

Micellar Effect on the Reaction of Picolinic Acid Catalyzed Chromium(VI) Oxidation of Dimethyl Sulfoxide in Aqueous Acidic Media: A Kinetic Study

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ABSTRACT: The kinetics and mechanism of picolinic acid (PA) catalyzed oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone by chromium(VI) in both aqueous H_2SO_4 and HClO_4 media have been studied in the absence and presence of surfactants at different temperatures. Cr(VI)–PA complex formed in preequilibrium steps is the active oxidant that experiences the nucleophilic attack by DMSO to form a positively charged intermediate ternary complex. Within the proposed ternary complex, an oxygen transfer or a ligand coupling or both occurs to generate the product, dimethyl sulfone. Cr(VI) is ultimately converted to Cr(III)–PA complex. Under the experimental conditions, the process shows a first-order dependence on each of the reactants (i.e., $[\text{Cr(VI)}]_T$, $[\text{PA}]_T$, $[\text{DMSO}]_T$, and $[\text{H}^+]$). HCrO_4^- has been found kinetically active. The reaction is catalyzed by sodium dodecyl sulfate (SDS, a representative anionic surfactant) monotonically, while cetylpyridinium chloride (CPC, a representative cationic surfactant) retards the reaction continuously. The observed micellar effects have been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants. A pseudo-phase ion exchange (PIE) model has been applied to explain the micellar effect. The Piszkiwicz cooperative model has been applied to determine the kinetic parameters, and it indicates the existence of catalytically productive submicellar aggregates. Because of this reactant-promoted micellization of the surfactant before or below the cmc value, the present systems do not show any discontinuity at the respective reported cmc values of the surfactants. © 2001 John Wiley & Sons, Inc. *Int J Chem Kinet* 33: 173–181, 2001

INTRODUCTION

Among the different chelating agents acting as catalysts [1–7] in Cr(VI) oxidation, picolinic acid (PA) is

quite unique [8–11]. It does not get cooxidized with the target reductant, but it is gradually lost during the reaction due to the formation of inert Cr(III)–PA complex. In this sense, PA is not a true catalyst; however, conventionally the reactions are described as PA-catalyzed reactions. Recently, we have investigated the mechanistic aspects of Cr(VI) oxidation of dimethyl

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sulfoxide (DMSO) in aqueous HClO₄ media in the presence of PA [11]. In fact, in the absence of any external catalyst, the title reaction practically does not go on in both aqueous HClO₄ and H₂SO₄ media. In fact, Cr(VI) can oxidize DMSO slowly without any catalyst only under drastic conditions [12,13]. The mechanistic aspects of oxidation of DMSO by Cr(VI) in the presence of PA and absence of PA are significantly different [11–13]. Our preliminary observation indicates that the different types of surfactants can significantly influence the PA-catalyzed oxidation of DMSO. The present paper describes the detailed micellar effect on the title reaction to provide a better insight to the reaction mechanism. It also explores the kinetics and reaction mechanism of the title reaction in aqueous H₂SO₄ media and compares the catalytic efficiency of PA in aqueous H₂SO₄ and HClO₄ media. This comparison is meaningful to understand the medium effect on the title reaction.

EXPERIMENTAL

Materials and Reagents

PA (Fluka) was used after recrystallization from methanol (m.p. 136°C). DMSO (SRL, AR) was purified and standardized as described previously [14]. Standard stock solution of Ce(IV) in aqueous H₂SO₄ media was prepared from Ce(SO₄)₂, 2(NH₄)₂SO₄ (AR, Himedia). K₂Cr₂O₇, sodium dodecyl sulfate (SDS), and cetylpyridinium chloride (CPC), and all other chemicals used were of AR/GR grade or purified by standard procedures.

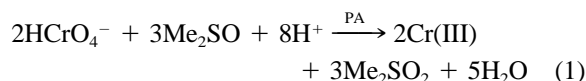
Procedure and Kinetic Measurements

The progress of the reaction was monitored by following the rate of disappearance of Cr(VI). The concentration of Cr(VI) at different time intervals was measured by titrimetric quenching technique using excess of standard Mohr's solution, and the unreacted Fe(II) was determined by standard Ce(IV) solution using fer-

roin indicator. The pseudo-first-order rate constants (k_{obs}) were calculated from the slopes of plots of $\log[\text{Cr(VI)}]$ vs. time (t), which were linear at least up to 3 half-lives. However, for very low [PA], the initial slopes were considered to evaluate k_{obs} . Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) during the time period of kinetic runs has been investigated in the absence of title substrate, and this path has been found kinetically insignificant. To circumvent the solubility problem, different acids—perchloric and sulfuric acids—have been used to follow the effects of anionic surfactant (SDS) and cationic surfactant (CPC), respectively. Errors associated with the different rate constants and activation parameters were estimated as usual [15].

Product Analysis and Stoichiometry

Under the kinetic conditions, DMSO is oxidized to dimethyl sulfone (Me₂SO₂), characterized by m.p. (109°C), and Cr(VI) is finally reduced to a Cr(III)–PA complex. The $\Delta[\text{Cr(VI)}] : \Delta[\text{DMSO}]$ ratio was also estimated. Completion of the reaction was indicated by the disappearance of Cr(VI) color. The unreacted DMSO was estimated by Ce(IV) [16]. The stoichiometry conforms to



RESULTS AND DISCUSSION

Dependence on [Cr(VI)]_T

Under the experimental conditions, the rate of disappearance of Cr(VI) shows a first-order dependence on [Cr(VI)]. The pseudo-first-order rate constant (k_{obs}) decreases with the increase of [Cr(VI)]_T but $k_{\text{obs}}[\text{Cr(VI)}]_T/[\text{HCrO}_4^-]$ remains more or less constant (cf. Table I). The values of [HCrO₄[−]] were calculated by using Eq. (2), considering the dimerization equilib-

Table I Effect of [Cr(VI)]_T on k_{obs} for the PA-Catalyzed Cr(VI) Oxidation of DMSO in the Presence of SDS at 35°C. [PA]_T = 0.03 mol dm^{−3}, [HClO₄] = 0.5 mol dm^{−3}, [SDS]_T = 0.02 mol dm^{−3}, I = 1.5 mol dm^{−3}

10 ³ [Cr(VI)] _T	:	0.70	1.0	1.5	2.0	2.4	2.75
10 ³ [HCrO ₄ [−]]	:	0.64	0.88	1.26	1.60	1.87	2.10
10 ⁴ k_{obs}/s^{-1}	:	5.80	5.60	5.40	5.20	5.10	4.95
10 ⁴ $k_{\text{obs}}\{[\text{Cr(VI)}]_T/[\text{HCrO}_4^-]\}$:	6.30	6.40	6.50	6.50	6.53	6.48

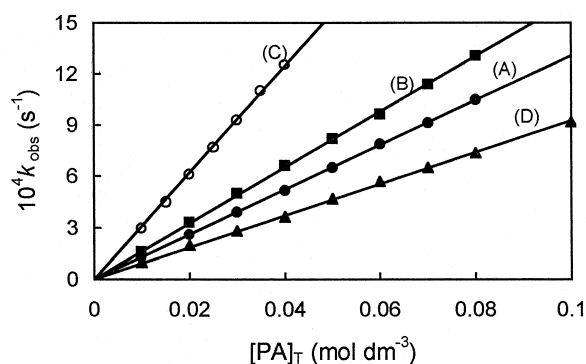


Figure 1 Effect of $[PA]_T$ on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous H_2SO_4 media in the presence (D) and absence (A, B, C) of the surfactant cetylpyridinium chloride (CPC). $[Cr(VI)]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.5 \text{ mol dm}^{-3}$; $[DMSO]_T = 0.2 \text{ mol dm}^{-3}$. A (30°C); B (35°C); C (45°C); D (35°C, $[CPC]_T = 0.004 \text{ mol dm}^{-3}$).

rium constant (Q_d) [17] of the process, $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, and neglecting the subsidiary equilibrium, $HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$. It indicates that under the experimental conditions, the monomeric species $HCrO_4^-$ is the kinetically active species [18,19].

$$[HCrO_4^-] = \{(1 + 8Q_d[Cr(VI)]_T)^{1/2} - 1\}/4Q_d \quad (2)$$

For the present studies, to explore the dependence of rate on other reactants and parameters, the Cr(VI) concentration used was $2 \times 10^{-3} \text{ mol dm}^{-3}$. The estimated k_{obs} values were used without any correction.

Dependence on $[PA]_T$

At fixed $[DMSO]_T$, $[Cr(VI)]_T$, and $[H_2SO_4]$, $[PA]_T$ was varied in the $0.01-0.08 \text{ mol dm}^{-3}$ range. The plots of k_{obs} vs. $[PA]_T$ (cf. Fig. 1) are linear ($r > 0.98$) without any intercept, indicating the nonexistence of the uncatalyzed path under the experimental conditions. This is also verified by carrying out an independent experiment in the absence of PA. Thus, the observation is expressed as

$$k_{\text{obs}} = k_{\text{cat}}[PA]_T \quad (3)$$

In aqueous $HClO_4$ media, the same observation has also been noted [11]. The first-order dependence on $[PA]_T$ is also maintained in the presence of both SDS and CPC [cf. Fig. 1].

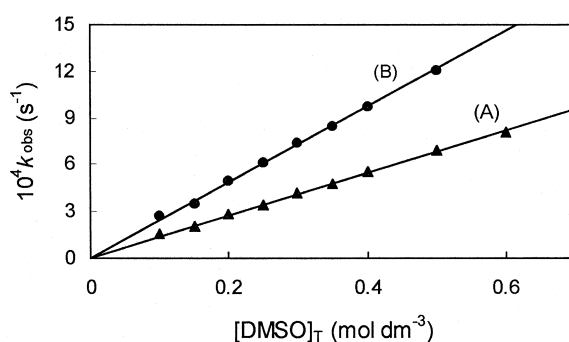


Figure 2 Effect of $[DMSO]_T$ on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous H_2SO_4 media in the presence (A) and absence (B) of the surfactant cetylpyridinium chloride (CPC). $[Cr(VI)]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 0.5 \text{ mol dm}^{-3}$; $[PA]_T = 0.03 \text{ mol dm}^{-3}$; 35°C. A ($[CPC]_T = 0.004 \text{ mol dm}^{-3}$); B (in the absence of CPC).

Dependence on $[DMSO]_T$

At fixed $[H^+]$, $[Cr(VI)]_T$, and $[PA]_T$, k_{obs} shows a first-order dependence on $[DMSO]_T$ both in the absence and presence of the surfactants (cf. Fig. 2), that is,

$$k_{\text{obs}} = k_s[DMSO]_T \quad (4)$$

Dependence on $[H^+]$

At fixed $[DMSO]_T$, $[Cr(VI)]_T$, and $[PA]_T$, k_{obs} shows a first-order dependence on $[H^+]$ both in the presence

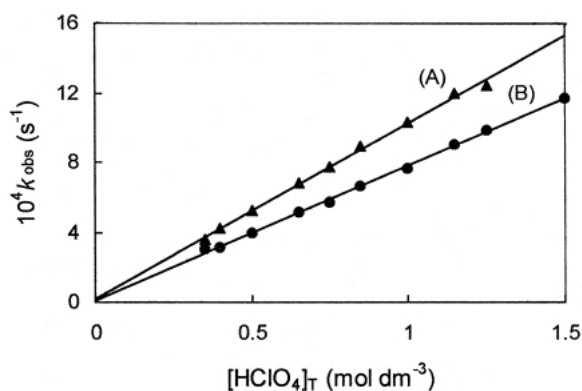


Figure 3 Effect of $[HClO_4]_T$ on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous $HClO_4$ media in the presence (A) and absence (B) of the surfactant sodium dodecyl sulfate (SDS). $[Cr(VI)]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $I = [HClO_4] + [NaClO_4] = 1.5 \text{ mol dm}^{-3}$; $[DMSO]_T = 0.1 \text{ mol dm}^{-3}$; 35°C. A ($[SDS]_T = 0.02 \text{ mol dm}^{-3}$); B (in the absence of SDS).

and absence of the surfactants (cf. Fig. 3), that is,

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

Dependence on $[\text{SDS}]_T$ and $[\text{CPC}]_T$

In the presence of both SDS and CPC, the first-order dependence on each of the reactants (i.e., $[\text{DMSO}]_T$, $[\text{H}^+]$, and $[\text{PA}]_T$) is maintained, but the rates are catalyzed in the presence of SDS and inhibited in the presence of CPC (cf. Figs. 4 and 5). We have already mentioned that to circumvent the solubility problem, different acids (i.e., HClO_4 and H_2SO_4) have been used for the anionic (SDS) and cationic (CPC) surfactants, respectively. The corresponding rate constants $k_{s(x)}$ and $k_{\text{cat}(x)}$ (i.e., $k_{s(w)}$, $k_{s(\text{CPC})}$, $k_{s(\text{SDS})}$, $k_{\text{cat}(w)}$, $k_{\text{cat}(\text{SDS})}$, and $k_{\text{cat}(\text{CPC})}$) are given in Table II. Here, the subscript x denotes the media (i.e., w indicates the values in the absence of any surfactant, CPC indicates the corresponding values in the presence of CPC, and similarly SDS indicates the corresponding values in the presence of SDS). From the plots of k_{obs} vs. $[\text{surfactant}]_T$ (cf. Figs. 4 and 5), it is evident that in the whole range of $[\text{surfactant}]_T$ used, the rate increases continuously for SDS and it decreases continuously for CPC.

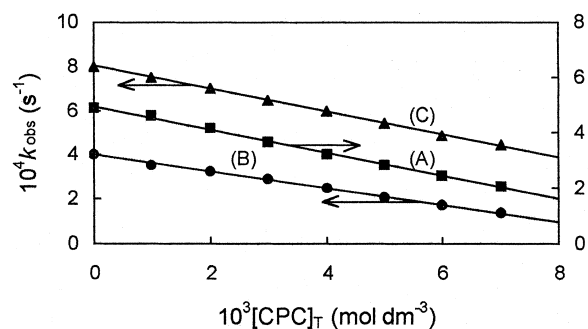


Figure 4 Effect of $[\text{CPC}]_T$ on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous H_2SO_4 media. $[\text{Cr(VI)}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$; $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$; $[\text{DMSO}]_T = 0.1 \text{ mol dm}^{-3}$. B (30°C); A (35°C); C (45°C).

Effect of Temperature

The effect of temperature on the rate constants (k_{obs}) in the presence and absence of surfactants has been followed, and the activation parameters have been estimated by using the Eyring equation. The dependence of activation parameters on $[\text{surfactant}]_T$ is shown in Figs. 6 and 7.

Table II Kinetic Parameters of the PA-Catalyzed Cr(VI) Oxidation of DMSO in the Presence and Absence of Surfactants, $[\text{Cr(VI)}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$

In Aqueous HClO_4 Media, (35°C, I = 1.5 mol dm^{-3})						
(a)		(b)		(c)		
$10^3 k_{\text{cat}(w)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{\text{cat}(\text{SDS})}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{\text{H}(w)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{\text{H}(\text{SDS})}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{s(w)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{s(\text{SDS})}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
12.0 ± 0.1	16.3 ± 0.2	0.78 ± 0.05	1.04 ± 0.06	4.1 ± 0.08	5.2 ± 0.07	
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	41 ± 3					
$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	-153 ± 9					
In Aqueous H_2SO_4 Media						
(d)				(e)		
$10^3 k_{\text{cat}(w)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$			$10^3 k_{\text{cat}(\text{CPC})}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{s(w)}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^3 k_{s(\text{CPC})}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	
30°C	35°C	45°C	35°C	35°C	35°C	
13.0 ± 0.2	16.2 ± 0.2	31.2 ± 1.0	9.2 ± 0.1	2.4 ± 0.07	1.4 ± 0.03	
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	46 ± 2					
$\Delta S^\ddagger/\text{J K}^{-1} \text{ mol}^{-1}$	-131 ± 8					

(a) $[\text{S}]_T = 0.1 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{SDS}]_T = 0.02 \text{ mol dm}^{-3}$, $[\text{PA}]_T = 0.01 - 0.12 \text{ mol dm}^{-3}$.

(b) $[\text{S}]_T = 0.1 \text{ mol dm}^{-3}$, $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$, $[\text{SDS}]_T = 0.02 \text{ mol dm}^{-3}$.

(c) $[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$, $[\text{SDS}]_T = 0.02 \text{ mol dm}^{-3}$.

(d) $[\text{S}]_T = 0.02 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $10^3[\text{CPC}]_T = 4.0 \text{ mol dm}^{-3}$, $[\text{PA}]_T = 0.01 - 0.10 \text{ mol dm}^{-3}$.

(e) $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$, $10^3[\text{CPC}]_T = 4.0 \text{ mol dm}^{-3}$.

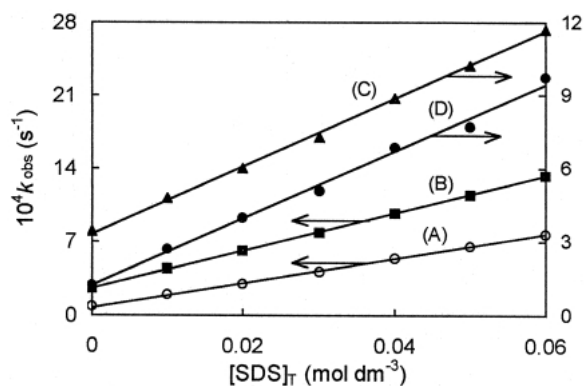


Figure 5 Effect of $[\text{SDS}]_T$ on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous HClO_4 media. $[\text{Cr(VI)}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HClO}_4] = 0.25 \text{ mol dm}^{-3}$; $I = [\text{HClO}_4] + [\text{NaClO}_4] = 1.5 \text{ mol dm}^{-3}$; $[\text{DMSO}]_T = 0.1 \text{ mol dm}^{-3}$ (A, B, D), $= 0.2 \text{ mol dm}^{-3}$ (C). A (30°C); D (35°C); B (45°C); C (35°C).

Test for Free-Radical Formation

Under the experimental conditions, acrylonitrile was added to the reaction mixture in the presence and absence of the said surfactants. It leads to polymerization of acrylonitrile on standing, indicating formation of free radicals in both cases.

Mechanism of the Reaction and Micellar Effect

It is suggested that Cr(VI)–PA complex (i.e., species II) undergoes complexation with DMSO, then “O”

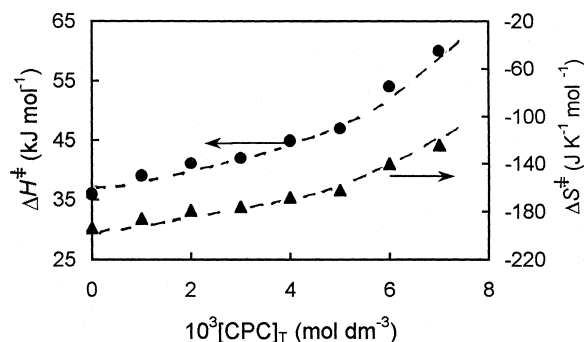


Figure 6 Effect of $[\text{CPC}]_T$ on the activation parameters (ΔH^\ddagger , ΔS^\ddagger) of k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous H_2SO_4 media in the presence of the surfactant cetylpyridinium chloride (CPC). $[\text{Cr(VI)}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$; $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$; $[\text{DMSO}]_T = 0.1 \text{ mol dm}^{-3}$.

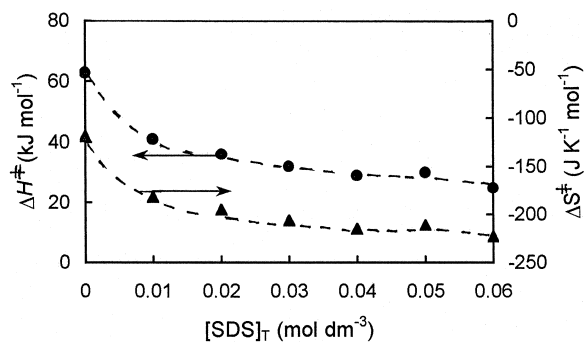


Figure 7 Effect of $[\text{SDS}]_T$ on the activation parameters (ΔH^\ddagger , ΔS^\ddagger) of k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous HClO_4 media in the presence of the surfactant sodium dodecyl sulfate (SDS). $[\text{Cr(VI)}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HClO}_4] = 0.25 \text{ mol dm}^{-3}$; $I = [\text{HClO}_4] + [\text{NaClO}_4] = 1.5 \text{ mol dm}^{-3}$; $[\text{PA}]_T = 0.03 \text{ mol dm}^{-3}$; $[\text{DMSO}]_T = 0.1 \text{ mol dm}^{-3}$.

transfer or ligand coupling leads to the product (cf. Scheme I). At the next faster steps, Cr(IV)–PA complex participates as given in Scheme I. Formation of the free radicals is evidenced through the polymerization of acrylonitrile. Under the steady-state approximation to the species III, Scheme I leads to the following rate equation, Eq. (14):

$$-d\ln[\text{HCrO}_4^-]/dt = k_{\text{obs}} = (2/3)(KK_a k_1 k [\text{PA}]_T / [\text{DMSO}]_T [\text{H}^+]^2) / \{(k_{-1} + k)([\text{H}^+] + K_a)\} \quad (14)$$

$$= m[\text{PA}]_T [\text{DMSO}]_T, \text{ (at fixed } [\text{H}^+]) \quad (15)$$

The rate law above can be derived from the following relations:

$$-d[\text{HCrO}_4^-]/dt = k[\text{III}] \quad (16)$$

$$d[\text{III}]/dt = 0 = k_1[\text{DMSO}]_T[\text{II}] - (k_{-1} + k)[\text{III}] \quad (17)$$

or,

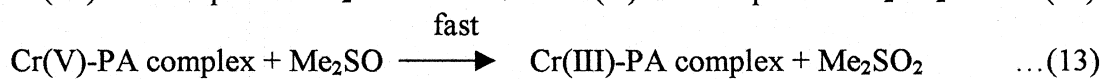
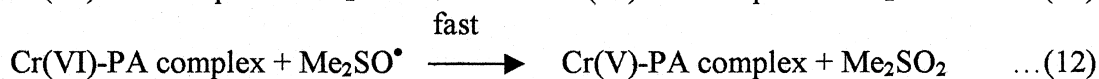
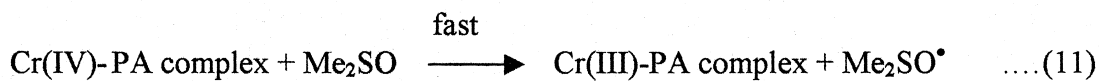
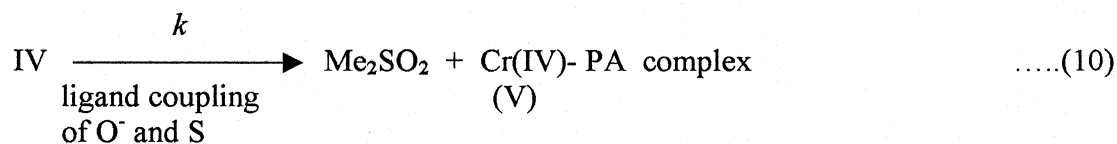
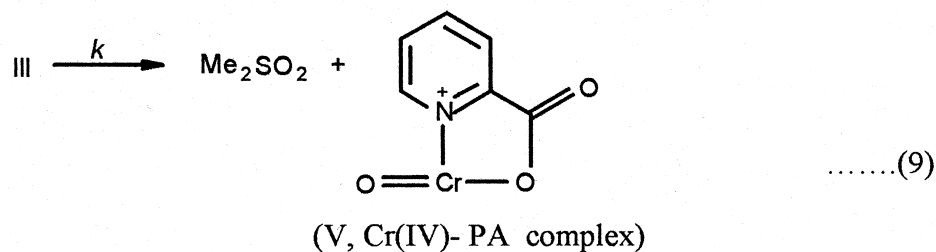
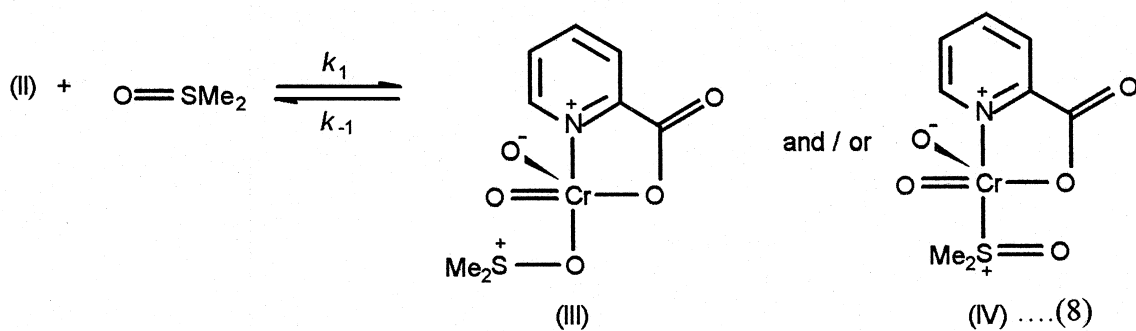
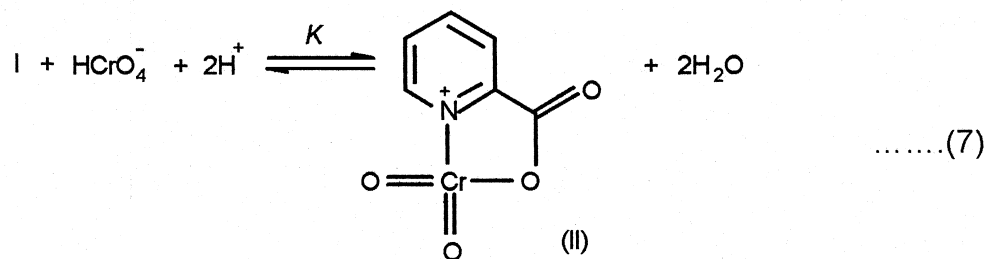
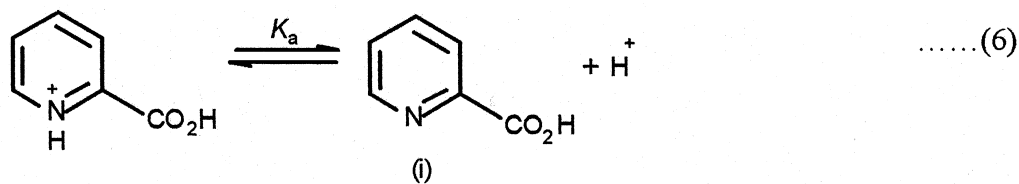
$$[\text{III}] = k_1[\text{DMSO}]_T[\text{II}] / (k_{-1} + k) \quad (18)$$

where $[\text{DMSO}] \approx [\text{DMSO}]_T$ under the condition $[\text{DMSO}]_T \gg [\text{Cr(VI)}]_T$.

$$\begin{aligned} [\text{II}] &= K[\text{PA}][\text{HCrO}_4^-][\text{H}^+]^2 \\ &= KK_a[\text{HCrO}_4^-][\text{H}^+]^2[\text{PA}]_T / (K_a + [\text{H}^+]) \end{aligned} \quad (19)$$

where

$$[\text{PA}]_T = [\text{PA}] + [\text{PAH}^+] \quad (20)$$

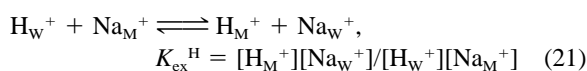


Scheme I

Thus, $k_{\text{cat}} = m[\text{DMSO}]_T$ and $k_s = m[\text{PA}]_T$. Neglecting K_a ($= 0.025 \text{ mol dm}^{-3}$ at 25°C) [20] compared to $[\text{H}^+]$ ($= 0.35\text{--}1.5 \text{ mol dm}^{-3}$), Eq. (14) explains the observed first-order dependence on $[\text{H}^+]$. The experimental observations indicate that the proposed reaction mechanism remains unchanged in the presence of surfactants. The catalytic efficiency of PA arises mainly due to the enhanced reduction potential of the Cr(VI)/Cr(IV) couple for the enhanced stability of Cr(IV) species [8].

The reaction is catalyzed by SDS and inhibited by CPC (cf. Figs. 4 and 5, Table II). In the PA catalyzed path, Cr(VI)–PA complex is the active oxidant, which is positively charged. Due to the electrostatic attraction, it is preferably partitioned in the SDS micellar phase that is also enriched with the neutral substrate concentration due to hydrophobic interaction. The process is strongly catalyzed by H^+ , and H^+ ions are also preferentially concentrated in the anionic micellar pseudo-phase. Thus, in the presence of SDS, the reaction in the micellar phase is facilitated, but the reaction also simultaneously goes on in the aqueous phase slowly. The rate enhancement in the micellar phase explains the overall increase of k_{obs} with the increase of $[\text{SDS}]_T$. On the other hand, in the cationic micellar phase, the neutral substrate is preferably accumulated due to hydrophobic interaction, but the other reactants (i.e., positively charged Cr(VI)–PA complex and H^+ ions) are repelled by the cationic micellar phase due to the electrostatic repulsion, and the reaction is mainly restricted in aqueous phase with a reduced concentration of DMSO. Consequently, the overall rate decreases with the increase of $[\text{CPC}]_T$. Thus, the observed micellar effects support the proposed mechanism. Here it is worth mentioning that the oxidation of DMSO involves the nucleophilic attack by DMSO on the Cr(VI)–PA complex, and it produces the build-up of positive charge on S (cf. Scheme I), which will be disfavored by the cationic micellar head groups. On the other hand, the build-up of such positive charge is electrostatically favored by the anionic surfactant.

For the analysis of observed micellar effect, the pseudo-phase ion exchange (PIE) model [21–23], which considers the micellar and aqueous phase as two distinct phases, can be considered. The reaction is acid catalyzed, and for SDS the following exchange equilibrium at the micellar surface is relevant:



Here, the subscripts M and W denote the micellar phase 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, $\lambda_M(\text{Na}^+)/\lambda_M(\text{H}^+)$ and $\lambda_W(\text{Na}^+)/\lambda_W(\text{H}^+)$ are each equal to

unity. The overall micellar binding parameter is given by

$$\beta = m_H + m_{\text{Na}} = [\text{H}_M^+]/[\text{D}_n] + [\text{Na}_M^+]/[\text{D}_n]$$

$$= ([\text{H}_M^+] + [\text{Na}_M^+])/[\text{D}_n] \quad (22)$$

Thus, β gives the fraction of micellar head-groups neutralized. Here, $[\text{D}_n]$ gives the micellized surfactant concentration (i.e., $[\text{D}_n] = [\text{SDS}]_T - \text{cmc}$). The various concentration terms are expressed as

$$[\text{H}_M^+] = m_H[\text{D}_n], [\text{H}_W^+] = [\text{H}^+]_T - [\text{H}_M^+]$$

$$= [\text{H}^+]_T - m_H[\text{D}_n],$$

$$[\text{Na}_W^+] = [\text{Na}^+]_T - [\text{Na}_M^+]$$

$$= [\text{Na}^+]_T - (\beta - m_H)[\text{D}_n];$$

$$[\text{Na}_M^+] = [\text{Na}^+]_T - [\text{Na}_W^+] = (\beta - m_H)[\text{D}_n].$$

The exchange equilibrium constant can be expressed as

$$K_{\text{ex}}^{\text{H}} = m_H\{[\text{Na}^+]_T - (\beta - m_H)[\text{D}_n]\}/$$

$$(\beta - m_H)([\text{H}^+]_T - m_H[\text{D}_n]) \quad (23)$$

Equation (23) on rearrangement yields

$$(m_H)^2(K_{\text{ex}}^{\text{H}} - 1)[\text{D}_n] - m_H\{K_{\text{ex}}^{\text{H}}[\text{H}^+]_T + [\text{Na}^+]_T$$

$$+ \beta[\text{D}_n](K_{\text{ex}}^{\text{H}} - 1)\} + K_{\text{ex}}^{\text{H}}\beta[\text{H}^+]_T = 0 \quad (24)$$

$[\text{H}_M^+]$ ($= m_H[\text{D}_n]$) can be calculated from Eq. (24). For the H^+ ions, K_{ex}^{H} is close to unity [22,23]. It indicates that there is no specific interaction for H^+ ion or Na^+ ion with the micellar surface, and consequently these ions are statistically distributed between the aqueous and micellar phases. If $K_{\text{ex}}^{\text{H}} \rightarrow 1$, then Eq. (24) leads to

$$[\text{H}_M^+] = ([\text{H}^+]_T\beta[\text{D}_n])/([\text{H}^+]_T + [\text{Na}^+]_T) \quad (25)$$

The value of β has been found ~ 0.7 [21,24]. It is evident that with the increase of $[\text{D}_n]$, $[\text{H}_M^+]$ increases in the micellar phase. The reaction rate is accelerated by SDS due to this enhanced concentration of H_M^+ , which reacts with the neutral reactants PA and H_2CrO_4 present in the micellar pseudo-phase (due to hydrophobic interaction) to generate the active oxidant (i.e., species II, which is positively charged). The reaction given by Eq. (7) may be considered as the H^+ catalyzed interaction between PA and H_2CrO_4 (which is suggested to be kinetically active under the experimental conditions [25–29]). The species II_M then reacts with DMSO, which is preferentially partitioned in the micellar pseudo-phase due to hydrophobic interaction to provide the rate benefit.

The rate enhancement can also be rationalized by considering the preferential partitioning of the positively charged Cr(VI)–PA complex (i.e., species II) in the an-

ionic micellar pseudo-phase. For the distribution of the positively charged species II (say, Ox^+), the following ion exchange equilibrium may be reasonably considered:



$[Ox_M^+]$ can also be calculated in terms of K_{ex}^{Ox} as in the case of $[H_M^+]$ [cf. Eqs. (24) and (26)]. Here it is also evident that $[Ox_M^+]$ also increases with increasing $[D_n]$, and consequently the rate increases with increasing the concentration of SDS.

The Piszkiwicz model [30–32], analogous to the Hill model applied to the enzyme-catalyzed reactions, may be considered here with some modifications. The model gives the following rate equation:

$$\begin{aligned} \log[(k_{obs} - k_w)/(k_m - k_{obs})] &= \log(P) \\ &= n \log[D]_T - \log K_D \quad (27) \end{aligned}$$

where K_D is the dissociation constant of micellized surfactant back to its components, n is the index of cooperativity, and $[D]_T$ gives the total surfactant concentration. Originally, Eq. (27) was developed for the micelle-catalyzed reactions showing a maximum rate followed by inhibition. In the present case, the plots of k_{obs} vs. $[\text{surfactant}]_T$ (cf. Figs. 4 and 5) are linear, showing the monotonic catalytic effects (positive effect by SDS and negative effect by CPC) of the surfactant in the whole range on the reaction. In such cases, Eq. (27) has also been applied by different workers to interpret the kinetic data [33–36,37]. Here, k_w is the k_{obs} without any surfactant, and k_m is the k_{obs} with the maximum amount of surfactant concentration within the given range. For the CPC-inhibited reactions ($k_m \approx 0$), the plots of $\log(P)$ vs. $\log[D]_T$ are linear (cf. Fig. 8). The advantage of this equation is that it does not require the knowledge of cmc values of the surfactant to interpret the micellar effect. For the CPC-inhibited reactions, under the experimental conditions of $[DMSO]_T = 0.01 \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$, $[Cr(VI)]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$, and $[PA]_T = 0.03 \text{ mol dm}^{-3}$, 35°C , it leads to $n = 1.543$, $\log K_B (= -\log K_D) = 3.42$. The values of n indicate positive cooperativity. The values of n are far less than the aggregation number (10–100) of detergent molecules in the micelles, and it indicates the existence of catalytically productive submicellar aggregates. Because of this reactant-promoted micellization of the surfactant before or below the cmc value, the present systems do not show any discontinuity at the respective reported cmc values of the surfactants. This explains the monotonic micellar effect on k_{obs} . In fact, it is well established that the external agents can promote micellization, and these submicellar aggregates below the cmc values are catalyti-

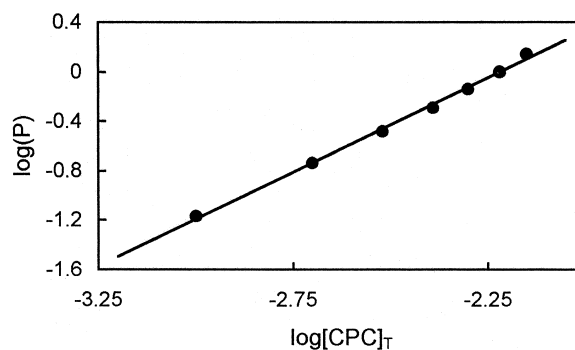


Figure 8 Applicability of the Piszkiwicz model to explain the micellar effect on k_{obs} for the picolinic acid (PA)-catalyzed oxidation of dimethyl sulfoxide (DMSO) by Cr(VI) in aqueous H_2SO_4 media in the presence of the surfactant cetylpyridinium chloride (CPC). $[Cr(VI)]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$; $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$; $[PA]_T = 0.03 \text{ mol dm}^{-3}$; $[DMSO]_T = 0.1 \text{ mol dm}^{-3}$; 35°C .

cally active. Here, the interaction measured by K_B is fairly high, and it is appropriate to consider n as representing average stoichiometry of the detergent – reactant aggregate.

Activation parameters (ΔH^\ddagger , ΔS^\ddagger) of k_{obs} for different surfactant concentrations have been estimated by using the Eyring equation. For the CPC-inhibited reaction, ΔH^\ddagger gradually increases with $[CPC]_T$, while for the SDS-catalyzed reaction ΔH^\ddagger gradually decreases (cf. Figs. 6 and 7). A similar observation has been noted in the reaction of ninhydrin with different amino acids [37].

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