

Kinetics and mechanism of picolinic acid promoted chromic acid oxidation of maleic acid in aqueous micellar media

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Abstract

The kinetics and mechanism of chromic acid oxidation of maleic acid in the presence and absence of picolinic acid (PA) in aqueous acid media have been studied under the conditions $[\text{maleic acid}] \gg [\text{Cr}^{\text{VI}}]_{\text{T}}$ at different temperatures. Under the kinetic conditions, the monomeric species of Cr^{VI} has been found kinetically active in the absence of PA while in the PA-catalysed path, Cr^{VI} -PA complex has been suggested as the active oxidant. In the PA-catalysed path, Cr^{VI} -PA complex receives a nucleophilic attack by the substrate to form a ternary complex, which subsequently experiences a 2e-transfer redox decomposition leading to the epoxide and Cr^{IV} -PA complex at the rate determining step. Subsequently, the epoxide produces pyruvic acid through the decarboxylation of β -keto acid in a faster step. Then Cr^{IV} -PA complex participates further in the oxidation of maleic acid in faster steps and ultimately is converted into the inert Cr^{III} -PA complex. In the uncatalysed path, Cr^{VI} -substrate ester experiences a redox decomposition through 2e-transfer at the rate determining step in the same way. The uncatalysed path shows a mixed order (i.e. first order + second order) dependence on $[\text{H}^+]$ while the PA-catalysed path shows a first order dependence on $[\text{H}^+]$. Both the uncatalysed path and PA-catalysed path show the first order dependence on both $[\text{maleic acid}]_{\text{T}}$ and $[\text{Cr}^{\text{VI}}]_{\text{T}}$. The PA-catalysed path is first order in $[\text{PA}]_{\text{T}}$. In the presence of surfactants like *N*-cetylpyridinium chloride (CPC, a cationic surfactant) and sodium dodecyl sulfate (SDS, an anionic surfactant), the reaction orders remain unchanged. CPC has been found to retard both the uncatalysed and PA-catalysed paths but the patterns are different while SDS shows the rate accelerating effect for the both paths in the same pattern. The observed micellar effects have been explained by considering hydrophobic and electrostatic interactions between the reactants and surfactants in terms of the proposed mechanism.

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1. Introduction

Picolinic acid (PA) is an efficient catalyst in chromic acid oxidation of different types of organic substrates [1–3]. Though PA is not co-oxidised but it is gradually lost during the reaction through the formation of inert Cr^{III} -PA complex. Studies on Cr^{VI} oxidation of alkenes are well known [4–9], but the micellar effect and effects of the chelating agents like PA are not reported in literature. The present investigation aims to follow the kinetics of oxidation of maleic acid by chromic acid. The studies have been carried out in aqueous micellar media with a view to substantiating the mechanistic paths proposed from the observed micellar effects.

2. Results and discussion

2.1. Dependence on $[\text{Cr}^{\text{VI}}]_{\text{T}}$

Both in the presence and absence of picolinic acid, under the experimental conditions $[\text{S}]_{\text{T}} \gg [\text{PA}]_{\text{T}} \gg [\text{Cr}^{\text{VI}}]_{\text{T}}$, the rate of disappearance of Cr^{VI} shows a first order dependence on Cr^{VI} . $[\text{S}]_{\text{T}}$ denotes the total substrate, i.e. maleic acid concentration. The pseudo first order rate constants (k_{obs}) have been evaluated from the linear plot of $\log[\text{Cr}^{\text{VI}}]_{\text{T}}$ versus time (t) as usual.

2.2. Dependence on $[\text{PA}]_{\text{T}}$

The effect of $[\text{PA}]_{\text{T}}$ on k_{obs} was followed in both aqueous H_2SO_4 and HClO_4 media. The plots of k_{obs} versus $[\text{PA}]_{\text{T}}$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower uncatalysed path

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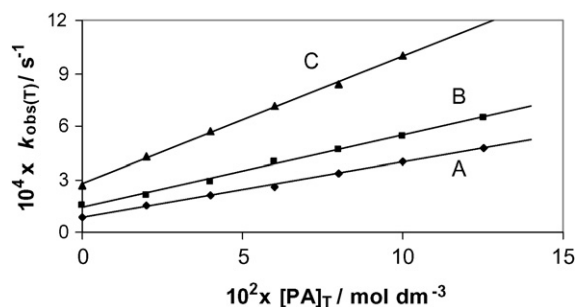


Fig. 1. Effect of $[PA]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of maleic acid in the presence of picolinic acid in aqueous $HClO_4$ media. $[Cr^{VI}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $HClO_4 = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[PA]_T = (0-12.5) \times 10^{-2} \text{ mol dm}^{-3}$; (A): $T = 30 \text{ }^\circ\text{C}$; (B): $T = 35 \text{ }^\circ\text{C}$; (C): $T = 45 \text{ }^\circ\text{C}$.

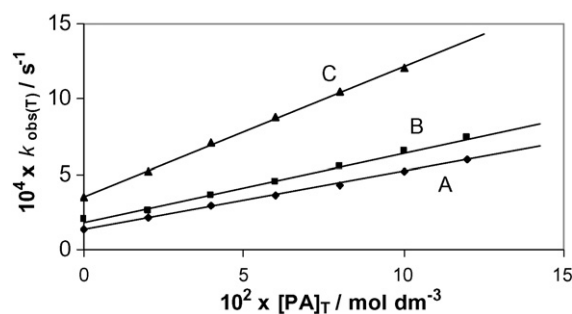


Fig. 2. Effect of $[PA]_T$ on $k_{obs(T)}$ for the Cr^{VI} oxidation of maleic acid in the presence of picolinic acid in aqueous H_2SO_4 media. $[Cr^{VI}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $H_2SO_4 = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = 0.3 \text{ mol dm}^{-3}$, $[PA]_T = (0-12) \times 10^{-2} \text{ mol dm}^{-3}$. (A): $[CPC]_T = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 35 \text{ }^\circ\text{C}$; (B): $[CPC]_T = 0 \text{ mol dm}^{-3}$, $T = 35 \text{ }^\circ\text{C}$; (C): $[CPC]_T = 0 \text{ mol dm}^{-3}$, $T = 45 \text{ }^\circ\text{C}$.

(cf. Figs. 1 and 2). The pseudo first order rate constants $k_{obs(u)}$ directly measured in the absence of catalyst, picolinic acid nicely agree with those obtained from the intercepts of the plot of $k_{obs(T)}$ versus $[PA]_T$. The observation is formulated as follows:

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

The values of k_{cat} with the activation parameters are given in Tables 1 and 2. During the progress of the reaction, PA is lost due to the formation of inert Cr^{III} -PA complex. Under the conditions $[PA]_T \gg [Cr^{VI}]_T$, during the progress of the reaction $[PA]_T$ remains more or less constant.

Table 1
Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of maleic acid in the presence and absence of picolinic acid (PA) in aqueous $HClO_4$ media

Temperature ($^\circ\text{C}$)	$10^4 k_{obs(u)(w)}/(s^{-1})^a$	$10^3 k_{cat(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^a$	$k_{eff(w)}^a$	$10^3 k_{s(u)(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^b$	$10^3 k_{s(c)(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^b$
30 $^\circ\text{C}$	0.8 ± 0.07	3.3 ± 0.30	1.63		
35 $^\circ\text{C}$	1.4 ± 0.09	4.2 ± 0.40	1.14	2.0 ± 0.15	1.96 ± 0.18
45 $^\circ\text{C}$	2.8 ± 0.12	7.3 ± 0.70	1.04		
ΔH^\ddagger (kJ mol^{-1})		43.26 ± 3.9			
ΔS^\ddagger ($\text{JK}^{-1} \text{ mol}^{-1}$)		-152.9 ± 7.2			

Subscript (u) for uncatalysed path; (c) for picolinic acid (PA) catalysed path; (w) for the value in the aqueous media.

^a $[Cr^{VI}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4] = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$, $[PA]_T = (0-12.5 \times 10^{-2}) \text{ mol dm}^{-3}$, $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[PA]_T = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$.

^b $[Cr^{VI}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[HClO_4] = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = (0-0.5) \text{ mol dm}^{-3}$, $[PA]_T = 4 \times 10^{-2} \text{ mol dm}^{-3}$.

Table 2
Kinetic parameters and some representative rate constants for the Cr^{VI} oxidation of maleic acid in the presence and absence of picolinic acid (PA) in aqueous H_2SO_4 media

Temperature ($^\circ\text{C}$)	$10^4 k_{obs(u)(w)}/(s^{-1})^a$	$10^3 k_{cat(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^a$	$k_{eff(w)}^a$	$10^3 k_{s(u)(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^b$	$10^3 k_{s(c)(w)}/(dm^3 \text{ mol}^{-1} s^{-1})^b$
30 $^\circ\text{C}$	1.2 ± 0.1	3.4 ± 0.35	1.08		
35 $^\circ\text{C}$	1.9 ± 0.2	4.5 ± 0.45	0.89		
45 $^\circ\text{C}$	3.5 ± 0.35	9.0 ± 0.85	1.0	1.13 ± 0.10	1.8 ± 0.08
ΔH^\ddagger (kJ mol^{-1})		49.52 ± 4.1			
ΔS^\ddagger ($\text{JK}^{-1} \text{ mol}^{-1}$)		-131.7 ± 5.4			

Subscript (u) for uncatalysed path; (c) for picolinic acid (PA) catalysed path; (w) for the value in the aqueous media.

^a $[Cr^{VI}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = 0.3 \text{ mol dm}^{-3}$, $[PA]_T = (0-12 \times 10^{-2}) \text{ mol dm}^{-3}$. $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[PA]_T = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$.

^b $[Cr^{VI}]_T = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$, $[maleic \text{ acid}]_T = (0-0.6) \text{ mol dm}^{-3}$, $[PA]_T = 6 \times 10^{-2} \text{ mol dm}^{-3}$.

2.3. Dependence on $[S]_T$

From the plot of k_{obs} versus $[S]_T$ (cf. Fig. 3), it is established that both the uncatalysed and catalysed paths show first order dependence on $[S]_T$, i.e.

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

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

The values of $k_{s(c)}$ and $k_{s(u)}$ are given in Tables 1–3. It is also worth mentioning that in the presence of surfactants, the same dependence pattern is maintained.

Table 3

Some representative rate constants for the Cr^{VI} oxidation of maleic acid in the presence and absence of picolinic (PA) in micellar acid media

Temperature (°C)	$10^3 k_{\text{cat(cpc)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{a}}$	$10^3 k_{\text{cat(sds)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{a}}$	$10^3 k_{\text{s(u)(cpc)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{b}}$	$10^3 k_{\text{s(c)(cpc)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{b}}$	$10^3 k_{\text{s(u)(sds)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{b}}$	$10^3 k_{\text{s(c)(sds)}} / (\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^{\text{b}}$
35	3.90 ± 0.40					
45		0.70 ± 0.06	0.75 ± 0.07	1.61 ± 0.15	2.7 ± 0.2	1.3 ± 0.05

Subscript (u) for uncatalysed path; (c) for picolinic acid (PA) catalysed path; (CPC) or (SDS) for the value in presence of the respective surfactant.

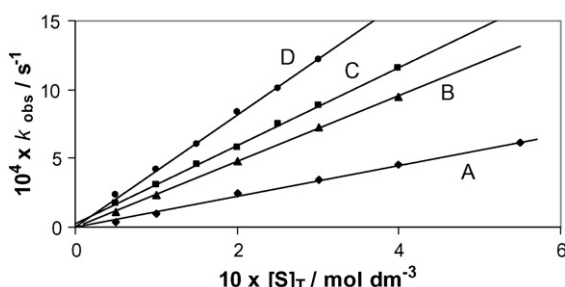
^a $[\text{Cr}^{\text{VI}}]_{\text{T}} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = 0.3 \text{ mol dm}^{-3}$, $[\text{PA}]_{\text{T}} = (0-12 \times 10^{-2}) \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 3 \times 10^{-2} \text{ mol dm}^{-3}$.^b $[\text{Cr}^{\text{VI}}]_{\text{T}} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.0 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = (0-0.6) \text{ mol dm}^{-3}$, $[\text{PA}]_{\text{T}} = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 3 \times 10^{-2} \text{ mol dm}^{-3}$.

Fig. 3. Effect of $[\text{maleic acid}]_{\text{T}}$ on k_{obs} for the Cr^{VI} oxidation of maleic acid in aqueous micellar acid media. $[\text{Cr}^{\text{VI}}]_{\text{T}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{H}_2\text{SO}_4 = 1.0 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = (0.5-5.5) \times 10^{-1} \text{ mol dm}^{-3}$, $T = 45^\circ \text{C}$. (A): $[\text{PA}]_{\text{T}} = 0 \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 0 \text{ mol dm}^{-3}$; (B): $[\text{PA}]_{\text{T}} = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 5 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 0 \text{ mol dm}^{-3}$; (C): $[\text{PA}]_{\text{T}} = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 0 \text{ mol dm}^{-3}$; (D): $[\text{PA}]_{\text{T}} = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{CPC}]_{\text{T}} = 0 \text{ mol dm}^{-3}$, $[\text{SDS}]_{\text{T}} = 3 \times 10^{-2} \text{ mol dm}^{-3}$.

2.4. Dependence on $[\text{H}^+]$

From the experimental fit (cf. Fig. 4), the acid dependence patterns for the uncatalysed and catalysed paths appear to be different. The observations (in both the presence and absence of SDS) are:

$$k_{\text{obs(c)}} = a[\text{S}]_{\text{T}}[\text{PA}]_{\text{T}}[\text{H}^+]^1 \quad (4)$$

$$k_{\text{obs(u)}} = b[\text{S}]_{\text{T}}[\text{H}^+]^1 + c[\text{S}]_{\text{T}}[\text{H}^+]^2 \quad (5)$$

$$k_{\text{obs(T)}} = k_{\text{obs(c)}} + k_{\text{obs(u)}}$$

$$k_{\text{obs(T)}} = a[\text{S}]_{\text{T}}[\text{PA}]_{\text{T}}[\text{H}^+]^1 + b[\text{S}]_{\text{T}}[\text{H}^+]^1 + c[\text{S}]_{\text{T}}[\text{H}^+]^2 \\ = \{a[\text{PA}]_{\text{T}} + b\}[\text{S}]_{\text{T}}[\text{H}^+]^1 + c[\text{S}]_{\text{T}}[\text{H}^+]^2 \quad (6)$$

2.5. Test for acrylonitrile polymerization

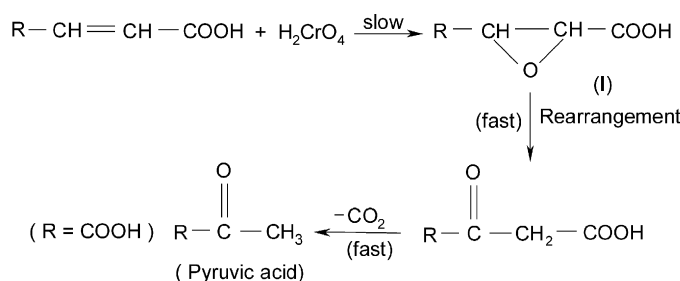
Under the experimental conditions, polymerization of acrylonitrile was observed under a nitrogen atmosphere.

2.6. Mechanism and interpretation

Mechanism of the reaction can be divided in two sections: (i) uncatalysed path and (ii) catalysed path.

2.6.1. Reaction mechanism for the uncatalysed chromic acid oxidation of maleic acid

Oxidation of olefinic compounds by different types of Cr^{VI} compounds like chromic acid, chromyl chloride, chromyl acetate, chlorochromate etc. has been widely studied [4–10]. These studies suggest the formation of an epoxide that subsequently participates in faster steps to give the product. In the present case, pyruvic acid has been detected as the final organic product. Thus, the overall reaction can be represented as follows:



Formation of the epoxide (I) can occur in different possible pathways [4–10] involving a three or five membered cyclic intermediate.

2.6.1.1. Formation of a five membered cyclic transition state. In this event, the double bond acts as a η^2 -ligand to produce a cyclic organometallic compound (III) that rearranges to (V) through the rupture of Cr-C bond [11]. Alternatively, the Π -complex

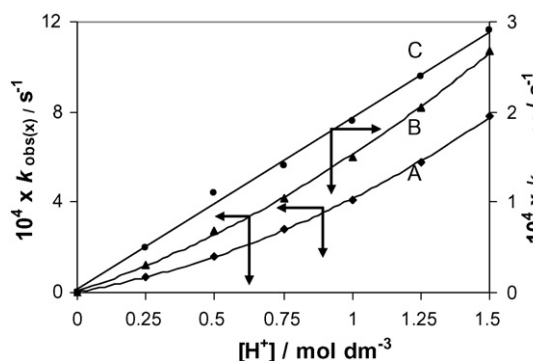
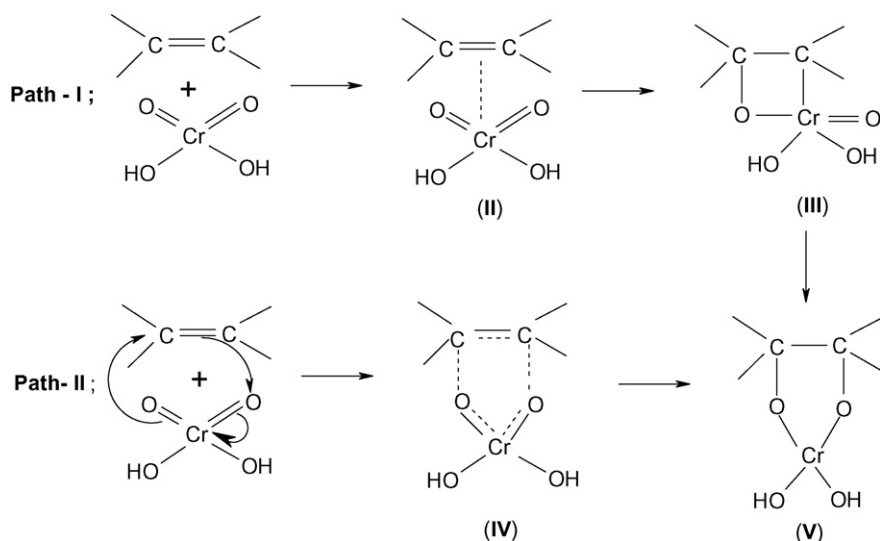


Fig. 4. Effect of $[\text{HClO}_4]_{\text{T}}$ on k_{obs} for the Cr^{VI} oxidation of maleic acid in the presence and absence of picolinic acid in aqueous HClO_4 media. $[\text{Cr}^{\text{VI}}]_{\text{T}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{HClO}_4 + \text{NaClO}_4] = 1.5 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = 0.3 \text{ mol dm}^{-3}$, $T = 45^\circ \text{C}$; (A): $k_{\text{obs(u)}}$ vs. $[\text{H}^+]$ plot, $[\text{PA}]_{\text{T}} = 0 \text{ mol dm}^{-3}$; (B): $k_{\text{obs(T)}}$ vs. $[\text{H}^+]$ plot, $[\text{PA}]_{\text{T}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$; (C): $k_{\text{obs(c)}}$ vs. $[\text{H}^+]$ plot.



Scheme 1. Formation of a five membered cyclic intermediate of CrVI in the oxidation of olefinic double bond.

(IV) may transform into (V) [4]. This path is energetically more feasible as it needs no bond breaking and it passes through the bond formation process only. These two possible paths are outlined in Scheme 1. This path is equivalent to cycloaddition to the double bond as in the case of oxidation by permanganate [10,12].

The five membered cyclic intermediate (V) produces the epoxide (I) [7–9]. This path may be acid catalysed. Protonation of the Cr–OH group facilitates the electron flow towards the Cr^{VI} centre. These are illustrated in Scheme 2.

2.6.1.2. Formation of a three membered cyclic transition state. It may occur in different possible ways outlined in Scheme 3.

In all these paths, the important event is the symmetric electrophilic attack on the double bond. In paths III and IV, the oxygen transfer to the double bond takes place from the nonprotonated oxygen while in paths V and VI, oxygen transfer takes place from the OH group which is definitely more electrophilic than the nonprotonated oxygen [9]. Thus, the paths V and VI are more reasonable. The redox decomposition of the intermediates

(i.e. VII, VIII, IX and X) leading to the epoxide (I) and Cr^{IV} can be catalysed through protonation of the ‘Cr=O’ or Cr–OH bond as it will facilitate the electron flow. This has been illustrated in Scheme 2.

Thus, the mechanism of chromic acid oxidation of maleic acid can be outlined as in Scheme 4.

In Scheme 4, the species ‘A’ actually denotes the five centered cyclic intermediate (V) of Cr^{VI} (cf. Scheme 1) or the three centered cyclic intermediate (VII, VIII, IX, X) of Cr^{VI} (cf. Scheme 3), the species ‘B’ is the protonated form of the species ‘A’ (cf. Scheme 2) and ‘C’ stands for the epoxide (I). Cr^{IV} generated at the rate-determining step is rapidly reduced to Cr^{III} in presence of Cr^{VI} and excess substrate. This may occur through the intermediacy of Cr^{II} or Cr^V or Cr^{IV} in different possible routes [2,3c,e,f,13–16].

Scheme 4 leads to the following rate law:

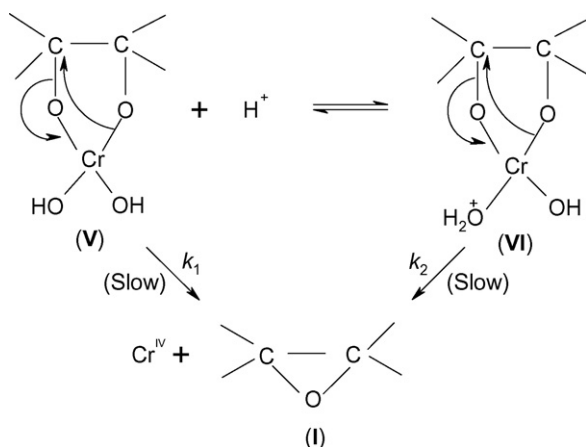
$$k_{\text{obs}(u)} = \frac{2}{3} \{K_1 k_1 [S]_T [H^+] + K_1 K_2 k_2 [S]_T [H^+]^2\}$$

$$= k_{u(1)} [S]_T [H^+] + k_{u(2)} [S]_T [H^+]^2 \quad (13)$$

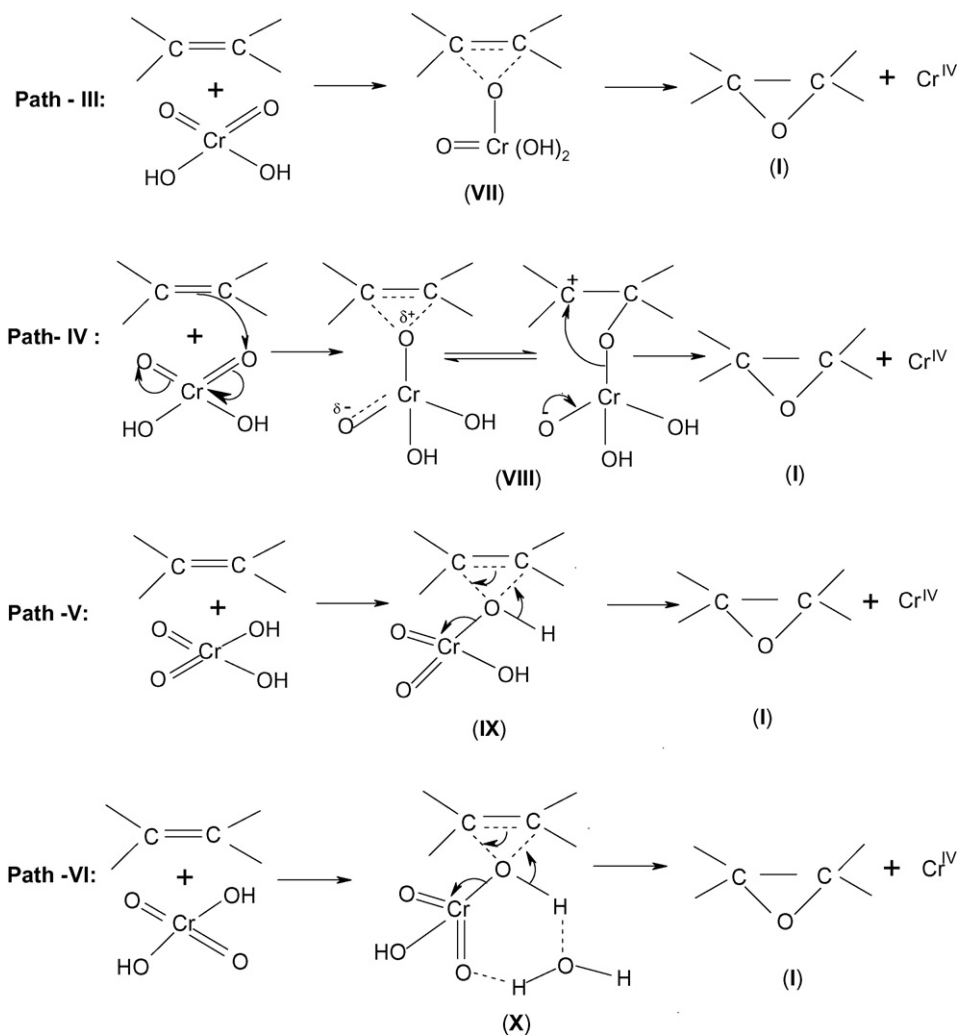
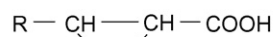
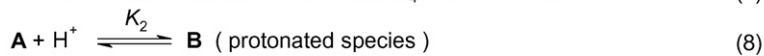
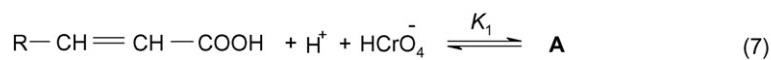
[S]_T stands for the substrate, i.e. maleic acid concentration.

2.6.2. Reaction mechanism for the PA-catalysed chromic acid oxidation of maleic acid

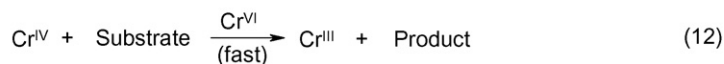
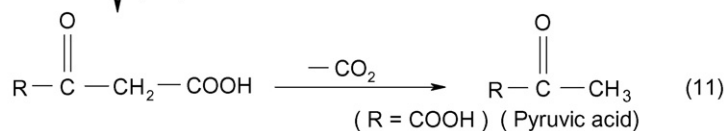
The findings for the PA-catalysed reactions can be explained by considering the reaction mechanism outlined in Scheme 5. Here, PA readily forms a reactive cyclic Cr^{VI}–PA complex ‘D’ in the acid catalysed reaction with HCrO₄[−] and this Cr^{VI}–PA complex is the active oxidant [1–3]. In the next step, Cr^{VI}–PA complex reacts with the substrate to form a ternary complex ‘E’, In the ternary complex ‘E’, the species XI and XII stand for the representative five membered and three membered cyclic intermediate, respectively. These cyclic intermediates are similar to those discussed for the uncatalysed reaction. The larger negative value of ΔS[#] (entropy of activation) (Tables 1 and 2) of the composite rate constant *k*_{cat} supports the suggested cyclic transition



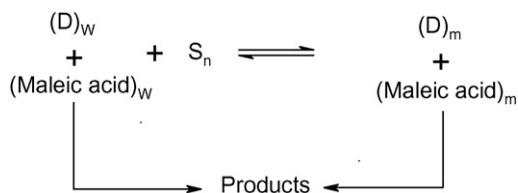
Scheme 2. Redox decomposition of the five membered cyclic intermediate (V) and its protonated form (VI) at the rate-determining step to give the epoxide (I).

Scheme 3. Formation of a three membered cyclic intermediate of Cr^{VI} in the oxidation of olefinic double bond.

(C)

rearrangement
(fast)

Scheme 4. Mechanistic steps of chromic acid oxidation of maleic acid.



Scheme 6. Distribution of the reactive species between the aqueous and micellar phases.

dodecyl sulfate (SDS). In the PA-catalysed path, CPC restricts the positively charged Cr^{VI} -PA complex (**D**), the active oxidant, in the aqueous phase and thus, the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction. Therefore, in the PA-catalysed path, the reaction is mainly restricted in the aqueous phase in which the concentration of the substrate is depleted due to its partitioning in the Stern layer of the micelle. Partitioning of the reactants between the aqueous and micellar phase is shown in Scheme 6 in which S_n represents the micellised surfactants where 'n' is the aggregation number.

2.7.2. Uncatalysed path

In the absence of picolinic acid (PA), i.e. uncatalysed path, the plot of $k_{\text{obs(u)}}$ versus $[\text{CPC}]_T$ (cf. Fig. 5) shows a different trend compared to the catalysed path. In the uncatalysed path, up to a certain concentration of CPC, the k_{obs} value remains unaffected but after a certain concentration level of CPC, it has been found to decrease with the further increase of CPC concentration and finally it tends to level off at higher concentration of CPC. At the lower concentration of CPC, the balancing effect can be explained by considering the parallel k_1 and k_2 paths. The k_1 path involves the reactants chromic acid (H_2CrO_4), which is kinetically active [21,22a] under the experimental condition and substrate. These are preferably accumulated in the Stern layer [2]. Thus, it is favoured. The k_2 path (i.e. acid catalysed path) needs the reactants chromic acid (H_2CrO_4), substrate and H^+ . Though chromic acid and substrate are favourably accumulated in the Stern layer of CPC, approach of H^+ is repelled by the positively charged micellar head groups. Thus, the rate accelerating effect of CPC in the k_1 path is opposed by the rate retarding effect of CPC in the k_2 path. This causes the balancing effect. But after a certain concentration of CPC, the rate retarding effect in the k_2 path becomes more predominant as the k_2 path is kinetically more important than the k_1 path.

2.8. Effect of SDS

Sodium dodecyl sulfate, a representative anionic surfactant accelerates both the uncatalysed and PA-catalysed path (cf. Fig. 6). In the PA-catalysed path, the rate accelerating effect arises owing to the preferential partitioning of the positively charged Cr^{VI} -PA complex (by electrostatic attraction) and neutral substrate (probably by hydrophobic attraction) in the micellar interphase. Thus, SDS permits the reaction to proceed in both aqueous and micellar interphase. The rate benefit

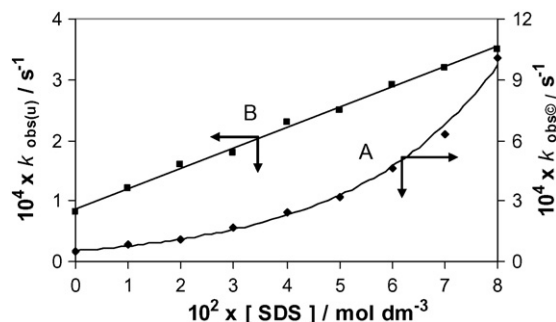
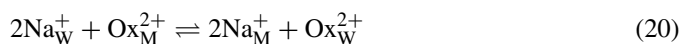


Fig. 6. Effect of $[\text{SDS}]_T$ on $k_{\text{obs(u)}}$ (absence of PA) and $k_{\text{obs(c)}}$ (presence of picolinic acid) for the Cr^{VI} oxidation of maleic acid in the presence of sodium dodecyl sulfate (SDS) in aqueous H_2SO_4 media. $[\text{Cr}^{\text{VI}}]_T = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{H}_2\text{SO}_4 = 1.25 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_T = 6 \times 10^{-2} \text{ mol dm}^{-3}$, $T = 47^\circ\text{C}$. (A): $k_{\text{obs(c)}}$ vs. $[\text{SDS}]_T$ plot, $[\text{PA}]_T = 2 \times 10^{-2} \text{ mol dm}^{-3}$; (B): $k_{\text{obs(u)}}$ vs. $[\text{SDS}]_T$ plot, $[\text{PA}]_T = 0 \text{ mol dm}^{-3}$.

arises due to the enhanced rate in the micellar phase where both the reactants are preferably accumulated. In the absence of PA, binding of kinetically active species H_2CrO_4 and the substrate to the SDS micelle has been argued by different workers [22]. However, possibility of partitioning of neutral Cr^{VI} -substrate ester (**A**, cf. Scheme 4) into the micellar phase cannot be ruled out. Simultaneous partitioning of H_2CrO_4 and substrate is equivalent to the partitioning of Cr^{VI} -substrate ester. The H^+ ions needed for the reactions are also preferably attracted to the micellar phase. Thus, SDS allows the reaction in both phases with a preferential rate enhancement in the micellar phase.

In the PA-catalysed reaction, the plot of $k_{\text{obs(c)}}$ versus $[\text{SDS}]_T$ (cf. Fig. 6) indicates that the rate increases in a continuous fashion up to the SDS concentration used. An increase of $[\text{SDS}]_T$ increases the micellar solubilisation of the reactants but at the same time an increase in $[\text{SDS}]_T$ increases the concentration of the micellar counterions (i.e. Na^+), which may replace H^+ and OX^+ ions (OX^+ stands for the cationic Cr^{VI} -PA complex, **D**) out of the micellar surface.



The plot of $k_{\text{obs(c)}}$ versus $[\text{SDS}]_T$ indicates that the solubilisation effect is greater than the counterion effect for the PA-catalysed path for the SDS concentration used. Here, it may be noted that the organic product pyruvic acid is also partitioned between the micellar (both cationic and anionic) and aqueous phases. However, this partitioning does not have any effect on the rate process or reaction mechanism.

3. Experimental

3.1. Materials and reagents

Picolinic acid (Fluka) was used after repeated crystallization from methanol (m.p. 136°C). Maleic acid (SRL), $\text{K}_2\text{Cr}_2\text{O}_7$ (BDH), sodium dodecyl sulfate (SRL), *N*-cetylpyridinium chlo-

ride, CPC (SRL) and all other chemicals used were of highest purity available commercially. The solutions were prepared in double distilled water.

3.2. Procedure and kinetic measurements

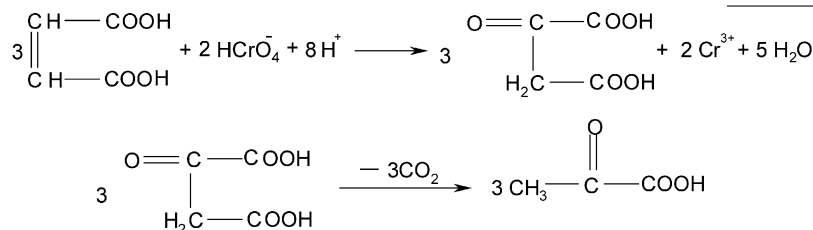
Solutions of the oxidant and reaction mixtures containing the known quantities of the substrate (S) (i.e. maleic acid), catalyst (picolinic acid), under the kinetic conditions $[\text{maleic acid}]_{\text{T}} \gg [\text{Cr}^{\text{VI}}]_{\text{T}}$ and $[\text{picolinic acid}]_{\text{T}} \gg [\text{Cr}^{\text{VI}}]_{\text{T}}$, 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 titrimetric quenching technique as discussed earlier [3a].

The pseudo first order constants (k_{obs}) were calculated as usual. Under the experimental conditions, possibility of decomposition of the surfactants by Cr^{VI} has been investigated and the rate of decomposition has been found negligible. Errors associated with the different rate constants and activation parameters were estimated as usual [23].

3.3. Product analysis and stoichiometry

Under the kinetic conditions (i.e. $[\text{S}]_{\text{T}} \gg [\text{Cr}^{\text{VI}}]_{\text{T}}$), qualitative identification of the reaction products was carried out by 2,4-dinitrophenylhydrazine test (DNP test) [4]. The reaction product solution was then treated with an excess of saturated solution of 2,4-dinitrophenylhydrazine. The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried, recrystallised from ethanol. The DNP derivative was found identical (m.p. 218 °C) with the DNP derivative of authentic pyruvic acid.

The product analysis was also carried out by another spot test, chromotropic acid test [24]. A few drops of the product solution were treated with magnesium powder in presence of dilute hydrochloric acid followed by the addition of moderately concentrated sulfuric acid and a little amount of chromotropic acid. The reaction mixture was heated in a water bath for about 10 min and then it developed a characteristic yellow colour obtained by using pure pyruvic acid in the same way. This spot test confirmed the reaction product as pyruvic acid. Thus, the stoichiometry of the reaction is:



The final fate of the Cr^{III} -species has been confirmed by spectroscopically. The UV–visible spectra (Figs. 7 and 8) were recorded by using the spectrophotometer (UV–VIS–NIR scanning spectrophotometer, UV-3101PC, Shimadzu). The reaction solution was scanned (in the range 350–700 nm) at regular intervals to follow the gradual development of the reaction

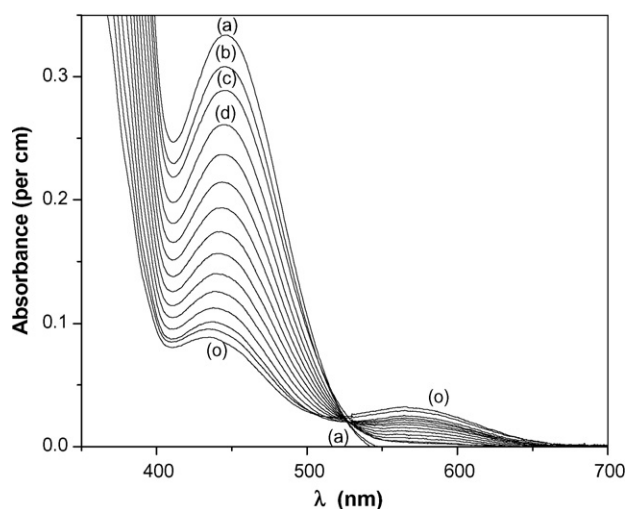


Fig. 7. Scanned absorption spectra of the reaction mixture at regular time intervals (5 min, e.g. (a) after 4 min at the beginning of reaction; (b) after 9 min; (c) after 14 min; and so on up to (o) after 74 min). Concentrations at the beginning of the reaction $[\text{Cr}^{\text{VI}}]_{\text{T}} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{PA}]_{\text{T}} = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.25 \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = 0.4 \text{ mol dm}^{-3}$, $T = 30$ °C.

intermediate (if any) and product spectrophotometrically. The scanned spectrum (Fig. 7) indicates the gradual disappearance of Cr^{VI} -species and appearance of Cr^{III} -species with the isobestic point at $\lambda = 525$ nm. Observation of this single isobestic point indicates the very low concentration of the probable intermediates [25] like Cr^{V} and Cr^{IV} under the present experimental conditions. In other words, it indicates the gradual decrease of Cr^{VI} with the concomitant increase of Cr^{III} . The characteristic part of electronic absorption spectrum of Cr^{III} -species lies in the range 360–600 nm [26]. The colours of the final solutions of the uncatalysed and PA-catalysed reaction are different due to the presence of different types of Cr^{III} -species. The colour of the final solution for the uncatalysed reaction (i.e. in absence of PA) under the experimental condition is pale blue ($\lambda_{\text{max}} = 412$ and 578 nm) and the corresponding transitions [26] are: 578 nm for ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$; and 412 nm for ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{F})$ of Cr^{III} -species. On the other hand, the colour of the final solution of the PA-catalysed reaction under the identical condition

is pale violet [$\lambda_{\text{max}} = 556$ nm for ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$ of Cr^{III} -species]. The spectra of the final solution of the uncatalysed reaction and pure chromic sulfate solution in aqueous sulfuric acid media are identical. It indicates that the final Cr^{III} -species is simply Cr^{III} -species for the uncatalysed reaction while for the PA-catalysed reaction; the final Cr^{III} -species is a different

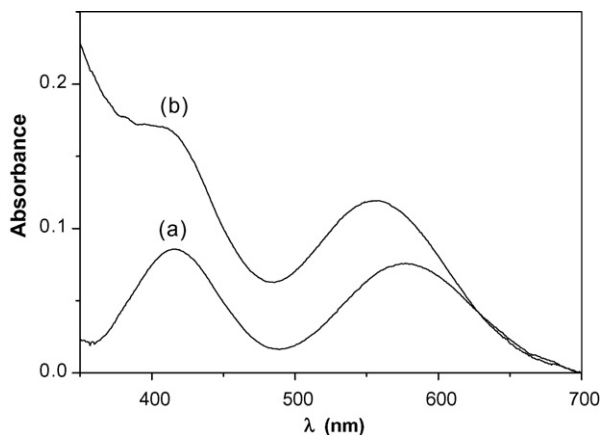


Fig. 8. (a) Absorption spectrum of the reaction mixture (after completion of reaction): $[\text{Cr}^{\text{VI}}]_{\text{T}} = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = 0.4 \text{ mol dm}^{-3}$, $[\text{PA}]_{\text{T}} = 0 \text{ mol dm}^{-3}$ (i.e. uncatalysed path), $[\text{H}_2\text{SO}_4] = 1.25 \text{ mol dm}^{-3}$ (the spectrum of the chromic sulfate is identical with this under the experimental condition.); (b) Absorption spectrum of the reaction mixture (after completion of reaction): $[\text{Cr}^{\text{VI}}]_{\text{T}} = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{maleic acid}]_{\text{T}} = 0.4 \text{ mol dm}^{-3}$, $[\text{PA}]_{\text{T}} = 15 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.25 \text{ mol dm}^{-3}$.

species, which is a $\text{Cr}^{\text{III}}\text{-PA}$ complex. It is very interesting to point out that for the final solution of the PA-catalysed reaction, there is a blue shift (Fig. 8) for the peak due to the transition ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$ compared to the final solution of the uncatalysed path. This blue shift is due to the presence of the strong field donor site, i.e. heteroaromatic *N*-donor site of PA. For the said $\text{Cr}^{\text{III}}\text{-PA}$ complex, the peak due to the transition ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{F})$ merges with a charge transfer band (Fig. 8). It may be noted that for $\text{Cr}(\text{aq})^{3+}$ species, there is also a large charge transfer band [26] at higher energy. In fact, the band at 270 nm due to ${}^4\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$ transition appears as a shoulder on the high energy charge transfer band [26a]. The appearance of the charge transfer band at much lower energy for the proposed $\text{Cr}^{\text{III}}\text{-PA}$ complex is quite reasonable because of the favoured metal to ligand charge transfer. In fact, in the vacant Π^* of PA favours the metal to ligand charge transfer. The existence of the charge transfer band (metal to ligand) at this lower energy for the PA-catalysed reaction indirectly supports the proposition of the $\text{Cr}^{\text{III}}\text{-PA}$ complex in the final solution.

4. Conclusions

The $\text{Cr}^{\text{VI}}\text{-PA}$ complex, a cationic species has been found to act as the active oxidant in the PA-catalysed chromic acid oxidation of unsaturated acid like maleic acid to give the product pyruvic acid. This cationic species reacts with the substrate maleic acid to form a ternary complex, which subsequently experiences a 2e-transfer redox decomposition leading to the epoxide and $\text{Cr}^{\text{IV}}\text{-PA}$ complex at the rate-determining step. Subsequently, the epoxide produces pyruvic acid through the decarboxylation of β -keto acid in a faster step. The reactions have been carried out in aqueous micellar media. The cationic surfactant (CPC) shows the rate retarding effect while the anionic surfactant (SDS) accelerates the rate both in the catalysed and

uncatalysed paths. The micellar effects support the proposed mechanistic pathways.

The state of Cr^{III} -species in the final solution has been detected by following the UV-visible spectra. In the uncatalysed reaction, the species is simply Cr^{III} -species (pale blue, $\lambda_{\text{max}} = 412 \text{ nm}$ and 578 nm) while for the PA-catalysed path; the corresponding species is a $\text{Cr}^{\text{III}}\text{-PA}$ complex (pale violet colour, $\lambda_{\text{max}} = 556 \text{ nm}$). This $\text{Cr}^{\text{III}}\text{-PA}$ complex is not formed by the interaction of PA with the Cr^{III} -species produced after reduction of Cr^{VI} as Cr^{III} ($t_{2\text{g}}^3$) is kinetically very inert. From an independent experiment, it has been noted that under the comparable conditions, the spectrum of a mixture containing $\text{Cr}(\text{aq})^{3+}$ and PA does not change within the reaction time (required for the present redox reaction initiated by Cr^{VI}). This is why, it is concluded that PA does not ligate with the Cr^{III} centre after its generation from Cr^{VI} . Existence of the $\text{Cr}^{\text{III}}\text{-PA}$ complex in the final solution supports the formation of $\text{Cr}^{\text{VI}}\text{-PA}$ complex in the pre-equilibrium step, as the Cr^{VI} centre is kinetically labile. This $\text{Cr}^{\text{VI}}\text{-PA}$ complex is finally reduced to $\text{Cr}^{\text{III}}\text{-PA}$ complex.

Acknowledgments

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Appendix A. Derivation of rate law considering Scheme 5

$$K_a = \frac{[\text{PA}][\text{H}^+]}{[\text{PAH}^+]} \quad (\text{i})$$

$$[\text{PA}]_{\text{T}} = [\text{PA}] + [\text{PAH}^+] \quad (\text{ii})$$

$$[\text{PA}]_{\text{T}} = [\text{PA}] + \frac{[\text{PA}][\text{H}^+]}{K_a} \text{ (from Eq. i)} = [\text{PA}] \left\{ 1 + \frac{[\text{H}^+]}{K_a} \right\}$$

or

$$[\text{PA}] = \frac{[\text{PA}]_{\text{T}} K_a}{K_a + [\text{H}^+]} \quad (\text{iii})$$

$$K_3 = \frac{[\text{D}]}{[\text{PA}][\text{HCrO}_4^-][\text{H}^+]^2} \quad (\text{iv})$$

or

$$[\text{D}] = K_3 [\text{PA}][\text{HCrO}_4^-][\text{H}^+]^2 = \frac{K_3 K_a [\text{PA}]_{\text{T}} [\text{HCrO}_4^-][\text{H}^+]^2}{K_a + [\text{H}^+]} \quad (\text{v})$$

Following the steady-state approximation,

$$\frac{d[\text{E}]}{dt} = 0 = k_3[\text{D}][\text{S}]_{\text{T}} - k_{-3}[\text{E}] - k_4[\text{E}] \quad (\text{vi})$$

or

$$k_3[\text{D}][\text{S}]_{\text{T}} = [\text{E}](k_{-3} + k_4) \quad (\text{vii})$$

or,

$$[E] = \frac{k_3[D][S]_T}{k_{-3} + k_4}$$

(where $[S] \approx [S]_T$ under the conditions $[S]_T \gg [Cr^{VI}]_T$)

$$\text{Rate} = -\frac{d[HCrO_4^-]}{dt} = k_4[E] = \frac{K_3 K_4 [D][S]_T}{k_{-3} + k_4} \quad (\text{viii})$$

$$\text{Rate} = \frac{K_3 K_a k_3 k_4 [S]_T [PA]_T [HCrO_4^-] [H^+]^2}{(k_{-3} + k_4)(K_a + [H^+])} \quad (\text{ix})$$

$$k_{\text{obs(c)}} = -\frac{d \ln[HCrO_4^-]}{dt} = \left(\frac{2}{3}\right) \frac{K_3 K_a k_3 k_4 [S]_T [PA]_T [H^+]^2}{(k_{-3} + k_4)(K_a + [H^+])} \quad (19)$$

$$k_{\text{obs(c)}} \approx \frac{(K_3 K_a k_3 k_4 [S]_T [PA]_T [H^+]^1)}{(k_{-3} + k_4)} = a[S]_T [PA]_T [H^+]^1 \quad (4)$$

where, $a = (2/3) (K_3 K_a k_3 k_4) / (k_{-3} + k_4)$ (under the condition $[H^+] (=0.25-1.5 \text{ mol dm}^{-3}) \gg K_a (=0.025 \text{ mol dm}^{-3})$)¹⁷ Eq. (19) reduces to (4) experimentally observed).

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