

Determination of the activation parameters ΔH^\ddagger and ΔS^\ddagger via a kinetic study of D,L-mandelic acid oxidation by using chromic acid in the presence of 1,10-phenanthroline as a promoter in an aqueous micellar acid medium

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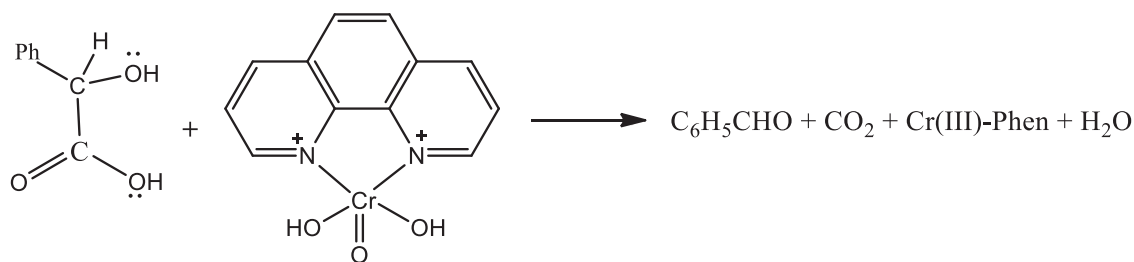
Abstract

Chromic acid oxidation of D,L-mandelic acid in the presence and absence of 1,10-phenanthroline (Phen) is studied in an aqueous micellar medium under kinetic conditions, $[D,L\text{-mandelic acid}] \gg [Phen]_T \gg [Cr(VI)]_T$ at different temperatures. From studies on the effect of temperature on the rate constant (k), the activation parameters ΔH^\ddagger (enthalpy of activation) and ΔS^\ddagger (entropy of activation) are evaluated by using the Eyring equation $[-\ln(kh/k_B T) = \Delta H^\ddagger/RT - \Delta S^\ddagger/R]$. The high value of ΔH^\ddagger indicates that the phen-catalysed path is favoured mainly due to very high negative value of ΔS^\ddagger . The negative value of ΔS^\ddagger and the composite rate constant k_{cat} support the suggested cyclic transition state. Both the catalysed and uncatalysed paths show a first-order dependence on $[H^+]$, and both also show a first-order dependence on $[D,L\text{-mandelic acid}]_T$ and $[Cr(VI)]_T$. The Phen-catalysed path is first order in $[Phen]_T$. These observations remain unaltered in the presence of externally added surfactants. The cationic surfactant *N*-cetylpyridinium chloride is found to retard the rate of the reaction.

Keywords

chromium(VI), D,L-mandelic acid, kinetics, *N*-cetylpyridinium chloride, Phen

Date received: 29 May 2021; accepted: 26 August 2021



Introduction

Chromium(VI) acts as a powerful oxidizing agent in different types of redox reactions and is converted into chromium(III). Different mechanistic routes have been suggested for the reduction of chromium(VI) to chromium(III) from analysis of kinetic data and other experimental findings. The mode of reduction largely depends on the nature of the reductant and the experimental conditions.^{1–4} Intermediates like Cr(V) and Cr(IV) have been identified and characterized in many cases. To explore

all these aspects, Cr(VI) has been extensively studied in redox kinetics. Here, it is important to note that Cr(VI) is

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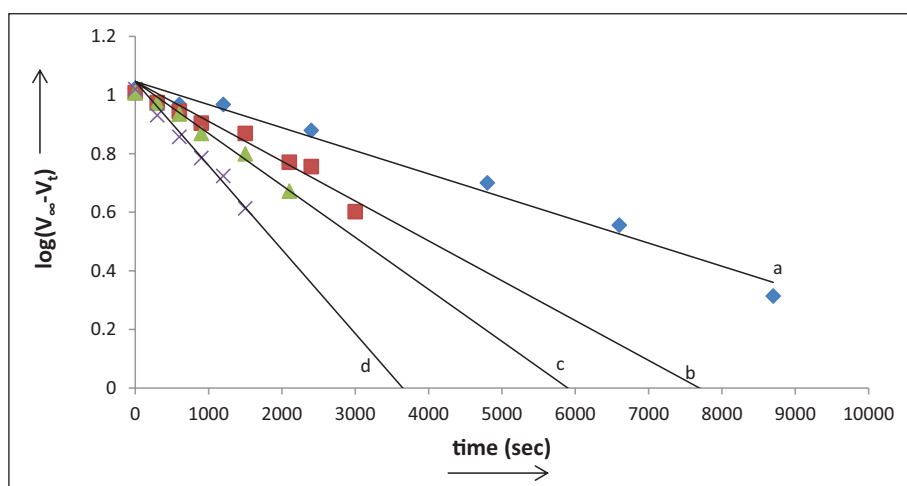


Figure 1. Plot of $\log[\text{Cr(VI)}]_T$ versus time (t): $[\text{Cr(VI)}]_T = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{D,L-mandelic acid}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $T = 30^\circ\text{C}$. Plot (a) $[\text{1,10-phen}] = 0 \text{ mol dm}^{-3}$, (b) $[\text{1,10-phen}] = 12 \times 10^{-4} \text{ mol dm}^{-3}$, (c) $[\text{1,10-phen}] = 24 \times 10^{-4} \text{ mol dm}^{-3}$ and (d) $[\text{1,10-phen}] = 36 \times 10^{-4} \text{ mol dm}^{-3}$.

hazardous because of its carcinogenic and mutagenic activity.⁵⁻⁸ This is why studies on the kinetics and mechanism of Cr(VI) oxidation of biologically relevant reducing agents are of interest to both biochemists and inorganic chemists.^{1,3} During the reduction of Cr(VI) to Cr(III), the intermediate oxidation states of chromium may interact with biologically active molecules and induce toxicity.³ Thus, in terms of chromate toxicity, it is reasonable to assume that the reducing agent may have an important role. The present research paper deals with three-electron (3e) transfer Cr(VI) oxidation of D,L-mandelic acid in the presence of 1,10-phenanthroline as a catalyst. It was reported by Dominic and Rocek^{9,10} that uncatalysed chromic acid oxidation of D,L-mandelic acid proceeds via three-electron transfer as the rate-determining step and involves simultaneous rupture of 'C-C' and 'C-H' bonds within a cyclic transition state. Here, it is worth mentioning that mandelic acid is quite interesting among α -hydroxy acids because on chromic acid oxidation it experiences 3e-transfer^{9,10} during the rate-determining step, while most other α -hydroxy acids experience 2e-transfer¹¹⁻¹⁵ under comparable conditions. In fairly recent work, Panigrahi and Sahu¹⁶ proposed a 2e-transfer process for the chromic acid oxidation of D,L-mandelic acid. According to them, D,L-mandelic acid behaves like other α -hydroxy acids during chromic acid oxidation. Hence, in the literature, there is a conflict in the behaviour of D,L-mandelic acid on chromic acid oxidation. This prompted us to carry out a detailed investigation under different conditions, that is, uncatalysed reactions and chelating-agent-catalysed reactions. The micellar effects on both the uncatalysed and Phen-catalysed reactions have been studied to substantiate the proposed reaction mechanism.

Results and discussion

Dependence on $[\text{Cr(VI)}]_T$

Under the experimental conditions, $[\text{D,L-mandelic acid}]_T \gg [\text{Phen}]_T \gg [\text{Cr(VI)}]_T$, both in the presence and

absence of Phen, the rate of disappearance of Cr(VI) shows a first-order dependence on Cr(VI). This first-order dependence on Cr(VI) is also maintained in the presence of the surfactant *N*-cetylpyridinium chloride (CPC). The pseudo first-order rate constants (k_{obs}) have been evaluated from the linear plot of $\log[\text{Cr(VI)}]_T$ versus time (t) (Figure 1).

Dependence on $[\text{Phen}]_T$

The plots of k_{obs} versus $[\text{Phen}]_T$ are linear ($r > 0.99$) with positive intercepts indicating the contribution of the relatively slower uncatalysed path (Figure 2). The pseudo first-order rate constants ($k_{\text{obs(u)}}$) directly measured in the absence of Phen under the same conditions nicely agree with those obtained from the intercepts of the plots of $k_{\text{obs(T)}}$ versus $[\text{PA}]_T$. In Figure 2, plots (a), (b) and (c) refer to the kinetic studies of the [1,10-phen] concentration variation at different temperatures (20°C , 30°C and 40°C), respectively.

Dependence on $[\text{S}]_T$, that is, $[\text{D,L-mandelic acid}]_T$

From the plot of k_{obs} versus $[\text{D,L-mandelic acid}]_T$ (Figure 3), it has been established that both the catalysed and uncatalysed paths show first-order dependence with respect to $[\text{S}]_T$, that is, the first-order dependence with respect to $[\text{S}]_T$ is also maintained in the presence of surfactants, for example, CPC. The values of $k_{\text{s(c)}}$ and $k_{\text{s(u)}}$ are given in Table 1.

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

The acid dependence patterns for the uncatalysed and catalysed paths are the same first-order dependence (Figure 4). From the experimental fit, the observations are as follows

$$k_{\text{obs(u)}} = k_{\text{o(u)}} + k_{\text{H(u)}} [\text{H}^+]$$

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

Thus, the observed rate laws are as follows

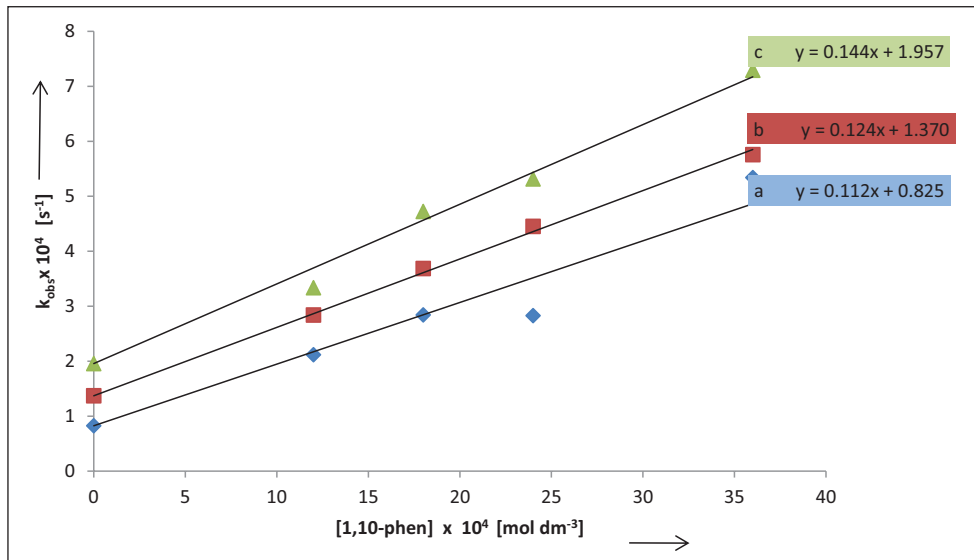


Figure 2. $[\text{Cr(VI)}]_{\text{T}} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{D,L-mandelic acid}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{1,10-phen}] = (0-36) \times 10^{-4} \text{ mol dm}^{-3}$. Plot (a) 20 °C, (b) 30 °C and (c) 40 °C.

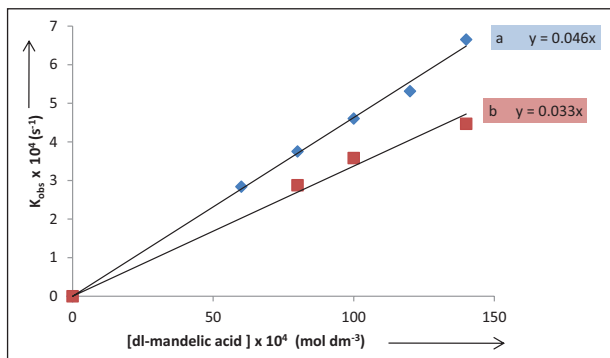


Figure 3. $[\text{Cr(VI)}]_{\text{T}} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{1,10-phen}] = 12 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{D,L-mandelic acid}] = (6-14) \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CPC}] = 20 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 30 \text{ °C}$. Plot (a) $[\text{CPC}] = 0 \text{ mol dm}^{-3}$, (b) $[\text{CPC}] = 20 \times 10^{-3} \text{ mol dm}^{-3}$.

$$k_{\text{obs(u)}} = \{k_{1(\text{u})} + k_{2(\text{u})} [\text{H}^+]\} [\text{MA}]_{\text{T}}$$

$$k_{\text{obs(c)}} = \{k_{1(\text{c})} + k_{2(\text{c})} [\text{H}^+]\} [\text{L}]_{\text{T}} [\text{MA}]_{\text{T}}$$

Test for acrylonitrile polymerization

Under the experimental conditions, polymerization of acrylonitrile occurred under a nitrogen atmosphere. This indicates the generation of free radicals during the reaction.

Evaluation of the activation parameters

From the studies of the effect of temperature on the rate constant (k), the activation parameters, ΔH^\ddagger (enthalpy of activation) and ΔS^\ddagger (entropy of activation), have been evaluated (Figure 5) by using the Eyring equation

$$-\ln(kh/k_{\text{B}}T) = \Delta H^\ddagger / RT - \Delta S^\ddagger / R$$

where k_{B} is the Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), h is Planck's constant ($6.62 \times 10^{-34} \text{ Js}^{-1}$) and R is the molar gas constant ($8.31 \text{ JK}^{-1} \text{ mol}^{-1}$). Free energy of activation (ΔG^\ddagger) and its errors can also be calculated from the following equations

$$\Delta G^\ddagger = RT \ln(k_{\text{B}}T / hk)$$

and

$$\delta \Delta G^\ddagger = RT(\delta k / k)$$

Mechanism and interpretation

Reaction mechanism for the Phen-assisted chromic acid oxidation of mandelic acid. The results obtained from the Phen-assisted reactions can be explained by considering the reaction mechanism outlined in Scheme 1. Here, Phen readily forms a reactive cyclic Cr(VI)-Phen complex **A** in the acid-catalysed reaction with HCrO_4^- , and this Cr(VI)-Phen complex is the active oxidant.^{8,15,18-22} In the next step, this Cr(VI)-Phen complex reacts with the substrate to form two ternary complexes **B** and **C**. Ternary complexes **B** and **C** differ only in the extent of protonation and both are kinetically active. These ternary complexes undergo redox decomposition through 3e-transfer within the cyclic transition state as the rate-determining step, involving simultaneous rupture of the C-C and C-H bonds leading to a benzoyl radical, carbon dioxide and a Cr(III)-Phen complex. Subsequently, the benzoyl radical reacts rapidly to form the benzaldehyde.

The observed rate law is

$$k_{\text{obs(c)}} = \{k_{1(\text{c})} + k_{2(\text{c})} [\text{H}^+]\} [\text{L}]_{\text{T}} [\text{MA}]_{\text{T}}$$

Table 1. Kinetic parameters and some representative rate constants for the Cr(VI) oxidation of D,L-mandelic acid in the presence of 1,10-phenanthroline in aqueous solution.

Temp (°C)	$10^4 k_{\text{obs}(u)(w)}^a$ (s ⁻¹)	$10^2 k_{\text{cat}(w)}^a$ (dm ³ mol ⁻¹ s ⁻¹)	$k_{s(c)(w)}^b$ (dm ³ mol ⁻¹ s ⁻¹)	$k_{s(c)(CPC)}^b$ (dm ³ mol ⁻¹ s ⁻¹)	$10^5 k_{H(u)(w)}^c$ (dm ³ mol ⁻¹ s ⁻¹)	$10^5 k_{H(c)(w)}^d$ (dm ³ mol ⁻¹ s ⁻¹)	$k_{\text{eff}(w)}$
20	0.8254	11.2					2.445
30	1.3708	12.4	0.046	0.033	3.936	7.23	1.688
40	1.957	14.4					1.414

ΔH^\ddagger (kJ mol⁻¹) 7.766.

ΔS^\ddagger (JK⁻¹ mol⁻¹) -239.18 (Islam and Das¹⁷).

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

$k_{\text{obs}(u)(w)}$ = rate constant of the uncatalysed reaction in aqueous medium.

$k_{\text{obs}(c)(w)}$ = rate constant of the 1,10-phenanthroline-catalysed reaction in aqueous medium.

$k_{\text{cat}(w)}$ = slope plot of $k_{\text{obs}(c)(w)}$ versus [1,10-phen] of the 1,10-phenanthroline-catalysed reaction in aqueous medium.

$k_{\text{eff}(w)} = (k_{\text{obs}(c)(w)} - k_{\text{obs}(u)(w)}) / k_{\text{obs}(u)(w)}$ calculated at [1,10-phen] = 18×10^{-4} mol dm⁻³; [Cr(VI)] = 6×10^{-4} mol dm⁻³; [D,L-mandelic acid] = 6×10^{-3} mol dm⁻³; [H₂SO₄] = 0.25 mol dm⁻³.

^a[Cr(VI)] = 6×10^{-4} mol dm⁻³; [D,L-mandelic acid] = 6×10^{-3} mol dm⁻³; [1,10-phen] = $(12-36) \times 10^{-4}$ mol dm⁻³; [H₂SO₄] = 0.25 mol dm⁻³.

^b[Cr(VI)] = 6×10^{-4} mol dm⁻³; [D,L-mandelic acid] = $(6-14) \times 10^{-3}$ mol dm⁻³; [1,10-phen] = 12×10^{-4} mol dm⁻³; [H₂SO₄] = 0.25 mol dm⁻³;

[CPC] = 20×10^{-3} mol dm⁻³.

^c[Cr(VI)] = 6×10^{-4} mol dm⁻³; [D,L-mandelic acid] = 8×10^{-3} mol dm⁻³; [H⁺] = (0.25-1.25) mol dm⁻³.

^d[Cr(VI)] = 6×10^{-4} mol dm⁻³; [D,L-mandelic acid] = 8×10^{-3} mol dm⁻³; [1,10-phen] = 12×10^{-4} mol dm⁻³; [H⁺] = (0.25-1.25) mol dm⁻³.

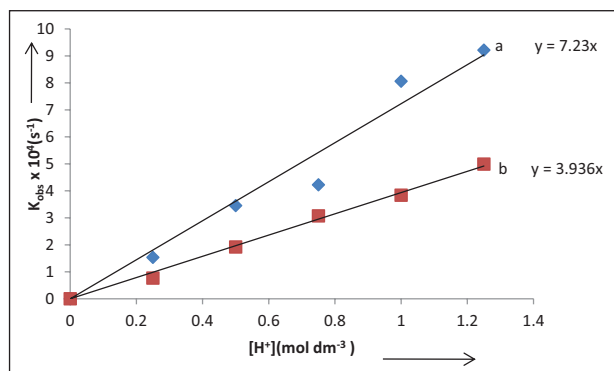


Figure 4. [Cr(VI)]_T = 6×10^{-4} mol dm⁻³, [1,10-phen] = 12×10^{-4} mol dm⁻³, [D,L-mandelic acid] = 8×10^{-3} mol dm⁻³, [H⁺] = (0.25-1.25) mol dm⁻³, [HClO₄ + NaClO₄] = 1.5 mol dm⁻³, T = 30 °C. Plot (a) [1,10-phen] = 12×10^{-4} mol dm⁻³ and (b) [1,10-phen] = 0 mol dm⁻³.

Effect of CPC

Catalysed path: For *N*-cetylpyridinium chloride (CPC), a representative cationic surfactant, the plot of $k_{\text{obs}(c)}$ versus [CPC]_T (Figure 6) shows a steady decrease and eventually levels off at higher concentration of CPC. This observation is similar to that observed by Bunton and Cerichelli²³ in the oxidation of ferrocene by ferric salts in the presence of the cationic surfactant cetyltrimethyl ammonium bromide (CTAB). Similar observations have also been noted by Panigrahi and Sahu²⁴ in the oxidation of acetophenone by Ce(IV) in the presence of *N*-dodecylpyridinium chloride (NDPC), by Sarada and Reddy,²⁵ in the oxalic acid-catalysed oxidation of aromatic azo-compounds by Cr(VI) in the presence of SDS, and by us in the chromic acid oxidation of D-glucose,²⁶ and propan-1-ol²⁷ in the presence of CPC.

The neutral substrate can be partitioned in the Stern layer of the micellar phase due to favourable H-bonding

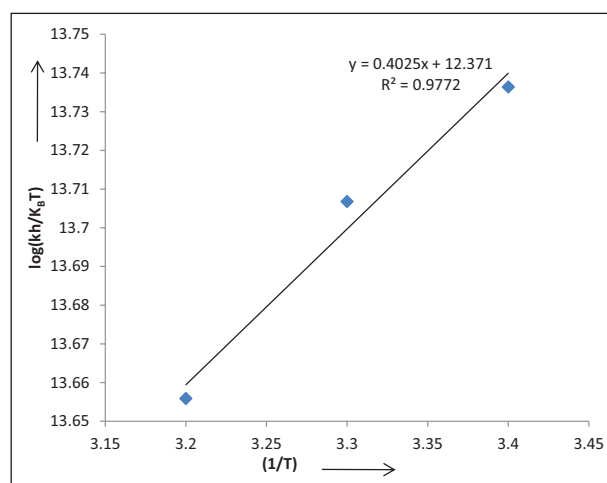
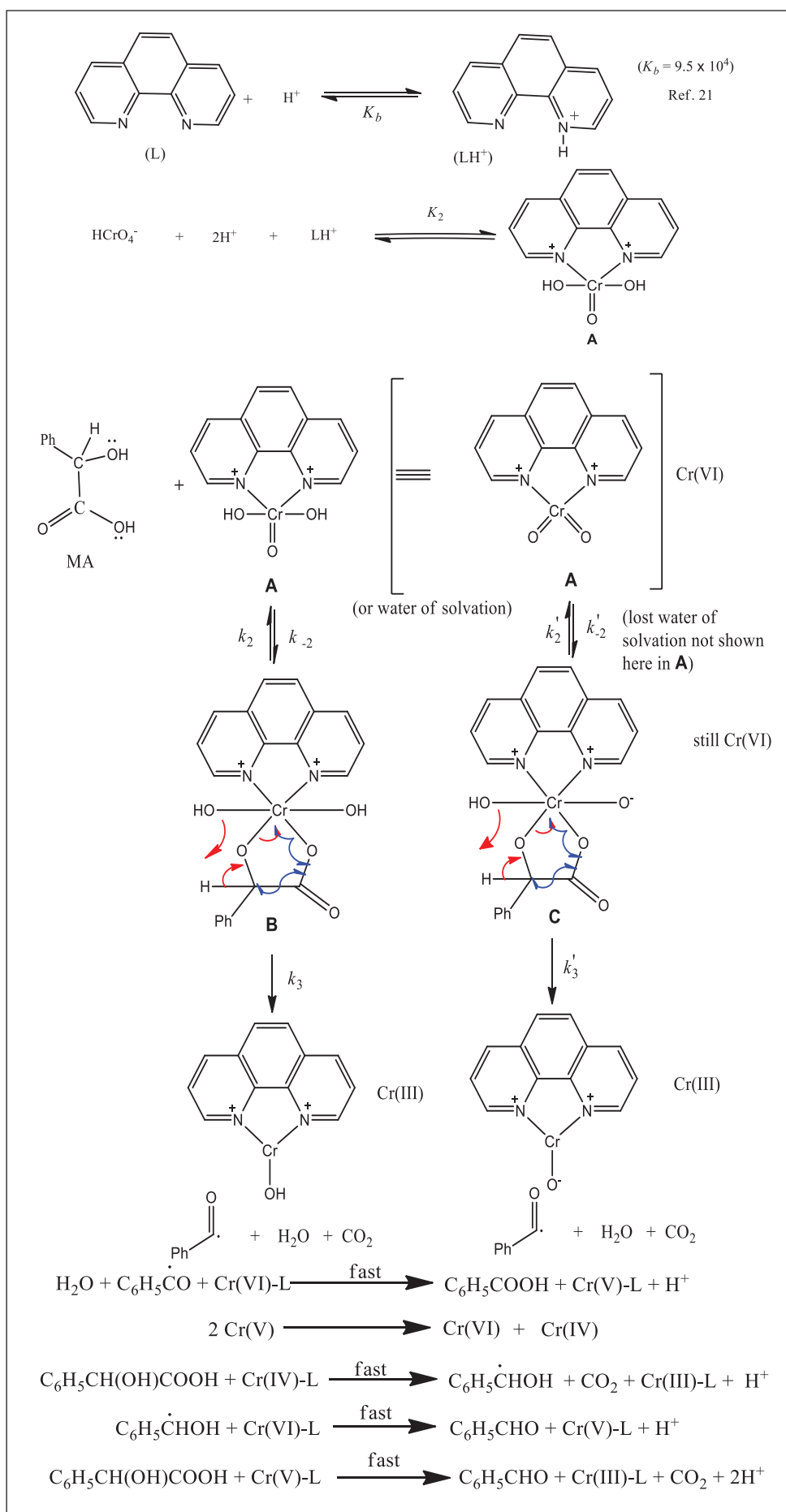


Figure 5. Plot of $-\log(kh/kBT)$ versus $1/T$ (T = 20 °C; 30 °C; 40 °C).

and ion-dipole interactions.¹ In the Phen-catalysed pathway, the positively charged micellar head groups of CPC electrostatically restrict the positively charged Cr(VI)-Phen complex **A** in the aqueous phase and thus the accumulated neutral substrate in the micellar phase (Stern layer) cannot participate in the reaction in the aqueous phase. Consequently, the overall rate is retarded. Partitioning of the reactants between the aqueous and micellar phases is shown in Scheme 2, in which S_n represents the micellized surfactants, n is the aggregation number, w is the aqueous medium and m is the micellar medium.

Conclusion

In the Phen-assisted path, a Cr(VI)-Phen complex, a cationic species has been found to act as the active oxidant. In the Phen-assisted path, the Cr(VI)-Phen complex undergoes a nucleophilic attack by the D,L-mandelic acid to form



Scheme 1. Oxidation of D,L-mandelic acid (MA) by Cr(VI) in the presence of 1,10-phenanthroline as the catalyst.

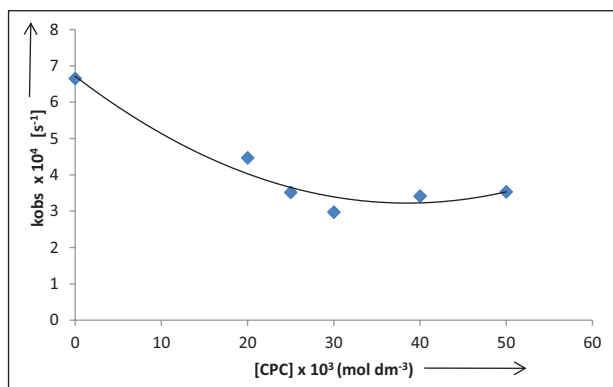


Figure 6. $[\text{Cr(VI)}]_{\text{T}} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[1,10\text{-phen}] = 12 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{D,L-mandelic acid}] = 14 \times 10^{-3} \text{ mol dm}^{-1}$, $[\text{CPC}] = (0-50) \times 10^{-3} \text{ mol dm}^{-3}$, $T = 30^\circ\text{C}$.

a ternary complex which subsequently undergoes a redox decomposition involving three-electron transfer leading to oxidative decarboxylation through C–C bond cleavage along with C–H bond cleavage. This rate-determining step produces a benzoyl radical, CO_2 and a Cr(III)-Phen complex. The benzoyl radical is subsequently oxidized to benzoic acid in a faster step. The reactions have been carried out in aqueous micellar media. The cationic surfactant CPC Phen-catalysed paths have been studied. CPC was found to retard the Phen-catalysed path. The high value of enthalpy of activation, ΔH^\ddagger , indicates that the phen-catalysed path is favoured mainly due to very high negative value of the entropy of activation, ΔS^\ddagger . The negative value of ΔS^\ddagger and the composite rate constant k_{cat} support the suggested cyclic transition state.

Experimental and methods

Materials and reagents

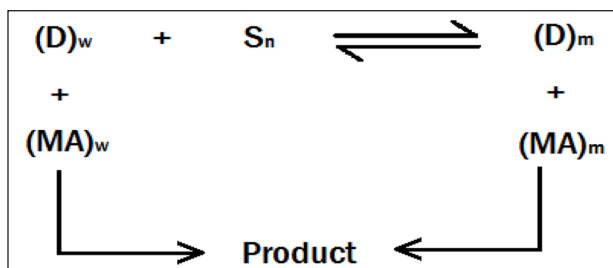
1,10-Phenanthroline (Qualigens) was used after repeated crystallization from methanol (m.p. 136°C). D,L-mandelic acid (Sisco Research Laboratories PVT Ltd., India), $\text{K}_2\text{Cr}_2\text{O}_7$ (BDH Chemicals, India), CPC (Sisco Research Laboratories PVT Ltd., India) and all other chemicals were of highest purity available commercially. Solutions were prepared in doubly distilled water.

Procedure and kinetic measurements

$T = 30^\circ\text{C}$, $[\text{S}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$ and $[\text{Phen}]_{\text{T}} \gg [\text{Cr(VI)}]_{\text{T}}$, acid and other necessary chemicals were separately thermostated ($\pm 0.1^\circ\text{C}$). Progress of the reactions was monitored by following the rate of disappearance of Cr(VI) by using the titrimetric quenching technique as discussed earlier.⁸ The pseudo first-order rate constants (k_{obs}) were calculated as usual. Errors associated with the different rate constants and activation parameters were estimated.²⁸

Product analysis and stoichiometry

Product analysis was carried out by using the 2,4-dinitrophenylhydrazine (DNP) test.²⁹ The solution of the

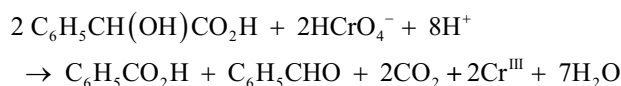


Scheme 2. Distribution of the reactive species between the aqueous and micellar phases. D: Cr(VI)-Phen complex; S: surfactant; MA: D,L-mandelic acid.

reaction product was treated with an excess of a saturated solution of DNP in dilute hydrochloric acid. The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried and recrystallized from ethanol. The melting point of the DNP derivative (230°C) was found to be lower than the melting point (239°C) of the DNP derivative of authentic benzaldehyde. This slight lowering of the m.p. was due to the presence of the DNP derivative of phenylglyoxylic acid produced as a by-product in a small amount. Thus, the product analysis agreed with the reports of Dominic and Rocek.⁹ Moreover, phenylglyoxylic acid was detected and confirmed by spot tests^{29,30} using a reagent solution prepared from a 0.3% solution of thiophene in benzene. The product solution was subjected to esterification by treatment with ethyl alcohol and concentrated sulfuric acid. A drop of the esterified solution was placed in a micro test tube and evaporated to dryness in a water bath. The residue was dissolved in three drops of concentrated sulfuric acid and treated with two drops of thiophene solution. A characteristic red colour appeared within 15 min. A similar observation was noted by using an authentic sample of phenylglyoxylic acid.

In the reaction mixture, benzoic acid was detected and confirmed by a spot test.²⁹ The product was extracted using n-hexane. One drop of the benzene solution was treated with a colourless saturated solution of Rhodamine B and an intense pink colour appeared. This colour intensified when the sample was shaken with an aqueous solution of uranyl acetate salts. The same identification was noted by using an authentic sample of benzoic acid.

Carbon dioxide was detected qualitatively³¹ under the kinetic conditions by purging dinitrogen through the reaction solution and passing the effluent gas through a narrow tube containing Ca(OH)_2 . Thus, the stoichiometry of the reaction is



The reaction mixture solutions were scanned (in the range 350–700 nm) at regular time intervals by using a UV-Vis spectrophotometer (UV-VIS-NIR Scanning Spectrophotometer, UV-1800 PC, Shimadzu) to follow the gradual development of the reaction intermediate and the product spectrophotometrically (Figure 7). The plots indicate the gradual disappearance of the Cr(VI) species and

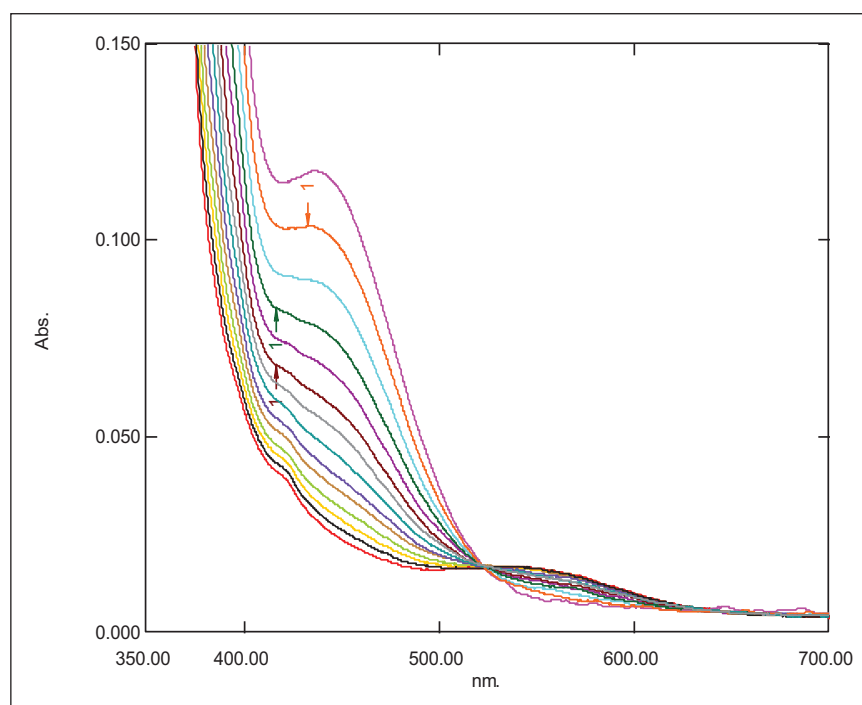


Figure 7. Absorption spectra of the reaction mixture in the presence of a catalyst at regular time intervals (7 min) from 0 to 92 min. Concentrations at the beginning of the reaction, $[\text{Cr(VI)}]_{\text{T}} = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Phen}]_{\text{T}} = 24 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{D,L-mandelic acid}]_{\text{T}} = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $T = 30^\circ\text{C}$, isosbestic point at $\lambda = 525 \text{ nm}$.

the appearance of a Cr(III) species with an isosbestic point at $\lambda = 525 \text{ nm}$.^{32,33} The observation of this single isosbestic point indicates the very low concentrations of probable intermediates such as Cr(V) and Cr(IV) under the present experimental conditions. In other words, a gradual decrease of Cr(VI) with a concomitant increase of Cr(III) occurs.

Acknowledgements

We acknowledge the Department of Chemistry, Seth Anandram Jaipuria College, Kolkata, for laboratory facilities. Cooperation from Dinesh Chandra Ghosh (of my Department) is gratefully appreciated.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship and/or publication of this article.

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