Kinetics and mechanism of 2,2'-bipyridine catalysed chromium(VI) oxidation of dimethyl sulfoxide in the presence and absence of surfactants†

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In the 2,2'-bipyridine (bipy) catalysed Cr^{VI} oxidation of dimethyl sulfoxide (DMSO) to dimethyl sulfone, the Cr^{VI}–bipy complex formed at the pre - equilibrium step undergoes a nucleophilic attack by the S or O of DMSO to form a positively charged reactive intermediate. This intermediate 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.

Keywords: kinetics, catalysis, 2,2'-bipyridine, Cr^{VI} oxidation, dimethyl sulfoxide, surfactants

Among the different chelating agents, such as 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy), 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. The mechanistic aspects of picolinic acid catalysed Cr^{VI} oxidation of dimethyl sulfoxide have been recently studied by us.[4] Because of the similarity between bipy and picolinic acid (both are heteroaromatic N- bases), the catalytic effect of bipy is worth exploring. Our preliminary observation indicates that Cr^{VI} oxidation of DMSO in both aqueous sulfuric and perchloric acid media is very slow but the process is catalysed effectively by bipy. This prompted us to explore the kinetic and mechanistic aspects of the reaction in detail and 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 also investigated. Under the experimental conditions (Table 1), DMSO (Me_2SO) is oxidised to dimethyl sulfone (Me_2SO_2) as characterised by m.p. (109 °C) and the Cr^{VI} precursor is finally reduced to a Cr^{III}-bipy complex.

$$2HCrO_4^- + 3Me_2SO + 8H^+ \longrightarrow 2Cr^{III} + 3Me_2SO_2 + 5H_2O \quad (1)$$

The rate of disappearance of Cr^{VI} shows a first order dependence on $[Cr^{VI}]$. The pseudo first order rate constants (k_{obs}) have been determined from the plots of $\ln[Cr^{VI}]_t$ *vs* time (t). The formation of a Cr^{III}-bipy complex (characterised spectroscopically) indicates that bipy undergoes complexation with the higher oxidation states (which are labile) of chromium. Because of the inertness of Cr^{III} (t_{2g}^3), bipy does not bind the Cr^{III} produced after the reduction of Cr^{VI}. Thus it is quite reasonable to consider that the Cr^{VI}-bipy complex formed at the pre-equilibrium step is the active oxidant.[5,6] It may be noted that there is no kinetic evidence for the formation of the said complex, as the strict first order dependence on bipy (Fig. 1) is maintained throughout the concentration range used. This indicates that the equilibrium constant for the formation of the complex is quite low.

The plot of k_{obs} *vs*. $[bipy]_T$ (Fig. 1) ($r > 0.989$), 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 bipy. At fixed $[H^+]$, $[DMSO]_T$ and $[Cr^{VI}]_T$, the dependence on [bipy] can be expressed as:

$$k_{obs(c)} = k_{cat}[bipy]_T \quad (2)$$

$k_{obs(c)}$ shows a first order dependence on $[DMSO]_T$ (Fig. 2) in presence and absence of surfactants when the other factors remain constant, *i.e*. at fixed $[H^+]$, $[Cr^{VI}]_T$, and $[bipy]_T$.

$$k_{obs(c)} = k_{s\,(c)}[DMSO]_T \quad (3)$$

$k_{obs(c)}$ shows a second order dependence on $[H^+]$ at fixed $[DMSO]_T$, $[Cr^{VI}]_T$, and $[bipy]_T$, both in presence and absence of surfactants (Fig. 3), *i.e*.

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

Thus the observed rate law is given by:

$$k_{obs(c)} = a[bipy]_T[DMSO]_T[H^+]^2, \quad (5)$$
(a = a constant)

These observations can be explained by Scheme 1, that involves the formation of a Cr^{VI}-bipy cyclic complex (**II**),

Table 1 Kinetic parameters of the bipy-catalysed Cr^{VI} oxidation of DMSO in the presence and absence of surfactants. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}

Temp (°C)	$10^2\,k_{cat(w)}$/ (dm^3 mol^{-1} s^{-1})[a]	$10^2\,k_{cat(cpc)}$/ (dm^3 mol^{-1} s^{-1})[a]	$10^2\,k_{cat(sds)}$/ (dm^3 mol^{-1} s^{-1})[a]	$10^2\,k_{s(c)(w)}$/ (dm^3 mol^{-1} s^{-1})[b]	$10^2\,k_{s(c)(cpc)}$/ (dm^3 mol^{-1} s^{-1})[b]	$10^2\,k_{s(c)(sds)}$/ (dm^3 mol^{-1} s^{-1})[b]	$10^4\,k_{H(c)(w)}$/ (dm^6 mol^{-2} s^{1})[c]	$10^4\,k_{H(c)(sds)}$/ (dm^6 mol^{-2} s^{1})[c]
25°C	7.0 ± 0.35							
35°C	12.90 ± 0.60	7.7 ± 0.40	16.40 ± 0.70	1.1 ± 0.07	0.75 ± 0.05	1.4 ± 0.10	4.0 ± 0.20	6.7 ± 0.35
40°C	17.00 ± 0.85							
$\Delta H^{\neq}$ (kJ mol^{-1})	42 ± 1.8							
$\Delta S^{\neq}$ (J K^{-1}mol^{-1})	-128 ± 6							

[a]$[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[DMSO]_T = 48 \times 10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[bipy]_T = (40 - 120) \times 10^{-4}$ mol dm^{-3}.
[b]$[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[bipy]_T = 40 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = 1.5 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 2 \times 10^{-2}$ mol dm^{-3}. $[DMSO]_T = (0 - 120) \times 10^{-3}$ mol dm^{-3}.
[c]$[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4]_T = 1.0$ mol dm^{-3}, $[bipy]_T = 40 \times 10^{-4}$ mol dm^{-3}, $[DMSO]_T = 35 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T = 4 \times 10^{-2}$ mol dm^{-3}.

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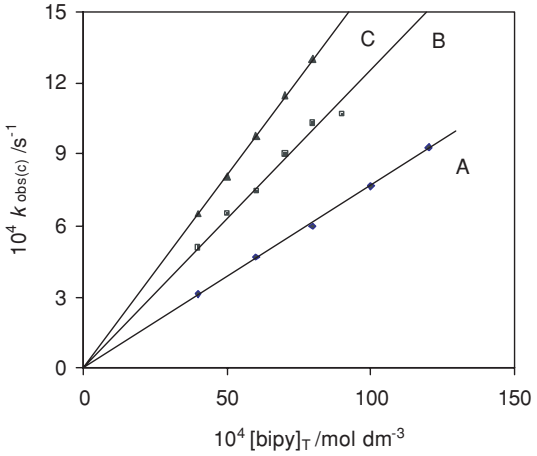


Fig. 1 Dependence of $k_{obs(c)}$ on $[bipy]_T$ for the Cr^{VI} oxidation of dimethyl sulfoxide at 35°C. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, $[DMSO]_T = 48 \times 10^{-3}$ mol dm^{-3}, A ($[CPC]_T = 2 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T$ = 0 mol dm^{-3}), B ($[CPC]_T = [SDS]_T$ = 0 mol dm^{-3}), C ($[SDS]_T = 2 \times 10^{-2}$ mol dm^{-3}, $[CPC]_T$ = 0 mol dm^{-3}).

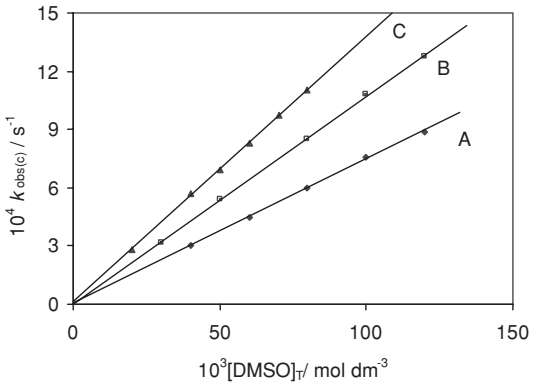


Fig. 2 Dependence of $k_{obs(c)}$ on $[DMSO]_T$ for the Cr^{VI} oxidation of dimethyl sulfoxide at 35°C. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, $[bipy]_T = 40 \times 10^{-4}$ mol dm^{-3}, A ($[CPC]_T = 1.50 \times 10^{-3}$ mol dm^{-3}, $[SDS]_T$ = 0 mol dm^{-3}), B ($[CPC]_T = [SDS]_T$ = 0 mol dm^{-3}), C ($[SDS]_T = 2 \times 10^{-2}$ mol dm^{-3}, $[CPC]_T$ = 0 mol dm^{-3}).

which is the active oxidant. Then **II** interacts with DMSO to give the reaction intermediate **III** and/or **IV** and/or **V**. In **III** and **V** 'O' transfer takes place through a four membered cyclic transition state to give the products. On the other hand, in **IV** ligand coupling of O^- and S occurs, leading to the formation of sulfone and a Cr^{IV}–bipy complex. This type of ligand coupling is well documented in the literature.[8] At the next faster steps, the Cr^{IV}–bipy complex (simply denoted as Cr^{IV}) is finally reduced to a Cr^{III}–bipy complex (simply denoted as Cr^{III}). This process might occur by different possible routes as given:

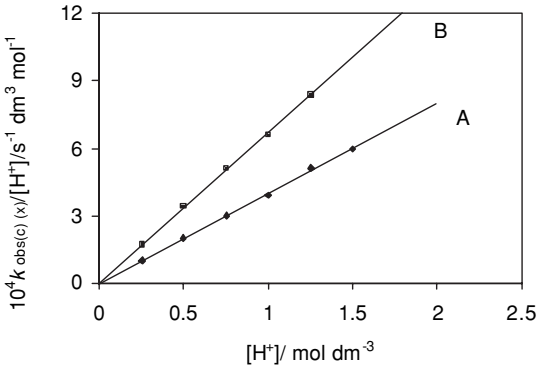


Fig. 3 Dependence of $k_{obs(c)(x)}$ (x = w or SDS) on $[H^+]$ for the Cr^{VI} oxidation of dimethyl sulfoxide at 35°C. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[HClO_4] + [NaClO_4]$ = 1.5 mol dm^{-3}, A ($[SDS]_T$ = 0 mol dm^{-3}, x = w), B ($[SDS]_T = 4 \times 10^{-2}$ mol dm^{-3}, x = SDS).

Route I: $Cr^{IV} + Cr^{VI} \rightarrow 2Cr^{V}$, $2Cr^{V} + 2S \rightarrow 2Cr^{III} + 2P$

Route II: $Cr^{IV} + S \rightarrow Cr^{III} + S^{\bullet}$, $Cr^{VI} + S^{\bullet} \rightarrow Cr^{V} + P$, $Cr^{V} + S \rightarrow Cr^{III} + P$

Route III: $Cr^{IV} + S \rightarrow Cr^{II} + P$, $Cr^{II} + Cr^{VI} \rightarrow Cr^{III} + Cr^{V}$, $Cr^{V} + S \rightarrow Cr^{III} + P$

S denotes the title substrate DMSO which is a 2*e* reductant and P denotes the oxidised product *i.e.* dimethyl sulfone. $S^{\bullet}$ denotes the partially oxidised substrate. In both the Watanabe-Westheimer mechanism[9] (*i.e.* **Route I)** and a Perez-Benito type mechanism[10,11] (*i.e.* **Route III**), the title substrate acts in all steps as a 2*e* reductant while it acts both as a 2*e* reductant and 1*e* reductant in the Rocek mechanism[12] (*i.e.* **Route II**). The partially oxidised substrate ($S^{\bullet}$ which is a free radical) is considered responsible for the acrylonitrile polymerisation. Previously, the Rocek mechanism was accepted widely in explaining the Cr^{VI} oxidation of organic reductants, however the Perez-Benito type mechanism has now been found to operate in Cr^{VI} oxidation of different types of 2*e* reductants (both organic and inorganic). Formation of Cr^{II} from Cr^{IV} might occur in the present case through an oxygen atom transfer. In fact, reduction of Cr^{IV} to Cr^{II} by different types of 2*e* inorganic reductants through the oxygen atom transfer process has also been suggested by Gould *et al.*[11]

Scheme 1 leads to eqn (11)

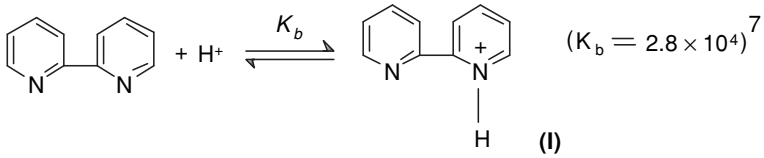
$$k_{obs(c)} = (2/3)K_1K_{ex}k[DMSO]_T[bipy]_T[H^+]^2 \qquad (11)$$

Here it is important to mention that in the case of picolinic acid (PA)-promoted chromic acid oxidation of the title substrate, a similar rate law has been found,[4] but the acid dependence pattern is totally different in the two cases. For the PA-promoted path, it shows a first order dependence on H^+ while for the bipy-promoted path, it shows a second order dependence on $[H^+]$. This difference arises due to the wide difference in basicity of these two chelating ligands (*cf.* pK_a of $bipyH^+$ = 4.45, pK_a of PAH^+ = 1.60).[7,13] Thus under the experimental conditions (*i.e.* strongly acidic), bipy exists predominately as $bipyH^+$ while PA exists in an equilibrium mixture of PA and PAH^+, *i.e.* $[bipy]_T \approx$

Table 2 Effect of $[SDS]_T$ and $[CPC]_T$ on $k_{obs(c)}$ for the bipy promoted Cr^{VI} oxidation of DMSO in aqueous acidic media. $[Cr^{VI}]_T = 4 \times 10^{-4}$ mol dm^{-3}, $[H_2SO_4]$ = 1.0 mol dm^{-3}, $[bipy]_T = 40 \times 10^{-4}$ mol dm^{-3}, 35°C

10^2 $[SDS]_T$/(mol dm^{-3})[a]:	0	2	4	6	8	10
10^4 k_{obs}/s^{-1}:	5.0	6.5	8.0	9.5	11.0	12.7
$10^3[CPC]_T$/(mol dm^{-3})[b]:	0	2	4	6	8	10
10^4 k_{obs}/s^{-1}:	8.5	5.3	3.9	2.9	2.4	2.3

[a]$[DMSO]_T = 48 \times 10^{-3}$ mol dm^{-3},
[b]$[DMSO]_T = 80 \times 10^{-3}$ mol dm^{-3}.



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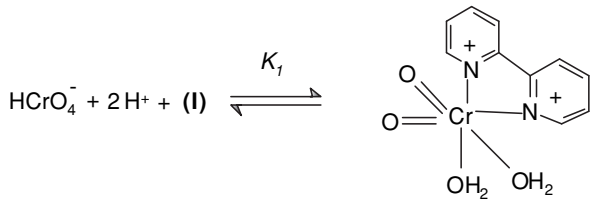

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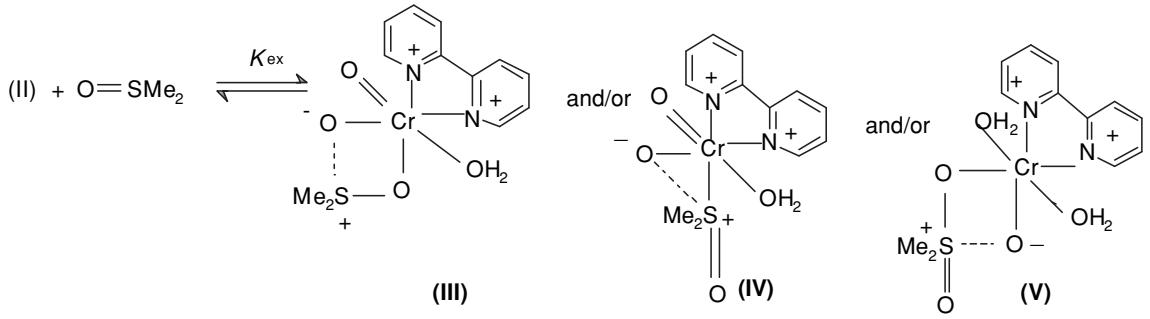

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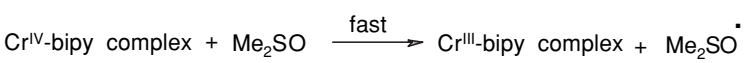

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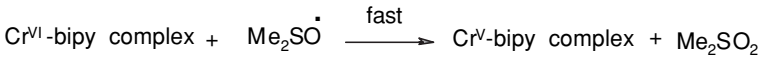

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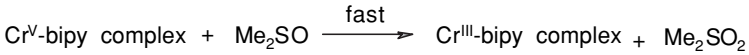


(12)

Scheme 1 Cr(VI) Oxidation of DMSO in presence of 2,2'- bipyridine.

[bipyH$^+$] and [PA]$_T$ = [PA] + [PAH$^+$], [PA] = K_a [PA]$_T$/([H$^+$] + K_a) ≈ K_a [PA]$_T$/[H$^+$] as K_a (= 0.025)[13] << [H$^+$]. By considering eqns. 6 and 7 of Scheme 1, we can express the concentration of the active oxidant (*i.e.* **II**) as follows:

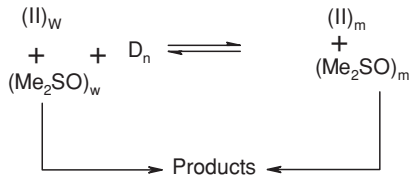
$$\text{For bipy: } [\mathbf{II}] = \{K_1K_b[H^+][\text{bipy}]_T[HCrO_4^-][H^+]^2\}/(1 + K_b[H^+]) \approx K_1[\text{bipy}]_T[HCrO_4^-][H^+]^2, (K_b[H^+] >> 1) \quad (12)$$

$$\text{For picolinic acid: } [\mathbf{II}] = \{K_1K_a[H^+]^2[PA]_T[HCrO_4^-]\}/(K_a + [H^+]), (K_a = 1/K_b) \approx K_1K_a[PA]_T[HCrO_4^-][H^+], ([H^+] >> K_a) \quad (13)$$

This difference between the ligands causes the first order dependence on [H$^+$] for the PA-catalysed path and second order dependence on [H$^+$] for the bipy-catalysed path.

It is evident that SDS catalyses (Table 1 and Table 2) the title reaction while CPC inhibits (Table 1 and Table 2) the process [Table 1: $k_{cat(x)}$, $k_{s(c)(x)}$, $k_{H(c)(x)}$ where $x = w$ (value in absence of surfactants), = SDS (value in presence of SDS surfactant), = CPC (value in presence of CPC surfactant)]. The results can be explained by considering the pseudo–phase ion exchange (PIE) model[14] that considers the micellar and aqueous phases as two distinct phases and in the present case, the redox reaction occurs in both phases. In presence of SDS, the rate acceleration is due to the preferential partitioning of the Cr^{VI}–bipy complex **II** (positively charged; favourable electrostatic attraction) and DMSO (neutral, favourable hydrophobic interaction) at the micellar phase. The overall process is acid catalysed. The increase in [H$^+$] increases[14] [H^+_m] (= concentration of H$^+$ in the micellar phase), which accelerates the redox reaction in the micellar phase. This explains why the overall rate increases in presence of SDS (Fig. 3).

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 concentration of reactants in the micellar phase is



Scheme 2 Partitioning of the reactive species between the aqueous and micellar phases.

higher than their stoichiometric concentrations. With the increase of $[SDS]_T$, the concentrations of the reactive species in the micellar phase increase, which explains the increase in k_{obs} (Table 2). Inhibition (Table 2) 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. A similar observation has been noted by Bunton *et al*.[15] in the oxidation of ferrocene by ferric salts in the presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB).

Oxidation of DMSO involves nucleophilic attack by 'S' or 'O' of DMSO on the active oxidant species **II** and it leads to the build-up of positive charge on S (species **III, IV, V**) that 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 formation of the proposed intermediate **III**, **IV**, **V,** where there is a build up of positive charge on S of DMSO, due to the nucleophilic attack by S or O of DMSO.

Experimental

DMSO (SRL, AR), 2,2´- bipyridine (Qualigens, AR, India), $K_2Cr_2O_7$ (AR, BDH), sodium dodecyl sulphate (SDS) (SRL, India), N-cetylpyridinium chloride (CPC) (SRL, India), $Ce(SO_4)_2$, $2(NH_4)_2SO_4$ (AR, Himedia, India) and all other chemicals used were of AR/GR grade or purified by standard procedures. Solutions were prepared in doubly distilled water. 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 a titrimetric quenching technique using excess of standard Mohr's solution and the unreacted Fe^{II} was estimated by a standard Ce^{IV} solution using ferroin indicator[16].

Thanks are due to CSIR and UGC, New Delhi and Visva Bharati for financial support.

Received 13 January 2005; accepted 4 April 2005
Paper 05/3007

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