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Heteroaromatic N-base ligands in 1,10-phenanthroline- and 2,2′-bipyridyl-assisted chromic acid oxidation of (−)-L-sorbose in aqueous micellar acid media: a kinetic study

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ABSTRACT

In aqueous sulfuric acid media, Cr(VI) oxidation of (−)-L-sorbose in the presence and absence of catalysts like 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy) have been carried out under the conditions, $[(-)\text{-L-sorbose}]_T \gg [Cr(VI)]_T$ at different temperatures. Under the experimental conditions, the monomeric species of Cr(VI) has been found kinetically active in the absence of phen and bipy catalysts, while in the heteroaromatic N-base catalysed path, the Cr(VI)–phen and Cr(VI)–bipy complexes have been suggested as the active oxidants. In the catalysed path, Cr(VI)–L complex (L = phen, bipy) receives a nucleophilic attack by the substrate to form a ternary complex which subsequently experiences a redox decomposition through two-electron transfer leading to the organic products and a Cr(IV)–L complex. Both the uncatalysed and catalysed paths show first-order dependence on $[(-)\text{-L-sorbose}]_T$ and $[Cr(VI)]_T$. The uncatalysed path shows second-order in $[H^+]$, while the catalysed path shows a first-order dependence on $[H^+]$. The heteroaromatic N-base catalysed path is first-order in $[phen]_T$ or $[bipy]_T$. These findings remain unchanged in the presence of externally added surfactants. The cationic surfactant (i.e., *N*-cetylpyridinium chloride (CPC)) inhibits the rate in both the catalysed and uncatalysed paths, whereas the anionic surfactant (i.e., sodium dodecyl sulfate (SDS)) shows the rate accelerating effect for both the uncatalysed and catalysed paths. The observed micellar effects have been rationalised by considering the distribution of the reactants between the micellar and aqueous phases in terms of the proposed reaction mechanism.

1. Introduction

The kinetic aspects of oxidative degradation of different types of reducing sugars by different higher valent metal ions including Cr(VI) have been studied by different workers under different conditions.[1–13] Reduction of Cr(VI) by different reducing sugars is relevant in understanding the chemistry of chromium in the environment[14] where Cr(VI) appears as a hazardous species because of its carcinogenic and mutagenic activity.[14–16] It is believed that during the reduction of Cr(VI) to Cr(III), the intermediate states of chromium probably interact with biological molecules to induce toxicity.[16] In this reduction process in vivo, it is quite reasonable to argue that reducing sugars may have some vital roles. Thus the studies of the kinetics of the interaction of Cr(VI) with the reducing sugars appear important. The present studies aim to contribute in this direction. The mechanistic aspects of oxidation of different ketohexoses by different transition metal ions in aqueous acid media have been reported.[1,5,17] Among the different types of chelating agents[8,18–38] to catalyse the Cr(VI) oxidation of different types of organic substrates, 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy), are unique and quite efficient.[39–43] These are never co-oxidised along with the substrate. The present investigations have been carried out in micro-heterogeneous systems relevant to biological systems in the presence of the chelating agents, 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy), to substantiate the proposed reaction mechanism and to mimic the in vivo reduction of Cr(VI).

2. Results and discussion

2.1. Dependence on $[Cr(VI)]_T$

Under the experimental conditions, $[(-)\text{-L-sorbose}]_T \gg [phen]_T$, and $[bipy]_T \gg [Cr(VI)]_T$, both in the presence and absence of the heteroaromatic N-bases, 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy), the rate of disappearance of Cr(VI) shows a first-order dependence on Cr(VI). This first-order dependence on Cr(VI) is also maintained in the presence of surfactants CPC and SDS. The pseudo-first-order rate constants (k_{obs}) have been evaluated from a linear plot of $\log[Cr(VI)]_t$ versus time (t) as usual.

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2.2. Dependence on $[phen]_T$ and $[bipy]_T$

The plots of k_{obs} versus $[phen]_T$ and k_{obs} versus $[bipy]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower uncatalysed path (cf. Fig. 1). The pseudo-first-order rate constants ($k_{obs(u)}$) directly measured in the absence of phen and bipy under the same conditions nicely agree with those obtained from the intercepts of the plots of $k_{obs(T)}$ versus $[phen]_T$ and $k_{obs(T)}$ versus $[bipy]_T$. These observations are formulated as follows:

$$k_{obs(T)} = k_{obs(u)} + k_{obs(c)} = k_{obs(u)} + k_{cat}[L]_T, \quad (L = phen, bipy) \quad (1)$$

Both in the presence and absence of surfactants (CPC and SDS), the above relationship is found to be maintained. The values of k_{cat} with the activation parameters are given in Tables 1 and 2. During the progress of reaction, phen and bipy are lost due to the formation of inert Cr(III)–phen and Cr(III)–bipy complexes. Under the conditions, $[phen]_T$ and $[bipy]_T \gg [Cr(VI)]_T$, during the progress of the reaction, $[phen]_T$ and $[bipy]_T$ remain more or less constant.

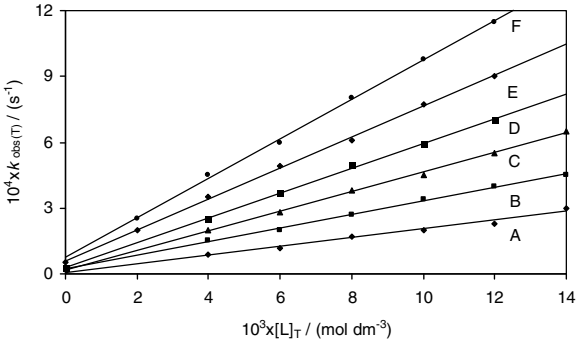


Figure 1. Effect of $[L]_T$ (L = phen, bipy) on $k_{obs(T)}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence of phen and bipy in aqueous H_2SO_4media. $[Cr(VI)]_T = 4 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.5$ mol dm^{-3}, $[(-)\text{-L-sorbose}]_T = 8 \times 10^{-3}$ mol dm^{-3}. (A) For bipy-catalysed reaction: $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}, $T = 30$ °C. (B) For phen-catalysed reaction: $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}, $T = 30$ °C. (C) For phen-catalysed reaction: T = 20 °C. (D) For bipy- catalysed reaction: T = 30 °C. (E) For bipy- catalysed reaction: T = 40 °C. (F) For phen- catalysed reaction: T = 40 °C.

2.3. Dependence on $[S]_T$ [(−)-L-sorbose]$_T$

From the plot of k_{obs} versus $[(-)\text{-L-sorbose}]_T$ (cf. Fig. 2), it has been established that the catalysed path shows the first-order dependence on $[S]_T$,

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{s(c)}[S]_T \quad (2)$$

$$k_{obs(u)} = k_{s(u)}[S]_T \quad (3)$$

The above first-order dependence on $[S]_T$ is also maintained in the presence of surfactants (i.e., CPC and SDS). The values of $k_{s(u)}$ and $k_{s(c)}$ are given in Tables 1 and 2.

2.4. Dependence on $[H^+]$

Acid dependence patterns for the uncatalysed and catalysed paths are different (cf. Fig. 3). From the experimental fit, the observations are as follows:

Table 1
Kinetic parameters and some representative rate constants for the Cr(VI) oxidation of (−)-L-sorbose in the presence of 1,10-phenanthroline catalyst in aqueous H_2SO_4 media

Temperature (°C)	$10^4 k_{obs(u)(w)}$[a] (s^{-1})	$10^2 k_{cat(w)}$[a] (dm^3 mol^{-1} s^{-1})	$10^2 k_{cat(cpc)}$[a] (dm^3 mol^{-1} s^{-1})	$10^2 k_{eff(w)}$[a]	$10^4 k_{H(c)(w)}$[b] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(w)}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(sds)}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(cpc)}$[c] (dm^3 mol^{-1} s^{-1})
20	0.1 ± 0.01	4.5 ± 0.3		45				
25					11.2 ± 0.20			
30	0.3 ± 0.03	6.5± 0.26	3.3± 0.15	22		4.0 ± 0.04	6.8 ± 0.25	1.5 ± 0.04
40	0.5 ± 0.04	9.3 ± 0.4		19				
$\Delta H^{\neq}$ (kJ mol^{-1})		28.9 ± 1.4						
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})		−175 ± 9.0						

Subscript (u) for uncatalysed path; (c) for 1,10-phen-catalysed path; (w) for the value in the absence of surfactant; (CPC) or (SDS) for the value in presence of the respective surfactant.

[a] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[S]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[1,10\text{-phen}]_T = (0–14 \times 10^{-3})$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}. $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[1,10\text{-phen}]_T = 10 \times 10^{-3}$ mol dm^{-3}.

[b] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[1,10\text{-phen}]_T = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+]_T = (0 – 1.0)$ mol dm^{-3}.

[c] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = (4\text{-}24) \times 10^{-3}$ mol dm^{-3}, $[1,10\text{-phen}]_T = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[SDS]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[CPC]_T = 4.0 \times 10^{-3}$ mol dm^{-3}.

Table 2
Kinetic parameters and some representative rate constants for the Cr(VI) oxidation of (−)-L-sorbose in the presence of 2,2′-bipyridyl catalyst in aqueous H_2SO_4 media

Temperature (°C)	$10^4 k_{obs(u)(w)}$[a] (s^{-1})	$10^2 k_{cat(w)}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{cat(cpc)}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{cat(sds)}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{eff(w)}$[a]	$10^4 k_{H(c)(w)}$[b] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(w)}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(sds)}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{s(c)(cpc)}$[c] (dm^3 mol^{-1} s^{-1})
20	0.1 ± 0.01	4.3 ± 0.18			43				
25						14.6 ± 0.15			
30	0.3 ± 0.03	5.6 ± 0.21	2.0 ± 0.1	8.3 ± 0.31	19		4.6 ± 0.04	6.15 ± 0.16	1.35 ± 0.10
40	0.5 ± 0.05	7.2 ± 0.30			14				
$\Delta H^{\neq}$ (kJ mol^{-1})	19.3 ± 1.1								
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−207 ± 10								

Subscript (u) for uncatalysed path; (c) for 2,2′-bipy-catalysed path; (w) for the value in the absence of surfactant; (CPC) or (SDS) for the value in presence of the respective surfactant.

[a] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = (0–14 \times 10^{-3})$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 4.0 \times 10^{-3}$ mol dm^{-3}. $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[2,2'\text{-bipy}]_T = 10 \times 10^{-3}$ mol dm^{-3}.

[b] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = 6.0 \times 10^{-3}$ mol dm^{-3}, $[H]_T = (0–1.0)$ mol dm^{-3}.

[c] $[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = (4–24) \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 4 \times 10^{-3}$ mol dm^{-3}.

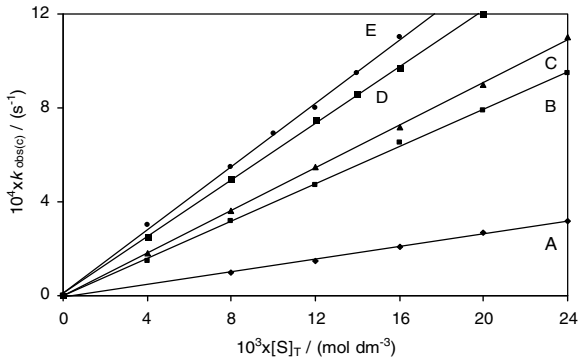


Figure 2. Effects of $[S]_T$ on $k_{obs(c)}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence of phen and bipy in aqueous H_2SO_4 media. $[Cr(VI)]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 30$ °C. (A) $[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}. (B) $[phen]_T = 5 \times 10^{-3}$ mol dm^{-3}. (C) $[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}. (D) $[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 4 \times 10^{-3}$ mol dm^{-3}. (E) $[phen]_T = 5 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 8 \times 10^{-3}$ mol dm^{-3}.

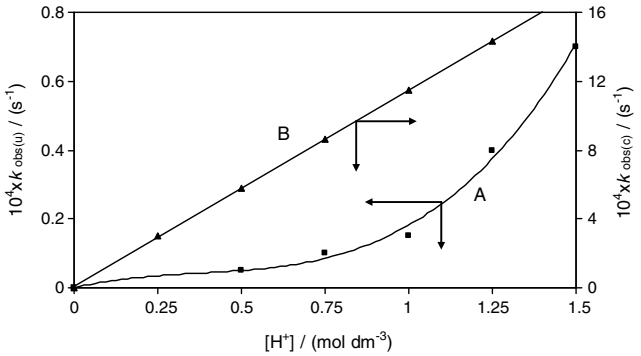


Figure 3. Effect of $[HClO_4]_T$ on $k_{obs(u)}$ and $k_{obs(c)}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence and absence of catalyst. $[Cr(VI)]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[(-)$-L-sorbose$]_T = 8 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] + [NaClO_4] = 1.5$ mol dm^{-3}, $T = 25$ °C. (A) For $k_{obs(u)}$ versus $[H^+]$ plot: $[bipy]_T = [phen]_T = 0$ mol dm^{-3}. (B) For $k_{obs(c)}$ versus $[H^+]$ plot: $[phen]_T = 4 \times 10^{-3}$ mol dm^{-3}.

$$k_{obs(u)} = k_{H(u)}[H^+]^2 \quad (4)$$

$$k_{obs(c)} = k_{H(c)}[H^+] \quad (5)$$

2.5. Effect of surfactants

From Figures 4 and 5, it has been noted that the cationic surfactant *N*-cetylpyridinium chloride (CPC) retards the rate of reaction, while the anionic surfactant sodium dodecyl sulfate (SDS) accelerates the rate of the reaction.

2.6. Test for acrylonitrile polymerisation

Under the experimental conditions, the existence of free radicals was indicated by polymerisation of acrylonitrile under a nitrogen atmosphere.

2.7. Reaction mechanism in presence and absence of heteroaromatic chelating ligands

The mechanism of the reaction can be described in two sections: (i) uncatalysed path and (ii) catalysed path. We have already established the uncatalysed path for (−)-L-sorbose[17] as that shown in Scheme 1, with the rate law:

$$k_{obs(u)} = (2/3)k_1K_1K_2[S]_T[H^+]^2 \quad (9)$$

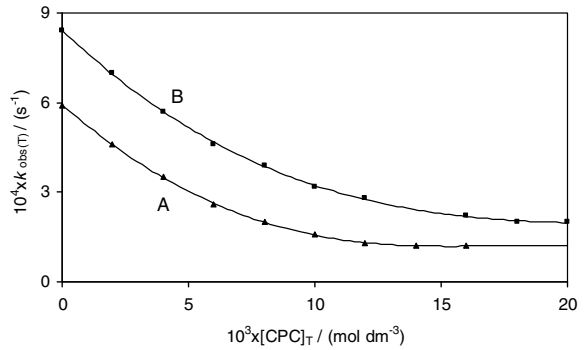


Figure 4. Effect of $[CPC]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence of phen and bipy in aqueous H_2SO_4 media. $[Cr(VI)]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 49$ °C. (A) $[bipy]_T = 10 \times 10^{-3}$ mol dm^{-3}, $[(-)$-L-sorbose$]_T = 8 \times 10^{-3}$ mol dm^{-3}. (B) $[phen]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[(-)$-L-sorbose$]_T = 10 \times 10^{-3}$ mol dm^{-3}.

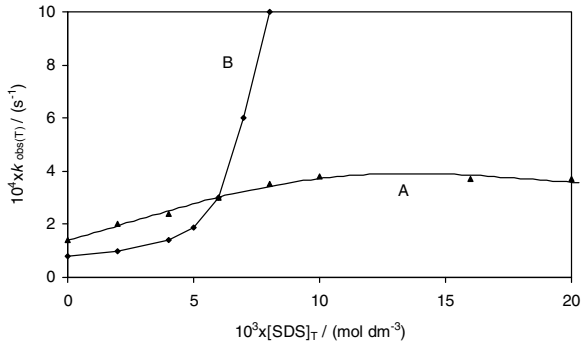
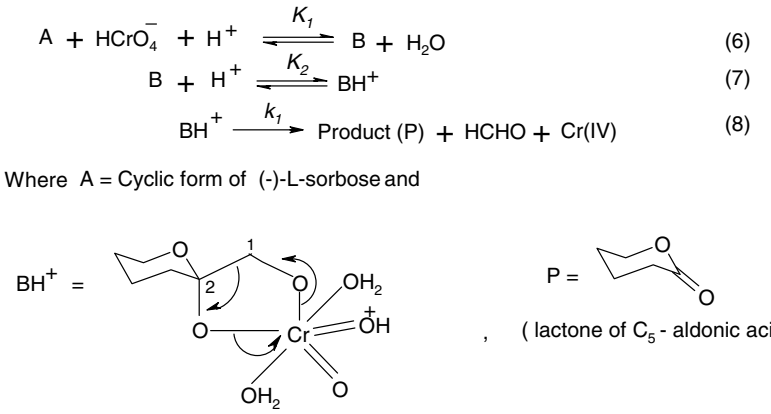


Figure 5. Effect of $[SDS]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence of phen and bipy in aqueous H_2SO_4 media. $[Cr(VI)]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[(-)$-L-sorbose$]_T = 6 \times 10^{-3}$ mol dm^{-3}. (A) $[phen]_T = 4 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.9$ mol dm^{-3}, $T = 24$ °C. (B) $[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}, $T = 20$ °C.

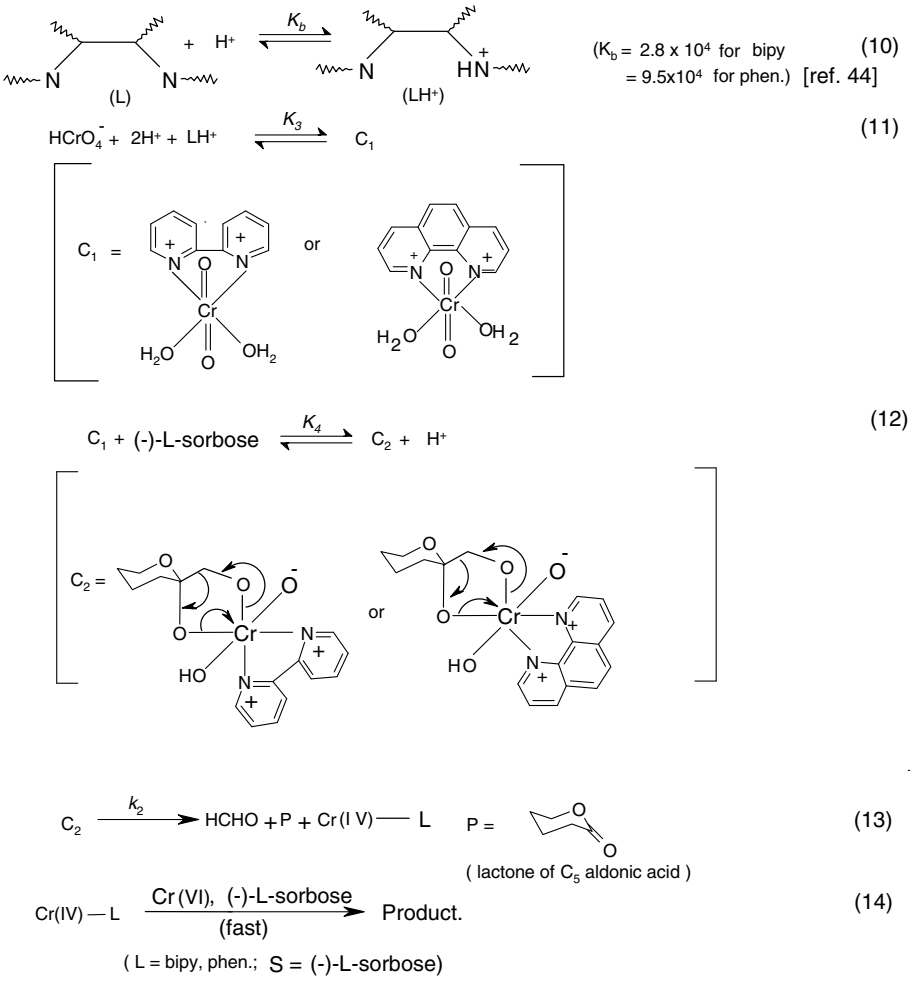
For the phen- and bipy-catalysed paths, Scheme 2 can explain all the experimental findings. The Scheme 2 leads to the following rate law:

$$k_{obs(c)} = (2/3)k_2K_3K_4[S]_T[L]_T[H^+] \quad (15)$$

With the heteroaromatic N-base ligand (L) like phen and bipy in the catalysed path, formation for the Cr(III)–phen and Cr(III)–bipy complexes, which were characterised spectroscopically, indicates that the ligands phen and bipy undergo complexation with the higher oxidation states (which are labile) of chromium. Because of the inertness of Cr(III) (t_{2g}^3), the catalyst ligands do not enter the inner coordination sphere of Cr(III) produced after the reduction of Cr(VI). Here phen and bipy react rapidly with the labile Cr(VI) centre in a pre-equilibrium step to form the reactive cyclic Cr(VI)–L (where L = phen, bipy) complex (C_1), which is the active oxidant.[39,40] Under the experimental conditions, the first-order dependence on $[phen]_T$ and $[bipy]_T$ is strictly maintained throughout the range of $[L]_T$ used. Hence it is reasonable to conclude that the equilibrium constant for the reaction leading to the cyclic Cr(VI)–L complex (C_1) is very low. This is why there is no kinetic evidence in favour of formation of the said complex (C_1). There is also no spectroscopic evidence for the said complex (i.e., the spectrum of chromic acid does not change with the addition of phen and bipy). The absence of spectroscopic evidence does not necessarily rule out the possibility of formation of the said complex,[45–48] however.



Scheme 1. Cr(VI) oxidation of (−)-L-sorbose in the absence of catalyst, that is, via an uncatalysed path.



Scheme 2. Cr(VI) oxidation of (−)-L-sorbose in the presence of bipy and phen. (See above-mentioned reference for further information.)

The ketohexose exists predominantly in aqueous solution as a cyclic hemiacetal which is in a dynamic equilibrium with the open-chain form (i.e., the acyclic form containing C2 as a keto group). The predominant form of (−)-L-sorbose is α-pyranoid.[49,50] Kinetically, the ketohexose can be considered as a polyol in which the reactivities of the alcoholic –OH groups are expected to be influenced by the presence of the carbonyl group.[51–55] In fact, hydroxy acetone is about 10^4 times more reactive than glycol towards V(V) oxidation.[51,52] Surprisingly, the reactivities of D-glucose and D-mannose are enhanced by a factor of about 15 only compared to glycol.[51,53] A similar situation arises for the Cr(VI) oxidation of D-glucose and glycol.[8,54] This dramatic fall in the reactivity of the monosaccharides compared to the acyclic polyols is quite interesting from the standpoint of the structural features of the monosaccharides. This decreased reactivity of the sugars can be explained by considering the fact that the reaction passes through the open-chain form whose concentration is negligibly small. It needs conversion of the cyclic form to the acyclic form through a

dynamic pre-equilibrium step, which is thermodynamically unfavourable. Here, it may be noted that the carbonyl group present in the open-chain form needs hydration in a pre-oxidative step.[46,47,56] Here, it is important to mention that the cyclic forms of the sugar can also participate in the redox reaction.[5–7] It is reasonable to conclude that the hydroxy groups in the cyclic hemiacetals are exposed better to interact with Cr(VI). In reality, thus it is reasonable to conclude that the pseudo-first-order rate constants are the sum contribution of the cyclic and acyclic forms remaining in a dynamic equilibrium. In the next step, the Cr(VI)–L complex reacts with the substrate to form a ternary complex (C_2) (Eq. 12, Scheme 2) which experiences a redox decomposition through a cyclic transition state. The large negative value of $\Delta S^{\neq}$ (entropy of activation, cf. Tables 1 and 2) of the composite rate constant k_{cat} supports the suggested cyclic transition state. The Cr(IV) species produced in the rate-limiting step participates in the next faster steps to give the final product.

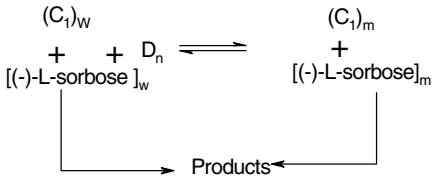
In the present case, formaldehyde initially produced may be further oxidised to formic acid. The Cr(IV) generated may subsequently participate in the faster reactions in different possible ways outlined below to be reduced to Cr(III). It may be pointed out that Cr(V) and Cr(IV) intermediates have been argued as efficient glycol-splitting agents.[48]

$$\begin{aligned}
&\text{Path I}: \mathrm{Cr(IV)} + \mathrm{Cr(VI)} \rightarrow 2\mathrm{Cr(V)}\\
&\qquad 2\mathrm{Cr(V)} + 2\mathrm{S} \rightarrow 2\mathrm{Cr(III)} + \text{Products}\\
&\text{Path II}: \mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \mathrm{S^{\cdot}}\\
&\qquad \mathrm{Cr(VI)} + \mathrm{S^{\cdot}} \rightarrow \mathrm{Cr(V)} + \text{Products}\\
&\qquad \mathrm{Cr(V)} + \mathrm{S} \rightarrow \mathrm{Cr(III)} + \text{Products}\\
&\text{Path III}: \mathrm{Cr(IV)} + \mathrm{S} \rightarrow \mathrm{Cr(II)} + \text{Products}\\
&\qquad \mathrm{Cr(II)} + \mathrm{Cr(VI)} \rightarrow \mathrm{Cr(III)} + \mathrm{Cr(V)}\\
&\qquad \mathrm{Cr(V)} + \mathrm{S} \rightarrow \text{Products} + \mathrm{Cr(III)}
\end{aligned}$$

In the above-mentioned possible paths, S denotes the substrate acting as a 2e reductant and $S^{\cdot}$ stands for the partially oxidised substrate. In both the Watanabe–Westheimer mechanism[57] (i.e., Path I) and the Perez-Bennito mechanism[58,59] (i.e., Path III), the title organic substrate acts in all steps as a 2e reductant, while it may act both as a 2e reductant and 1e reductant in the Rocek mechanism[60] (i.e., Path II). Previously, the Rocek mechanism was accepted widely in explaining the Cr(VI)oxidation of different organic substrates and the Perez-Bennito mechanism was discarded due to the instability of Cr(II). But recently, it has been established[58,59] that for the oxidation of different 2e organic reductants, Cr(II) is formed from Cr(IV) through hydride transfer. Thus, the carbocationic centre generated is responsible for acrylonitrile polymerisation.[61] It may be pointed out that in the Rocek mechanism, the free radical $S^{\cdot}$ is mainly responsible for acrylonitrile polymerisation.

2.8. Effect of CPC

N-Cetylpyridinium chloride (CPC, a representative cationic surfactant) is found to retard both the uncatalysed (already established)[17] and the catalysed paths. The plots of $k_{obs(T)}$ versus $[CPC]_T$ (cf. Fig. 4) show a continuous decrease that tends to level off at higher concentrations of CPC. This observation is identical to that noted by Bunton and Cerichelli[62] in the oxidation of ferrocene by ferric salts in the presence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB). The present observation is also similar to those observed by Panigrahi and Sahu[63] in the oxidation of acetophenone by Ce(IV) in the presence of *N*-dodecylpyridinium chloride (NDPC) and by Sarada and Reddi[23] in the oxalic acid-catalysed oxidation of aromatic azo-compounds by Cr(VI) in the presence of SDS. In the catalysed path, CPC restricts the positively charged Cr(VI)-catalyst complex (C_1) (cf. Eq. 11, Scheme 2), the active oxidant, in the aqueous phase and thus the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction. Hence in the catalysed path, the reaction is mainly restricted in the aqueous phase in which concentration of the substrate is depleted due to its partitioning in the Stern layer of the micelle. Partitioning of the reactants between the aqueous and micellar phase is shown in Scheme 3 in which D_n represents micellised surfactants where '*n*' is the aggregation number.



Scheme 3. Partitioning of the reactive species between the aqueous and micellar phases.

2.9. Effect of SDS

Sodium dodecyl sulfate (SDS, a representative anionic surfactant) is found to accelerate both the uncatalysed (already established)[17] and the catalysed path. In the catalysed path, Cr(VI)-catalyst complex (C_1) (cf. Eq. 11, Scheme 2), a cationic complex, has been argued as the active oxidant. Due to the electrostatic attraction, it can preferably be distributed in the micellar pseudo phase of the anionic surfactant SDS. Thus, in the presence of SDS, the reaction can go on in both the micellar pseudo phase (where both the active oxidant and substrate are preferably concentrated) and in the aqueous phase to give the observed rate benefit. The plot of $k_{obs(T)}$ versus $[SDS]_T$ (cf. Fig. 5) shows a continuous increase up to the concentration of SDS used for the bipy-catalysed reaction. For the phen-catalysed reaction, the rate increases with the increase of $[SDS]_T$ and attains a limiting value, followed by a very slight rate retardation. The rate acceleration arises owing to the preferential partitioning of the positively charged (by electrostatic attraction) and the neutral substrate in the micellar interphase (Stern layer). Thus SDS allows the reaction to proceed in both aqueous and micellar interphases. This rate retardation at very high $[SDS]_T$ is probably due to the dilution of reactants in the micellar phase. An increase in $[SDS]_T$ increases the micellar solubilisation of the reactants, but at the same time an increase in $[SDS]_T$ increases the concentration of the micellar counterions (i.e., Na^+) which may displace H^+ and Ox^{2+} ions (C_1) out of micellar surface:

$$\mathrm{Na_W^{+}} + \mathrm{Ox_M^{2+}} \rightleftharpoons \mathrm{Na_M^{+}} + \mathrm{Ox_W^{2+}} \quad (16)$$

$$\mathrm{Na_W^{+}} + \mathrm{H_M^{+}} \rightleftharpoons \mathrm{Na_M^{+}} + \mathrm{H_W^{+}} \quad (17)$$

The above equilibria lead to decrease the value of $[H_M]^+$ and $[Ox_M]^{2+}$ (C_1) to inhibit the rate process. These two effects are opposite in nature to determine the rate of reaction. In the case of the phen-catalysed path, these two effects roughly nullify each other at higher concentration to attain the rate saturation. But in the case of the bipy-catalysed path, the former effect (solubilisation effect) is greater than the later effect (i.e., the counterion effect) up to the SDS concentration used.

3. Experimental

3.1. Materials and reagents

(−)-L-Sorbose (AR, SRL, India), 1,10-phenanthroline (phen) (AR, Qualigens, India), 2,2′-bipyridyl (bipy) (AR, Qualigens, India), $K_2Cr_2O_7$ (AR, BDH), *N*-cetylpyridinium chloride (CPC) (AR, SRL,

India), sodium dodecyl sulfate (SDS) (AR, SRL, India) and all other chemicals used were of highest purity commercially available. Solutions were prepared in doubly distilled water.

3.2. Procedure and kinetic measurements

Under the experimental conditions, solutions of the oxidant and mixtures containing the known quantities of the substrate (S) (i.e., (−)-L-sorbose), catalyst (phen and bipy) (under the conditions $[S]_T \gg [Cr(VI)]_T$ and $[catalyst]_T \gg [Cr(VI)]_T$), acid and other necessary chemicals were separately thermostated (±0.1 °C). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was monitored by following the rate of disappearance of Cr(VI) by a titrimetric quenching technique.[29] The pseudo-first-order rate constants (k_{obs}) were calculated as usual. Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was investigated, and the rate of decomposition in this path was found to be kinetically negligible. Errors associated with the different rate constants and activation parameters were estimated as usual.[64]

3.3. Product analysis and stoichiometry

Under the experimental conditions (i.e., $[(-)\text{-L-sorbose}]_T \gg [Cr(VI)]_T$), qualitative identification of the reaction products was carried out by paper chromatography.[4–7] The aldonic acid (C_5-acid) was identified as the main product. To characterise the oxidation products, a series of aldopentoses and aldohexoses were oxidised with nitric acid and bromine water.[65] Thus the oxidised products obtained were purified, and these were taken as the standards in the chromatographic procedure. Paper chromatography was effected using 4:1:5 BuOH–HOAC–H_2O as elutant. Formaldehyde was detected in the reaction mixture as such by the chromotropic acid test.[66–68] After reduction of the reaction mixture with Zn–HCl, the resultant solution was subjected to the chromotropic acid test under identical conditions in a control experiment, and the intensity of the colour (at $\lambda = 570$ nm) was found to be higher than that obtained from the direct reaction mixture. This result indicates that formic acid is also produced in part during the reaction.

The final fate of the Cr(III) species was confirmed spectroscopically. The UV–vis spectra (cf. Fig. 6) were recorded by using a scanning spectrophotometer (UV-3101PC, Shimadzu). The characteristic part of electronic absorption spectrum of the Cr(III) species lies in the range of 360–600 nm.[69,70] The colours of the final solutions of the uncatalysed and phen- and bipy-catalysed reactions are different due to the presence of different types of Cr(III) species. The colour of the final solution for the uncatalysed reaction (i.e., in absence of phen, bipy) under the experimental condition is pale blue ($\lambda_{max} = 412$ and 578 nm), and the corresponding transitions[69,70] are as follows: 578 nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$; and 412 nm for $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ of Cr(III) species. On the other hand, the colour of the final solution of the phen- and bipy-catalysed reactions under identical conditions is pale violet [phen-catalysed reaction; $\lambda_{max} = 553$ nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr(III) species and bipy-catalysed reaction; $\lambda_{max} = 548$ nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr(III) species]. The spectra of the final solution of the uncatalysed reaction and pure chromic sulfate solution in aqueous sulfuric acid media are identical. These results indicate that the final Cr(III) species is simply the Cr(III) species for the uncatalysed reaction, while for the phen- and bipy-catalysed reaction, the final Cr(III) species is different, which is a Cr(III)–phen and Cr(III)–bipy complex. Similar results have been noted by earlier workers.[39,40] It is very interesting to point out that for the final solution of the phen- and bipy-catalysed reaction, there is a blue shift (Fig. 6) for the peak due to the transition $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ compared to the final solution of the uncatalysed path. This blue shift is due to the presence of the strong field-donor site, that is, the heteroaromatic N-donor site of phen and bipy. For the said Cr(III)–phen and Cr(III)–bipy complex, the peak due to the transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ merges with a charge-transfer band (Fig. 6). It may be noted that for $Cr(aq)^{3+}$ species, there is also a large charge-transfer band[69,70] at higher energy. In fact, the band at 270 nm due to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition appears as a shoulder on the high-energy charge-transfer band.[69] The appearance of the charge-transfer band at much lower energy for the proposed Cr(III)–phen and Cr(III)–bipy complex is quite reasonable because of the favoured metal-to-ligand charge transfer. In fact, in the vacant Π^* of phen and bipy favours the metal to ligand charge transfer. The existence of the charge-transfer band (metal to ligand) at this lower energy for the phen- and bipy-catalysed reaction indirectly supports the proposition of the Cr(III)–phen and Cr(III)–bipy complex in the final solution.

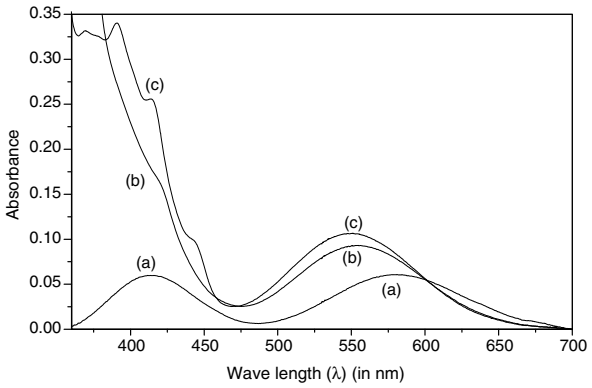


Figure 6. (a) Absorption spectrum of the reaction mixture (after completion of reaction): $[Cr(VI)]_T = 4.0 \times 10^{-3}$ mol dm^{-3}, $[(-)\text{-L-sorbose}]_T = 60 \times 10^{-3}$ mol dm^{-3}, $[phen]_T = [bipy]_T = 0$ mol dm^{-3}(i.e., uncatalysed path), $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 25$ °C. (The spectrum of the chromic sulfate is identical with this under the experimental condition.) (b) Absorption spectrum of the reaction mixture (after completion of reaction): $[Cr(VI)]_T = 4.0 \times 10^{-3}$ mol dm^{-3}, $[(-)\text{-L-sorbose}]_T = 60 \times 10^{-3}$ mol dm^{-3}, $[phen]_T = 8 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 25$ °C. (c) Absorption spectrum of the reaction mixture (after completion of reaction): $[Cr(VI)]_T = 4.0 \times 10^{-3}$ mol dm^{-3}, $[(-)\text{-L-sorbose}]_T = 60 \times 10^{-3}$ mol dm^{-3}, $[bipy]_T = 8 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 25$ °C.

4. Conclusions

The Cr(VI)-catalyst (catalyst = phen and bipy) complex, a cationic species, has been found to act as the active oxidant in the 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy) catalysed chromic acid oxidation of (−)-L-sorbose to give the product, a lactone of C_5-aldonic acid. The cationic species reacts with the substrate (−)-L-sorbose to form a ternary complex that subsequently experiences a two-electron transfer redox decomposition leading to the organic products, a lactone of a C_5-aldonic acid and formaldehyde. The reactions have been carried out in aqueous micellar media. The cationic surfactant like *N*-cetylpyridinium chloride (CPC) shows the rate-retarding effect, while an anionic surfactant like sodium dodecyl sulfate (SDS) accelerates the rate, both in the catalysed and uncatalysed paths. Micellar effects support the proposed mechanistic pathways.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.05.017.

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