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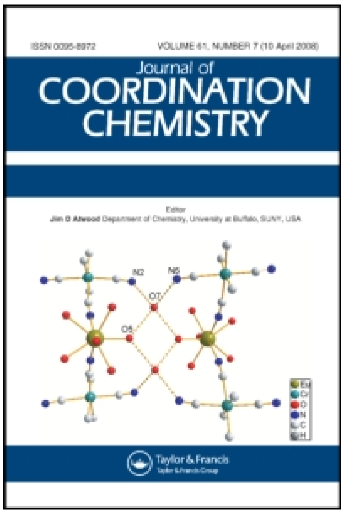

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Micellar catalysis of chromium(VI) oxidation of ethane-1,2-diol in the presence and absence of 2,2′-bipyridine in aqueous acid media

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The kinetics and mechanism of the Cr(VI) oxidation of ethane-1,2-diol in the presence and absence of 2,2′-bipyridine (bipy) in aqueous acid media were studied under the conditions $[\text{ethane-1,2-diol}]_T \gg [\text{Cr(VI)}]_T$. Under the kinetic conditions, monomeric Cr(VI) was found to be kinetically active in the absence of bipy, whereas in the bipy-catalyzed path the Cr(VI)-bipy complex was the active oxidant. In this path, the Cr(VI)-bipy complex undergoes nucleophilic attack by the substrate to form a ternary complex which subsequently undergoes redox decomposition (through 2e transfer) leading to hydroxyethanol and the Cr(IV)-bipy complex. The Cr(IV)-bipy complex then participates further in oxidation of organic substrate, ultimately converted into inert Cr(III)-bipy complex. The uncatalyzed path shows a second-order dependence on $[H^+]$, while the bipy-catalyzed path shows a first-order dependence on $[H^+]$. Both the uncatalyzed and bipy-catalyzed paths show first-order dependence on $[\text{ethane-1,2-diol}]_T$ and on $[\text{Cr(VI)}]_T$. The bipy-catalyzed path is first-order in $[\text{bipy}]_T$. All these patterns remain unaltered in the presence of externally added surfactants. The effects of a cationic surfactant, *N*-cetylpyridinium chloride (CPC), and an anionic surfactant, sodium dodecyl sulfate (SDS), on both the uncatalyzed and bipy-catalyzed paths were studied. CPC inhibits both the uncatalyzed and bipy-catalyzed paths, whereas SDS catalyzes the reactions. The observed micellar effects are explained by considering a distribution pattern of the reactants between the micellar and aqueous phases.

Keywords: Kinetics; Catalysis; Surfactants; Ethane-1,2-diol; Chromium(VI)

1. Introduction

Organized assemblies may have an important effect [1, 2] on the rate of electron transfer reactions. Micellar systems have been well studied for various separation [3] and catalytic processes [4, 5]. For catalytic processes micellar solutions provide a way for alternative routes in an aqueous medium. In an aqueous phase surfactant molecules aggregate, at ambient conditions, forming micelles with a hydrophobic cora and hydrophilic corona [6]. Oxidations are key reactions in the synthesis of organic molecules and fine chemicals [7, 8] with Cr(VI) a universal oxidant. Picolinic acid (PA), a chelating agent, is well known [9–12] to catalyze Cr(VI) oxidations. The structure of 2,2′-bipyridine (bipy) is comparable to that of PA and both are chelating

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heteroaromatic nitrogen bases. PA and 2,2′- bipyridine are not true catalysts being lost during the course of the reaction, but are promoters. To maintain steady concentration a huge amount of these chelating agents compared to oxidant is used. Recently we reported bipyridine promoted Cr(VI) oxidations of D-fructose [13], D-glucose [14], and hexitols [15]. The present article deals with micellar effects on 2,2′-bipyridine (bipy) promoted Cr(VI) oxidation of ethane-1,2-diol. The studies have been carried out in aqueous micellar media to substantiate paths proposed for micellar effects.

2. Experimental and methods

2.1. *Materials and reagents*

Ethane-1,2-diol (AR, BDH) was dried over anhydrous Na_2SO_4 for 7 days and distilled at low pressure (*ca* 4 mm Hg) and the 92–94°C fraction was collected. The purity of the distillate was further checked by density measurement. 2,2′-Bipyridine (bipy) (AR, Qualigen, India), $K_2Cr_2O_7$ (AR, BDH), sodium dodecyl sulfate (SDS) (AR, SRL, India), *N*-cetylpyridinium chloride (CPC) (AR, SRL, India) and all others chemicals were of highest purity available commercially. Solutions were prepared in doubly distilled water.

2.2. *Procedure and kinetic measurements*

Solutions of oxidant and reaction mixtures containing known quantities of the substrate (S) (i.e. ethane-1,2-diol), 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 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 [16]. 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 from this path was kinetically negligible.

2.3. *Product analysis and stoichiometry*

In a typical experiment, the substrate (0.25 mol), Cr(VI) (0.02 mol) and bipy (0.2 mol) were dissolved in 1.0 mol dm^{-3} H_2SO_4 (75 cm^3). The reaction mixture was allowed to stand in the dark for 24 h to ensure complexation, as indicated by the disappearance of the Cr(VI) color. Then the reaction mixture was treated overnight with an excess (*ca* 200 cm^3) of a saturated solution of 2,4-dinitrophenylhydrazine (DNP) in 2 mol dm^{-3} HCl. The precipitated 2,4-dinitrophenylhydrazone of product was filtered off, dried, and recrystallized from ethanol. The hydrazone had m.p. 155–157°C which conforms [17] to that of the hydrazone of hydroxyethanol. The overall stoichiometry of the reaction may be represented as

$$2HCrO_4^- + 3(CH_2OH)_2 + 8H^+ \rightarrow 2Cr(III) + 3HOCH_2CHO + 8H_2O \qquad (1)$$

3. Results and discussion

3.1. *Dependence on [Cr(VI)]$_T$*

The rate of disappearance of Cr(VI) shows first-order dependence on Cr(VI) in the presence and absence of bipy under the conditions $[\text{ethane-1,2-diol}]_T \gg [\text{bipy}]_T \gg [\text{Cr(VI)}]_T$ and $[\text{bipy}]_T \gg [\text{Cr(VI)}]_T$. 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 linear plots of log[Cr(VI)] *versus* time (t).

3.2. *Dependence on [bipy]$_T$*

Plots of k_{obs} *versus* $[\text{bipy}]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower unanalyzed path (figure 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* $[\text{bipy}]_T$, consistent with

$$k_{obs(T)} = k_{obs(u)} + k_{obs(c)} = k_{obs(u)} + k_{cat}[\text{bipy}]_T \tag{2}$$

3.3. *Dependence on [ethane-1,2-diol]$_T$*

From the plot of k_{obs} *versus* $[\text{ethane-1,2-diol}]_T$ (figure 2), both catalyzed and uncatalyzed paths show a first-order dependence on $[S]_T$, S is ethane-1,2-diol,

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{s(c)}[S]_T \tag{3}$$

$$k_{obs(u)} = k_{s(u)}[S]_T \tag{4}$$

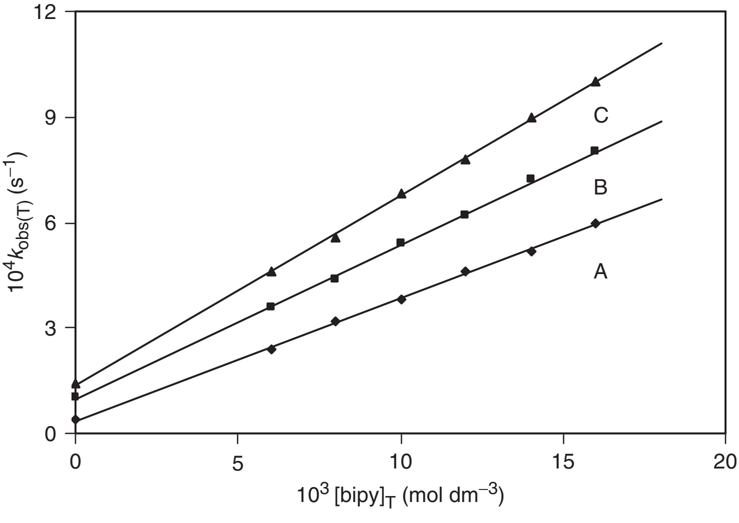


Figure 1. Effect of $[\text{bipy}]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of ethane-1,2-diol in the presence of bipyridine in aqueous H_2SO_4. $[\text{Cr(VI)}]_T = 6 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.75$ mol dm^{-3}, $[\text{ethane-1,2-diol}]_T = 12 \times 10^{-2}$ mol dm^{-3} at 35°C. A ($[\text{CPC}]_T = 4 \times 10^{-3}$ mol dm^{-3}); B ($[\text{CPC}]_T = [\text{SDS}]_T = 0$ mol dm^{-3}); C ($[\text{SDS}]_T = 3 \times 10^{-2}$ mol dm^{-3}).

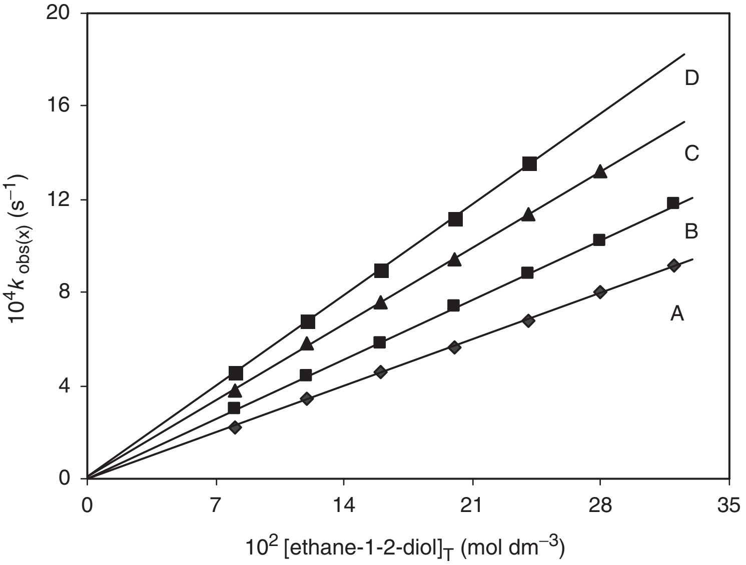


Figure 2. Effect of [ethane-1,2-diol]$_T$ on $k_{obs(x)}$ (where $x = u$ or T) for the Cr(VI) oxidation of ethane-1,2-diol in the presence (i.e. $k_{obs(T)}$ for B and D) and absence (i.e. $k_{obs(u)}$ for A and C) of 2,2′-bipyridine in aqueous H_2SO_4 media at 35°C. [Cr(VI)]$_T = 6 \times 10^{-4}$ mol dm^{-3}, [H_2SO_4] $= 0.75$ mol dm^{-3}. A ([CPC]$_T = 4 \times 10^{-3}$ mol dm^{-3}); B ([bipy]$_T = 11 \times 10^{-3}$ mol dm^{-3}, [CPC]$_T = 4 \times 10^{-3}$ mol dm^{-3}); C ([SDS]$_T = 3 \times 10^{-2}$ mol dm^{-3}); D ([bipy]$_T = 6 \times 10^{-3}$ mol dm^{-3}, [SDS]$_T = 3 \times 10^{-2}$ mol dm^{-3}).

3.4. *Dependence on [H$^+$]*

Acid dependence patterns for uncatalyzed and catalyzed paths are totally different (figure 3). From the experimental fit, the observations are

$$k_{obs(u)} = k_{H(u)}[H^+]^2 \tag{5}$$

$$k_{obs(c)} = k_{H(c)}[H^+] \tag{6}$$

A similar dependence pattern is also observed in the presence of SDS with enhanced rate constants.

3.5. *Test for acrylonitrile polymerization*

Under the experimental conditions, polymerization of acrylonitrile occurred under a nitrogen atmosphere, supporting the existence of free radicals.

3.6. *Mechanism of the reaction*

The mechanism of the reaction can be divided into the uncatalyzed path (scheme 1) and the catalyzed path (scheme 2). In the uncatalyzed path (i.e. in absence of bipy), the reactions of scheme 1 lead to

$$k_{obs(u)} = (2/3)K_1K_2k_1[CH_2OHCH_2OH]_T[H^+]^2 \tag{7}$$

Figures 2 and 3 support the observed rate law. In the catalyzed path, with $[\text{ethane-1,2-diol}]_T \gg [\text{Cr(VI)}]_T$ and $[\text{bipy}]_T \gg [\text{Cr(VI)}]_T$, scheme 2 leads to

$$k_{\text{obs(c)}} = (2/3)K_3K_4k_2[\text{CH}_2\text{OHCH}_2\text{OH}]_T[\text{bipy}]_T[\text{H}^+] \tag{8}$$

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

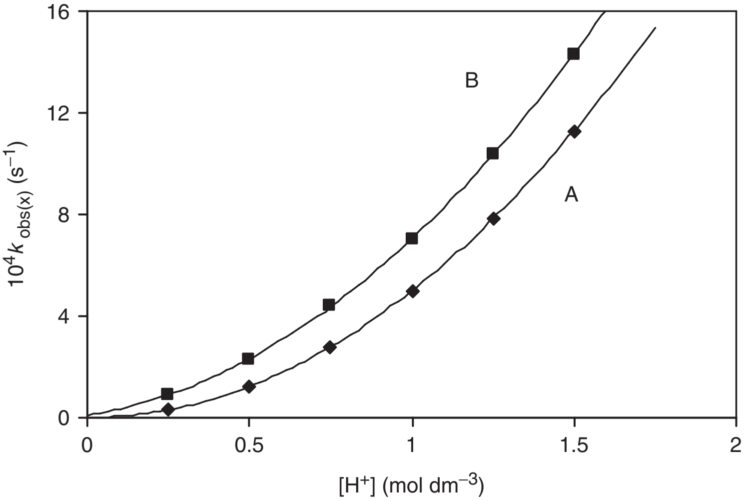
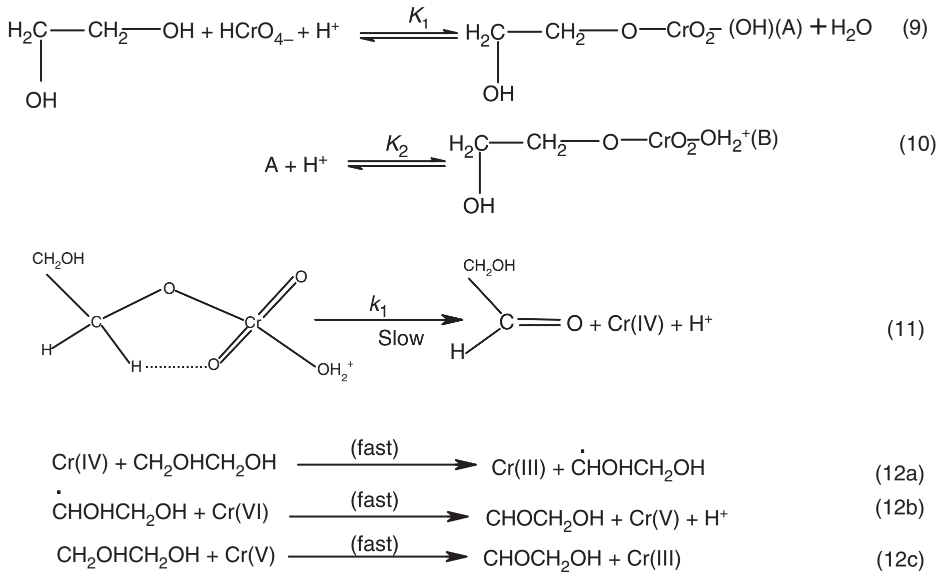
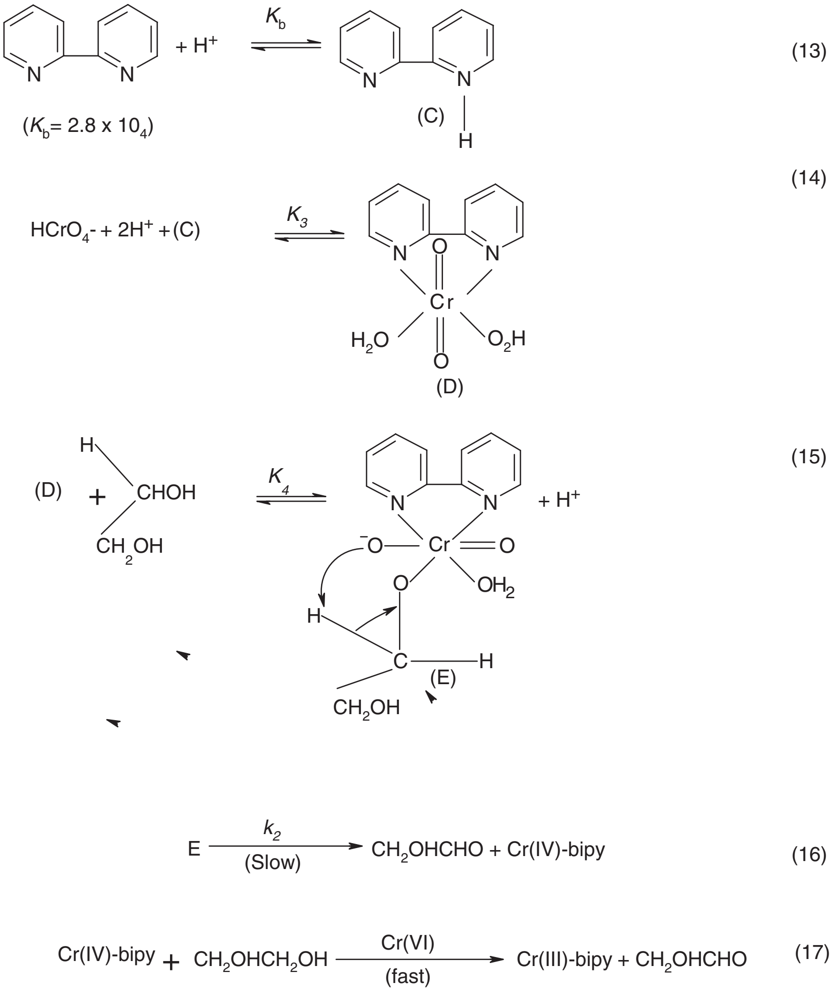


Figure 3. Effect of $[\text{HClO}_4]_T$ on $k_{\text{obs}(x)}$ (where $x = \text{u}$ or T) for the Cr(VI) oxidation of ethane-1,2-diol in the presence (i.e. $k_{\text{obs(T)}}$ for B) and absence (i.e. $k_{\text{obs(u)}}$ for A) of 2,2′-bipyridine in aqueous HClO_4 at 25°C. $\text{I} = [\text{HClO}_4] + [\text{NaClO}_4] = 1.5$, $[\text{Cr(VI)}]_T = 5 \times 10^{-4}\,\text{mol dm}^{-3}$, $[\text{ethane-1,2-diol}]_T = 8 \times 10^{-3}\,\text{mol dm}^{-3}$, $[\text{SDS}]_T = 4 \times 10^{-2}\,\text{mol dm}^{-3}$, $[\text{bipy}]_T = 6 \times 10^{-3}\,\text{mol dm}^{-3}$.



Scheme 1. Cr(VI) oxidation of ethane-1,2-diol in absence of bipy.



Scheme 2. Cr(VI) oxidation of ethane-1,2-diol in presence of 2,2′-bipyridine.

3.7. *Effect of CPC*

CPC, a cationic surfactant, retards both uncatalyzed and catalyzed paths (figure 4). The plots of $k_{obs(x)}$ *versus* $[CPC]_T$ (figure 4) show a continuous decrease, finally leveling off at high concentration of CPC. This observation is similar to that noted by Bunton and Cerichelli [18] in oxidation of ferrocene by ferric salts in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB). Similar findings have also been reported by Panigrahi and Sahu [19] in oxidation of acetophenone by Ce(IV) in the presence of *N*-dodecyl pyridinium chloride (NDPC). In the uncatalyzed path, the neutral Cr(VI)-substrate ester (A, equation 10, scheme 1) formed is partitioned in the micellar pseudo-phase of the surfactant; CPC restricts H^+ ions in aqueous phase due to the electrostatic repulsion needed for protonation of A (equation 10, scheme 1). Thus, the reaction has lower concentration of A and reaction rate is retarded. In the catalyzed path, CPC restricts the positively charged Cr(VI)-catalyst complex

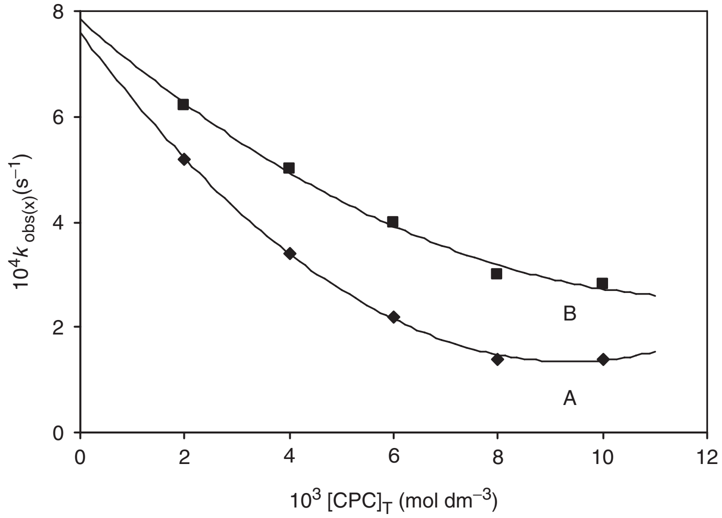


Figure 4. Effect of $[CPC]_T$ on $k_{obs(x)}$ (where $x = u$ or T) for the Cr(VI) oxidation of ethane-1,2-diol in the presence of CPC aqueous H_2SO_4 media at 40°C. $[Cr(VI)]_T = 6 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.75$ mol dm^{-3}, [ethane-1,2-diol]$_T = 12 \times 10^{-2}$ mol dm^{-3}. A ($[bipy]_T = 0$ mol dm^{-3}); B ($[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}).

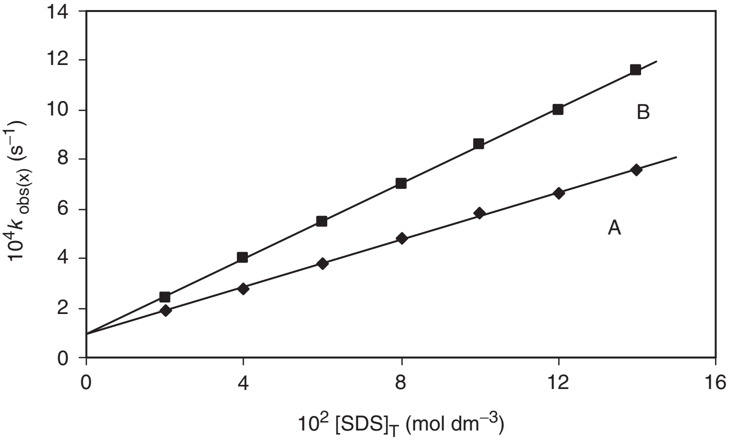


Figure 5. Effect of $[SDS]_T$ on $k_{obs(x)}$ (where $x = u$ or T) for the Cr(VI) oxidation of ethane-1,2-diol in the presence of SDS aqueous H_2SO_4 media at 35°C. $[Cr(VI)]_T = 6 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 0.50$ mol dm^{-3}, [ethane-1,2-diol]$_T = 12 \times 10^{-2}$ mol dm^{-3}. A ($[bipy]_T = 0$ mol dm^{-3}); B ($[bipy]_T = 6 \times 10^{-3}$ mol dm^{-3}).

(D, equation 14, scheme 2) in the aqueous phase and the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction. Hence in the catalyzed path, the reaction is restricted in the aqueous phase with concentration of the substrate depleted due to its partitioning in the Stern layer of the micelle.

3.8. *Effect of SDS*

Sodium dodecyl sulfate, an anionic surfactant, accelerates both the uncatalyzed and bipy-catalyzed path (figure 5). In the bipy-catalyzed path, the rate accelerating effect arises from preferential partitioning of the positively charged Cr(VI)-bipy complex (by electrostatic attraction) and neutral substrate (probably by hydrophobic attraction) in the micellar interphase. Thus, SDS permits the reaction to proceed in both aqueous and micellar interphase. The rate benefit arises due to the enhanced rate in the micellar phase where both the reactants are preferentially accumulated. In the absence of bipy, binding of H_2CrO_4 and the substrate to the SDS micelle has been argued by different workers [20, 21]. The H^+ ions needed for the reactions are also preferably attracted to the micellar phase. Thus, SDS allows the reaction in both phases with a preferential rate enhancement in the micellar phase.

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