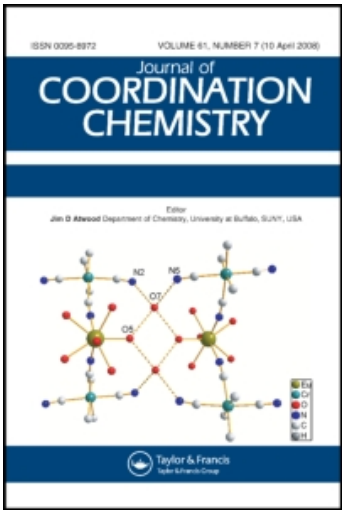

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Kinetics and mechanism of 2,2′-bipyridine-catalyzed chromium(VI) oxidation of propan-2-ol in the presence and absence of surfactants§

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Under kinetic conditions, monomeric Cr(VI) has been found kinetically active in the absence of bipy while in the bipy-catalyzed path, Cr(VI)-bipy complex has been suggested as the active oxidant. The uncatalyzed path shows the second-order dependence on $[H^+]$ while the bipy-catalyzed path shows the first-order dependence on $[H^+]$. Both the uncatalyzed and bipy-catalyzed paths show the first-order dependence on $[\text{propan-2-ol}]_T$ and $[Cr(VI)]_T$. The bipy-catalyzed path is the first order in $[\text{bipy}]_T$. Cetylpyridiniumchloride inhibits the reactions while sodium dodecyl sulfate catalyzes the reactions in the presence and in the absence of bipy.

Keywords: Cr(VI); Oxidation; Propan-2-ol; 2,2′-Bipyridine; Surfactant

1. Introduction

Reactions with *in-situ* separation have great potential to improve conversion and selectivity. Micellar systems seem well suited for various separation and catalytic process [1]. Oxidations are key reactions in the synthesis of organic molecules and fine chemicals [2a, b]; Cr(VI) is a universal oxidant [2c]. Alcohol oxidation is an important reaction. Among the different chelating agents, such as picolinic acid (PA), 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), ethylenediaminetetraaceticacid, oxalic acid, etc. acting as catalysts [3] in Cr(VI) oxidation of different subtrates, the catalytic ability [4–8] of PA is unique. The structure of bipy is comparable to that of PA as both chelating agents are heteroaromatic nitrogen bases. Recently, we reported bipy-promoted Cr(VI) oxidation of D-fructose [9], D-glucose [10], hexitols [11a], and ethane-1,2-diol [11b] in micellar media. It has been found [1a, 3–11] that micelles significantly influence the kinetic and the mechanistic aspects of Cr(VI) oxidation of different organic substrates and the observed micellar effect can substantiate the proposed reaction mechanism.

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2. Experimental

Propan-2-ol (SRL, AR) was distilled and the absence of any carbonyl compound in the distillate was checked by Schiff's reagent and 2,4-dinitrophenylhydrazine. $K_2Cr_2O_7$ (BDH, AR), cetylpyridiniumchloride (CPC) (SRL, AR), sodium dodecyl sulfate (SDS) (SRL, AR), and all other chemicals used were of the highest purity available commercially. Under the reaction conditions $[\text{propan-2-ol}]_T \gg [Cr(VI)]_T$, oxidation of propan-2-ol yields acetone which was identified by the preparation of 2,4dinitrophenylhydrazone derivatives [12]. The progress of the reaction was followed by quenching titrimetric technique [13]. The solutions of the oxidant and the reaction mixtures containing known quantities of the substrate (S) (propan-2-ol), bipy {under the conditions: $[S]_T \gg [Cr(VI)]_T$ and $[bipy]_T \gg [Cr(VI)]_T$}, surfactant, acid and other necessary chemicals were separately thermostated ($\pm 0.1^\circ$C). The reaction was initiated by mixing requisite amounts of oxidant with the reaction mixture. At different time intervals, 5 mL of reaction mixture was withdrawn and quenched in excess ferrous sulfate solution and then excess ferrous sulfate is back titrated by cerric sulfate solution using ferroin as a redox indicator. The overall stoichiometry of the reaction may be represented as

$$3CH_3CHOHCH_3 + 2HCrO_4^- + 8H^+ \rightarrow 2Cr(III) + 3CH_3COCH_3 + 8H_2O \qquad (1)$$

3. Results and discussion

The rate of disappearance of Cr(VI) shows the first-order dependence on $[Cr(VI)]_T$. The pseudo first-order rate constants (k_{obs}) have been determined from plots of $\ln[Cr(VI)]_t$ *versus* time using the equation $\ln[Cr(VI)]_t = \ln[Cr(VI)]_0 - kt$. In the catalyzed path the formation of a Cr(III)–bipy complex (characterized spectroscopically) [10] indicates that bipy undergoes complexation with the higher oxidation states (which are labile) of chromium. Because of the inertness of Cr(III), bipy does not bind the Cr(III) produced after reduction of Cr(VI). Thus, it is reasonable to consider that the Cr(VI)–bipy complex formed at the pre-equilibrium step is the active oxidant [14, 15]. In scheme 1, in the cyclic transition state (5), reduction of Cr(VI) to Cr(IV) is the rate-determining step. By considering the stoichiometry of the reaction, scheme 2 leads to

$$k_{obs(u)} = (2/3)K_1K_2k_1[CH_3CHOHCH_3]_T[H^+]^2 \qquad (2)$$

The observed rate law is supported by figures 1 and 2. In the cyclic transition state (2), reduction of Cr(VI) to Cr(IV) occurs [16] either through H^+ or H^- transfer and it is the rate-determining step. In the next step, Cr(IV) is further reduced to Cr(III) [17–19] as shown below.

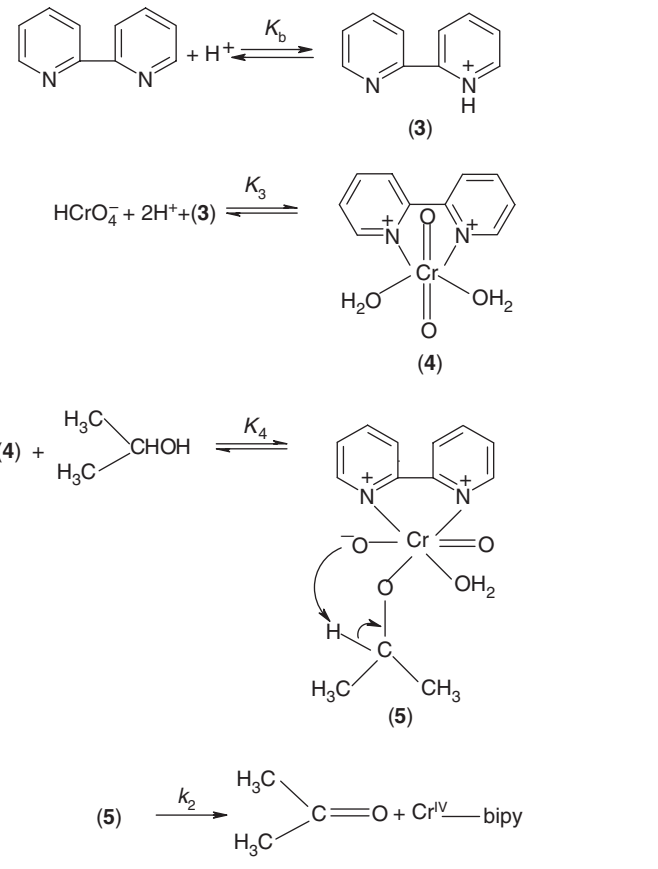
Route 1 $Cr(IV) + Cr(VI) \rightarrow 2Cr(V)$

$2Cr(V) + 2CH_3CHOHCH_3 \rightarrow 2Cr(III) + 2CH_3COCH_3$

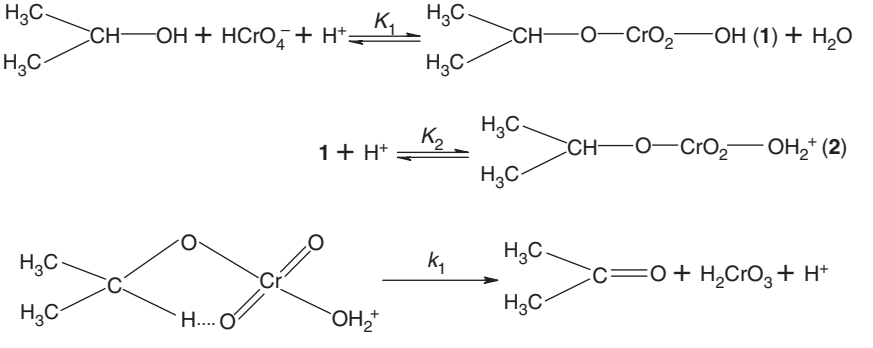
Route 2 $Cr(IV) + CH_3CHOHCH_3 \rightarrow Cr(III) + CH_3COHCH_3$

$Cr(VI) + CH_3COHCH_3 \rightarrow Cr(V) + CH_3COCH_3$

$Cr(V) + S \rightarrow Cr(III) + P$



Scheme 1. Cr(VI) oxidation of propan-2-ol in the presence of bipy.



Scheme 2. Cr(VI) oxidation of propan-2-ol in the absence of catalyst.

Route 3 $Cr(IV) + CH_3CHOHCH_3 \rightarrow Cr(II) + CH_3COCH_3$

$Cr(VI) + Cr(II) \rightarrow Cr(III) + Cr(V)$

$Cr(V) + CH_3CHOHCH_3 \rightarrow Cr(III) + CH_3COCH_3$

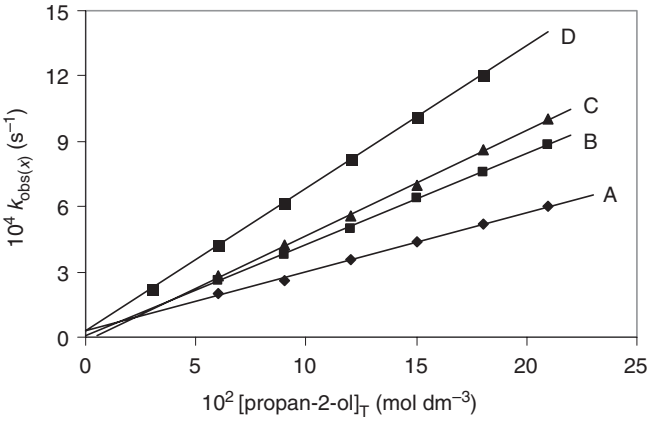


Figure 1. Dependence of $[propan\text{-}2\text{-}ol]_T$ on $k_{obs(x)}$ (where $x = u$ or T) for Cr(VI) oxidation of propan-2-ol in the presence (i.e., $k_{obs(T)}$ for B and D) and absence (i.e., $k_{obs(u)}$ for A and C) of 2,2′-bipyridine in aqueous H_2SO_4 at 30°C. $[Cr(VI)]_T = 10^{-3}$ mol dm^{-3}. A $[(H_2SO_4) = 1.0$ mol dm^{-3}, $(CPC)_T = 4 \times 10^{-3}$ mol dm$^{-3}]$; B $[(H_2SO_4) = 1.0$ mol dm^{-3}, $(bipy)_T = 14 \times 10^{-3}$ mol dm^{-3}, $(CPC)_T = 4 \times 10^{-3}$ mol dm$^{-3}]$; C $[(H_2SO_4) = 1.0$ mol dm^{-3}, $(SDS)_T = 2 \times 10^{-2}$ mol dm$^{-3}]$; D $[(H_2SO_4) = 1.0$ mol dm^{-3}, $(bipy) = 1 \times 10^{-2}$ mol dm^{-3}, $(SDS) = 2 \times 10^{-2}$ mol dm$^{-3}]$.

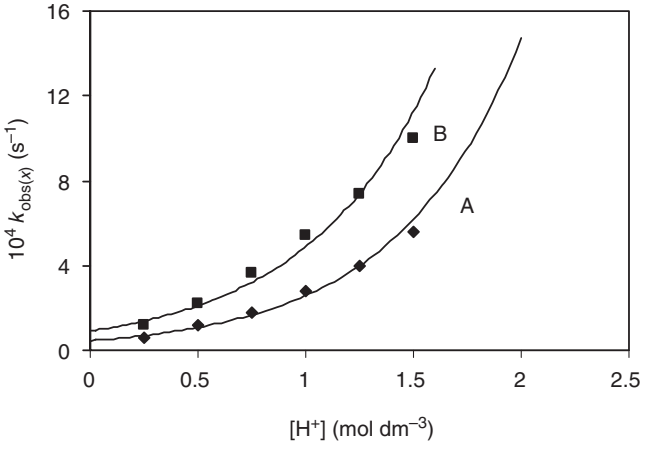


Figure 2. Dependence of $[HClO_4]_T$ in $k_{obs(x)}$ (where $x = U$ or T) for the Cr(VI) oxidation of propan-2-ol in the presence ($k_{obs(T)}$ for B) and absence ($k_{obs(U)}$ for A) of bipyridine in aqueous $HClO_4$ at 25°C. $[HClO_4] + [NaClO_4] = 1.5$, $[propan\text{-}2\text{-}ol]_T = 15 \times 10^{-2}$ mol dm^{-3}, $[Cr(VI)]_T = 1 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 3 \times 10^{-2}$ mol dm^{-3}, $[bipy]_T = 10 \times 10^{-3}$ mol dm^{-3}.

In the above routes, $CH_3CHOHCH_3$ is a $2e^-$ reductant and CH_3COHCH_3 is deprotonated and further oxidized to acetone.

There is no kinetic evidence for the formation of the said complex, as the strict first-order dependence on bipy (figure 3) is maintained throughout the concentration range used, indicating that the equilibrium constant for formation of the complex is quite low. By considering the stoichiometry of the reaction, scheme 1 leads to

$$k_{obs} = (2/3)K_3K_4k_2[propan\text{-}2\text{-}ol]_T[bipy]_T[H^+] \quad (3)$$

Figures 1, 2 and 3 confirm the above rate law.

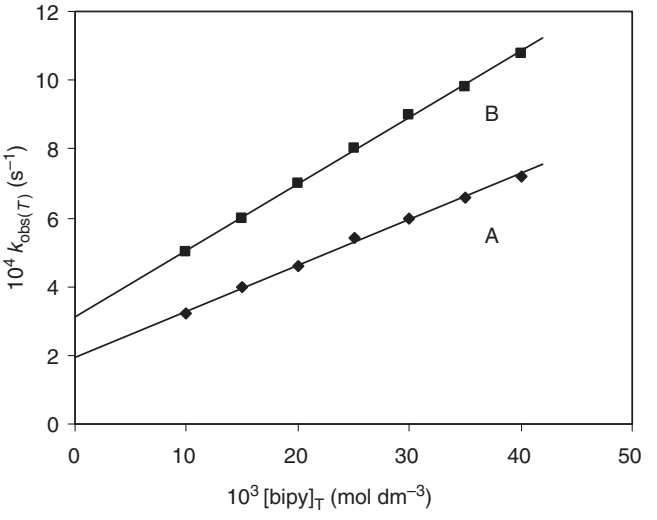


Figure 3. Dependence of $k_{obs(T)}$ on $[bipy]_T$ for Cr(VI) oxidation of propan-2-ol in aqueous H_2SO_4 at 25°C. $[propan\text{-}2\text{-}ol]_T = 45 \times 10^{-3}$ mol dm^{-3}, $[Cr(VI)]_T = 1 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}. A ($[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}); B (CPC = SDS = 0 mol dm^{-3}).

Table 1. Effect of $[SDS]_T$ and $[CPC]_T$ on $k_{obs(U)}$ for Cr(VI) oxidation of propan-2-ol in aqueous acidic media at 30°C.

$10^2[SDS]_T$ (mol dm^{-3})	2	4	6	8	10
$10^4\,k_{obs}$ (s^{-1})	3.0	4.0	5.0	6.0	7.0
$10^3[CPC]_T$ (mol dm^{-3})	2	4	6	8	10
$10^4\,k_{obs}$ (s^{-1})	3.6	2.0	1.0	0.5	0.5

$[Propan\text{-}2\text{-}ol]_T = 60 \times 10^{-3}$ mol dm^{-3}, $[Cr(VI)]_T = 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}.

Table 2. Effect of $[SDS]_T$ and $[CPC]_T$ on $k_{obs(T)}$ for the bipy promoted Cr(VI) oxidation of propan-2-ol in aqueous acidic media at 30°C.

$10^2[SDS]_T$ (mol dm^{-3})	2	4	6	8	10
$10^4 k_{obs}$ (s^{-1})	4	5.6	7.2	8.6	10.0
$10^3[CPC]_T$ (mol dm^{-3})	2	4	6	8	10
$10^4 k_{obs}$ (s^{-1})	4.0	2.8	2.0	1.4	1.4

$[Propan\text{-}2\text{-}ol]_T = 60 \times 10^{-3}$, $[Cr(VI)]_T = 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[bipy]_T = 10^{-2}$ mol dm^{-3}.

CPC(a representative cationic surfactant) inhibits both the uncatalyzed and catalyzed paths (tables 1 and 2) with a continuous decrease, finally attaining a limiting value at higher CPC concentration. A similar observation has been noted by Bunton and Cerichelli [20] in oxidation of ferrocene by ferric salts in the presence of the cationic surfactant. This rate-retarding by surfactants has been previously reported [6, 8–11]. Propan-2-ol is likely preferably partitioned in the micellar phase, and the kinetically active H_2CrO_4 [21, 22] may remain concentrated in the stern layer of the micellar phase. This leads to generation of Cr(VI)–propan-2-ol ester (scheme 2, **1**) in the micellar interphase. In the uncatalyzed path, the neutral Cr(VI)–substrate ester (scheme 2, **1**) is

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

partitioned in the micellar pseudo phase of the surfactant but the cationic surfactant repels H^+ needed for the reaction. In the bipy catalyzed path, CPC restricts the positively charged complex in the aqueous phase and thus, the accumulated neutral substrate in the micellar phase cannot participate in the reaction and the reaction rate is retarded. Thus, in both the uncatalyzed and bipy-catalyzed paths the reaction is mainly in the aqueous phase, where the reactant concentrations decrease due to their partitioning in the micellar phase. Partitioning of the reactant between the aqueous and the micellar phase is shown in scheme 3.

SDS (a representative anionic surfactant) catalyzes the reactions, both in the presence and absence of bipy (tables 1 and 2). In the bipy-catalyzed path, rate acceleration is due to preferential partitioning of the positively catalyzed Cr(VI)–bipy complex (scheme 1, **4**) by electrostatic attraction with neutral substrate in the micellar surface. Thus, SDS allows the reaction to proceed in both aqueous and micellar interphases. In the absence of bipy, Cr(VI)–substrate ester (scheme 2, **1**) partitioned into the micellar phase with H^+ needed for the reaction. Thus, SDS permits the reaction in both phases with a preferential rate enhancement in the micellar phase.

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