Convention Special Issue - 2019

J. Indian Chem. Soc.,
Vol. 96, October 2019, pp. 1333-1342

Kinetics and mechanism of hetero-aromatic N-base ligand 1,10-phenanthroline assisted chromic acid oxidation of DL-malic acid in aqueous micellar acid media

Monirul Islam

Department of Chemistry, Seth Anandram Jaipuria College, Kolkata-700 005, India

E-mail: monirul_vu@yahoo.co.in, michem989@gmail.com

Manuscript received online 18 September 2019, accepted 24 September 2019

Hetero-aromatic N-base ligand like 1,10-phenanthroline (phen) assisted chromic acid oxidation of malic acid in aqueous sulfuric acid media have been studied under the experimental conditions, $[\text{malic acid}]_T >> [\text{Cr(VI)}_T]$ at different temperatures. Under the kinetic conditions, $HCrO_4^-$ has been found kinetically active in the absence of phen catalyst while in the phen catalyzed path Cr(VI)-phen complex has been suggested in the active oxidant. In the catalysed path, Cr(VI)-phen complex receives a nucleophilic attack by the substrate to form a ternary complex which subsequently experiences a two-electron transfer redox decomposition leading to Cr(IV)-phen complex. Then Cr(IV)-phen complex participates further in the oxidation of malic acid and ultimately is converted into Cr(III)-phen complex. Both the paths show first-order dependence on $[\text{malic acid}]_T$ and $[\text{Cr(VI)}]_T$. The phen catalyzed path is first-order in $[\text{phen}]_T$. These observations remain unaltered in the presence of externally added surfactants. Effect of anionic surfactant sodium dodecyl sulfate (SDS) and cationic surfactant N-cetylpyridinium chloride (CPC) on the phen-catalysed path has been studied. SDS accelerates the phen-catalysed path and CPC shows the rate retarding effect on the path. The observes micellar effects have been explained by considering the hydrophobic and electrostatic interaction between the surfactants and reactants.

Keywords: Kinetics, catalysis, DL-malic acid, chromium(VI), 1,10-phenanthroline, surfactants.

1. Introduction

In chromic acid oxidation of organic substrates various chelating agents[1–29] such as oxalic acid, ethylenediammine tetraacetic acid (EDTA), 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been employed as catalysts, 1,10-phenanthroline (phen) is quite unique[20,21,30–34]. It does not get itself co-oxidized with the target reductant but it is gradually lost due to the formation of an inert Cr(III)-phen complex. Thus, phen is not a true catalyst and it is better described[20] as an oxidation catalyst, however, conventionally the reactions are described as phen-catalysed reactions. The present paper describes the micellar effect on the title reaction in the presence of 1,10-phenanthroline catalyst to provide a better insight to the reaction mechanisms. It also explores the kinetics and reaction mechanism of the title reaction in aqueous sulfuric acid media to substantiate the proposed reaction mechanism. Activation parameters have been determined in order to rationalize the mechanistic steps. The micellar effect on the oxidation reaction by higher valent metal ions[23,24,26,35–39] have been studied to substantiate the proposed reaction mechanism. In the present investigation the high value of enthalphy of activation, $\Delta H^{\neq}$ indicates that the phen-catalysed path is favoured mainly due to very high negative value of entropy of activation, $\Delta S^{\neq}$. The negative value of $\Delta S^{\neq}$ and the composite rate constant k_{cat} supports the suggested cyclic transition state.

2. Experimental

2.1. Materials and reagents

Standard stock solution of Ce(IV) in aqueous sulfuric acid media was prepared from $CeSO_4.2(NH_4)_2SO_4.2H_2O$ (A.R., E. Merck), 1,10-phenanthroline (Qualigens, India), *dl*-malic acid (SRL), $K_2Cr_2O_7$ (BDH), sodium dodecyl sulfate, SDS (SRL), *N*-cetylpyridinium chloride, CPC (SRL) and all other chemicals used were of highest purity available commercially. The solutions were prepared in doubly distilled water.

2.2. Procedure and kinetic measurements

Under the kinetic conditions, $[S]_T >> [\text{Cr(VI)}]_T$ and $[\text{phen}]_T$

>> $[Cr(VI)]_T$, the solutions of the oxidant and the reaction mixture containing the required quantities of the substrate (S) (DL-malic acid), catalyst (phen), 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. The rate of progress of the reaction was followed by measuring the concentration of Cr(VI) at different time intervals by quenching titrimetric methods as discussed earlier[15]. The pseudo-first order rate 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[40].

2.3. Product analysis and stoichiometry

Under the kinetic conditions {i.e. $[malic\ acid]_T >> [Cr(VI)]_T$}, the oxidized reaction mixture was completely neutralized by sodium bicarbonate and then extracted with ether. The ethereal layer was used for the detection of very small amounts of acetaldehyde while the aqueous layer was used to detect and estimate the main product, pyruvic acid. Aqueous HCl solution of 2,4-dinitro phenyl hydrazine was used to precipitate the hydrazones. The products were qualitatively checked by m.p. of hydrazones of pyruvic acid (m.p. 218°C) and that of acetaldehyde (m.p. 168°C)[41]. Under the experimental conditions, $[malic\ acid]_T >> [Cr(VI)]_T$ and $[phen]_T >> [Cr(VI)]_T$, the overall stoichiometry of the reactions may be represented as follows:

$$3CH_2(COOH)CH(OH)CO_2H + 2HCrO_4^- + 8H^+ \rightarrow$$
$$3CH_3COCO_2H + 3CO_2 + 2Cr(III) + 8H_2O \quad (I)$$

The reaction mixtures solutions were scanned (in the range 350–700 nm) at regular time intervals (*cf.* Figs. 1, 2 and 3) by using the spectrophotometer (UV-Vis-NIR Scanning Spectrophotometer, UV-3101PC, Shimadzu) to follow the gradual development of the reaction intermediate and product spectrophotometrically. The scanned spectrum (Figs. 1 and 3) indicates the gradual disappearance of Cr(VI)-species and appearance of Cr(III)-species with the isosbestic point at λ = 525 nm. Observation of this single isosbestic point indicates the very low concentration of the probable intermediates[42] 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[43,44]. The colour of the final solutions of the uncatalysed and phen-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 under the experimental condition is pale blue (λ_{max} = 412 and 578 nm) and the colour of the final solution of the

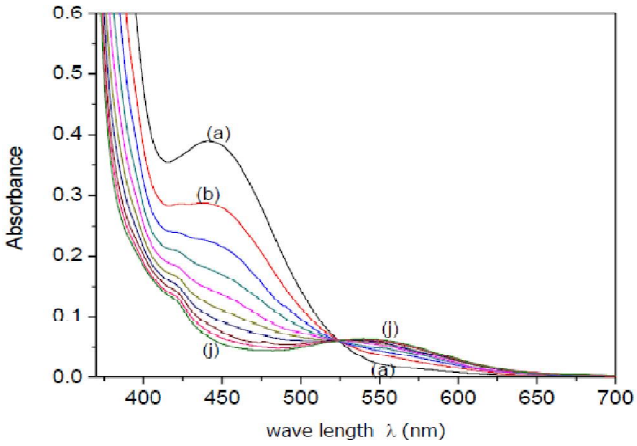


Fig. 1. Scanned absorption spectra of the reaction mixture in presence of catalyst at a regular time intervals (5 min) from beginning (a) to upto 45 min (j). Concentrations at the beginning of the reaction, $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[phen]_T = 9.0\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.00$ mol dm^{-3}, $[malic\ acid]_T = 30.0\times10^{-3}$ mol dm^{-3}, T = 25°C, isosbestic point at λ = 525 nm.

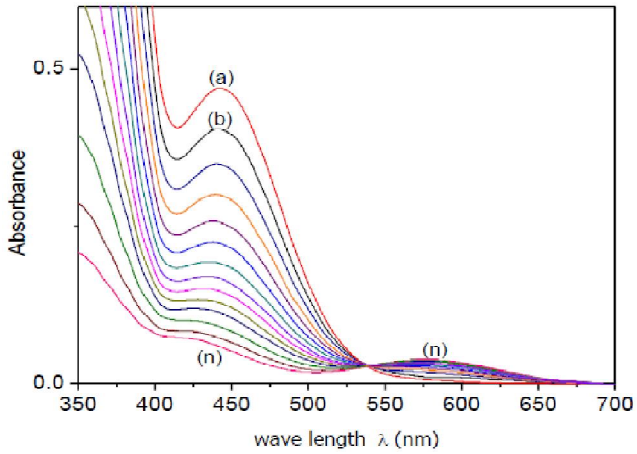


Fig. 2. Scanned absorption spectra of the reaction mixture in absence of catalyst (i.e. uncatalysed path) at a regular time intervals (5 min) from beginning (a) to upto 90 min (n). Concentrations at the beginning of the reaction, $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.00$ mol dm^{-3}, $[malic\ acid]_T = 60.0\times10^{-3}$ mol dm^{-3}, T = 25°C , isosbestic point at λ = 536 nm.

phen-catalysed reaction under the identical condition is pale violet [λ_{max} = 553 nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr(III)-species].

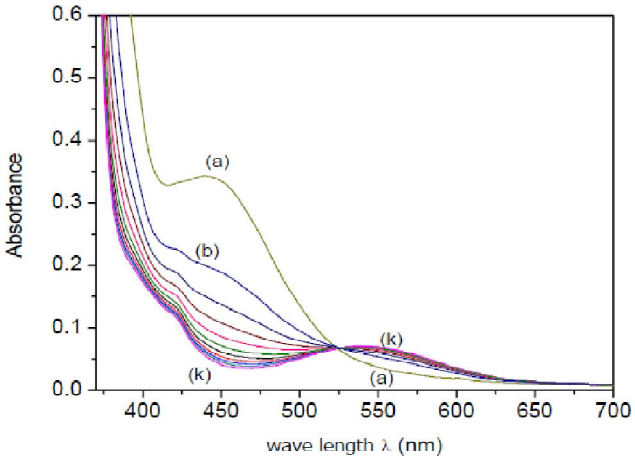


Fig. 3. Scanned absorption spectra of the reaction mixture in presence of catalyst at a time intervals from beginning (a) to upto 55 min (k). Concentrations at the beginning of the reaction, $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[phen]_T = 12.0\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.00$ mol dm^{-3}, $[malic\ acid]_T = 30.0\times10^{-3}$ mol dm^{-3}, T = 25°C , isosbestic point at λ = 525 nm.

The state of Cr(III)-species in the final solution has been detected by the following UV-Visible spectra. The UV-Visible spectra (Fig. 4) was recorded by using the spectrophotometer (UV-Vis-NIR Scanning Spectrophotometer, UV-3101PC, Shimadzu). In the uncatalyzed reaction, the species is simply Cr(III)-species, under the experimental condition is pale blue (λ_{max} = 412 and 578 nm) and the corresponding transitions[43,44] are: 578 nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$; and 412 nm for $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ of Cr(III)-species. On the other hand, the colour of the final solution of the phen-catalysed reaction under the identical condition is pale violet [λ_{max} = 553 nm for $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ of Cr(III)-phen]. The spectra of the final solution of the uncatalysed reaction and pure chromic sulfate solution in aqueous sulfuric acid media are identical. These results indicates that the final Cr(III)-species is simply Cr(III)-species for the uncatalysed reaction while for the phen-catalysed reaction, the final Cr(III)-species is a different species which is a Cr(III)-phen complex. Similar results have been noted by earlier workers[31,32]. It is very interesting to point out that for the final solution of the phen-catalysed reaction, there is a blue shift (Fig. 4) for the peak due to the transition

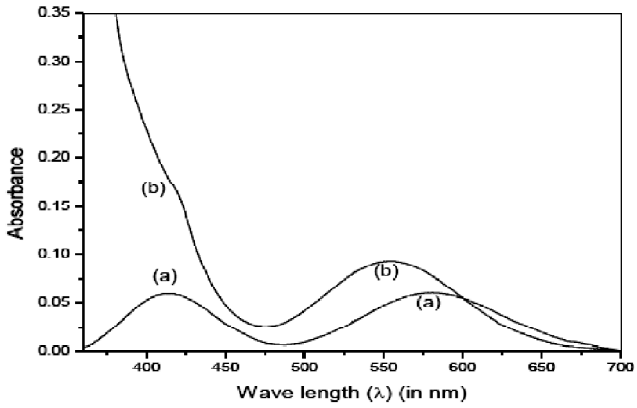


Fig. 4 (a) Absorption spectrum of the reaction mixture (after completion of reaction): $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 50\times10^{-3}$ mol dm^{-3}, $[phen]_T = 0$ mol dm^{-3} (i.e. uncatalysed path), $[H_2SO_4] = 1.0$ mol dm^{-3}, T = 25°C (The spectrum of the chromic sulfate is identical with this under the experimental condition). (b) Absorption spectrum of the reaction mixture (after completion of reaction): $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 50\times10^{-3}$ mol dm^{-3}, $[phen]_T = 8\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, T = 25°C.

$^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ compared to the final solution of the uncatalysed path. This blue shift is due to the presence of the strong field donar site i.e. heteroaromatic N-donar site of phen. For the said Cr(III)-phen complex, the peak due to the transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ merges with a charge transfer band (Fig. 4). It may be pointed out that for $Cr(aq)^{3+}$ species, there is also a large charge transfer band[43,44] at higher energy. In fact, the band at 270 nm due to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition appears as a shoulder on the high energy charge transfer band[43,44]. The appearance of the charge transfer band at much lower energy for the proposed Cr(III)-phen complex is quite reasonable because of the favored M→L charge transfer transition. In fact, the vacant Π* in phen favours the M→L charge transfer band. The existence of the charge transfer band (M→L) at this lower energy for the phen-catalysed reaction in the final solution directly supports formation of Cr(III)-phen complex .

3. Results and discussion

3.1. Dependence on $[Cr(VI)]_T$

Under the kinetic conditions, $[S]_T >> [Cr(VI)]_T$ and $[phen]_T >> [Cr(VI)]_T$, the rate of disappearance of Cr(VI) shows a first-order dependence on $[Cr(VI)]_T$ for both the presence and absence of phen. The first-order dependence remains unal-

tered in the presence of surfactants CPC and SDS. The pseudo-first order rate constants (k_{obs}) were estimated as usual from the linear plot of log $[Cr(VI)]_T$ versus *t*.

3.2. Dependence on $[S]_T$

From the plot of k_{obs} vs $[S]_T$ (*cf.* Fig. 5), it is established that k_{obs} shows a first-order dependence on $[S]_T$ in the presence and absence of $[phen]_T$, 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 valus of $k_{s(c)}$ and $k_{s(u)}$ are given in Table 1. In the presence of surfactants, the same dependence pattern is maintained.

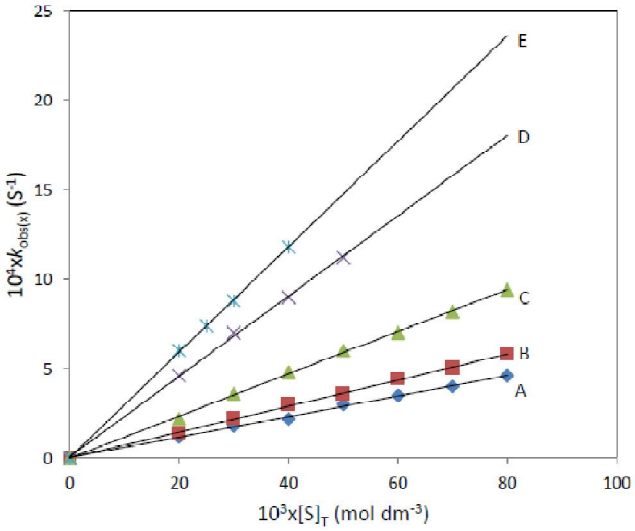


Fig. 5. Effects of $[S]_T$ on $k_{obs(x)}$ (x = u or T) for the Cr(VI) oxidation of DL-malic acid in the presence of phen in aqueous H_2SO_4 media. $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, T = 37°C . $[malic\ acid]_T = (0–80)\times10^{-3}$ mol dm^{-3}. (A) : $[phen]_T = 6\times10^{-3}$ mol dm^{-3}, $[CPC]_T = 12\times10^{-3}$ mol dm^{-3}. (B) : $[phen]_T = 0$ mol dm^{-3}. (C) : $[phen]_T = 6\times10^{-3}$ mol dm^{-3}. (D) : $[phen]_T = 6\times10^{-3}$ mol dm^{-3}, $[SDS]_T = 3\times10^{-2}$ mol dm^{-3}. (E) : $[phen]_T = 10\times10^{-3}$ mol dm^{-3}, $[SDS]_T = 10\times10^{-3}$ mol dm^{-3}.

3.3. Dependence on $[phen]_T$

The effect of $[phen]_T$ on k_{obs} has been followed in aqueous sulfuric acid media. The plots of $k_{obs(T)}$ vs $[phen]_T$ are linear ($r > 0.99$) with positive intercepts measuring the contribution of the relatively slower unanalyzed path (*cf.* Fig. 6). The pseudo-first order rate constants $\{k_{obs(u)}\}$ directly measured in the absence of phen nicely agree with those obtained from the intercepts of the plots of $k_{obs(T)}$ vs $[phen]_T$.

Table 1. Kinetic parameters and some representative rate constants for the chromic acid oxidation of DL-malic acid in the presence of 1,10-phenanthroline in aqueous H_2SO_4 media

Temp. (°C)	$10^4\,k_{obs(u)(w)}$ (s^{-1})[a]	$10^2\,k_{cat(w)}$ ($dm^3\,mol^{-1}\,s^{-1}$)[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]	$10^2\,k_{eff(w)}$[a]	$k_{H(c)(w)}$ ($dm^3\,mol^{-1}\,s^{-1}$)[b]	$10^2\,k_{s(c)(w)}$ ($dm^3\,mol^{-1}\,s^{-1}$)[c]	$10^2\,k_{s(c)(CPC)}$ ($dm^3\,mol^{-1}\,s^{-1}$)[c]	$10^2\,k_{s(c)(SDS)}$ ($dm^3\,mol^{-1}\,s^{-1}$)[c]
27°C	2.0±0.2	3.3±0.25		4.9±0.30	17.0				
37°C	2.8±0.2	4.7±0.40			16.0	7.6±0.10	1.2±0.03	0.55±0.05	2.4±0.02
47°C	5.8±0.4	7.0±0.35	5.0±0.25		11.2				
$\Delta H^{\neq}$ (kJ mol^{-1})		53.7±5.17							
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})		−265.95±12							

Subscript (u) for uncatalysed path; (c) for 1,10-phen catalysed path; (w) for the value in the absence of surfactant; (CPC) or (SDS) for the value in presence of the respective surfactant.

[a] $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 30.0\times10^{-3}$ mol dm^{-3}, $[1,10\text{-}phen]_T = (0–14.0\times10^{-3})$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = 10.0\times10^{-3}$ mol dm^{-3}, $[SDS]_T = 3.0\times10^{-2}$ mol dm^{-3}. $k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)}$ and $k_{eff(w)}$ calculated at $[1,10\text{-}phen]_T = 1.0\times10^{-2}$ mol dm^{-3}.

[b] $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 25\times10^{-3}$ mol dm^{-3}, $[1,10\text{-}phen]_T = 8.0\times10^{-3}$ mol dm^{-3}, $[H]_T = (0.2–1.0)$ mol dm^{-3}, $[HClO_4]_T + [NaClO_4]_T = 1.5$ mol dm^{-3}.

[c] $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = (20.0–80.0)\times10^{-3}$ mol dm^{-3}, $[1,10\text{-}phen]_T = 6.0\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = 12\times10^{-3}$ mol dm^{-3}, $[SDS]_T = 3\times10^{-2}$ mol dm^{-3}.

The observation is represented as follows:

$$k_{obs(T)} = k_{obs(u)} + k_{obs(c)} = k_{obs(u)} + k_{cat}[phen]_T \quad (4)$$

The values of k_{cat} with the activation parameters are given in Table 1. During the progress of reaction, phen is lost due to the formation of inert Cr(III)-phen complex. The nature of dependence on phen remains unaltered in the presence of the surfactants. Under the kinetic conditions, $[phen]_T >> [Cr(VI)]_T$, during the progress of the reaction, $[phen]_T$ remains more or less constant. The catalytic efficiency at a particular value of $[phen]_T$ has been measured by considering the following parameters.

$$k_{eff(w)} = [k_{obs(T)} - k_{obs(u)}]/k_{obs(u)} \quad (5)$$

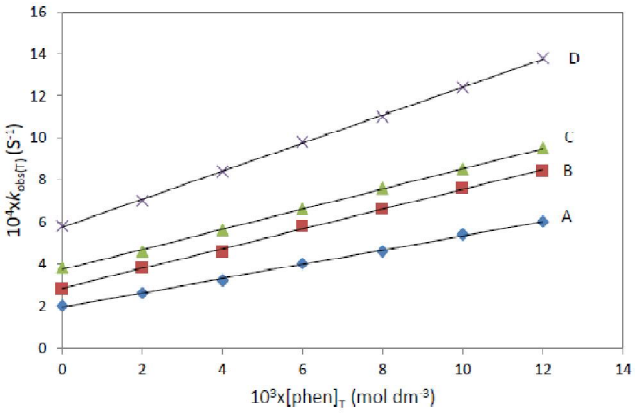


Fig. 6. Effect of $[phen]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of DL-malic acid in the presence of phen in aqueous H_2SO_4 media. $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $H_2SO_4 = 1.0$ mol dm^{-3}, $[phen]_T = (0–12)\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 30\times10^{-3}$ mol dm^{-3}. (A) For phen-catalysed reaction: T = 27°C. (B) For phen-catalysed reaction: T = 37°C. (C) For phen-catalysed reaction: T = 47°C, $[CPC]_T = 10\times10^{-3}$ mol dm^{-3}. (D) For phen-catalysed reaction: T = 47°C.

3.4. Dependence on $[H]^+$

The acid dependence was followed in aqueous $HClO_4$ media at fixed $[Cr(VI)]_T$ and $[malic\ acid]_T$.

From the experimental fit, the observation fit, the observations are as given in eqs. (6) and (7)

$$k_{obs(u)} = k_{H(u)}[H^+] \quad (6)$$

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{H(c)}[H^+] \quad (7)$$

For malic acid $10^4\ k_{H(C)(w)}$ ($dm^3\ mol^{-1}\ s^{-1}$) = 7.6±0.10 at 37°C for $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[S]_T = 25.0\times10^{-3}$ mol dm^{-3}, $[phen]_T = 8\times10^{-3}$ mol dm^{-3}, $[H]_T = (0.2–1.0)$ mol dm^{-3}. $[HClO_4]_T + [HClO_4]_T = 1.5$ mol dm^{-3}.

3.5 Test for acrylonitrile polymerization

Under the experimental conditions, existence of free-radical was indicated by polymerization of acrylonitrile under a nitrogen atmosphere.

3.6. Effect of surfactants

It has been noted that the anionic surfactant sodium dodecyl sulfate (SDS) accelerates (*cf*. Fig. 7) the rate of the reaction while the cationic surfactant N-cetylpyridinium chloride (CPC) retards (*cf*. Fig. 8) the rate of the reaction.

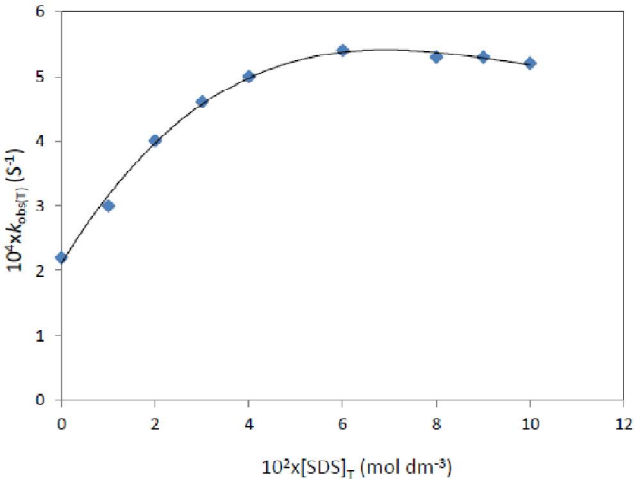


Fig. 7. Effect of $[SDS]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of DL-malic acid in the presence of phen in aqueous H_2SO_4 media. $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 20\times10^{-3}$ mol dm^{-3}. $[phen]_T = 6\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[SDS]_T = (0–10)\times10^{-2}$ mol dm^{-2}, T = 37°C.

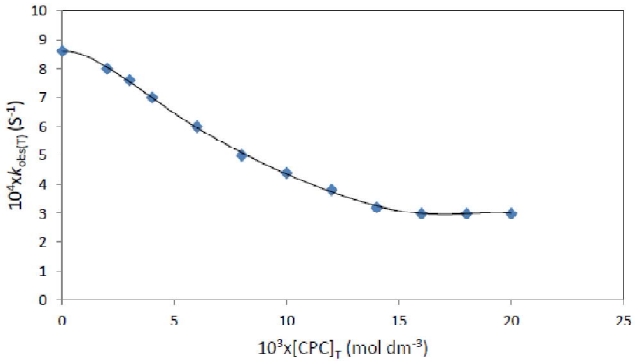


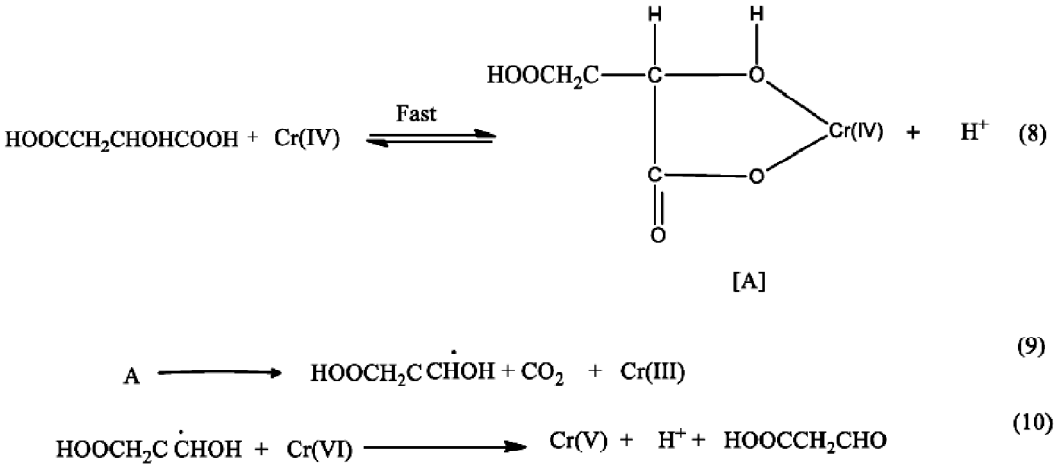
Fig. 8. Effect of $[CPC]_T$ on $k_{obs(T)}$ for the Cr(VI) oxidation of DL-malic acid in the presence of phen in aqueous H_2SO_4 media. $[Cr(VI)]_T = 2.5\times10^{-3}$ mol dm^{-3}, $[malic\ acid]_T = 30\times10^{-3}$ mol dm^{-3}. $[phen]_T = 6\times10^{-3}$ mol dm^{-3}, $[H_2SO_4] = 1.0$ mol dm^{-3}, $[CPC]_T = (0–20)\times10^{-3}$ mol dm^{-2}, T = 47°C.

3.7. Reaction mechanism and interpretation

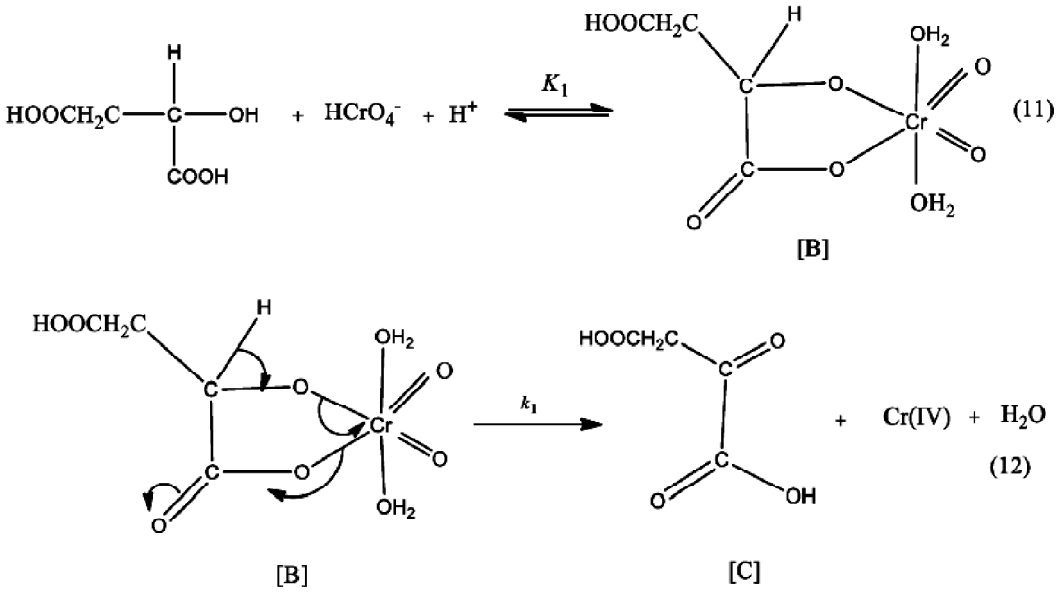
The mechanism of the reaction can be divided in two parts as (i) the uncatalysed path (Scheme 1 and Scheme 2) and (ii) the catalysed path (Scheme 3).

For the heteroaromatic-N base ligand 1,10-phenanthroline (phen) catalysed path, the reaction in Scheme 3 can explain the experimental findings and lead to the following rate law:

$$k_{obs(c)} = (2/3)k_2K_3K_4[S]_T[phen]_T[H^+] \quad (18)$$



Scheme 1. Cleavage of C-C bond by Cr(IV).

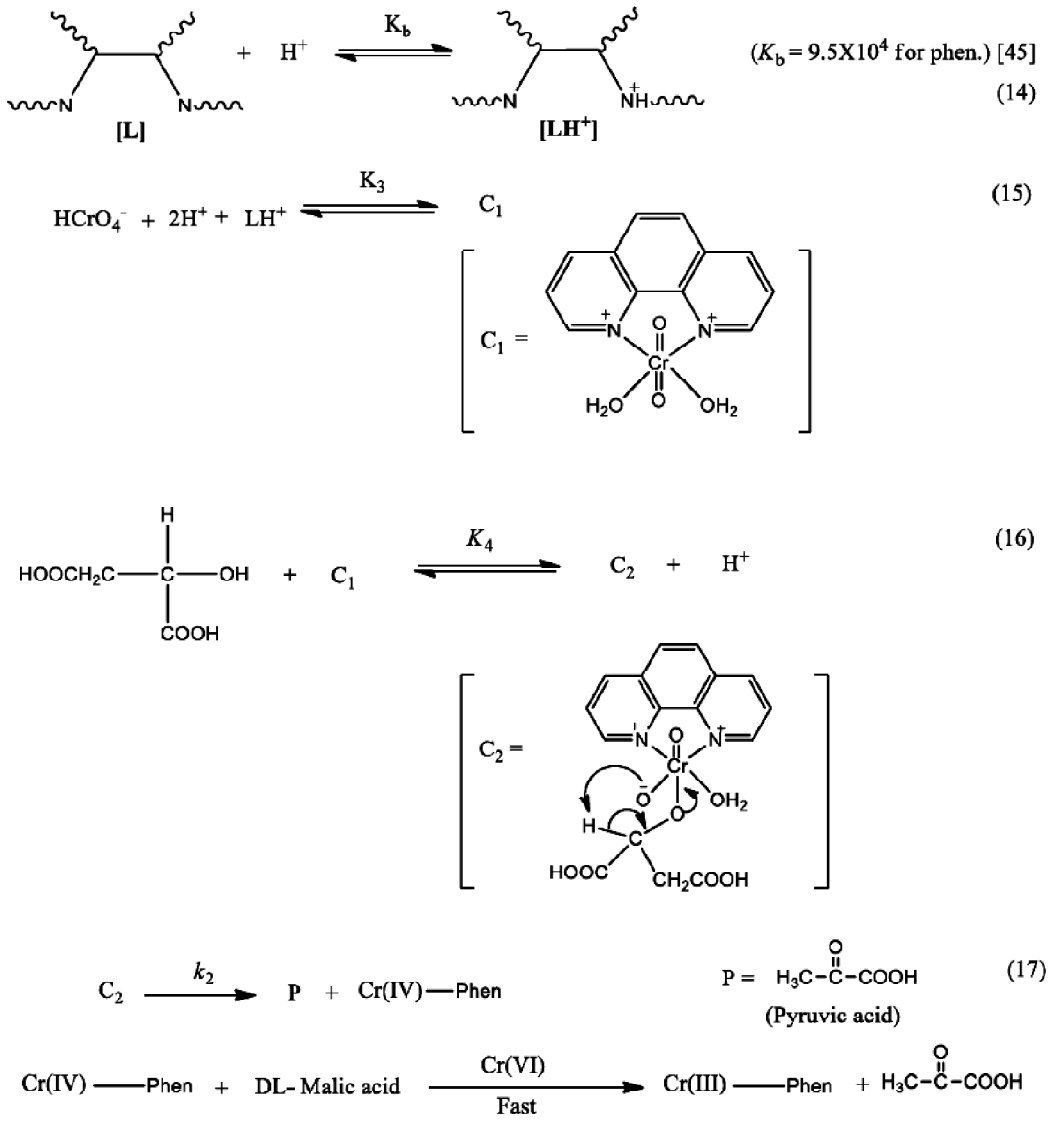


Scheme 2. Cr(VI) oxidation of malic acid in absence of catalyst.

We have already established the uncatalysed path for the malic acid[17] as that shown in Scheme 1 and Scheme 2 and with the rate law:

$$k_{obs(u)} = (2/3)k_1K_1[S]_T[H^+] = k_{s(u)}[S]_T = k_{H(u)}[H^+] \quad (13)$$

Under the reaction conditions, the first-order dependence on $[phen]_T$ is strictly maintained throughout the range of $[phen]_T$ used. The Cr(VI)-species typically labile and undergoes complexation at the first step with the chelating agent (L) to pro-



Scheme 3. Chromic acid oxidation of malic acid in presence of 1,10-phenanthroline catalyst.

duce chelating complex (C_1), which is to be the kinetically active oxidant[31,32]. As Cr(III) (t_{2g}^3) is an inert species, it is reasonable to consider that the heteroaromatic nitrogen base (i.e. phen) does not bind to the Cr(III) centre after its formation from the reduction of Cr(VI). The Cr(III)-phen complex has been characterized spectroscopically[31,32]. Thus, it is reasonable to conclude that the equilibrium constant for the reaction leading to Cr(VI)-phen complex (C_1) is low. In the next step, Cr(VI)-phen complex reacts with the substrate to form a ternary complex (C_2) which experiences a redox decomposition at a rate limiting step giving rise to the organic product and Cr(IV)-phen complex. The high value of enthalphy of activation, $\Delta H^{\neq}$ (Table 1) indicates that the phen-catalysed path is favoured mainly due to very high negative value of entropy of activation, $\Delta S^{\neq}$ (Table 1). The negative value of $\Delta S^{\neq}$ and the composite rate constant k_{cat} supports the suggested cyclic transition state. The Cr(IV) generated may subsequently participated in the faster reactions in different possible ways outlined below to be reduced to Cr(III).

Path I: Cr(IV)+ Cr(VI) $\rightarrow$ 2Cr(V)

2Cr(V) + 2S$\rightarrow$ 2Cr(III) + Products

Path II: Cr(IV) + S $\rightarrow$ Cr(III)+ S$^{\bullet}$

Cr(VI) + S$^{\bullet}$ $\rightarrow$ Cr(V) + Products

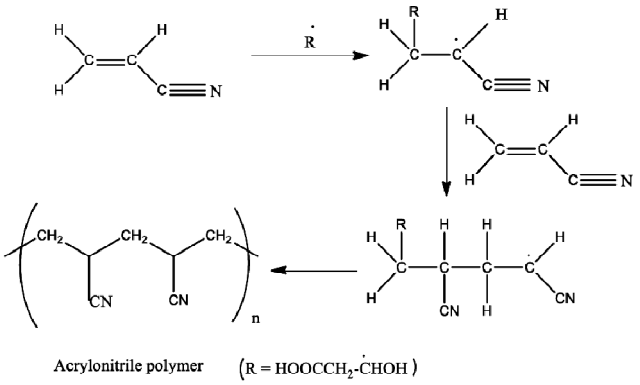
$$Cr(V) + S \rightarrow Cr(III) + Products$$

Path III: $Cr(IV) + S \rightarrow Cr(II) + Products$

$$Cr(II) + Cr(VI) \rightarrow Cr(III) + Cr(V)$$

$$Cr(V) + S \rightarrow Products + Cr(III)$$

In the above mentioned possible paths, S denotes the 2e-reductant and $S^{\bullet}$ stands for the partially oxidized substrate. In both the Watanabe-Westheimer mechanism[46] (i.e. Path I) and the Perez-Benito mechanism[47,48] (i.e. Path III), the title organic substrates acts in all steps as a 2e-reductant, while it may act both as a 2e-reductant and 1e-reductant in the Rocek mechanism[49] (i.e. Path II). Previously, the Rocek mechanism was accepted widely in explaining the Cr(VI) oxidation of different organic substrates and Perez-Benito mechanism was discarded because of the instability of Cr(II). But it has been established[47,48] that for the oxidation of different 2e-organic reductants, Cr(II) is produced from Cr(IV) through hydride ion transfer. Thus the carbo-cationic centre generated is responsible for acrylonitrile polymerization[50]. It may be noted that in Rocek mechanism, the free radical ($S^{\bullet}$) is responsible for the acrylonitrile polymerization. This mechanism was also supported by Haight *et al.*[51]. For the reaction pathway, radical mediated acrylonitrile polymerization form under the condition in following ways[52].



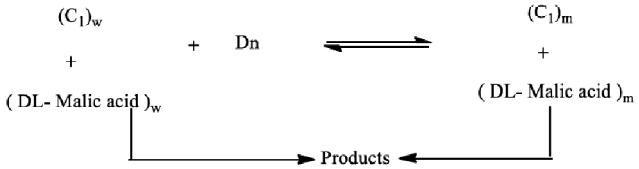
3.8. Effect of SDS

Sodium dodecyl sulfate (SDS), a representative anionic surfactant is found to accelerate the phen-catalysed path. The plot of $k_{obs(T)}$ vs $[SDS]_T$ shows a rate accelerating effect with the increase of $[SDS]_T$ (*cf.* Fig. 7) and attains a limiting value followed by a slight rate retardation. The nature of the plot arises due to the preferential partitioning of the positively charged Cr(VI)-phen complex by electrostatic attraction and neutral substrate by hydrophobic attraction in the micellar interphase. Thus SDS allows the reaction to proceed in both aqueous and micellar interphases. After a certain concentration of $[SDS]_T$. The rate retardation is probably due to the dilution of the reactants in the micellar phase. An increase in $[SDS]_T$ increases the micellar solubilisation of the reactants but at the same time an increase in $[SDS]_T$ increases the concentration of the micellar counter ions (i.e. Na^+) which may displace H^+ and Ox^{2+} and (C_1) out of micellar surface.

$$2Na_w^+ + Ox_M^{2+} \rightleftharpoons 2Na_M^+ + Ox_w^{2+} \quad (19)$$

$$Na_w^+ + H_M^+ \rightleftharpoons Na_M^+ + H_w^+ \quad (20)$$

The above equilibria lead to decrease the value of $[H_M]^+$ and $[OX_M]^{2+}$ (C_1) to inhibit the rate process. These two effects are opposite in nature to determine the rate of the reaction. In the phen-catalysed path, these two effects roughly nullify each other at higher concentration to attain the rate saturation.



Scheme 4. Partitioning of the reactive species between the aqueous and micellar phases.

3.9. Effect of CPC

N-Cetylpyridinium chloride (CPC), a representative cationic surfactant is found to retard the phen-catalysed path. The plot of $k_{obs(T)}$ vs $[CPC]_T$ (*cf.* Fig. 8) shows a continuous decrease that tends to level off at higher concentration of CPC. Bunton and Cerichelli noted a similar observation in the oxidation of ferrocene by Fe(III) salts in the presence of cationic surfactant cetyl trimethyl ammonium bromide [CTAB][53]. Similar micellar effects have been noted in the oxidation of acetophenone by Ce(IV)[54] and oxalic acid catalysed oxidation of aromatic azo compounds by chromic acid[8].

In the phen-catalysed path, Cr(VI)-phen complex (C_1), a cationic complex, has been argued as the active oxidant. The active oxidant (C_1) is electro statically repelled by the cationic micellar head groups of CPC. In the presence of CPC, the reaction is mainly restricted in aqueous phase where

concentration of the neutral substrate is depleted. This explains the rate retarding effect of CPC for the phen-catalysed path.

In the phen-catalysed path, CPC restricts the positively charged Cr(VI)-catalyst complex (C_1) (*cf*. eq. Scheme 3), the active oxidant, in the aqueous phase and thus the accumulated neutral substrate in the micellar phase (stern layer) cannot participate in the reaction. Hence in the 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 4 in which D_n represents the micellised surfactants where 'n' is the aggregation number.

Conclusions

In the hetero aromatic N-base ligand 1,10-phenanthroline assisted chromic acid oxidation of DL-malic acid in aqueous micellar media Cr(VI)-phen complex has been found to act as the active oxidant. Cr(VI)-phen complex receives a nucleophilic attack by the substrate to form a ternary complex which subsequently experiences a two-electron transfer redox decomposition leading to the organic products, pyruvic acid. The scanned spectrum in catalysed path indicates the gradual disappearance of Cr(VI)-species and appearance of Cr(III)-species with the isosbestic point at λ = 525 nm. Observation of this single isosbestic point indicates the very low concentration of the probable intermediates 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 reactions have been carried out in aqueous micellar media. The anionic surfactant SDS accelerates the rate while the cationic surfactant CPC shows the rate retarding effect.

Acknowledgement

Financial support from UGC (New Delhi, India) Minor Research Project is thankfully acknowledged.

References

1. A. Granzow, A. Wilson and F. Ramirez, *J. Am. Chem. Soc*., 1974, **96**, 2454.
2. F. Hasan and J. Rocek, *J. Am. Chem. Soc*., 1972, **94** , 3181.
3. F. Hasan and J. Rocek, *J. Am. Chem. Soc*., 1974, **96** , 534.
4. R. Hintze and J. Rocek, *J. Am. Chem. Soc*., 1977, **99**, 132.
5. T. Lin, *J. Chin. Chem. Soc*., 1981, **28**, 21.
6. J. Rocek and T. Peng, *J. Am. Chem. Soc*., 1977, **99**, 7622.
7. P. Rao, V. S. Murty, K. S. Murty and R. V. S. Murty, *J. Indian Chem. Soc*., 1979, **56**, 604.
8. C. N. Sarada and A. K. Reddy, *J. Indian. Chem. Soc*., 1993, **70**, 35.
9. T. Lin, *J. Chin. Chem. Soc*., 1981, **28**, 149.
10. M. T. Beck and D. A. Durham, *J. Inorg. Nucl. Chem*., 1971, **33**, 461.
11. S. Meenakshisundaram and R. Vinothini, *Croatica Chemica Acta*, 2003, **76(1)**, 75.
12. V. M. S. Ramanujam, S. Sundaram and N. Venkatasubramanian, *Inorganica Chemica Acta*, 1975, **13**, 133.
13. M. Islam, B. Saha and A. K. Das, *J. Mol. Catal. A: Chem*., 2007, **266**, 21.
14. A. K. Das, *Coord. Chem. Rev*., 2004, **248**, 81.
15. A. K. Das, *Inorg. React. Mech*., 1999, **1**, 161.
16. A. K. Das, S. K. Mondal, D. Kar and M. Das, *Int. J. Chem. Kinet*., 2001, **33**, 173.
17. B. Saha, M. Islam and A. K. Das, *Inorg. React. Mech*., 2006, **6**, 141.
18. R. Bayen, M. Islam and A. K. Das, *Indian J. Chem*., 2009, **48A**, 1055.
19. R. Bayen, M. Islam, B. Saha and A. K. Das, *Carbohydr. Res*., 2005, **340**, 2163.
20. S. Meenakshisundaram, *Trans. Met. Chem*., 2004, **29**, 308.
21. S. Malik and B. Saha, *Tenside Surfactants Detergents*, 2015, **6**, 502.
22. A. Ghosh, R. Saha and B. Saha, *J. Ind. Eng. Chem*., 2014, **20**, 345.
23. P. Sar, A. Ghosh, S. Malik, D. Ray, B. Das and B. Saha, *J. Ind. Eng. Chem*., 2016, **42**, 53.
24. S. Malik, D. Saha, M. H. Mondal, P. Sar, A. Ghosh, K. Mahali and B. Saha, *J. Mol. Liq*., 2017, **225**, 207.
25. K. Mukherjee, R. Saha, A. Ghosh, S. K. Ghosh and B. Saha, *J. Mol. Liq*., 2013, **179**, 1.
26. R. Saha, A. Ghosh and B. Saha, *Spectrochim. Acta, Part A*, 2014, **124**, 130.
27. K. Mukherjee, A. Ghosh, R. Saha, P. Sar, S. Malik, S. S. Bhattacharyya and B. Saha, *Spectrochim. Acta, Part A*, 2014, **122**, 204.
28. R. Saha, A. Ghosh, P. Sar, I. Saha, S. K. Ghosh, K. Mukherjee and B. Saha, *Spectrochim. Acta, Part A*, 2013, **116**, 524.
29. A. Ghosh, R. Saha, K. Mukerjee, S. K. Ghosh and B. Saha, *Spectrochim. Acta, Part A*, 2013, **109**, 55.
30. B. Saha, M. Islam and A. K. Das, *J. Chem. Res. (S)*, 2005, 471.
31. T. Y. Lin, H. W. Zeng and C. M. Chuo, *J. Chin. Chem.*

Soc., 1995, **42**, 43.

32. Z. Khan and Kabir-ud-Din, *Trans. Met. Chem*., 2002, **27**, 832.
33. M. Islam, B. Saha and A. K. Das, *Int. J. Chem. Kinet*., 2006, **38(9)**, 531.
34. A. K. Das, M. Islam, R. Das and D. Kar, *Progress in React. Kinet. and Mechs*., 2010, **35**, 387.
35. P. Sar, A. Ghosh and D. Ghosh, *Res. Chem. Intermediat*, 2014, **41(8)**.
36. B. Saha, S. Sarkar and K. M. Chowdhury, *Int. J. Chem. Kinet*., 2008, **40**, 282.
37. A. K. Das, M. Islam and R. Bayen., *Int. J. Chem. Kinet*., 2008, **40**, 445.
38. A. Ghosh, R. Saha, P. Sar and B. Saha, *J. Mol. Liq*., 2013, **186**, 122.
39. A. Ghosh, K. Sengupta, R. Saha and B. Saha, *J. Mol. Liq*., 2014, **198**, 369.
40. L. Lyons, "A Practical Guide to Data Analysis for Physical Science Student", Cambridge University Press, Cambridge, 1991.
41. F. Feigl, "Spot Tests in Organic Analysis", 5th ed., Elsevier, 1956, p. 331.
42. V. Daier, S. Signorella, M. Rizzotto, M. I. Frascaroli, C. Palopoli, C. Brondino, J. M. Salas-Peregrin and L. F. Sala, *Can. J. Chem*., 1999, **77**, 57.
43. B. N. Figgis, "Introduction to Ligand Fields", Wiley Eastern Limited, 1966, p. 222.
44. C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press Ltd., 1964, p. 290.
45. Stability Constants of Metal-Ion Complexes, The Chemical Society, London, Suppl. 1, Special Publication No. 25, 1971, pp. 598, 676.
46. W. Watanabe and F. H. Westheimer, *J. Chem. Phys*., 1949, **17**, 61.
47. J. F. Perez-Bennito, C. Arias and D. Lamrhari, *J. Chem. Soc., Chem. Commun*., 1992, 472.
48. J. F. Perez-Bennito and C. Arias, *Can. J. Chem*., 1993, **71**, 649.
49. F. Hasan and J. Rocek, *Tetrahedron*, 1974, **30**, 21.
50. F. W. Bilmer, "Text Book of Polymer Sciences", Wiley, New York, 1984, p. 85.
51. G. P. Haight, Gregory M. Jurisch, M. Terry Kelso and Patrick J. Merrill, *Inorg. Chem*., 1985, **24**, 2740.
52. P. S. Kalsi, "Organic Reactions and their Mechanism", New Age International (P.) Limited Publishers, 1998, p. 545, First reprint.
53. C. H. Bunton and G. Cerichelli, *Int. J. Chem. Kinet*., 1980, **12** , 519.
54. G. P. Panigrahi and B. P. Sahu, *J. Indian Chem. Soc*., 1991, **68**, 239.