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Kinetics and mechanism of 2,2′-bipyridyl and 1,10-phenanthroline-catalysed chromium(VI) oxidation of D-fructose in aqueous micellar media

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Abstract

The kinetics and mechanism of Cr^{VI} oxidation of fructose in the presence and absence of 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) in aqueous acid media have been studied under the condition $[sugar]_T \gg [Cr^{VI}]_T$ at different temperatures. Under the kinetic conditions, both the slower uncatalysed and faster catalysed (by heteroaromatic N-bases i.e., bipy, phen) paths go on. The monomeric species of Cr^{VI} has been found to be kinetically active in the absence of bipy and phen whereas in the heteroaromatic N-base catalysed path, the Cr^{VI}-bipy and Cr^{VI}-phen complexes have been found to be the active oxidants. Both the paths show the first-order dependence on $[sugar]_T$ and $[Cr^{VI}]_T$. The uncatalysed path shows a second-order dependence on $[H^+]$. But the catalysed path shows a first-order dependence on $[H^+]$. The heteroaromatic N-base-catalysed path is first-order in $[bipy]_T$ or $[phen]_T$. These observations remain unaltered in the presence of externally added surfactants. Effect of the cationic surfactant (i.e. CPC) and anionic surfactant (i.e. SDS) on both the uncatalysed and heteroaromatic N-base-catalysed paths has been studied. CPC inhibits both the uncatalysed and catalysed paths while SDS accelerates the reactions. The observed effects have been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants.

Keywords: Kinetics; Oxidations; Catalysis; D-Fructose; Chromium(VI); 1,10-Phenanthroline; 2,2′-Bipyridine; Surfactants

1. Introduction

The kinetics of oxidative degradation of sugars by different metal ions have been the subject of numerous studies to explore the chelating and reducing properties of the sugars under different conditions [1,2]. Reduction of Cr^{VI} by different reducing sugars is relevant in understanding the chemistry of chromium in the environment where Cr^{VI} appears as a hazardous one because of its mutagenic and carcinogenic activity [1,3]. The kinetics and mechanistic aspects of the interactions of different types of sugars with Cr^{VI} have been investigated by different workers [4,5] under different conditions. The proposed mechanisms involve two-electron transfer at the rate-determining step and Cr^{V} has also been proposed to exist in the oxidative degradation of the sugars. Comparison of the kinetics of oxidation of different sugars by Ce^{IV}, Cr^{VI} and V^{V} has been carried out by Virtanen and Lindroos-Heinanen [2a]. Here it is worth mentioning that regarding the reaction mechanism, the conclusions drawn by Sengupta and Basu [4a] are different compared to those given by Sala et al. [4d] in many aspects. It may be pointed out that these two groups of workers used different types of sugars. Picolonic acid (PA) is well known [5–8] to catalyse the Cr^{VI} oxidation reactions. Kinetics and mechanistic aspects of PA-catalysed oxidation of different sugars have been reported by us recently [5]. Because of the structural similarity among bipyridyl, phenanthroline and picolinic acid (all are heteroaromatic N-bases), the catalytic effects of bipyridyl and phenanthroline are of interest. The present paper deals with the mechanism of bipy and phen catalysis in Cr^{VI} oxidation of a ketohexose (D-fructose)

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along with the micellar effect on the bipy and phen-catalysed paths.

2. Results and discussion

2.1. Dependence on $[Cr^{VI}]_T$

Both in the presence and absence of heteroaromatic N-bases bipy and phen, under the experimental conditions: [D-fructose]$_T \gg$ [bipy]$_T$ and [phen]$_T \gg [Cr^{VI}]_T$, the rate of disappearance of Cr^{VI} shows a first-order dependence on Cr^{VI}. In the presence of surfactants, the first-order dependence on Cr^{VI} remains also unaltered. The pseudo-first-order rate constants (k_{obs}) were evaluated from the linear plot of log$[Cr^{VI}]_T$ versus time (t) as usual.

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

The plots of k_{obs} versus [bipy]$_T$ and k_{obs} versus [phen]$_T$ 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 absence of bipy or phen nicely agree with those obtained from the intercepts of the plots of $k_{obs(T)}$ versus [bipy]$_T$ and $k_{obs(T)}$ versus [phen]$_T$. These observations are formulated as follows:

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

The values of k_{cat} with the activation parameters are given in Tables 1 and 2. During the progress of reaction bipy, phen are lost due to the formation of inert Cr^{III}-bipy and Cr^{III}-phen complexes. Under the conditions: [bipy]$_T$ and [phen]$_T \gg [Cr^{VI}]_T$, during the progress of the reaction [bipy]$_T$ and [phen]$_T$ remain more or less constant.

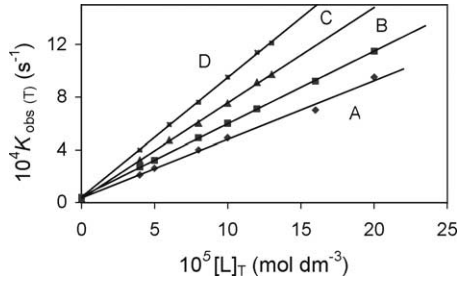


Fig. 1. Effect of [bipy]$_T$ and [phen]$_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}. (A) For bipy-catalysed reaction: [D-fructose]$_T = 60 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.5$ mol dm^{-3}, $T = 30\,^\circ$C; (B) for bipy-catalysed reaction: [D-fructose]$_T = 60 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.5$ mol dm^{-3}, $T = 40\,^\circ$C; (C) for phen-catalysed reaction: [D-fructose]$_T = 50 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.25$ mol dm^{-3}, $T = 45\,^\circ$C; (D) for phen-catalysed reaction: [D-fructose]$_T = 50 \times 10^{-4}$ mol dm^{-3}, $H_2SO_4 = 0.25$ mol dm^{-3}, $T = 55\,^\circ$C.

Table 1
Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of D-fructose in the presence of 1,10-phenanthroline in aqueous H_2SO_4 media

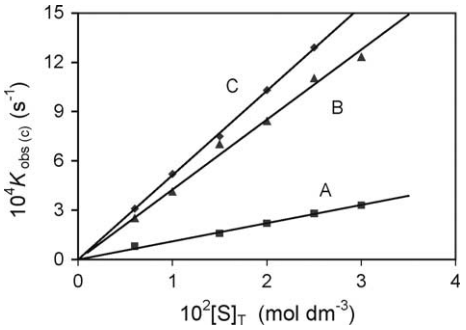
Temperature (°C)	$k_{obs(u)(w)}$ ($\times 10^4$ s^{-1})[a]	$k_{cat(w)}$ ($\times 10^2$ dm^3 mol^{-1} s^{-1})[a]	$k_{cat(pc)}$ ($\times 10^2$ dm^3 mol^{-1} s^{-1})[a]	$k_{eff(w)}$ ($\times 10^2$)[a]	$k_{H(c)(w)}$ (dm^3 mol^{-1} s^{-1})[b]	$k_{S(c)(w)}$ ($\times 10^2$ dm^3 mol^{-1} s^{-1})[c]	$k_{S(c)(sds)}$ ($\times 10^2$ dm^3 mol^{-1} s^{-1})[c]	$k_{S(c)(cpc)}$ ($\times 10^2$ dm^3 mol^{-1} s^{-1})[c]
30						4.1 ± 0.05	5.8 ± 0.15	1.2 ± 0.04
35	0.1 ± 0.01	5.0 ± 0.18		49	17.7 ± 0.30			
45	0.3 ± 0.03	7.2 ± 0.26	5.3 ± 0.20	24				
55	0.4 ± 0.04	9.1 ± 0.33		23				
$\Delta H^{\neq}$ (kJ mol^{-1})		19.8 ± 0.91						
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})		−208 ± 9.5						

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}, $[H_2SO_4] = 0.25$ mol dm^{-3}, $[S]_T = 5.0 \times 10^{-3}$ mol dm^{-3}, [1,10-phen]$_T = (0–1.3) \times 10^{-2}$ mol dm^{-3}, $[CPC]_T = 2 \times 10^{-3}$ mol dm^{-3}. $k_{eff(w)} = (k_{obs(T)} - k_{obs(u)})/k_{obs(u)}$ and $k_{eff(w)}$ calculated at [1,10-phen]$_T = 1.0 \times 10^{-2}$ mol dm^{-3}.
[b] $[Cr^{VI}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = 6.0 \times 10^{-3}$ mol dm^{-3}, [1,10-phen]$_T = 0.4 \times 10^{-2}$ mol dm^{-3}, $[H^+]_T = (0.2–1.0)$ mol dm^{-3}.
[c] $[Cr^{VI}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = (0.6–4.0) \times 10^{-2}$ mol dm^{-3}, [1,10-phen]$_T = 0.4 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}, $[SDS]_T = 0.75 \times 10^{-2}$ mol dm^{-3}, $[CPC]_T = 0.4 \times 10^{-2}$ mol dm^{-3}.

Table 2
Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of D-fructose in the presence of 2,2′-bipyridyl in aqueous H_2SO_4 media

Temperature (°C)	$k_{obs(u)(w)}$ ($\times 10^4\ s^{-1}$)[a]	$k_{cat(w)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[a]	$k_{cat(cpc)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[a]	$k_{cat(sds)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[a]	$k_{eff(w)}$ ($\times 10^2$)[a]	$k_{H(c)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[b]	$k_{s(c)(w)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[b]	$k_{s(c)(cpc)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[c]	$k_{s(c)(sds)}$ ($\times 10^2\ dm^3\ mol^{-1}\ s^{-1}$)[c]
30	0.3 ± 0.03	4.6 ± 0.15			15.3		4.0 ± 0.03	1.1 ± 0.10	5.7 ± 0.15
35						10.1 ± 0.10			
40	0.4 ± 0.04	5.9 ± 0.20	4.4 ± 0.20	8.4 ± 0.30	13.8				
50	0.6 ± 0.06	7.5 ± 0.25			12.3				
$\Delta H^{\neq}$ (kJ mol^{-1})	18.3 ± 0.87								
$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	−213 ± 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}, $[S]_T = 6.0 \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = (0–2.5) \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[CPC]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 1.5 \times 10^{-2}$ mol dm^{-3}.
$k_{eff(w)} = (k_{obs(T)} - k_{obs(u)})/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[2,2'\text{-bipy}]_T = 1.0 \times 10^{-2}$ mol dm^{-3}.
[b] $[Cr^{VI}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = 6.0 \times 10^{-3}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = 0.5 \times 10^{-2}$ mol dm^{-3}, $[H]_T = (0.2–1.0)$ mol dm^{-3}.
[c] $[Cr^{VI}]_T = 4.0 \times 10^{-4}$ mol dm^{-3}, $[S]_T = (0.6–3.0) \times 10^{-2}$ mol dm^{-3}, $[2,2'\text{-bipy}]_T = 0.5 \times 10^{-2}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[CPC]_T = 6 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 4 \times 10^{-3}$ mol dm^{-3}.



ig. 2. Effects of $[S]_T$ on $k_{obs(c)}$ for the Cr^{VI} oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}: (A) $[bipy]_T = 5 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[CPC]_T = 6 \times 10^{-3}$ mol dm^{-3}, $T = 30$ °C; (B) $[bipy]_T = 5 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $T = 30$ °C; (C) $[phen]_T = 4 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}, $T = 30$ °C.

2.3. Dependence on [D-fructose]$_T$, i.e. [S]$_T$

From the plot of k_{obs} versus $[S]_T$ (cf. Fig. 2), it is established that the catalysed path shows the first-order dependence on $[S]_T$, i.e.:

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

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

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:

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

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

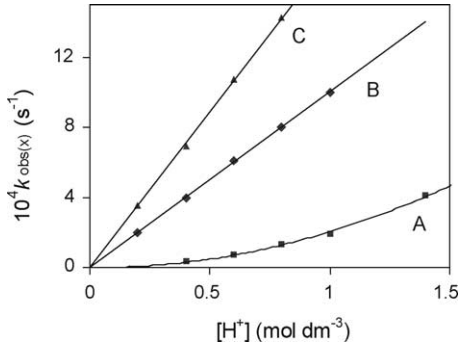
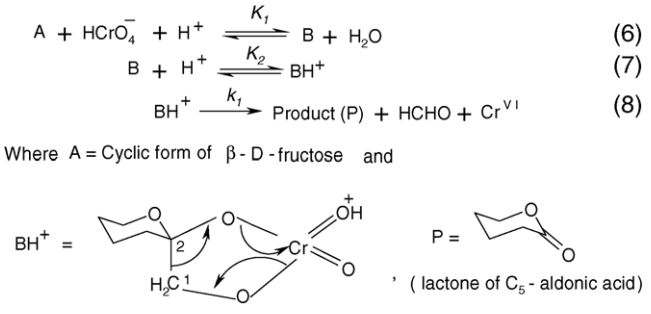


Fig. 3. Effect of $[HClO_4]_T$ on $k_{obs(x)}$ (x = u or c) for the Cr^{VI} oxidation of D-fructose in the presence and absence of bipy, phen in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, [D-fructose]$_T = 60 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] + [NaClO_4] = 1.5$ mol dm^{-3}, $T = 35$ °C: (A) x = u, $[bipy]_T = [phen]_T = 0$ mol dm^{-3}; (B) x = c, $[bipy]_T = 50 \times 10^{-4}$ mol dm^{-3}; (C) x = c, $[phen]_T = 40 \times 10^{-4}$ mol dm^{-3}.



Scheme 1. Cr^{VI} oxidation of D-fructose in the absence of catalyst.

2.5. Test for free radical formation

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

2.6. Reaction mechanism

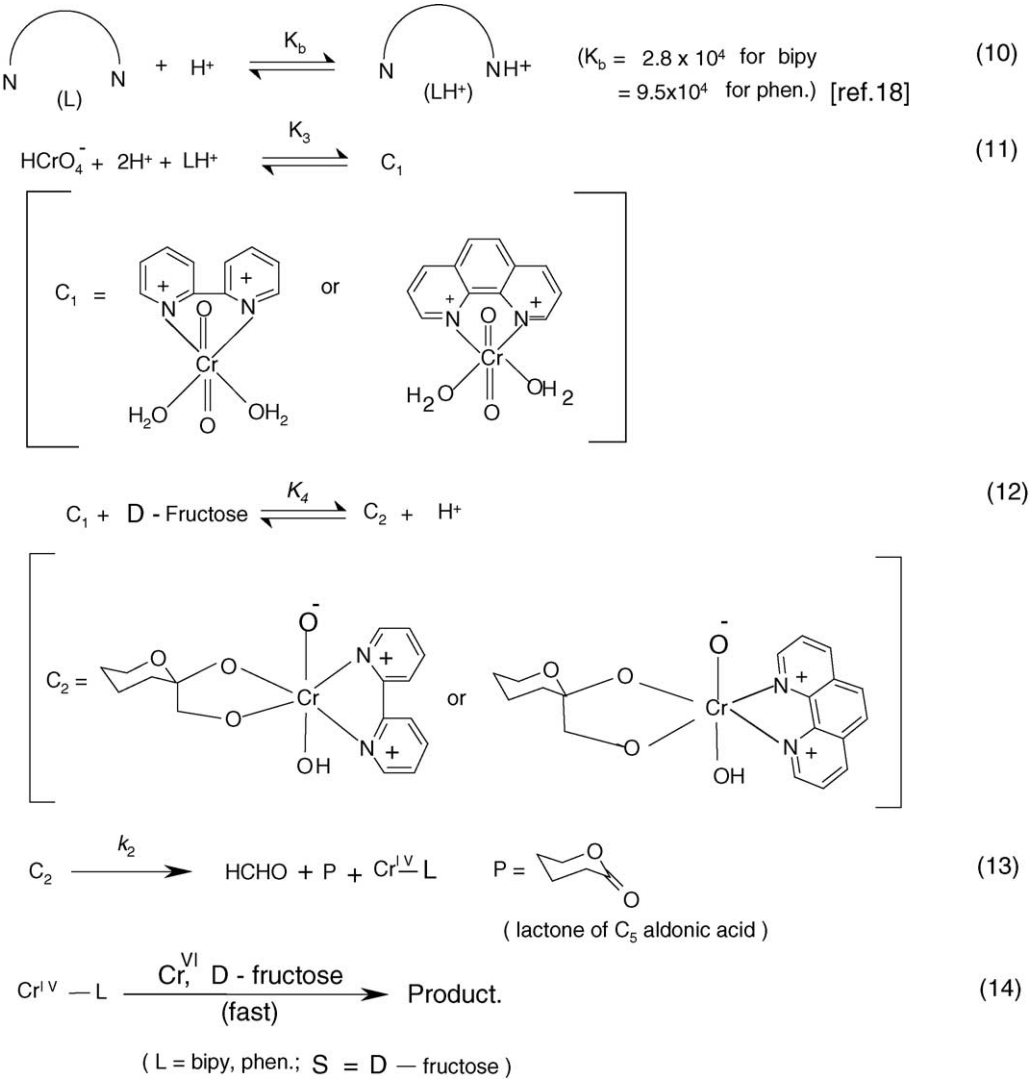
The mechanism of the reaction can be divided in two sections: (i) uncatalysed path and (ii) catalysed path. We have already established the uncatalysed path (Scheme 1) for D-fructose [5a] as:

$$k_{obs(u)} = \left(\frac{2}{3}\right) k_1 K_1 K_2 [S]_T [H^+]^2 \quad (9)$$

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

$$k_{obs(c)} = \left(\frac{2}{3}\right) K_3 K_4 k_2 [S]_T [L]_T [H^+] \quad (15)$$

Formation of Cr^{III}-L complex characterised spectroscopically indicates that the ligand heteroaromatic N-base (*L*) undergoes complexation with the higher oxidation states (which are labile) of chromium. Because of the inertness of Cr^{III}



Scheme 2. Cr^{VI} oxidation of D-fructose in presence of bipy and phen.

(t_{2g}^3), ligand does not enter to Cr^{III} produced after the reduction of Cr^{VI}. Here bipy and phen readily form the reactive cyclic Cr^{VI}-L (where L = bipy, phen) complex (C_1), which is the active oxidant [9]. Under the experimental conditions, the first-order dependence on $[bipy]_T$ and $[phen]_T$ 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 cyclic Cr^{VI}-L complex (C_1) is low. Kinetically, the monosaccharides can be considered as polyols in which the reactivities of alcoholic –OH groups were expected to be increase by the presence of the adjacent carbonyl group. In fact, in the case of oxidations by V^V, the rate constant for hydroxy acetone is about 10^4 times [10,11] greater than that for glycol, but the rate constants for D-glucose and D-mannose are only about 15 times [10,12] higher than that for glycol. A similar observation has been noted by us for Cr^{VI} oxidation of glycols [7a] and D-glucose [5c]. In aqueous media, D-fructose remains mainly as cyclic hemiacetals, which are in a dynamic equilibrium with the acyclic form. Between the furanoid and pyranoid cyclic forms, the latter is more stable [13]. Hence the preponderant form of the D-fructose is β-pyranoid. By considering the open chain structures of the sugars, it is reasonable to expect that the sugars should react much faster than glycol. The observed decreased rate constant for the sugars have been explained by some workers [12] by considering the fact that the oxidation goes predominantly through the open chain form whose concentration is very low. However, some workers have also suggested [4b,d,e] the participation of the cyclic forms in the redox reaction mechanism. It has been assumed that in the cyclic hemiacetal forms, the hydroxy groups are better exposed to interact with Cr^{VI} species [4d]. In reality, the pseudo-first-order rate constants are the sum contribution of each furanoid and pyranoid form in addition to the possible contribution of the open chain form remaining in a dynamic equilibrium with the cyclic forms. In the next step, the Cr^{VI}-L complex reacts with the substrate to form a ternary complex (C_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) supports the suggested cyclic transition state. The rate limiting step giving rise to the organic product and the Cr^{IV}-L complex. Then the Cr^{1V}-species i.e., Cr^{IV}-L complex participates in the next faster steps as discussed below:

$$\text{Path I}: \quad Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V},$$

$$2Cr^{V} + 2S \rightarrow 2Cr^{III} + \text{Products}$$

$$\text{Path II}: \quad Cr^{IV} + S \rightarrow Cr^{III} + S^{\bullet},$$

$$Cr^{VI} + S^{\bullet} \rightarrow Cr^{V} + \text{Products},$$

$$Cr^{V} + S \rightarrow Cr^{III} + \text{Products}$$

$$\text{Path III}: \quad Cr^{IV} + S \rightarrow Cr^{II} + \text{Products},$$

$$Cr^{II} + Cr^{VI} \rightarrow Cr^{III} + Cr^{V},$$

$$Cr^{V} + S \rightarrow \text{Products} + Cr^{III}$$

In the above-mentioned possible paths, S denotes the substrate acting as a 2e reductant and $S^{\bullet}$ stands for the partially oxidised substrate. In both the Watanabe–Westheimer mechanism [14] (i.e. Path I) and the Perez–Bennito mechanism [15] (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 [16] (i.e. Path II). Previously, the Rocek mechanism [16] was accepted widely in explaining the Cr^{VI} oxidation of different organic substrates and the Perez–Bennito mechanism [15] was discarded because of the instability of Cr^{II}. But recently, it has been established [15] that for the oxidation of different 2e organic reductants, Cr^{II} is produced from Cr^{IV} through hydride transfer. Thus, the carbocationic centre generated is responsible for acrylonitrile polymerisation [17]. It may be noted that in Rocek mechanism [16], the free radical $S^{\bullet}$ is supposed to be responsible for acrylonitrile polymerisation.

2.7. Effect of CPC

CPC, a representative cationic surfactant is found to retard both the uncatalysed (already established) [5a] and catalysed paths. The plots of $k_{obs(T)}$ versus $[CPC]_T$ (Fig. 4) shows a continuous decrease and finally it tends to level off at higher concentrations of CPC. This observation is similar to that noted by Bunton and Cerichelli [19] in the oxidation of ferrocene by ferric salts in the presence of cationic surfactant cetyl trimethyl ammonium bromide (CTAB). The similar findings have also been reported by Panigrahi and Sahu [20] in the oxidation of acetophenone by Ce^{IV} in the presence of *N*-dodecyl pyridinium chloride (NDPC), by Sarada and Reddi [21] in the oxalic acid catalysed oxidation of aromatic azocompounds by Cr^{VI} in the presence of SDS and by us in the oxidation of D-glucose [5c], D-fructose [5a] and L-sorbose [5b] by Cr^{VI} in the presence of CPC. In the catalysed path, CPC restricts the positively charged Cr^{VI}-catalyst complex (C_1) (cf. Eq. (11), Scheme 2) 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

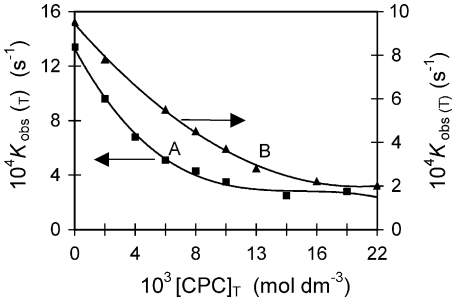
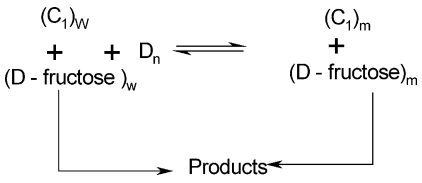


Fig. 4. Effect of $[CPC]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}: (A) $[phen]_T = 50 \times 10^{-4}$ mol dm^{-3}, $[D\text{-fructose}]_T = 140 \times 10^{-4}$ mol dm^{-3}, $T = 40\,^{\circ}C$; (B) $[bipy]_T = 120 \times 10^{-4}$ mol dm^{-3}, $[D\text{-fructose}]_T = 60 \times 10^{-4}$ mol dm^{-3}, $T = 50\,^{\circ}C$.



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

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.

2.8. Effect of SDS

SDS, a representative anionic surfactant, accelerates both the uncatalysed and catalysed paths. In the catalysed path, the rate acceleration arises owing to the preferential partitioning of the positively charged Cr^{VI}-catalyst complex (C_1) (cf. Eq. (11), Scheme 2) (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. The plot of $k_{obs(T)}$ versus $[SDS]_T$ (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 slight rate retardation. This rate retardation 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:

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

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

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 phen-catalysed path, these two effects roughly

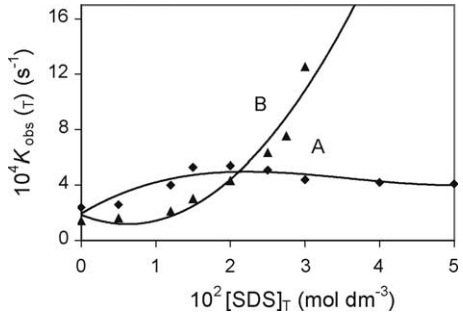


Fig. 5. Effect of $[SDS]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-fructose in the presence of bipy and phen in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.25$ mol dm^{-3}, $T = 35\,^\circ$C: (A) $[D\text{-fructose}]_T = 50 \times 10^{-4}$ mol dm^{-3}, $[phen]_T = 40 \times 10^{-4}$ mol dm^{-3}; (B) $[D\text{-fructose}]_T = 60 \times 10^{-4}$ mol dm^{-3}, $[bipy]_T = 40 \times 10^{-4}$ mol dm^{-3}.

nullify each other at higher concentration to attain the rate saturation. But in the case of bipy-catalysed path, the former effect (solubilisation effect) is greater than the later effect (i.e., counterion effect) up to the used SDS concentration.

3. Experimental

3.1. Materials and reagents

2,2′-Bipyridyl (bipy) (AR, Qualigens, India), 1,10-phenanthroline (phen) (AR, Qualigens, India), D-fructose (AR, SRL, India), $K_2Cr_2O_7$ (AR, BDH), sodium dodecyl sulphate (SDS) (AR, SRL, India), *N*-cetylpyridinium chloride (CPC) (AR, SRL, India) and all other chemicals used were of highest purity available commercially. Solutions were prepared in doubly distilled water.

3.2. Procedure and kinetic measurements

Solutions of the oxidant and mixtures containing the known quantities of the substrate (S) (i.e. D-fructose), catalyst (bipy or phen) (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 titrimetric quenching technique [8b]. 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 [22].

3.3. Product analysis and stoichiometry

Under the kinetic conditions (i.e. $[S]_T \gg [Cr^{VI}]_T$), qualitative identification of the reaction products was carried out by paper-chromatography [4b,d,e]. Paper chromatograph was effected by using butan-1-ol–acetic acid–water (4:1:5) as eluent. To characterise the oxidation products, a series of aldopentoses and aldohexoses were oxidised with nitric acid and bromine water [23] separately and the purified products were taken as the standards in the chromatographic procedure. Aldonic acid (C_5-acid) corresponding to arabinose was identified as the main product. Formaldehyde was detected in the reaction mixture as such by the chromotropic acid test [24]. After reduction of the reaction mixture with Zn–HCl, the 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 not subjected to reduction with Zn–HCl. This indicates that formic acid is also produced in part in the reaction mixture.

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Appendix A

Derivation of rate law (considering Scheme 2):

$$\text{Rate} = k_2[C_2] \quad \text{(i)}$$

$$K_4 = \frac{[C_2][H^+]}{[C_1][S]}$$

$$\text{or,} \quad [C_2] = \frac{K_4[C_1][S]}{[H^+]} \quad \text{(ii)}$$

$$K_3 = \frac{[C_1]}{[HCrO_4^-][H^+]^2[LH^+]} \quad \text{(iii)}$$

$$\text{or,} \quad [C_1] = K_3[HCrO_4^-][H^+]^2[LH^+]$$

The total concentration of L (= bipy or phen) is given by:

$$[L]_T = [L] + [LH^+] \quad \text{(iv)}$$

$$K_b = \frac{[LH^+]}{[L][H^+]}; \quad \text{or,} \quad [L] = \frac{[LH^+]}{K_b[H^+]} \quad \text{(v)}$$

$$\text{or,} \quad [L]_T = \frac{[LH^+]}{K_b[H^+]} + [LH^+]$$

$$= [LH^+]\left[1 + \frac{1}{K_b[H^+]}\right]$$

$$= [LH^+]\left[\frac{K_b[H^+] + 1}{K_b[H^+]}\right] \approx [LH^+] \quad \text{(vi)}$$

Since $K_b[H^+] \gg 1$ ($K_b = 2.8 \times 10^4$ for bipy, $= 9.5 \times 10^4$ for phen) [18]

It leads to : $[C_2] \approx K_3K_4[S]_T[HCrO_4^-][H^+][L]_T$

$$\text{Rate} = \frac{K_3K_4k_2[S]_T[HCrO_4^-][L]_T[H^+]^2}{[H^+]}$$

$$= K_3K_4k_2[S]_T[HCrO_4^-][L]_T[H^+] \quad \text{and,}$$

$$-\frac{d\ln[HCrO_4^-]}{dt} = k_{obs(c)}$$

$$= \left(\frac{2}{3}\right) K_3K_4k_2[S]_T[L]_T[H^+] \quad (15)$$

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