Kinetics and Mechanism of Picolinic Acid Promoted Chromium(VI) Oxidation of Dimethyl Sulfoxide in the Presence and Absence of Surfactants†

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In the picolinic acid (PA) promoted Cr^{VI} oxidation of dimethyl sulfoxide (DMSO), the Cr^{VI}–PA complex formed at the pre-equilibrium step undergoes nucleophilic attack by the S of DMSO to form a positively charged reactive intermediate which experiences an oxygen transfer or a ligand coupling to give the products; the anionic surfactant (SDS) accelerates the process while the cationic surfactant (CPC) retards the reaction.

Among the different chelating agents like 1,10-phenanthroline, 2,2′-bipyridyl, ethylenediaminetetraacetic acid, oxalic acid, *etc*. acting as catalysts[1] in Cr^{VI} oxidation of different substrates, the catalytic ability[2,3] of picolinic acid (PA) is unique and of considerable interest as was first reported by Rocek *et al*.[2] In the case of catalysis by oxalic acid[1d] or α-hydroxy acids[1e] the catalysts are also often co-oxidised along with the substrates *e.g*. alcohols. In the case of PA catalysis, PA is not itself oxidised but lost during the reaction due to the formation of an inert Cr^{III}–PA complex. Thus PA is not a true catalyst and it is better described[1a] as a promoter. In fact, the mechanistic aspects of PA catalysis in Cr^{VI} oxidation have been explored only in a very few cases.[2,3] Cr^{VI} oxidation of dimethyl sulfoxide (DMSO) is kinetically sluggish. Our preliminary observation indicates that Cr^{VI} oxidation of DMSO in both aqueous sulfuric and perchloric acid media is catalysed effectively by PA. It prompted us to explore the kinetic behaviour and mechanistic aspects of the title reaction in detail. To substantiate the proposed reaction mechanism, the effects of surfactants *e.g*. sodium dodecyl sulfate (SDS, a representative anionic surfactant) and cetylpyridinium chloride (CPC, a representative cationic surfactant) on the title reaction were investigated.

Under the experimental conditions (*cf*. Tables 1 and 2), DMSO is oxidised to dimethyl sulfone (Me_2SO_2) characterised by mp (109 °C) and Cr^{VI} is finally reduced to a Cr^{III}–PA complex. The rate of disappearance of Cr^{VI} shows a first-order dependence on $[Cr^{VI}]$. The pseudo-first-order rate constant (k_{obs}) determined from plots of $\ln[Cr^{VI}]_t$ *versus* time (t) decreases with $[Cr^{VI}]_T$ but $k_{obs}([Cr^{VI}]_T/[HCrO_4^-])$ remains constant (*cf*. Table 1). The values of $[HCrO_4^-]$ were calculated by considering the equilibrium constants (K_d)[4] of the process, $HCrO_4^-/Cr_2O_7^{2-}$, neglecting the subsidiary equilibrium $HCrO_4^-/CrO_4^{2-}$. Thus, under the experimental conditions, the monomeric species $HCrO_4^-$ is the effective oxidant. k_{obs} shows a first-order dependence on $[DMSO]_T$ when the other factors remain constant, *i.e*. eqn. (1).

$$k_{obs} = k_s[DMSO]_T \quad (1)$$

The values of $10^3\,k_S/dm^3\,mol^{-1}\,s^{-1}$ are: 3.2 ± 0.06 (30 °C), 4.1 ± 0.08 (35 °C) and 6.8 ± 0.1 (45 °C) under the conditions $10^3[Cr^{VI}]_T = 2.0$ mol dm^{-3}; $[HClO_4] = 0.5$ mol dm^{-3}; $I = [HClO_4] + [NaClO_4] = 1.5$ mol dm^{-3}, $[PA]_T = 0.03$ mol dm^{-3}. Similarly, k_{obs} shows strictly a first-order dependence on $[PA]_T$ and the plot of k_{obs} *versus* $[PA]_T$ ($r > 0.989$) without any intercept indicates that the uncatalysed path is kinetically nonexistent under the experimental conditions. It is also experimentally verified by carrying out an independent kinetic run in the absence of PA.

Table 1 Effect of $[Cr^{VI}]_T$ on k_{obs} for the PA promoted Cr^{VI} oxidation of DMSO. $[DMSO]_T = 0.1$ mol dm^{-3}, $[PA]_T = 0.03$ mol dm^{-3}, $[HClO_4] = 1.0$ mol dm^{-3}, $I = [HClO_4] + [NaClO_4] = 1.5$ mol dm^{-3}, 35 °C, $K_d = 76.0$ (ref. 4)

$10^3[Cr^{VI}]_T$/mol dm^{-3}	:	0.67	1.33	2.0	2.67
$10^4\,k_{obs}$/s^{-1}	:	8.5	8.1	7.7	7.4
$10^4\,k_{obs}\,([Cr^{VI}]_T/[HCrO_4^-])$/s^{-1}	:	9.3	9.5	9.6	9.7

$$k_{obs} = k_p[PA]_T \quad (2)$$

The values of $10^3\,k_p/dm^3\,mol^{-1}\,s^{-1}$ are: 9.2 ± 0.1 (30 °C), 12.0 ± 0.1 (35 °C) and 20.8 ± 0.2 (45 °C) with $\Delta H^{\neq} = 41 \pm 3$ kJ mol^{-1} and $\Delta S^{\neq} = -153 \pm 9$ J K^{-1} mol^{-1} under the conditions $10^3[Cr^{VI}]_T = 2.0$ mol dm^{-3}, $[DMSO]_T = 0.1$ mol dm^{-3}, $[HClO_4] = 0.5$ mol dm^{-3} and $I = 1.5$ mol dm^{-3}. k_{obs} shows a first-order dependence on $[H^+]$ (=0.35–1.5 mol dm^{-3}) at 35 °C.

$$k_{obs} = k_H[H^+] \quad (3)$$

$10^3\,k_H = 0.78 \pm 0.05$ dm^3 mol^{-1} s^{-1} at $[DMSO]_T = 0.1$ mol dm^{-3}, $[PA]_T = 0.03$ mol dm^{-3}, $I = 1.5$ mol dm^{-3} and 35 °C.

The observations can be explained by Scheme 1 involving the formation of $HCrO_4$–PA cyclic complex (**II**) which is the active oxidant. Then, **II** interacts with the DMSO to give the reaction intermediate **III** and/or **IV**. In **III**, nucleophilic attack on 'O' of the Cr^{VI}–PA complex by the S of DMSO occurs. Then 'O' transfer to DMSO leads to the products, *i.e*. Me_2SO_2 and Cr^{IV}–PA complex. Such possibilities have been proposed[5] by many workers. On the other hand, the nucleophilic attack of S of DMSO on Cr of Cr^{VI}–PA complex leads to **IV** followed by the ligand coupling[6] of O^- and S leading to the formation of sulfone and Cr^{IV}–PA complex. At the next faster steps, the Cr^{IV}–PA complex participates as given in Scheme 1. Formation of the free radicals is evidenced through the polymerisation of acrylonitrile. Scheme 1 leads to the eqns. (12) and (13) which conform to the experimental findings:

$$\frac{-\mathrm{d}\ln[HCrO_4^-]}{\mathrm{d}t} = k_{obs} = (2/3)\frac{K_a K k_1 k[PA]_T[DMSO]_T[H^+]^2}{(k_{-1}+k)([H^+]+K_a)} \quad (12)$$

$$= m[PA]_T[DMSO]_T, \text{ (at fixed } [H^+]). \quad (13)$$

The calculated values of m/dm^6 mol^{-2} s^{-1} [=0.9 (30 °C), 1.2 (35 °C), 2.1 (45 °C) from k_p; =1.0 (30 °C), 1.4 (35 °C), 2.3 (45 °C) from k_s] obtained from the [PA] variation experiments (*i.e*. k_p) agree well with those obtained from $[DMSO]_T$ variation experiments (*i.e*. k_s) as expected from the above eqns. [*cf*. eqns. (1), (2) and (12)]. k_p is a composite rate constant and this is why interpretation of its activation parameters is not so straightforward. However, highly negative entropy of activation may be due to the complexation leading to the transition state. Neglecting K_a (=0.025 mol dm^{-3} at 25 °C)[7] compared to

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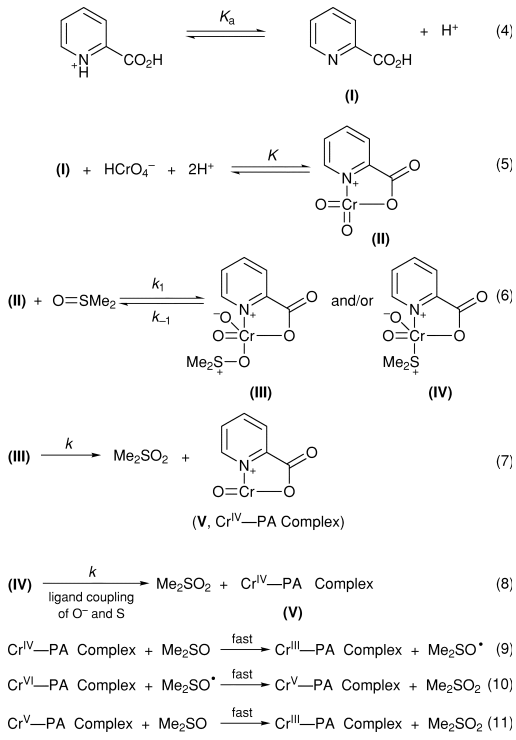
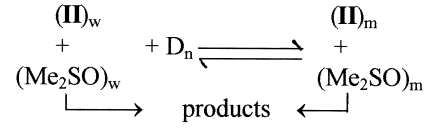


Scheme 1

$[H^+]$ (=0.35–1.5 mol dm^3), eqn. (12) explains the observed first order dependence on $[H^+]$. From the $[H^+]$ dependence, the calculated values of k_s ($=3.9\times10^{-3}$ dm^3 mol^{-1} s^{-1}) and k_p ($=12.8\times10^{-3}$ dm^3 mol^{-1} s^{-1}) at 35 °C nicely agree with those obtained from $[DMSO]_T$ and $[PA]_T$ dependence, respectively. The catalytic efficiency of PA in the present system is argued[2] as being mainly due to enhanced Cr^{VI}/Cr^{IV} and Cr^{IV}/Cr^{IIII} reduction potentials in the presence of PA.

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. It is evident that SDS catalyses (*cf.* Table 3) the title reaction while CPC inhibits (*cf.* Table 3) the process. The results can be explained by considering the pseudo-phase ion exchange (PIE) model[8] which considers the micellar and aqueous phases as two distinct phases and in the present case the redox reaction occurs in the both phases. In the presence of SDS, the rate acceleration is due to the preferential partitioning of the Cr^{VI}–PA complex **II** (positively charged; favourable electrostatic attraction) and DMSO (neutral, favourable hydrophobic interaction) at the micellar phase. The overall process is acid catalysed and this explains why the increase in $[H^+]$ increases[8] $[H_m^+]$ (=concentration of H^+ in the micellar phase) which accelerates the redox reaction in the micellar phase. The observation in the anionic micellar phase can be rationalised by considering Scheme 2 where the subscripts m and w denote the micellar and aqueous phase respectively.

The reaction occurs in the aqueous phase as well as in the micellar phase. The reaction is catalysed by SDS because the local concentrations of the reactants in the micellar phase are higher than their stoichiometric concentrations. With the increase of $[SDS]_T$, the concentrations of the reactive species in the micellar phase increase which explains



Scheme 2

Table 3 Effect of $[SDS]_T$ and $[CPC]_T$ on k_{obs} for the PA-promoted Cr^{VI} oxidation of DMSO in aqueous acidic media. $[Cr^{VI}]=2\times10^{-3}$ mol dm^{-3}, $[DMSO]_T=0.2$ mol dm^{-3}, $[PA]_T=0.03$ mol dm^{-3}, 35 °C

$10^2[SDS]_T{}^a$/mol dm^{-3} :	0.0	1.0	2.0	3.0	4.0	5.0	6.0
$10^4 k_{obs}/s^{-1}$:	3.4	4.7	6.0	7.2	8.9	10.2	11.8
$10^3[CPC]_T{}^b$/mol dm^{-3} :	0.0	1.0	2.0	3.0	4.0	5.0	
$10^4 k_{obs}/s^{-1}$:	4.9	4.3	3.6	3.2	2.8	2.0	

[a] $[HClO_4]=0.25$ mol dm^{-3}; $I=1.5$ mol dm^{-3}. [b] $[H_2SO_4]=0.5$ mol dm^{-3}.

the increase in k_{obs}. Inhibition by the cationic micelle (*i.e.* CPC) is due to the fact that DMSO is distributed preferably in the micellar phase due to hydrophobic interaction, but the approach of the other reactive species **II** (positively charged) is repelled. The process is catalysed by H^+, whose approach to the micellar phase is prevented due to the repulsion from the cationic surfactant.

Lastly it is worth mentioning that the oxidation of DMSO involves the nucleophilic attack of 'S' of DMSO on the oxidant species **II** and it leads to the build-up of positive charge on S (*cf.* species **III**, **IV**) which will be disfavoured by the cationic micellar head groups. On the other hand, development of such positive charge on S in DMSO is coulombically favoured in the anionic surfactants. Thus the micellar effects support the proposed mechanism involving positively charged reactive oxidant species **II** and the proposed intermediate **III/IV** where there is a build-up of positive charge on S of DMSO due to the nucleophilic attack by S.

Experimental

PA was used after repeated recrystallisation from methanol (mp 136 °C). DMSO was purified and standardised as described previously.[9] All other chemicals used were of analytical or general reagent grade or purified by standard procedures. The rate of disappearance of Cr^{VI} was followed by the titremetric quenching technique using excess standard Mohr's solution and the unreacted Fe^{II} was determined[9] by standard Ce^{IV} solution using ferroin indicator. The pseudo-first-order rate constants were obtained from the slopes of $\ln[Cr^{VI}]_t$ *versus* time (t). Initial slopes were used for the sets with very low $[PA]_T$.

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