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Oxidation of D-glucose in the presence of 2,2′-bipyridine by Cr^{VI} in aqueous micellar media: a kinetic study

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Abstract—The kinetics of Cr^{VI} oxidation of D-glucose to the corresponding lactone in the presence and absence of 2,2′-bipyridine (bipy) has been carried out under the conditions, $[\text{D-glucose}]_T \gg [Cr^{VI}]_T$ at different temperatures in aqueous micellar media. The monomeric Cr^{VI} species has been found to be kinetically active in the absence of bipy whereas in the bipy-catalysed path, the Cr^{VI}–bipy complex has been found to be the active oxidant. In the bipy-catalysed path, the Cr^{VI}–bipy complex undergoes nucleophilic attack by the substrate to form a ternary complex. The ternary complex spontaneously experiences a redox decomposition (through two-electron transfer) in the rate-determining step leading to the product lactone and Cr^{IV}–bipy complex. The Cr^{IV}–bipy complex then takes part in faster steps in the further oxidation of D-glucose and is ultimately converted into a Cr^{III}–bipy complex. In the uncatalysed path, the Cr^{VI}-substrate ester experiences acid catalysed redox decomposition (two-electron transfer) in the rate-determining step. The uncatalysed path shows a second order dependence on $[H^+]$ and a first order dependence on each of the reactants $[\text{D-glucose}]_T$ and $[Cr^{VI}]_T$. In contrast, the bipy-catalysed path shows a first order dependence on each of the reactants $[H^+]$, $[\text{D-glucose}]_T$ and $[Cr^{VI}]_T$. The bipy-catalysed path is first order in $[\text{bipy}]_T$. These observations remain unaltered in the presence of externally added surfactants. The effect of the cationic surfactant, *N*-cetylpyridinium chloride (CPC) and anionic surfactant, sodium dodecyl sulfate (SDS) on both the uncatalysed and bipy-catalysed path has been studied. CPC inhibits both the uncatalysed and bipy-catalysed path, while SDS catalyses these reactions. The observed micellar effects have been explained by considering hydrophobic and electrostatic interactions between the surfactants and reactants.

Keywords: Kinetics; Oxidations; Catalysis; D-Glucose; Chromium(VI); 2,2′-Bipyridine (bipy); Surfactants

1. Introduction

Due to the carcinogenic and toxic effects of Cr^{VI},[1–3] studies on the kinetics and mechanism of Cr^{VI} oxidation of biologically relevant reducing agents is of interest to both biochemists and inorganic chemists.[3,4] During the reduction of Cr^{VI} to Cr^{III}, the intermediate oxidation states of chromium may interact with biologically active molecules to induce toxicity.[3] Thus, in chromate toxicity, it is reasonable to assume that the reducing agents may have an important role. The kinetics of oxidative degradation of different sugars by metal ions including Cr^{VI} has been studied under different conditions.[5–11] The present studies aims to contribute in this direction and we note that in regard to the reaction mechanism, the conclusions drawn by Sengupta and Basu[7] differ from those of Sala et al.[10] in many aspects. The present investigations have been carried out in micro-heterogeneous systems relevant to biological systems in the presence of the chelating agent bipyridine (bipy). Picolinic acid (PA) is a chelating agent that is well known[12–23] to catalyse Cr^{VI} oxidation reactions. The structure of bipyridine is comparable to that of picolinic acid in many respects and, in particular, both chelating agents are heteroaromatic nitrogen bases.

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2. Results and discussion

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

The rate of disappearance of Cr^{VI} shows a first order dependence on Cr^{VI} in the presence and absence of bipy under the conditions, $[\text{D-glucose}]_T \gg [\text{bipy}]_T \gg [Cr^{VI}]_T$ and $[\text{bipy}]_T \gg [Cr^{VI}]_T$. In the presence of surfactants, the first order dependence on Cr^{VI} remains 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 $[\text{bipy}]_T$

At $[\text{D-glucose}]_T = 6 \times 10^{-3}$ mol/dm^3 and $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $[H_2SO_4] = 0.5$ mol/dm^3, the effect of bipy on k_{obs} has been studied. The plots of k_{obs} versus $[\text{bipy}]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower uncatalysed path (Fig. 1). The pseudo first order rate constants ($k_{obs(u)}$) directly measured in the absence of bipy agree well with those obtained from the intercepts of the plots of $k_{obs(T)}$ versus $[\text{bipy}]_T$. The observation is formulated as follows:

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

The values of k_{cat} with the activation parameters are given in Table 1. During the progress of the reaction, bipy is lost due to the formation of the inert Cr^{III}–bipy complex. Under the conditions, $[\text{bipy}]_T \gg [Cr^{VI}]_T$, the $[\text{bipy}]_T$ remains more or less constant over the course of the reaction.

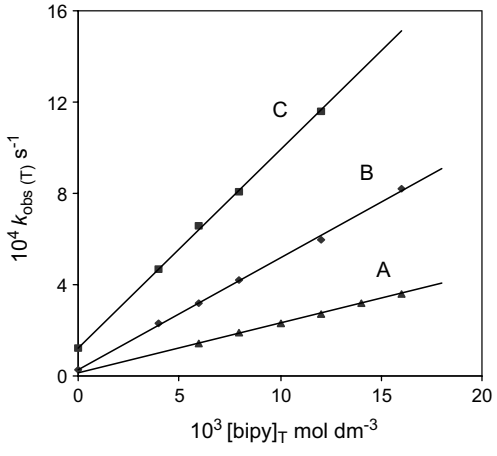


Figure 1. Effect of $[\text{bipy}]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-glucose in the presence of bipy in aqueous H_2SO_4 media. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $[\text{D-glucose}]_T = 6 \times 10^{-3}$ mol/dm^3, $H_2SO_4 = 0.5$ mol/dm^3. (A) $[\text{CPC}]_T = 3 \times 10^{-3}$ mol/dm^3, $T = 35$ °C. (B) CPC = 0 mol/dm^3, $T = 35$ °C. (C) CPC = 0 mol/dm^3, $T = 55$ °C.

Table 1. Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of D-glucose in the presence of 2,2′-bipyridyl in aqueous H_2SO_4 media (precession in the concentration of reagents are used within ±2.0%)[a]

Temp (°C)	$k_{obs(u)(w)}$ ($\times 10^4$, s^{-1})[b]	$k_{cat(w)}$ ($\times 10^2$, dm^3/mol s)[b]	$k_{cat(cpc)}$ ($\times 10^2$, dm^3/mol s)[b]	$k_{cat(sds)}$ ($\times 10^2$, dm^3/mol s)[b]	$k_{eff(w)}$[a]	$k_{H(c)(w)}$ ($\times 10^4$, dm^3/mol s)[c]	$k_{s(c)(w)}$ ($\times 10^2$, dm^3/mol s)[d]	$k_{s(c)(sds)}$ ($\times 10^2$, dm^3/mol s)[d]	$k_{s(c)(cpc)}$ ($\times 10^2$, dm^3/mol s)[d]
30							1.9 ± 0.1	2.9 ± 0.1	0.5 ± 0.01
35	0.3	4.9 ± 0.2	2.2 ± 0.1	6.8 ± 0.3	16.3	11.7 ± 0.2			
45	0.6	6.8 ± 0.3			11.3				
55	1.2	8.8 ± 0.4			7.3				
$\Delta H^{\ddagger}$ (kJ mol^{-1})		20 ± 0.2							
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})		−206 ± 11							

[a] Subscript (u) for uncatalysed path; (c) for bipy catalysed path; (w) for the value in the absence of surfactant; (CPC) or (SDS) for the value in presence of the respective surfactant.
[b] $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $[S]_T = 6.0 \times 10^{-3}$ mol/dm^3, $[H_2SO_4] = 0.5$ mol/dm^3, $[\text{bipy}]_T = 0$–1.6×10^{-2} mol/dm^3, $[\text{CPC}]_T = 3 \times 10^{-3}$ mol/dm^3, $[\text{SDS}]_T = 5 \times 10^{-3}$ mol/dm^3 and $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[\text{bipy}]_T = 1.0 \times 10^{-2}$ mol/dm^3.
[c] $[Cr^{VI}]_T = 4.0 \times 10^{-4}$ mol/dm^3, $[S]_T = 8.0 \times 10^{-3}$ mol/dm^3, $[\text{bipy}]_T = 0.5 \times 10^{-2}$ mol/dm^3, $[H^+]_T = 0.2$–1.0 mol/dm^3, $[HClO_4]_T + [NaClO_4]_T = 1.5$ mol/dm^3.
[d] $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $[S]_T = 1$–10×10^{-2} mol/dm^3, $[\text{bipy}]_T = 0.4 \times 10^{-2}$ mol/dm^3, $[H_2SO_4] = 0.25$ mol/dm^3, $[\text{CPC}]_T = 3 \times 10^{-3}$ mol/dm^3, $[\text{SDS}]_T = 6 \times 10^{-3}$ mol/dm^3.

2.3. Dependence on [D-glucose]$_T$

From the plot of k_{obs} versus [D-glucose]$_T$ (Fig. 2) it was established that the catalysed path shows a first order dependence on [S]$_T$ where S denotes D-glucose, that is

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

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

2.4. Dependence on [H$^+$]

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

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

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

2.5. Test for free radical formation

The existence of free radicals has been indicated by polymerisation of acrylonitrile under a nitrogen atmosphere under the experimental conditions.

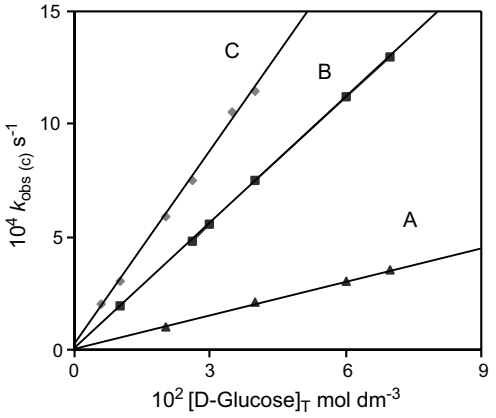


Figure 2. Effect of [S]$_T$ on $k_{obs(c)}$ for the Cr^{VI} oxidation of D-glucose in the presence of bipy in aqueous H_2SO_4 media. [Cr^{VI}]$_T = 4 \times 10^{-4}$ mol/dm^3, [H_2SO_4] = 0.25 mol/dm^3, [bipy]$_T = 4 \times 10^{-3}$ mol/dm^3, $T = 30$ °C. (A) [CPC]$_T = 3 \times 10^{-3}$ mol/dm^3, (B) CPC = 0 mol/dm^3, SDS = 0 mol/dm^3, (C) SDS $= 6 \times 10^{-3}$ mol/dm^3.

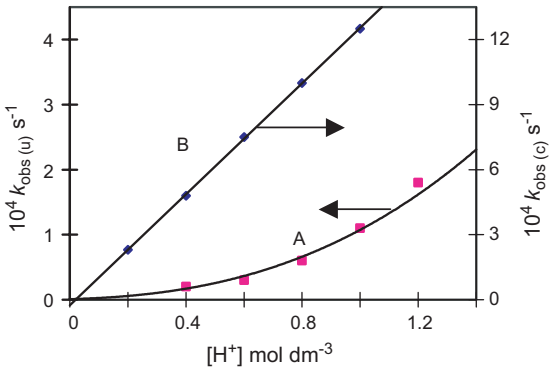


Figure 3. Effect of [$HClO_4$]$_T$ on $k_{obs(u)}$ and $k_{obs(c)}$ for the Cr^{VI} oxidation of D-glucose in the presence and absence of bipy. [Cr^{VI}]$_T = 4 \times 10^{-4}$ mol/dm^3, [D-glucose]$_T = 80 \times 10^{-4}$ mol/dm^3, [$HClO_4$] + [$NaClO_4$] = 1.5 mol/dm^3, $T = 35$ °C. (A) for $k_{obs(u)}$: [bipy]$_T = 0$ mol/dm^3; (B) for $k_{obs(c)}$: [bipy]$_T = 50 \times 10^{-4}$ mol/dm^3.

2.6. Mechanism of the reaction

The mechanism of the reaction can be divided in two parts as (i) the uncatalysed path (Scheme 1) and (ii) the catalysed path (Scheme 2).

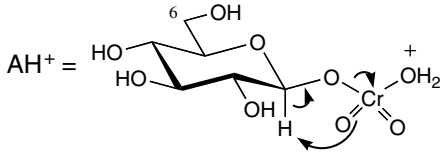
$$\text{Glu-OH} + HCrO_4^- + H^+ \overset{K_1}{\rightleftarrows} \underset{(A)}{\text{Glu-OCrO}_3\text{H}} + H_2O \quad (5)$$

$$A + H^+ \overset{K_2}{\rightleftarrows} \text{Glu-OCrO}_3\text{H}_2^+\ (AH^+) \quad (6)$$

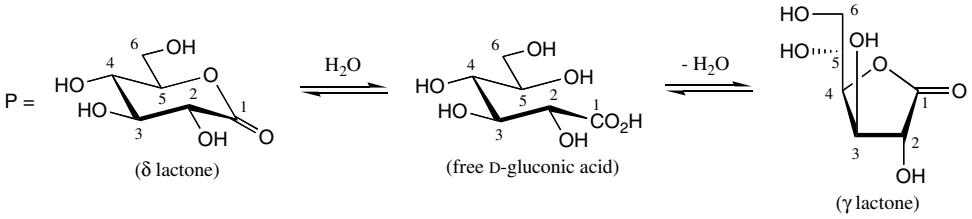
$$AH^+ \overset{k_1}{\rightarrow} \text{Product(P)} + Cr^{IV} \quad (7)$$

$$Cr^{IV} \xrightarrow{Cr^{VI},\text{Glu-OH}} \text{Product(P)} + Cr^{III} \quad (8)$$

where



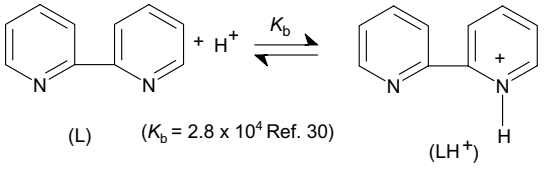
2.6.1. Uncatalysed path. In aqueous acidic media, D-glucose exists predominantly in hemiacetal cyclic pyranose forms as a mixture of α (OH-1, axial) and β (OH-1, equatorial) anomers.[7,24,25] The concentration of the open chain aldehyde form,[26,27] the intermediate



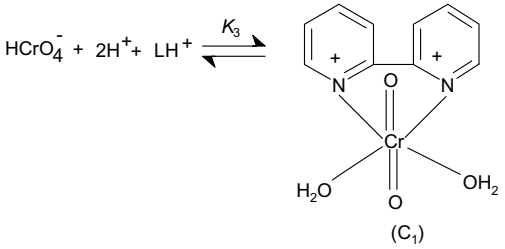
Scheme 1. Cr^{VI} oxidation of D-glucose (denoted by Glu–OH) in the absence of 2,2′-bipyridine.

in the dynamic equilibrium between the anomers, is very small. The rate of mutarotation (i.e., α-D-glucose ↔ β-D-glucose) is known to be acid catalysed[28] and, under these oxidation conditions, the mutarotation equilibrium is immediately attained.[28] Thus, the rate of oxidation of D-glucose is the summation of rates contributed by each of the α- and β-anomers in addition to the possible contribution from the open chain aldehyde form.[11] The cyclic hemiacetal forms are expected to be more reactive species because the hydroxy groups are better exposed to interact with the Cr^{VI} species.[10] In fact, esterification of the –OH group of the substrate with chromic acid is the first step of Cr^{VI} oxidation of D-glucose. Among the α- and β-anomers, the β-form bearing the –OH group at C1 at the equatorial position is more suitably exposed[29] to attack the chromic acid. Thus, D-glucose is mainly oxidised as the β-pyranose form and the initial product is the corresponding lactone. We have already established the kinetics for the uncatalysed path (Scheme 1) for D-glucose[18] as follows:

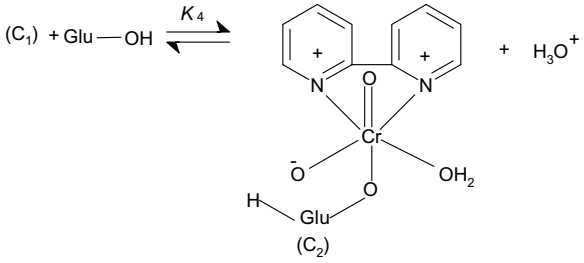
$$k_{obs(u)} = (2/3)k_1K_1K_2[S]_T[H^+]^2 \quad (9)$$



(10)

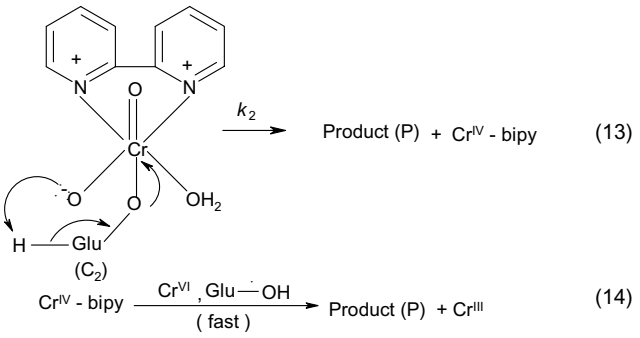


(11)



(12)

2.6.2. Catalysed path. For the bipy-catalysed path, the reactions in Scheme 2 can explain the experimental findings and lead to the following rate law:



Scheme 2. Cr^{VI} oxidation of D-glucose denoted by (Glu–OH) in the presence of 2,2′-bipyridine.

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

The final Cr^{III}–bipy complex has been characterised spectroscopically and are outlined below. As Cr^{III} (t_{2g}^3) is an inert species, it is reasonable to consider that the heteroaromatic nitrogen base (i.e., bipy) does not bind to the Cr^{III}-centre after its formation from the reduction of Cr^{VI}. Therefore, we suggest that the heteroaromatic nitrogen base (denoted by L) undergoes complexation with the higher oxidation states of chromium, which are labile. The Cr^{VI}-species (i.e., chromic acid) is typically labile and undergoes complexation at the first step with the chelating agent (L) to produce the chelate complex (C_1), which is believed to be the kinetically active oxidant.[31] Under these reaction conditions, the first order dependence on $[bipy]_T$ is strictly maintained throughout the range of $[bipy]_T$ used. Thus, it is reasonable to conclude that the equilibrium constant for the reaction leading to Cr^{VI}–bipy complex (C_1) is low. In the next step, the Cr^{VI}–bipy complex reacts with the substrate to form a ternary complex (Eq. 12), which experiences redox decomposition through a cyclic transition state in the rate-limiting step giving rise to the organic product and Cr^{IV}–bipy complex. The negative value of $\Delta S^{\ddagger}$ (entropy of activation, Table 1) of the composite rate constant k_{cat} supports the suggested cyclic transition state. The fairly high $\Delta H^{\ddagger}$ (enthalpy of activation) value (Table 1) indicates that the bipy-catalysed path is favoured mainly due to the very high negative value of $\Delta S^{\ddagger}$. The Cr^{IV}-species produced in the rate-limiting step participates in the next faster steps to give the final product. The different possible routes are given below:

Path I

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

Path II

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

Path III

$$Cr^{IV} + S \rightarrow Products + Cr^{II}$$
$$Cr^{II} + Cr^{VI} \rightarrow Cr^{III} + Cr^{V}$$
$$Cr^{V} + S \rightarrow Products + Cr^{III}$$

In the aforementioned possible paths, S denotes the substrate acting as a two-electron reductant and S˙ stands for the partially oxidised substrate. In both the Watanabe–Westheimer mechanism[32] (i.e., *Path I*) and the Perez-Bennito mechanism[33,34] (i.e., *Path III*), the title organic substrate acts in all steps as a two-electron reductant, while it acts both as a two-electron reductant and a one-electron reductant in the Rocek mechanism[35] (i.e., *Path II*). Previously, the Rocek mechanism[35] was accepted widely in explaining the Cr^{VI} oxidation of different organic substrates and the Perez-Bennito mechanism[33,34] was discarded because of the instability of Cr^{II}. Recently, however, it has been proven[33,34] that for the oxidation of different two-electron organic reductants, Cr^{II} is produced from Cr^{IV} through hydride transfer. Thus, the carbocationic centre generated is responsible for acrylonitrile polymerisation.[36] It may be noted that in the Rocek mechanism,[35] the free radical S˙ is supposed to be responsible for acrylonitrile polymerisation.

2.7. Effect of CPC

Cetyl pyridinium chloride (CPC), a representative cationic surfactant, has been found to show the rate retarding effect both in the uncatalysed and catalysed paths. The plot of $k_{obs(T)}$ versus $[CPC]_T$ (Fig. 4) indicates that the rate decreases in a continuous manner, and it tends to level off at higher CPC concentration. Bunton and Cerichelli[37] noted a similar observation in the oxidation of ferrocene by Fe^{III} 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[38] in the oxidation of acetophenone by Ce^{IV}, by Sarada and Reddi[39] in the oxalic acid catalysed oxidation of aromatic azo-compounds by Cr^{VI}in the presence of surfactant sodium dodecyl sulfate (SDS). In the uncatalysed path, the neutral Cr^{VI}-substrate ester (A) formed (Eq. 5) can be partitioned in the micellar pseudo-phase of the surfactant but the cationic surfactant repelling H^+ needed for the redox decomposition of the ester (Eqs. 6 and 7) inhibits the reaction. In the bipy-catalysed path, CPC restricts the positively charged Cr^{VI}–bipy complex (C_1), the active oxidant, in the aqueous phase and thus the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction. Therefore in both the uncatalysed and bipy-catalysed paths, the reaction is mainly restricted to the aqueous phase in which the 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.

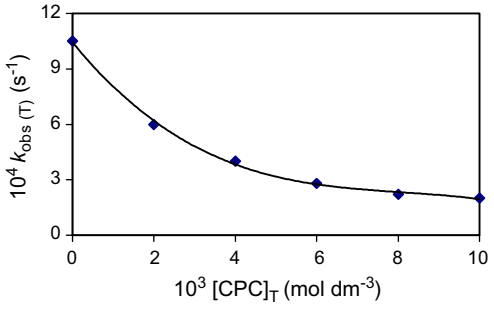
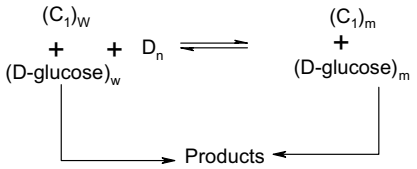


Figure 4. Effect of $[CPC]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-glucose in the presence of bipy in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $H_2SO_4 = 0.5$ mol/dm^3. $[D\text{-glucose}]_T = 180 \times 10^{-4}$ mol/dm^3, $[bipy]_T = 60 \times 10^{-4}$ mol/dm^3, $T = 35$ °C.



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

2.8. Effect of SDS

Sodium dodecyl sulfate (SDS), a representative anionic surfactant, catalyses the oxidation reaction both in the presence and absence of bipy. In the bipy-catalysed path, the rate acceleration arises due to the preferential partitioning of the positively charged Cr^{VI}–bipy complex (C_1) by an electrostatic attraction and the neutral substrate in the micellar surface Stern layer. In the uncatalysed path, the neutral Cr^{VI}-substrate ester (A) is partitioned in the micellar phase (Stern layer) and the H^+ ions needed for the redox decomposition of the ester (A) (Eqs. 6 and 7) are also preferentially accumulated in the micellar interphase due to an electrostatic attraction. Thus, SDS allows the reaction to proceed in both the aqueous and micellar interphases. However, the reaction is more favoured in the micellar pseudo-phase because of the enhanced concentration of the reactants (i.e., A and H^+) in the micellar interphase. In the bipy-catalysed reaction, the plot of $k_{obs(T)}$ versus $[SDS]_T$ (Fig. 5) indicates that the rate increases in a continuous fashion up to the SDS concentration used. 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 counter ions

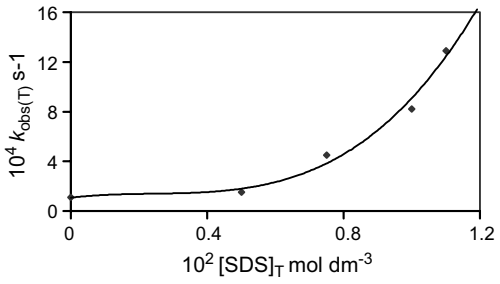


Figure 5. Effect of $[SDS]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of D-glucose in the presence of bipy in aqueous H_2SO_4 media, $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol/dm^3, $[bipy]_T = 4 \times 10^{-3}$ mol/dm^3, $[H_2SO_4] = 0.25$ mol/dm^3, [D-glucose]$_T = 6 \times 10^{-3}$ mol/dm^3, $T = 30$ °C.

(i.e., Na^+), which may displace H^+ and OX^{2+} ions (C_1) out of the micellar surface.

$$2Na^+_W + OX^{2+}_M \rightleftarrows 2Na^+_M + OX^{2+}_W \quad (16)$$

$$Na^+_W + H^+_M \rightleftarrows Na^+_M + H^+_W \quad (17)$$

The plot of $k_{obs(T)}$ versus $[SDS]_T$ indicates that the solubilisation effect is greater than the counter-ion effect for the bipy-catalysed path up to the SDS concentration used. Here, it may be pointed out that the organic product D-gluconic acid is also partitioned between the micellar (both cationic and anionic) and aqueous phases. However, this partitioning does not have any effect on the rate process or reaction mechanism.

3. Experimental

3.1. Materials and reagents

2,2′-Bipyridine (Qualigens, India) D-glucose (SRL), $K_2Cr_2O_7$ (BDH), sodium dodecyl sulfate (SRL), *N*-cetylpyridinium chloride (SRL), H_2SO_4 (E. Merck), $HClO_4$ (E. Merck) and all other chemicals used were of highest purity available commercially. The solutions were prepared in doubly distilled water.

3.2. Procedure and kinetic measurements

Solutions of the oxidant and reaction mixtures containing known quantities of the substrate (S) (i.e., D-glucose), catalyst (bipy) (under the conditions $[S]_T \gg [Cr^{VI}]_T$ and $[bipy]_T \gg [Cr^{VI}]_T$) acid and other necessary chemicals were separately thermostated (±0.1 °C). The reaction was started by mixing the requisite amounts of the oxidant with the substrate. The progress of the reaction was monitored by following the rate of disappearance of Cr^{VI} by a titrimetric quenching technique.[40] 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.

3.3. Product analysis and stoichiometry

Under the kinetic conditions (i.e., [D-glucose]$_T \gg [Cr^{VI}]_T$), qualitative identification of the organic reaction product was carried out by paper-chromatography,[8,10,11] using *n*-butyl alcohol–acetic acid–water (4:1:5) as the eluant. To characterise the oxidation products, a series aldopentoses and aldohexoses were oxidised with nitric acid and bromine water[41] separately and the purified products were used as authentic standards in the chromatographic procedure. D-Gluconic acid and the corresponding lactone were identified[42] as the only reaction products. The observed R_f value for D-gluconic acid is also in good agreement with the reported value.[43] The paper chromatogram developed from the product solution also indicates the presence of unreacted substrate D-glucose ($R_f = 0.18$). The observed R_f value of D-glucose was also compared with that of authentic sample under the same conditions. The observed R_f value for glucose agrees well with the reported value ($R_f = 0.19$).[43] The paper chromatogram obtained from the product solution indicates the absence of any other organic compounds. Thus, it is evident that during the reaction the substrate did not degrade under these conditions.

The final fate of Cr^{III}-species was confirmed spectroscopically. The UV–vis spectra (Fig. 6) were recorded on a UV–vis–NIR scanning spectrophotometer, (UV-3101PC, Shimadzu). The characteristic part of electronic

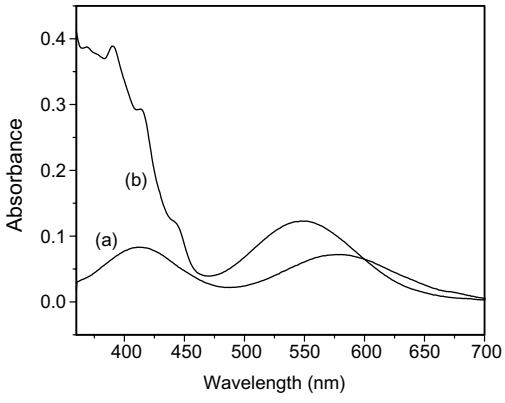


Figure 6. (a) Absorption spectra (absorbance per cm) of the reaction mixture (after completion of reaction): $[Cr^{VI}]_T = 3.85 \times 10^{-4}$ mol/dm^3, [D-glucose]$_T = 60 \times 10^{-3}$ mol/dm^3, $[bipy]_T = 0$ mol/dm^3 (i.e., uncatalysed path), $[H_2SO_4] = 0.5$ mol/dm^3. (The spectrum of the chromic sulfate is identical under the experimental conditions.) (b) Absorption spectra (absorbance per cm) of the reaction mixture (after completion of reaction): $[Cr^{VI}]_T = 3.85 \times 10^{-4}$ mol/dm^3, [D-glucose]$_T = 60 \times 10^{-3}$ mol/dm^3, $[bipy]_T = 8 \times 10^{-3}$ mol/dm^3, $[H_2SO_4] = 0.5$ mol/dm^3.

absorption spectra of Cr^{III} species lies in the range 360–600 nm. The colour of the final solution of bipy-catalysed reaction in aqueous H_2SO_4 media is pale violet [$\lambda_{max} = 548$ nm for $^4A_{2g} \rightarrow {}^4T_{2g}$] while the colour of the final solution for the uncatalysed reaction (i.e., in the absence of bipy) under identical conditions is pale blue [$\lambda_{max} = 578$ nm for $^4A_{2g} \rightarrow {}^4T_{2g}$; and 412 nm for $^4A_{2g} \rightarrow {}^4T_{1g}(F)$]. The spectrum of the final solution of the uncatalysed reaction and pure chromic sulfate solution in aqueous sulfuric acid media is identical. This indicates that the final Cr^{III}-species is simply chromic sulfate for the uncatalysed reaction while for the bipy-catalysed reaction, the final Cr^{III}-species is a Cr^{III}–bipy complex. Similar results have been noted by the earlier workers.[31,44] It is interesting to note that for the final solution of the bipy-catalysed reaction, there is a blue shift (Fig. 6) for the peak due to the transition $^4A_{2g} \rightarrow {}^4T_{2g}$. This blue shift is due to the presence of the strong field ligand like bipy. For the Cr^{III}–bipy complex, the peak due to the transition $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ merges with a charge transfer band (Fig. 6).

4. Conclusions

The cationic Cr^{VI}–bipy complex has been found to act as the active oxidant for the bipy-catalysed path of oxidation of D-glucose to D-gluconic acid in aqueous acidic media. This complex is produced in a rapid pre-equilibrium step in the reaction of Cr^{VI} and bipy, which then reacts with D-glucose to produce a ternary complex that experiences the redox decomposition (two-electron transfer) in the rate-determining step. The reactions have been carried out in aqueous micellar media. The effects of both the cationic and anionic surfactants have been followed and the observed micellar effects are in agreement with the proposed reaction mechanism. The mechanistic path of the uncatalysed and bipy-catalysed chromic acid oxidation of D-glucose have been compared.

The organic product, D-gluconic acid, was identified by paper chromatography and the observed R_f value has been found in good agreement with the reported value. This was further supported by comparison with an authentic sample of D-gluconic acid under the same conditions. In the reaction, Cr^{VI} is finally reduced to Cr^{III}. The fate of Cr^{III}-species in the final solution was determined by following the UV–vis spectra. In the uncatalysed reaction, the species is simply chromic sulfate (pale blue, $\lambda_{max} = 412$ and 578 nm) while for the bipy-catalysed reaction, the corresponding species is a Cr^{III}–bipy complex (pale violet colour, $\lambda_{max} = 548$ nm). In the Cr^{III}–bipy complex, the peak at 548 nm (due to the transition $^4A_{2g} \rightarrow {}^4T_{2g}$) experiences a blue shift (with respect to the simply chromic sulfate species obtained in the case of uncatalysed reaction) due to the presence of the strong field ligand bipy. The existence of Cr^{III}–bipy complex in the final product solution for the bipy-catalysed reaction supports the formation of Cr^{VI}–bipy complex in the pre-equilibrium step. This is a reasonable proposal as the Cr^{VI} centre is kinetically labile and the Cr^{VI}–bipy complex is finally reduced to a Cr^{III}–bipy complex. In contrast, formation of Cr^{III}–bipy complex after the reduction of Cr^{VI} to Cr^{III} is ruled out as Cr^{III} (t_{2g}^3) is a kinetically inert centre.

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Appendix A. Derivation of rate law for D-glucose (considering Scheme 2)

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

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

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

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

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

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

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

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

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

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

Since $K_b[H^+] \gg 1$ ($K_b = 2.8 \times 10^4$ for bipy) (Ref. 30)
It leads to: $[C_2] \approx K_3K_4[S]_T[HCrO_4^-][H^+][L]_T$

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

$$= K_3K_4k_2[S]_T[HCrO_4^-][L]_T[H^+]$$

and,

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

$$= (2/3)K_3K_4k_2[S]_T[L]_T[H^+] \quad (15)$$

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