in Fig. 5. From Fig. 5 it can be seen that the replacement of one hydrogen of ammonia (obtained through extrapolating to zero) by one $-CH_2CH_2OH$ group (MEA) reduces V(V) with the k'_{obs}/[reductant] value of 3.40×10^{-5} min^{-1} M^{-1}, and subsequent replacement of a second (DEA) and a third (TEA) hydrogen atom increases the reduction rate by 8.0×10^{-5} and 18.66×10^{-5} min^{-1} M^{-1}, respectively. Thus, the role of the hydroxy groups in the succesive increase in reducing abilities of these compounds is demonstrated.

(e) L-*Cysteine.* The reduction of V(V) by L-Cys at the same ratios as those carried out for the monosaccharides, glycols, and ethanolamines, instantaneously produced VO^{2+} species that could not be monitored due to instrumental limitations. However, the reductions were performed using the ratios 1:1, 1:2, 1:3, and 1:4, the ratios 1:3 and 1:4 being monitored in the time-scan mode. The slope of the plot k'_{obs} versus [L-Cys] was calculated to be 6.50 min^{-1} M^{-1}. The reducing ability of L-Cys is generally higher by about 1–4 orders of magnitude compared with the other reductants reported here.

(f) L-*Ascorbic acid.* Under similar conditions, the reduction by L-ascorbic acid was also found to be instantaneous, even at a ratio as low as 1:1. Therefore, the reactions could not be monitored even in the time-scan mode. These reactions need to be monitored on a milli-/micro-second time-scale. Thus, under present conditions, the reduction by L-ascorbic acid was the fastest of all the reductants used for V(V) reduction.

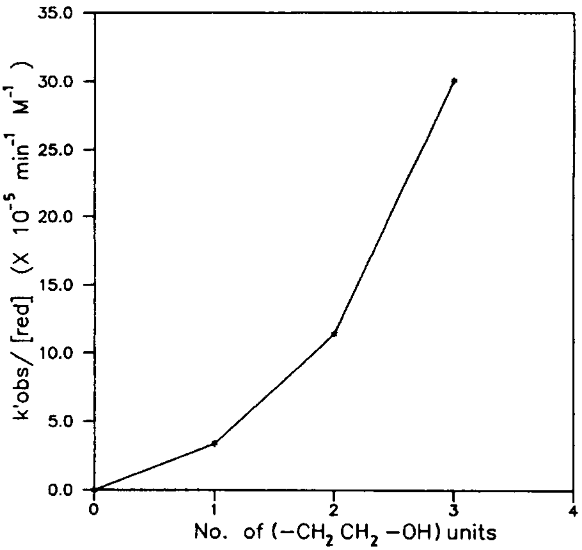

Fig. 5. Plots of k'_{obs} /[reductant] vs. number of $-CH_2CH_2OH$ units for V(V) reduction by ethanolamines.

Based on the above observations, the V(V) reducing abilities of all the compounds taken together follow a trend: L-ascorbic acid > L-Cys ≫ D-Fru (5700) > D-Rib (337) > D-Xyl (247) > D-Gal (83) > D-Glc (55) > Etol (21) > Polygol (10) ≥ TEA (9) ≥ Trigol (8) = Tetragol (8) ≥ Digol (7) > DEA (3) > MEA (1). The values in parentheses denote the relative reducing abilities of compounds compared with that of MEA. A similar trend was also observed for the reduction of chromate as reported earlier [3].

Reduction of Mo(VI).—Molybdate exists as a tetrahedral anion, MoO_4^{2-}, in aqueous solution, like chromate. Although this anion can be reduced in solution, it is a weaker oxidant than chromate. Molybdenum oxoanions give complexes with sulfate and hydroxy compounds such as glycerol, tartrate ion, and sugars [7a]. It is not usually possible to obtain samples of the molybdoenzymes containing only the Mo(V) oxidation state, since the Mo(VI)/Mo(V) and Mo(V)/Mo(IV) redox couples have similar potentials. Therefore, addition of a single reducing equivalent to Mo(VI) results in the formation of all these three oxidation states of Mo [7b]. But an extensive range of Mo(V) compounds can be obtained by the reduction of molybdates in acid solutions [7a]. The chemical speciation suggests the presence of an oxochloride anion, $MoO_2Cl_4^{2-}$ in 12 N HCl and $MoO_2Cl_2(H_2O)_2$ in 6 N HCl. Selection of HCl concentration was made as mentioned earlier in the case of V(V) reduction, and a 5.5 N HCl concentration was chosen for the Mo(VI) reduction studies. The reductants, freshly prepared in 5.5 N HCl, were added to the Mo(VI) solution, and the progress of the reaction was monitored by an increase in the band at ~ 700 nm due to Mo(V) in the absorption spectra. The formation of Mo(V) in the final reaction mixtures was also confirmed from EPR spectra with a strong signal at $g = 1.945 \pm 0.001$ due to ^{96}Mo(V) ($I = 0$, $S = 1/2$) and six very weak lines in the vicinity, due to ^{95}Mo and ^{97}Mo ($I = 5/2$) isotopes, having identical g values and a hyperfine coupling constant A of ~52 Gauss (Fig. 6).

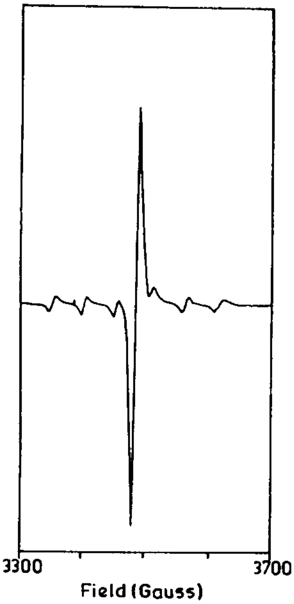

Fig. 6. X-Band EPR spectrum of final reaction mixture indicating the presence of ^{96}Mo(V) in 5.5 N HCl. Field marker = TCNE (g = 2.00277). Six weak lines due to ^{95}Mo and ^{97}Mo isotopes (I = 5/2).

(a) Hexoses. Reduction of Mo(VI) by D-Glc, D-Fru, and D-Gal followed first-order kinetics like that of the V(V) reduction. The slopes (k'_{obs}/[reductant]) obtained were 2.45×10^{-5}, 1.90×10^{-4}, and 2.04×10^{-5} min^{-1} M^{-1}, respectively, for reduction by D-Glc, D-Fru, and D-Gal. It is noted from the k'_{obs}/[reductant] values that, compared with D-Gal, the reduction by D-Fru is about nine times faster, while that by D-Glc is almost the same (1.2 times). Hence, the relative reducing ability of hexoses towards Mo(VI) reduction follows a trend: D-Fru > D-Glc ≥ D-Gal. Compared with the V(V) reduction by D-Fru, the relative reduction by D-Fru is only nine times faster than that of other hexoses, probably due to opening of the furanose ring at an HCl concentration of 5.5 N.

(b) Glycols. The reduction of Mo(VI) by glycols follows pseudo-first-order kinetics similar to those of V(V) and Cr(VI) reductions. Based on the k'_{obs}/[reductant] (min^{-1} M^{-1}) values derived as mentioned earlier, the reducing ability of glycols towards Mo(VI) follows a trend: Digol (1.35×10^{-4}) > Polygol (1.53×10^{-5}) ≥ Trigol (1.36×10^{-5}) ≥ Tetragol (1.08×10^{-5}) > Etol (6.38×10^{-6}). A plot of number of glycol units vs. the reducing abilities (k'_{obs}/[reductant]) is shown in Fig. 7. While the reducing ability of Digol increases by about an order of magnitude compared with that of Etol, further addition of glycol units results in a large decrease in their reactivity. Thus, the results show that the presence of two glycol units (as in Digol) is necessary for the reduction of Mo(VI). This suggests the most favourable binding of Digol to Mo to form two five-membered rings, and that increase in the chain length reduces the binding nature of the OH groups through greater flexibility and reduced chelating effect. Similar

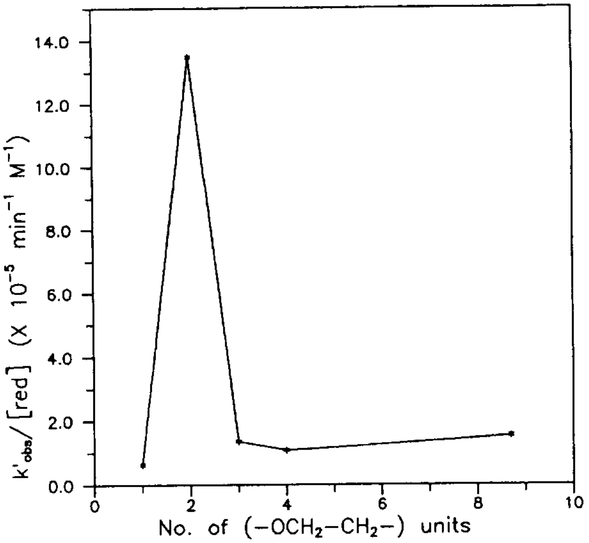

Fig. 7. Plot of k'_{obs} /[reductant] vs. number of $-OCH_2CH_2-$ units for Mo(VI) reduction by glycols.

results were obtained in the case of the Cr(VI) reduction by these reductants, as reported earlier [3c].

(c) L-*Cysteine.* The reduction by L-Cys was carried out at lower ratios, namely, 1:4, 1:6, and 1:8, owing to its faster rate of reduction at the ratios studied compared with other reductants reported. The first-order formation of Mo(V) was also calculated as for other reductants, and the k'_{obs}/[reductant] value was found to be 7.56×10^{-3} min^{-1} M^{-1}. Thus, on a relative basis, the reduction by L-Cys is about 40 times faster than that of D-Fru and 56 times faster than that of Digol.

(d) L-*Ascorbic acid.* The reduction of Mo(VI) by L-ascorbic acid at 5.5 N HCl concentration was instantaneous, even at a low ratio such as 1:1. Hence, the formation of Mo(V) could not be monitored on the time-scale of the instrument. Thus, on a qualitative basis, the reduction was found to be faster than that of L-Cys, and hence the fastest of all the reductants studied for the Mo(VI) reduction.

From the results and discussion presented above, an overall trend for the Mo(VI) reduction is: L-ascorbic acid > L-Cys ≫ D-Fru (30) > Digol (21) > D-Glc (4) ≥ D-Gal (3) ≥ Polygol (2.5) ≥ Trigol (2) = Tetragol (2) > Etol (1). The values in parentheses denote the relative reducing abilities of the compounds compared with Etol.

4. Conclusions

The present study shows the results of the reduction of V(V) and Mo(VI) in acidic media by various monosaccharides, glycols, ethanolamines, L-ascorbic acid, and L-Cys, under identical conditions. The role of these compounds in the reduction of V(V) and Mo(VI) is addressed based on their relative reducing abilities. The reductions by L-ascorbic acid are instantaneous, and hence fastest, and those by L-Cys are about 2–3 orders of magnitude higher than those of the monosaccharides and other reductants at the same acid strength. Amongst the monosaccharides, the ketoses are better reductants than the aldoses; however, the aldopentoses exhibit better reducing ability than the aldohexoses. Thus, while the reducing ability of D-Fru is ~1–2 orders of magnitude higher than that of D-Glc or D-Gal, the reducing abilities are comparable between D-Glc and D-Gal reactions, but lower by an order of magnitude compared with D-Xyl and D-Rib. Of the glycols studied while Etol is an efficient reductant of V(V), it is the Digol, which possesses two glycol units, that is an efficient reductant of Mo(VI). This reflects the optimal chelating abilities, respectively, for V and Mo, depending upon the available coordination sites after replacing labile ligands such as Cl^- and/or H_2O. Digol showed efficient reduction, even in the case of Cr(VI) [3c]. The ethanolamines show the effect that increasing the number of ethanol groups results in a successive increase in reducing abilities; however, their overall reducing ability is the lowest amongst the categories of reductants studied. The Cr(VI) reductions carried out with the reductants as reported earlier were found to be faster even at the low acid strength of 1 M HCl, whereas similar reductions of V(V) and Mo(VI) were considerably slower. Since these reactions are acid catalysed, the reductions of V(V) and Mo(VI) were accelerated using a higher concentration of HCl to study the relative reducing abilities. Hence, the relative oxidizing properties of the metal ions towards the reductants follows the trend, Cr(VI) > V(V) > Mo(VI), which is in accord with their redox potentials. In all the three metal ions, reducing abilities follow a general trend, L-ascorbic acid > L-Cys > monosaccharides > glycols > ethanolamines [not studied for Mo(VI) reduction]. Thus, while L-ascorbic acid and L-Cys are very efficient reductants of these metal ions, the saccharides and related hydroxy-containing compounds are also important, to some extent, in the reduction and complexation of various metal ions.

Acknowledgements

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