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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, $[(-)\text{-L-sorbose}]_T \gg [\mathrm{Cr(VI)}]_T$ 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 $[\mathrm{Cr(VI)}]_T$. The uncatalysed path shows second-order in $[\mathrm{H}^+]$, while the catalysed path shows a first-order dependence on $[\mathrm{H}^+]$. The heteroaromatic N-base catalysed path is first-order in $[\mathrm{phen}]_T$ or $[\mathrm{bipy}]_T$. 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 $[\mathrm{Cr(VI)}]_T$

Under the experimental conditions, $[(-)\text{-L-sorbose}]_T \gg [\mathrm{phen}]_T$, and $[\mathrm{bipy}]_T \gg [\mathrm{Cr(VI)}]_T$, 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 $\log[\mathrm{Cr(VI)}]_t$ versus time (t) as usual.

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2.2. Dependence on $[\text{phen}]_T$ and $[\text{bipy}]_T$

The plots of k_{obs} versus $[\text{phen}]_T$ and k_{obs} versus $[\text{bipy}]_T$ 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 ($k_{\text{obs(u)}}$) 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 $k_{\text{obs(T)}}$ versus $[\text{phen}]_T$ and $k_{\text{obs(T)}}$ versus $[\text{bipy}]_T$. These observations are formulated as follows:

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

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, $[\text{phen}]_T$ and $[\text{bipy}]_T \gg [\text{Cr(VI)}]_T$, during the progress of the reaction, $[\text{phen}]_T$ and $[\text{bipy}]_T$ remain more or less constant.

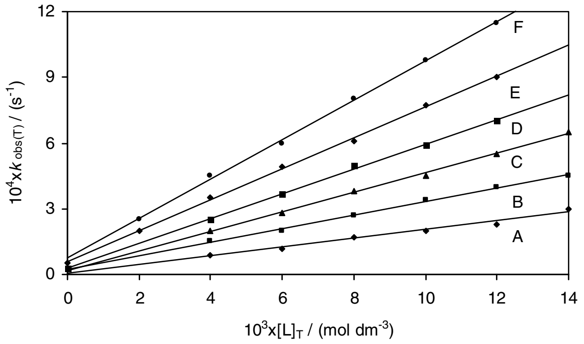

Figure 1. Effect of $[\text{L}]_T$ (L = phen, bipy) on $k_{\text{obs(T)}}$ for the Cr(VI) oxidation of (−)-L-sorbose in the presence of phen and bipy in aqueous H_2SO_4media. $[\text{Cr(VI)}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.5$ mol dm^{-3}, $[(-)\text{-L-sorbose}]_T = 8 \times 10^{-3}$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

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

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

The above first-order dependence on $[\text{S}]_T$ 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 $[\text{H}^+]$

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)	$10^4 k_{\text{obs(u)(w)}}$[a] (s^{-1})	$10^2 k_{\text{cat(w)}}$[a] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{cat(cpc)}}$[a] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{eff(w)}}$[a]	$10^4 k_{\text{H(c)(w)}}$[b] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(w)}}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(sds)}}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(cpc)}}$[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] $[\text{Cr(VI)}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[\text{S}]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[1,10\text{-phen}]_T = (0\text{–}14 \times 10^{-3})$ mol dm^{-3}, $[\text{CPC}]_T = 4 \times 10^{-3}$ mol dm^{-3}. $k_{\text{eff(w)}} = [k_{\text{obs(T)}} - k_{\text{obs(u)}}]/k_{\text{obs(u)}}$ and $k_{\text{eff(w)}}$ calculated at $[1,10\text{-phen}]_T = 10 \times 10^{-3}$ mol dm^{-3}.

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

[c] $[\text{Cr(VI)}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[\text{S}]_T = (4\text{-}24) \times 10^{-3}$ mol dm^{-3}, $[1,10\text{-phen}]_T = 5.0 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[\text{SDS}]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[\text{CPC}]_T = 4.0 \times 10^{-3}$ 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)	$10^4 k_{\text{obs(u)(w)}}$[a] (s^{-1})	$10^2 k_{\text{cat(w)}}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{\text{cat(cpc)}}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{\text{cat(sds)}}$[a] (dm^3 mol^{-1} s^1)	$10^2 k_{\text{eff(w)}}$[a]	$10^4 k_{\text{H(c)(w)}}$[b] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(w)}}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(sds)}}$[c] (dm^3 mol^{-1} s^{-1})	$10^2 k_{\text{s(c)(cpc)}}$[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] $[\text{Cr(VI)}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[\text{S}]_T = 8.0 \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = (0\text{–}14 \times 10^{-3})$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[\text{CPC}]_T = 4 \times 10^{-3}$ mol dm^{-3}, $[\text{SDS}]_T = 4.0 \times 10^{-3}$ mol dm^{-3}. $k_{\text{eff(w)}} = [k_{\text{obs(T)}} - k_{\text{obs(u)}}]/k_{\text{obs(u)}}$ and $k_{\text{eff(w)}}$ calculated at $[2,2'\text{-bipy}]_T = 10 \times 10^{-3}$ mol dm^{-3}.

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

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