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Micellar effect on the reaction of chromium(VI) oxidation of D-fructose in the presence and absence of picolinic acid in aqueous media: a kinetic study

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ABSTRACT: The kinetics and mechanism of the Cr(VI) oxidation of D-fructose in the presence and absence of picolinic acid (PA) in aqueous acid media were studied under the conditions $[\text{D-fructose}]_T \gg [\text{Cr(VI)}]_T$ at different temperatures. Under the kinetic conditions, the monomeric species of Cr(VI) was found to be kinetically active in the absence of PA whereas in the PA-catalysed path, the Cr(VI)–PA complex was considered to be the active oxidant. In this path, the Cr(VI)–PA complex undergoes a nucleophilic attack by the substrate to form a ternary complex which subsequently experiences a redox decomposition through glycol splitting leading to the lactone of C_5-aldonic acid along with formaldehyde and the Cr(IV)–PA complex. The primary product formaldehyde undergoes further oxidation (in part) to form formic acid. Then the Cr(IV)–PA complex participates further in the oxidation of D-fructose and ultimately is converted into the inert Cr(III)–PA complex. In the uncatalysed path, the Cr(VI)–substrate ester experiences an acid-catalysed redox decomposition (2e transfer) in the rate-determining step giving rise to the products. The uncatalysed path shows a second-order dependence on $[H^+]$ whereas the PA catalysed path shows a fractional order in $[H^+]$. Both paths show a first-order dependence on $[\text{D-fructose}]_T$ and $[\text{Cr(VI)}]_T$. The PA-catalysed path is first order in $[\text{PA}]_T$. 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 uncatalysed and PA-catalysed paths were studied. CPC inhibits both the uncatalysed and PA-catalysed paths whereas SDS catalyses the reactions. The observed micellar effects are explained by considering a distribution pattern of the reactants between the micellar and aqueous phases. The applicability of different kinetic models, e.g. the pseudo-phase ion-exchange model, the Menger–Portnoy model and the Piszkiewicz cooperative model, was tested to explain the observed micellar effects. The effect of $[\text{surfactant}]_T$ on the activation parameters was explored to rationalize the micellar effect. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: kinetics; oxidation; catalysis; D-fructose; chromium(VI); picolinic acid; surfactants

INTRODUCTION

From the standpoint of the biochemical importance of D-fructose in metabolic systems,[1] its physico-chemical properties in solution have been extensively studied.[2] The kinetics and mechanism of the oxidation of ketohexoses by different transition metal ions have been reported.[3] Different ketohexoses including D-fructose have been subjected[3c,e] to kinetic studies of Cr(VI) oxidation in aqueous acidic media. Because of the carcinogenic and mutagenic activity of Cr(VI), the chemistry of chromium in biological systems[4] has become important to both biochemists and inorganic chemists. It is believed that reducing sugars including D-fructose play an important role in monitoring the toxicity[4] of chromium. Hence fresh interest has arisen among kineticists to explore the kinetic aspects[5] of interaction of Cr(VI) with reducing sugars and their different metabolic intermediates. This paper deals with the kinetics and mechanism of the Cr(VI) oxidation of D-fructose in the presence and absence of picolinic acid (PA), which is unique[5e,6,7] in catalysing the Cr(VI) oxidation of organic substrates containing OH groups. D-Fructose is basically a polyol but the reactivities of the OH groups are markedly influenced by the adjacent carbonyl group. Hence the effect of PA in the present kinetic study is of interest. Micellar effects on both the uncatalysed and PA-catalysed reactions were studied to substantiate the proposed mechanism.

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EXPERIMENTAL

Materials and reagents. PA (Fluka) was used after repeated crystallization from methanol (m.p. 136 °C). D-Fructose (SRL), $K_2Cr_2O_7$ (BDH), sodium dodecyl sulfate

(SDS) (SRL), *N*-cetylpyridinium chloride (CPC) (SRL) and all other chemicals used were of highest purity available commercially. Solutions were prepared in doubly distilled water.

Procedure and kinetic measurements. Solutions of the oxidant and reaction mixtures containing known quantities of the substrate (S) (D-fructose), catalyst (PA) {under the conditions $[S]_T \gg [Cr(VI)]_T$ and $[PA]_T \gg [Cr(VI)]_T$}, 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 a titrimetric quenching technique as discussed earlier.[7] 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. To circumvent the solubility problem, different acids ($HClO_4$ and H_2SO_4) were used to follow the effects of the anionic surfactant and cationic surfactant (CPC). The catalytic efficiencies of PA in aqueous H_2SO_4 and $HClO_4$ were compared. Errors associated with the different rate constants and activation parameters were estimated as usual.[8]

RESULTS AND DISCUSSION

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.[5a,b,9] To characterize the oxidation products of D-fructose, a series of aldopentoses and aldohexoses were oxidized with nitric acid and bromine water[10] separately and the purified products were taken as the standards in the chromatographic procedure. The aldonic acid (C_5-acid) corresponding to arabinose was identified as the main product of D-fructose oxidation. Paper chromatography was effected by using butan-1-ol–acetic acid–water (4:1:5) as eluent. Formaldehyde was detected in the reaction mixture as such by the chromotropic acid test.[11] 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.

Dependence on $[Cr(VI)]_T$

Both in the presence and absence of PA, under the experimental conditions, $[S]_T \gg [PA]_T \gg 10^3[Cr(VI)]_T$, and $[PA]_T \gg 10^3[Cr(VI)]_T$, 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 unaltered. The pseudo-first-order rate constants (k_{obs}) were evaluated from the linear plot of $\log[Cr(VI)]_t$ vs time (t) as usual.

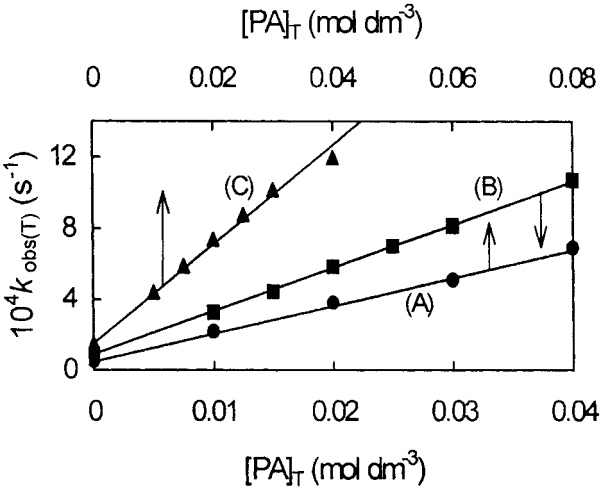


Figure 1. Effect of $[PA]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of D-fructose in the presence of PA in aqueous $HClO_4$ media. $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.45$ mol dm^{-3}, $I = [HClO_4] + [NaClO_4] = 1.0$ mol dm^{-3}, $[D\text{-fructose}]_T = 0.017$ mol dm^{-3}. (A) 25 °C; (B) 35 °C; (C) 40 °C

Dependence on $[PA]_T$

At $[S]_T = 0.017$ mol dm^{-3} and $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, the effect of $[PA]_T$ on k_{obs} was followed in both aqueous $HClO_4$ and H_2SO_4 media. The plots of k_{obs} vs $[PA]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower uncatalysed paths (Fig. 1). The pseudo-first-order rate constants [$k_{obs(u)}$] directly measured in the absence of PA agree well with those obtained from the intercepts of the plots of $k_{obs(T)}$ vs $[PA]_T$. The relevant equation is

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

The values of k_{cat} with the activation parameters are given in Table 1. During the progress of the reaction, PA is lost owing to the formation of an inert Cr(III)–PA complex. The nature of the dependence on $[PA]_T$ remains unaltered also in the presence of the surfactants. Under the condition $[PA]_T \gg [Cr(VI)]_T$ during the progress of the reaction, $[PA]_T$ remains more or less constant.

Dependence on $[S]_T$

From the plot of k_{obs} vs $[S]_T$ (Fig. 2), it is established that

Table 1. Kinetic parameters for the Cr(VI) oxidation of D-fructose in the presence and absence of picolinic acid (PA) under different conditions

In aqueous H_2SO_4 medium							
Temperature (°C)	$10^4 k_{obs(u)(w)}$ (s^{-1})[a]	$10^3 k_{cat(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[a]	$k_{eff(w)}$[b]	$10^3 k_{s(u)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[c]	$10^3 k_{s(u)(CPC)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[d]	$10^3 k_{s(c)(CPC)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[d]	$10^3 k_{s(u)(SDS)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[c]
25	0.5	11.0 ± 0.2	9				
35	0.9	17.8 ± 0.3	8	11.5 ± 0.3	7.0 ± 0.2	9.4 ± 0.2	13.6 ± 0.2
40	1.1	22.0 ± 0.3	8				
$\Delta H^{\neq}$ (kJ mol^{-1})		33 ± 3					
$\Delta S^{\neq}$ (J $K^{-1}\ mol^{-1}$)		-175 ± 10					

In aqueous $HClO_4$ medium						
Temperature (°C)	$10^4 k_{obs(u)(w)}$ (s^{-1})[e]	$10^3 k_{cat(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[e]	$k_{eff(w)}$[f]	$10^3 k_{s(u)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)	$10^3 k_{s(c)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)	$10^4 k_{H(u)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$)[i]
25	0.5	15.6 ± 0.3	13			
35	0.9	24.4 ± 0.3	11	(6.7 ± 0.1)[g] (32.5 ± 0.4)[h]	(29.3 ± 0.3)[g]	9.2 ± 0.1
40	1.5	29.3 ± 0.4	8			
$\Delta H^{\neq}$ (kJ mol^{-1})		29.6 ± 2.5				
$\Delta S^{\neq}$ (J $K^{-1}\ mol^{-1}$)		-182 ± 9				

[a] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 0.5$ mol dm^{-3}, $[S]_T = 0.017$ mol dm^{-3}, $[PA]_T = 0 - 0.08$ mol dm^{-3}.
[b] Conditions as in (a) and $k_{eff} = \{k_{obs(T)} - k_{obs(u)}\}/k_{obs(u)}$ and k_{eff} calculated at $[PA]_T = 0.04$ mol dm^{-3}.
[c] $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[SDS]_T = 0.04$ mol dm^{-3}, $[S]_T = 0.015$–0.085 mol dm^{-3}.
[d] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[PA]_T = 0.02$ mol dm^{-3}, $[CPC]_T = 4 \times 10^{-3}$ mol dm^{-3}.
[e] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.45$ mol dm^{-3}, $[S]_T = 0.017$ mol dm^{-3}, $[PA]_T = 0$–0.07 mol dm^{-3}.
[f] $k_{eff(w)}$ calculated for $[PA]_T = 0.04$ mol dm^{-3}.
[g] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 0.45$ mol dm^{-3}, $[PA]_T = 0.02$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}.
[h] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[HClO_4] = 1.0$ mol dm^{-3}, $I = 1.5$ mol dm^{-3}.
[i] $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[S]_T = 0.03$ mol dm^{-3}, $I = 1.5$ mol dm^{-3}.

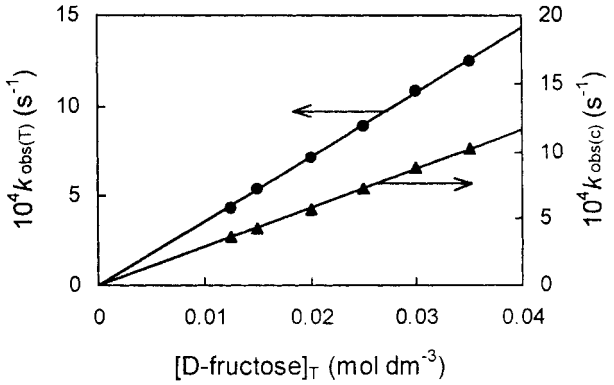


Figure 2. Effect of [D-fructose]$_T$ on k_{obs} for the Cr(VI) oxidation of D-fructose in the presence of PA in aqueous $HClO_4$ media. [Cr(VI)]$_T$ = 1.13×10^{-3} mol dm^{-3}, [PA]$_T$ = 0.02 mol dm^{-3}, [$HClO_4$] = 0.45 mol dm^{-3}, I = [$HClO_4$] + [$NaClO_4$] = 1.0 mol dm^{-3}, 35 °C

both the uncatalysed and catalysed paths show a first-order dependence on [S]$_T$, i.e.

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

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

In the presence of surfactants, the same dependence pattern is also found. The values of $k_{s(c)}$ and $k_{s(u)}$ under different conditions are given in Table 1.

Dependence on [H^+]

The acid concentration dependence patterns for the uncatalysed and catalysed paths are different (Fig. 3).

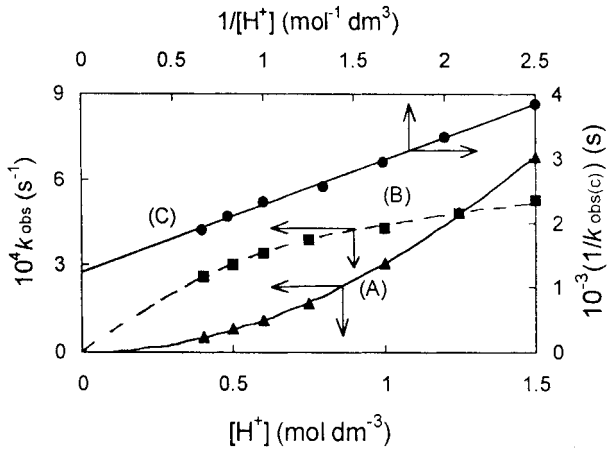


Figure 3. Effect of [$HClO_4$]$_T$ on k_{obs} for the Cr(VI) oxidation of D-fructose in the presence of PA in aqueous $HClO_4$ media. [Cr(VI)]$_T$ = 1.0×10^{-3} mol dm^{-3}, I = [$HClO_4$] + [$NaClO_4$] = 1.5 mol dm^{-3}, [D-fructose]$_T$ = 0.011 mol dm^{-3}, [PA]$_T$ = 0.02 mol dm^{-3}, 35 °C (A) For $k_{obs(u)}$; (B) and (C) for $k_{obs(c)}$, i.e. PA-catalysed path

From the experimental fit, the observations (in both the presence and absence of SDS) are

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

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = a[S]_T[PA]_T[H^+]/(b + m[H^+]) \quad (5)$$

where a, b and m are constants, or

$$1/k_{obs(c)} = b/(a[S]_T[PA]_T[H^+]) + (m/a)(1/[S]_T[PA]_T) \quad (6)$$

The linear plots (Fig. 3) of $k_{obs(u)}/[H^+]$ vs [H^+] and $1/k_{obs(c)}$ vs [H^+] support the above equations.

Test for acrylonitrile polymerization

Under the experimental conditions, polymerization of acrylonitrile was observed under a nitrogen atmosphere.

Mechanism of the reaction

In aqueous solution, D-fructose exists mainly as cyclic hemiacetals which are in dynamic equilibrium with the acyclic form (where C_2 is present as a keto group). Of the pyranoid and furanoid cyclic forms, the former is more stable.[12] Hence the preponderant form of the D-fructose is β-pyranoid. Kinetically, the monosaccharides can be considered as polyols in which the reactivities of alcohol groups are expected to be increased by the presence of the carbonyl group. In fact, in the case of oxidations by V(V), the rate constant for hydroxyacetone is about 10^4 times[3b,13] greater than that for glycol, but the rate constants for D-glucose and D-mannose are only about 15 times[3b,14] higher than that for glycol. A similar observation has been noted by us[5e,15] for Cr(VI) oxidation of glycols and D-glucose.

By considering the open-chain structures of the sugars, it is reasonable to expect that the sugars should react much faster than glycol. This decreased rate constant for the sugars has been explained by some workers[14] by considering the fact that the oxidation goes predominantly through the open-chain form whose concentration is very small. Thus the oxidation process needs the conversion of cyclic forms into open-chain forms through a dynamic pre-equilibrium step. The carbonyl group present in the open-chain form will undergo hydration[15,16] and the hydrated compound is kinetically active.[17] In fact, this pre-oxidative hydration step is well documented[17] for carbonyl compounds.

The apparent low reactivities[3b,e] (compared with the pure acyclic compound, e.g. hydroxyacetophenone) of the monosaccharides and the increase in the reactivity of

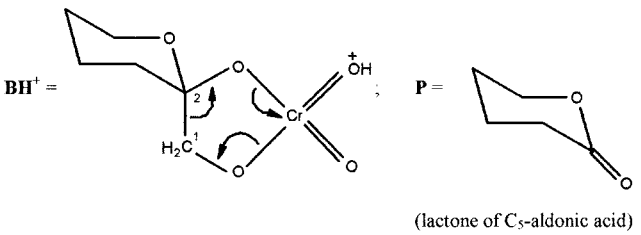
the sugars with increase in the relative amount of the open-chain form [e.g. for Cr(VI) oxidation, the rate sequences D-galactose >D-mannose >D-glucose; D-ribose >L-arabinose >D-xylose and D-fructose >L-sorbose follow the same sequence of relative amounts of the open-chain forms of the sugars] strongly indicate that the kinetic path involving the open-chain form of the sugar definitely makes a significant contribution to the overall reaction. However, some workers have also proposed[3c,5a,b,9] the participation of the cyclic forms in the redox reaction mechanism. It has been argued that in the cyclic hemiacetal forms, the hydroxyl groups are better exposed to interact with Cr(VI).[5a] Scheme 1 presents the reaction mechanism by considering the β-pyranoid form of D-fructose. In reality, the pseudo-first-order rate constants are the sum contribution of each pyranoid and furanoid form in addition to the possible contribution of the open-chain form remaining in dynamic equilibrium with the cyclic forms.

$$\mathbf{A} + HCrO_4^- + H^+ \overset{K_1}{\rightleftharpoons} \mathbf{B} + H_2O \quad (7)$$

$$\mathbf{B} + H^+ \overset{K_2}{\rightleftharpoons} \mathbf{BH}^+ \quad (8)$$

$$\mathbf{BH}^+ \overset{k_1}{\longrightarrow} \text{product (P)} + HCHO + Cr(VI) \quad (9)$$

where **A** = cyclic form of β-D-fructose and



Scheme 1. Cr(VI) oxidation of D-fructose in the absence of PA

In Scheme 1, B denotes the Cr(VI) ester formed through chelation. It is important to mention that the intermediate ester could not be characterized and no kinetic evidence for the intermediate ester formation was available. However, such an ester formation mechanism for the oxidation of alcohols is well documented.[17,18] B experiences acid-catalysed redox decomposition through glycol splitting[18] (i.e. splitting of the C—C bond) giving rise to the lactone of the corresponding C_5-aldonic acid and formaldehyde. The acid-catalysed redox decomposition of C may be considered to involve protonation on the oxygen of the Cr—O bond to generate BH^+ before the electron movement. In fact, such protonation will favour the electron movement towards the chromium centre. A similar observation has been noted by Sala and coworkers.[5a,b] It is worth noting that in the case of glucose, no glycol splitting occurs. This is probably due to the fact that for the cyclic β-pyranoid form of D-glucose, the reactive OH groups are not suitably oriented for chelation with Cr(VI). In the case of the β-form of D-glucose, the equatorial HO-1 group is readily attacked by Cr(VI) to generate the corresponding ester.[9] The glycol splitting in the case of D-fructose generates formaldehyde, which may be further oxidized to formic acid. The Cr(IV) generated may participate in the subsequent faster reactions in different ways [Eqns. ((10)–(14))].[9] It is important to mention that Cr(IV) and Cr(V) intermediates have also been argued[18b] as efficient oxidants to cause glycol splitting.

$$\textbf{Route I:}\ Cr(IV) \overset{Cr(VI)}{\longrightarrow} 2Cr(V) \overset{S}{\longrightarrow} 2Cr(III) \quad (10)$$

$$\textbf{Route II:}\ Cr(IV) \overset{S}{\longrightarrow} Cr(III) + S^{\cdot} \quad (11)$$

$$Cr(VI) \overset{S^{\cdot}}{\longrightarrow} Cr(V) \overset{S}{\longrightarrow} Cr(III) \quad (12)$$

$$\textbf{Route III:}\ Cr(IV) \overset{S}{\longrightarrow} Cr(II) \overset{Cr(VI)}{\longrightarrow} Cr(III) + Cr(V) \quad (13)$$

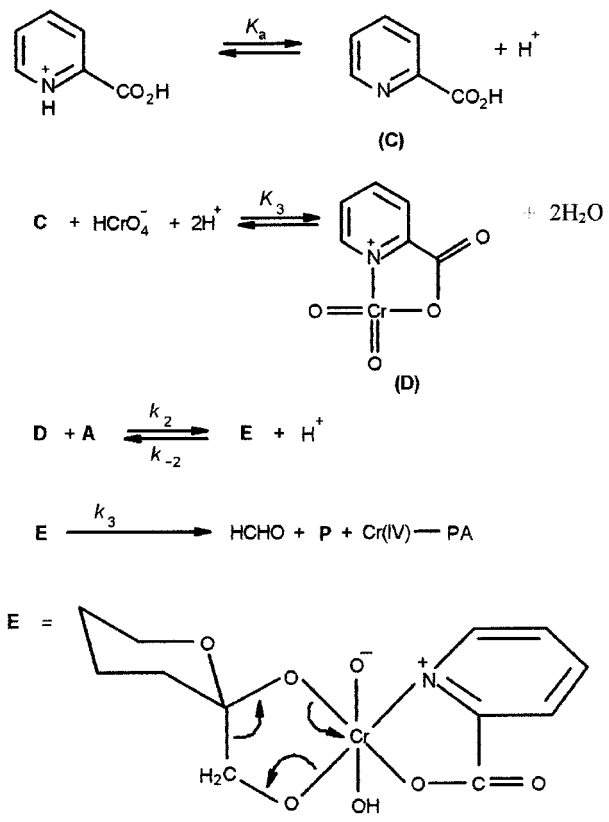
$$Cr(V) \overset{S}{\longrightarrow} Cr(III) \quad (14)$$

In the above routes S is a 2e reductant and $S^{\cdot}$ is the partially oxidized product. In both the Watanabe–Westheimer mechanism[19a] (i.e. Route I) and Perez-Benito Mechanism[20] (i.e. route III), the title organic substrate behaves as a 2e reductant throughout the reaction sequence, but in the Rocek mechanism[19b] (i.e. route I), the organic substrate acts as a 1e reductant towards Cr(IV) and as a 2e reductant towards both Cr(VI) and Cr(V). The Rocek mechanism has been widely accepted for the Cr(VI) oxidation of many organic compounds. Previously, the route involving Cr(II) (i.e. Perez-Benito mechanism) was discarded because of the instability of Cr(II), but in the recent past it has been established[20] that this mechanism operates for the different organic compounds known to act as 2e reductants toward Cr(VI). It has been suggested that in such cases, Cr(IV) is reduced to Cr(II) through a hydride transfer mechanism. By considering the oxidation of D-fructose to formaldehyde and the lactone of C_5-aldonic acid, Scheme **1** leads to the following rate equation:

$$k_{obs(u)} = (2/3)k_1K_1K_2[S]_T[H^+]^2 \quad (15)$$

For the PA-catalysed path, Scheme 2 is reasonable to explain the findings. Here, PA readily forms a reactive cyclic Cr(VI)–PA complex (**D**) which is the active oxidant. Under the experimental conditions, the first-order dependence on $[PA]_T$ is strictly maintained throughout the range of $[PA]_T$ used. Hence it is reasonable to conclude that the equilibrium constant for the

reaction leading to the cyclic Cr(VI)–PA complex is low. In the next step, the Cr(VI)–PA complex reacts with the substrate to form a ternary complex (**E**) which experiences a redox decomposition through glycol splitting with a rate-limiting step giving rise to the organic products and the Cr(IV)–PA complex. Then the Cr(IV)–PA complex may participate in the next faster steps as outlined for the uncatalysed reactions.



P = lactone of C_5-aldonic acid

Scheme 2. Mechanistic aspects of Cr(VI) oxidation of D-fructose in the presence of PA

By considering the glycol splitting as the main reaction, Scheme 2 leads to the following rate equation under the steady-state conditions of the ternary complex **E**:

$$k_{obs(c)} = (2/3)(K_aK_3k_2k_3[PA]_T[S]_T[H^+]^2)/\{(k_{-2}[H^+] + k_3)([H^+] + K_a)\} \quad (20)$$

Neglecting K_a (= 0.025 mol dm^{-3} at 25 °C)[21] compared with [H^+] (= 0.45 –1.20 mol dm^{-3}), Eqn. (20) reduces to

$$k_{obs(c)} = (2/3)(K_aK_3k_2k_3[PA]_T[S]_T[H^+])/(k_{-2}[H^+] + k_3) = k_{cat}[PA]_T \quad (21)$$

which explains the hydrogen ion dependence. Equation (21) conforms to the experimentally observed equation [Eqn. (5)]. Comparison of Eqns (5) and (21) leads to $a = (2/3)(K_aK_3k_2k_3)$, $b = k_3$ and $m = k_{-2}$. Polymerization of acrylonitrile under the experimental conditions was observed in both the presence and absence of PA. Probably the reaction between formaldehyde and Cr(IV) produced in the first step initiates acrylonitrile polymerization. In terms of the Rocek mechanism,[19b] it is believed that Cr(IV) acts as a 1e oxidant towards the 2e reductant giving rise to the organic free radical which initiates the polymerization. On the other hand, according to the Perez-Benito mechanism,[20] Cr(IV) reacts with the 2e reductant through a hydride ion transfer mechanism yielding Cr(II) and a carbocation centre, which is responsible[22] for acrylonitrile polymerization.

The different rate parameters for both the uncatalysed and catalysed paths are given in Table 1. To represent the rate constants in the presence of surfactants, the subscripts CPC and SDS are used and for the values in the absence of surfactants the subscript W is used. The catalytic efficiency of PA is believed to be due to the enhanced $E_{Cr(VI)/Cr(IV)}$ and $E_{Cr(VI)/Cr(III)}$ potentials in the presence of PA. The catalytic efficiency measured by k_{eff} [= $k_{obs(c)}/k_{obs(u)}$] at 0.04 mol dm^{-3} and $H^+ \approx 0.5$ mol dm^{-3} is about 10 (cf. Table 1), which is considerably lower than for acyclic alcohol oxidation.[6a] The highly negative value of $\Delta S^{\neq}$ is inconsistent with the proposed cyclic transition state for glycol splitting (cf. Scheme 2).

Effect of CPC

CPC, a representative cationic surfactant, is found to retard both the uncatalysed and catalysed paths. The plot of k_{obs} vs [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 observed by

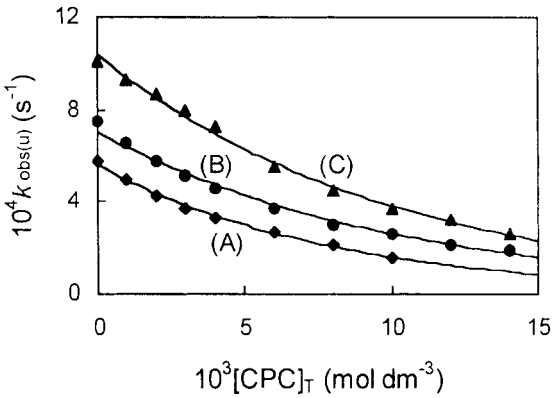


Figure 4. Effect of [CPC]$_T$ on $k_{obs(u)}$ for the Cr(VI) oxidation of D-fructose in the presence of CPC in aqueous H_2SO_4 media. [Cr(VI)]$_T$ = 2 × 10^{-3} mol dm^{-3}, [H_2SO_4] = 1.0 mol dm^{-3}, [D-fructose]$_T$ = 0.07 mol dm^{-3}. (A) 30 °C; (B) 35 °C; (C) 40 °C

Bunton and Cerichelli[23] in the oxidation of ferrocene by Fe(III) salts in the presence of cationic cetyltrimethylammonium bromide (CTAB). Similar observations have also been noted by Panigrahi and Sahu[24] in the oxidation of acetophenone by Ce(IV) and by Sarada and Reddy[25] in the oxalic acid-catalysed oxidation of aromatic azo compounds by Cr(VI) in the presence of SDS. In the uncatalysed path, the neutral Cr(VI)–substrate ester formed [cf. Eqn. (7)] 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 [cf. Eqn. (8)] inhibits the reaction. The Cr(VI)–ester species is likely to be present in the Stern layer. It may be noted that for the uncatalysed reaction, the other species H_2CrO_4 and/or substrate (i.e. D-fructose) may also be partitioned in the micellar interphase. Simultaneous partitioning of both H_2CrO_4 and substrate is equivalent to the partitioning of the Cr(VI)–ester. In the PA-catalysed path, CPC restricts the positively charged Cr(VI)–PA complex [cf. Eqn. (17)] in the aqueous phase and thus the accumulated neutral substrate in the micellar phase cannot participate in the reaction. Hence in both the uncatalysed and PA-catalysed paths the reaction is mainly restricted to the aqueous phase.

To interpret the observed kinetic data, the applicability of the pseudo-phase kinetic model proposed by Menger and Portnoy[26] may be considered. This model considers the partitioning of one reactant between the aqueous and micellar phases and leads to the following rate equation:

$$k_{obs} = (k_w + k_m K_B[D_n])/(1 + K_B[D_n]) \qquad (22)$$

where k_w and k_m are the first-order rate constants in the aqueous and micellar phase, respectively, and include the concentration of the other reactant in these pseudo-phases. K_B gives the measure of the binding constant of the reactant (which is partitioned) with the micelles. $[D_n]$ is the concentration of the micelles and is related to the stoichiometric concentration of the surfactant ($[D]_T$), critical micellar concentration (cmc) and the aggregation number (N), i.e. $[D_n] = ([D]_T - \text{cmc})/N$. Equation (22) leads to

$$1/(k_w - k_{obs}) = 1/(k_w - k_m) + (N/K_B)\{1/([D]_T - \text{cmc})\}\{1/(k_w - k_m)\} \qquad (23)$$

$$(k_w - k_{obs})/(k_{obs} - k_m) = P = (K_B/N)[D]_T - (K_B/N)(\text{cmc}) \qquad (24)$$

To deal with Eqns (23) and (24) one requires the knowledge of the cmc, which is not available under the present kinetic conditions. However, by taking the literature value[27] of cmc (= 8×10^{-4} mol dm^{-3}) under comparable conditions at 35 °C, the plot of $1/(k_w - k_{obs})$ vs $1/([D] - \text{cmc})$ is linear (Fig. 5) at fixed concentrations of the other reactants. This leads to $k_m \approx 0$ for both $k_{obs(u)}$ and $k_{obs(c)}$. Taking $k_m \approx 0$, Eqn. (22) takes the form

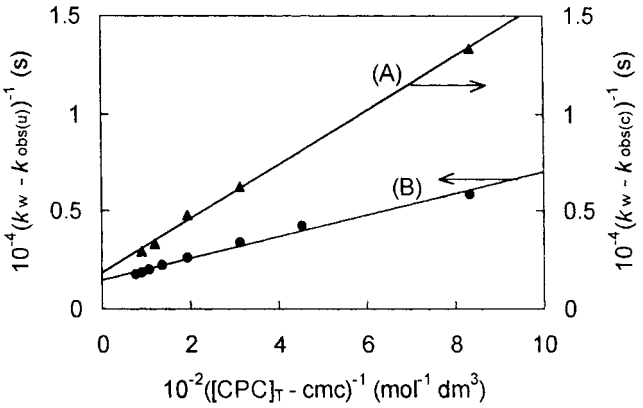


Figure 5. Applicability of the Menger–Portnoy model [i.e plot of $(k_w - k_{obs(x)})^{-1}$ vs $([CPC]_T - cmc)^{-1}$, where x = u or c] to explain the micellar effect on $k_{obs(x)}$ for the Cr(VI) oxidation of D-fructose in the presence of CPC in aqueous H_2SO_4 media (taking cmc = 8×10^{-4} mol dm^{-3}). (A) $k_{obs(c)}$, i.e. PA-catalysed path, $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, $[PA]_T = 0.02$ mol dm^{-3}, $[D\text{-fructose}]_T$ = 0.04 mol dm^{-3}, 35 °C. (B) $k_{obs(u)}$, i.e. in the absence of PA, $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[D\text{-fructose}]_T = 0.07$ mol dm^{-3}, 35 °C

$$1/k_{obs} = 1/k_w + (K_B/N)\{([D]_T - \text{cmc})/k_w\} \qquad (25)$$

The linearity of the plot of $1/k_{obs}$ vs $([D]_T - \text{cmc})$ was verified (not shown) and indicates that the reaction occurs predominantly in the aqueous phase. The k_w value obtained from the intercept agrees well with the experimentally observed value. The magnitude of the binding constant (K_B/N) indicates the depletion of the concentration of the reactant (which may be either the neutral Cr(VI)–substrate ester complex or substrate) in the aqueous phase. This brings about a lowering of the rate with increasing surfactant concentration. In fact, the reaction is strongly acid catalysed, but H^+ ions are not available in the cationic micellar phase produced by CPC owing to electrostatic repulsion. Consequently, the reaction cannot proceed in the micellar phase even when Cr(VI)–substrate ester [which needs H^+ for its redox decomposition, cf. Eqn. (9)] is absorbed in the micellar pseudo-phase.

The rate data in the presence of surfactants were subjected to the Piszkiewicz model[28] analogous to the Hill model applied to the enzyme-catalysed reactions. The Piszkiewicz model relates cooperativity between the neutral species and surfactant to aggregate to form the reactive micelles and its contribution to the rate is given by

$$\log[(k_{obs} - k_w)/(k_m - k_{obs})] = \log P = n \log[D]_T - \log K_D \qquad (26)$$

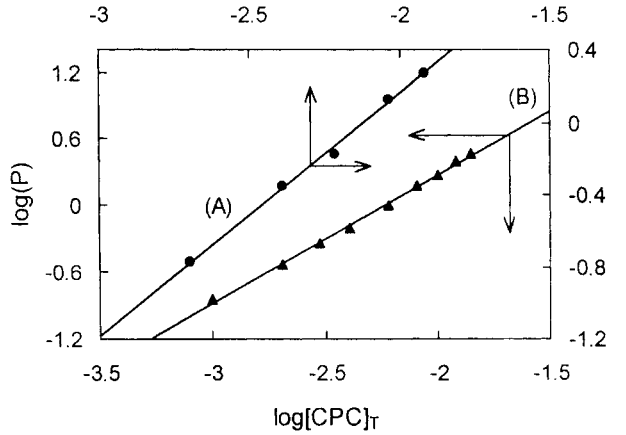


Figure 6. Applicability of the Piszkiewicz model (i.e. plot of log$P$ vs log$[CPC]_T$) to explain the micellar effect on $k_{obs(x)}$ (where x = u or c) for the Cr(VI) oxidation of D-fructose in the presence of CPC in aqueous H_2SO_4 media. (A) PA-catalysed path, i.e. $k_{obs(c)}$, $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, $[PA]_T = 0.02$ mol dm^{-3}, $[D\text{-fructose}]_T$ = 0.04 mol dm^{-3}, 35 °C. (B) Uncatalysed path, i.e. $k_{obs(u)}$, $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[D\text{-fructose}]_T$ = 0.07 mol dm^{-3}, 35 °C P is defined as $P = [k_w - k_{obs(x)}]/[k_{obs(x)} - k_m]$

Table 2. Kinetic parameters (35 °C) of micellar effect for the Cr(VI) oxidation of D-fructose in the presence and absence of PA

Parameters	Effect of CPC		Effect of SDS[g]
	PA absent[a]	PA present[b]	
$\text{Log}(K_B/N)$	2.32[c] 2.30[d] 2.30[e]		
$-\text{Log}K_D$	2.68[f]	2.85	2.61
n	1.2	1.35	1.8
$-\text{Log}[D]_{50}$ (calculated)	2.23	2.13	1.45
$-\text{Log}[D]_{50}$ (found)	2.20	2.10	1.4

[a] In the absence of PA [i.e. $k_{obs(u)}$]: $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[S]_T = 0.07$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}.
[b] For PA-catalysed path [i.e. $k_{obs(c)}$]: $[Cr(VI)]_T = 1.13 \times 10^{-3}$ mol dm^{-3}, $[S]_T = 0.04$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[PA]_T = 0.02$ mol dm^{-3}.
[c] cf. Eqn. (23).
[d] cf. Eqn. (24).
[e] cf. Eqn. (25).
[f] cf. Eqn. (26).
[g] In the absence of PA [i.e. $k_{obs(u)}$]: $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[S]_T = 0.03$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}.

where K_D is the dissociation constant of micellized surfactant back to its components and n is the index of cooperativity. The advantage of Eqn. (26) is that it does not require the knowledge of the cmc of the surfactant used. This helps a larger number of data to come under the purview of analysis. Although Eqn. (26) was originally developed for micelle-catalysed reactions showing a maximum rate followed by inhibition, the model has been applied by different workers[24,25,29] to explain the micellar effect in which the reaction is inhibited or catalysed by the micelle over the whole range as observed in the present system. By using Eqn. (26), i.e. the plot of log P vs $\log[D]_T$ (Fig. 6), the different parameters n, $\log[D]_{50}$ (where $\log[D]_{50}$ represents the concentration of surfactant required for half-maximum catalysis or inhibition) and $\log K_D$ have been determined (cf. Table 2). The calculated $\log[D]_{50}$ values conform well with the experimentally observed values. The values of n = 1–2, far less than the aggregation number (20–100) of the surfactant molecules[28] leading to micelles, indicate the existence of catalytically productive submicellar aggregates. The non-integral values of n indicate the existence of multiple equilibria in the formation of catalytically active submicellar aggregates. When the interaction (measured by $-\log K_D$) is fairly high, it is appropriate to consider n as representing the average stoichiometry of the detergent–reactant aggregate. The simultaneous applicability of the different kinetic models (i.e. Menger–Portnoy model[26] and Piszkiewicz model[28]) based on different mathematical assumptions is not surprising. In fact, both of these models lead to similar final equations [Eqns (24) and (26)]. From the effect of $[CPC]_T$ on the activation parameters (Fig. 7), it is evident that the rate retardation in the presence of CPC mainly arises due to the higher $\Delta H^{\neq}$ values.

Effect of SDS

SDS, a representative anionic surfactant, catalyses both the uncatalysed and PA-catalysed paths. In the PA-catalysed path, the rate acceleration arises owing to the preferential partitioning of the positively charged Cr(VI)–PA complex (by electrostatic attraction) and neutral substrate in the micellar interphase. Thus SDS allows the reaction to proceed in both aqueous and

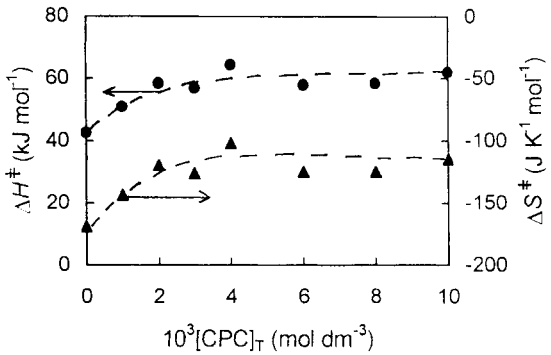


Figure 7. Effect of $[CPC]_T$ on the activation parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) of $k_{obs(u)}$ for the Cr(VI) oxidation of D-fructose in the presence of CPC in aqueous H_2SO_4 media. $[Cr(VI)]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[D\text{-fructose}]_T$ = 0.07 mol dm^{-3}

micellar interphases. In the absence of PA, binding of H_2CrO_4 (kinetically active species[30a,b]) and substrate to the SDS micelles has been argued by different workers.[30c,d] However, the possibility of partitioning of the neutral Cr(VI)–substrate ester [*cf.* Eqn. (7)] into the micellar phase cannot be ruled out. However, simultaneous partitioning of H_2CrO_4 and substrate is equivalent to the partitioning of Cr(VI)–substrate ester. Hence it leads to higher local concentrations of both the reactants at the micelle-water interphase compared with their stoichiometric concentrations. The H^+ ions needed for the reactions are also preferably attracted to the micellar phase. Thus SDS allows the reaction in both the phases with a preferential rate enhancement in the micellar phase. The observed catalysis can be explained by considering the pseudo-phase ion-exchange (PIE) model,[31] which considers the micellar and aqueous phase as two distinct phases and in the present system the title redox reaction occurs in both the phases. The reaction is acid catalysed and the corresponding exchange equilibrium between H^+ ion and Na^+ ion at the micellar surface is

$$H_W{}^+ + Na_M{}^+ \rightleftharpoons H_M{}^+ + Na_W{}^+ \qquad (27)$$

The ion-exchange equilibrium constant ($K_{ex}{}^H$) is defined as

$$K_{ex}{}^H = [H_M{}^+][Na_W{}^+]/[H_W{}^+][Na_M{}^+] \qquad (28)$$

where the subscripts M and W denote the micellar and aqueous phase, respectively. The concentrations are expressed in terms of the total solution volume and it is further assumed that the activity coefficient ratios, $\gamma_M(Na^+)/\gamma_M(H^+)$ and $\gamma_W(Na^+)/\gamma_W(H^+)$, are each equal to unity. Considering the competition between Na^+ and H^+ only, the overall micellar binding parameter is given by

$$\begin{aligned}\beta &= m_H + m_{Na} = [H_M{}^+]/[D_n] + [Na_M{}^+]/[D_n] \\ &= ([H_M{}^+] + [Na_M{}^+])/[D_n] \end{aligned} \qquad (29)$$

Thus, β gives the fraction of micellar head-groups neutralized. $[D_n]$ gives the micellized surfactant concentration, i.e. $[D_n] = [SDS]_T - cmc$. The various concentration terms are expressed as $[H_M^+] = m_H[D_n]$, $[H_W^+] = [H^+]_T - [H_M^+] = [H^+]_T - m_H[D_n]$, $[Na_W^+] = [Na^+]_T - [Na_M^+] = [Na^+]_T - (\beta - m_H)[D_n]$ and $[Na_M^+] = [Na^+]_T - [Na_W^+] = (\beta - m_H)[D_n]$.

The ion-exchange equilibrium constant can be expressed as:

$$\begin{aligned}K_{ex}{}^H = m_H\{[Na^+]_T - (\beta - m_H)[D_n]\}/(\beta \\ - m_H)([H^+]_T - m_H[D_n])\end{aligned} \qquad (30)$$

On rearrangement Eqn. (30) yields

$$\begin{aligned}&(m_H)^2(K_{ex}{}^H - 1)[D_n] - m_H\{K_{ex}{}^H[H^+]_T + [Na^+]_T \\ &+ \beta[D_n](K_{ex}{}^H - 1)\} + K_{ex}{}^H\beta[H^+]_T \\ &= 0\end{aligned} \qquad (31)$$

Thus $[H_M^+]$ (= $m_H[D_n]$) can be calculated by using Eqn. (31). The positively charged Cr(VI)–PA complex is the active oxidant (Ox^+) in the PA-catalysed path and it may also participate in a similar exchange equilibrium:

$$Ox_W{}^+ + Na_M{}^+ \rightleftharpoons Ox_M{}^+ + Na_W{}^+, \; K_{ex}{}^{Ox} \qquad (32)$$

The magnitude of $[Ox_M^+]$ can also be calculated by using the analogous equation [*cf.* Eqn. (31)] involving $K_{ex}{}^{Ox}$. For H^+ ions, $K_{ex}{}^H$ is close to unity.[30d,32] This indicates that there is no specific interaction of H^+ ions or Na^+ ions with the micellar surface and consequently these ions are statistically distributed between the aqueous and micellar phases. If $K_{ex}{}^H \rightarrow 1$, then Eqn. (31) leads to

$$[H_M{}^+] = ([H^+]_T\beta[D_n])/([H^+]_T + [Na^+]_T) \qquad (33)$$

The value of β has been found to be in the range 0.6–0.85 from conductivity measurements.[30d,31] It is evident that $[H_M^+]$ increases with increase in $[D_n]$. It is important to mention that the change in polarity of the medium (specifically in the intermicellar zone in which the reactants are positioned) with the addition of surfactant may also influence the observed micellar effect.[30d] From the plot of k_{obs} vs $[SDS]_T$ (not shown), it is evident that the rate initially increases, but it tends to level off at higher $[SDS]_T$. In fact, an increase in $[SDS]_T$ increases the micellar counterions (i.e. Na^+) which may displace H^+ and Ox^+ ions, from the micellar surface to drive the equilibria (27) and (32) to the left. This reduces $[H_M^+]$ and $[Ox_M^+]$ to inhibit the rate process in the micellar phase. Owing to these opposing factors (i.e. dilution of all reactants over micelles at higher $[SDS]_T$), k_{obs} initially increases with increase in $[SDS]_T$, but it attains a limiting value at higher $[SDS]_T$.

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