Hexavalent Chromium Removal By MANDELIC ACID In The Presence And Absence Of Surfactants

Jayashree Mandal, Ankita Basu, Rumpa Saha, Sumanta Kr Ghosh and Bidyut Saha*

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Abstract- **The chromic acid oxidations of dl-mandelic acid (MA) in the presence and absence of bipyridine (bpy) as catalyst have been studied in aqueous micellar media under the kinetic condition, $[\text{dl-mandelic acid}]_T >> [Cr(VI)]_T$ at various temperatures. The unanalyzed path is first order with respect to $[H^+]$, $[\text{dl-mandelic acid}]_T$ and $[Cr(VI)]_T$. The bpy catalyzed path gives zero order dependency on $[H^+]$. This path also shows a first order dependence on $[bpy]_T$. $HCrO_4^-$ has been found to be kinetically active in the absence of bpy while in the bpy catalyzed path, a Cr(VI)-bpy complex was considered to be the active oxidant. In this path the Cr(VI)-bpy complex undergoes a nucleophilic attack by the mandelic acid to form a ternary complex which subsequently experiences a redox decomposition involving 3e transfer leading to benzoyl radical, CO_2 and corresponding Cr(VI)-bpy complex. Benzoyl radical is then oxidized to form benzoic acid. In the unanalyzed path, the Cr(VI)-substrate ester undergoes an acid-catalyzed redox decomposition through 3e-transfer as the rate-determining step. It is striking to note that unanalyzed paths show a first order dependence on $[H^+]$ and catalysed path shows zero order dependence on $[H^+]$ and boh paths also show a first order dependence on $[\text{dl-mandelic acid}]_T$ and $[Cr(VI)]_T$.The bpy catalyzed path is first order in $[bpy]_T$. All these patterns remain unaltered in the presence of externally added surfactants. The effects of an anionic surfactant, sodium dodecyl sulphate (SDS), on both the unanalyzed and catalyzed paths were studied.**

Keywords- kinetics, dl-mandelic acid, chromium(VI), bipyridine, sds.

I. INTRODUCTION

Chromium toxicity among workers in tanneries and other chromium-based industries have been known for a long time. The workers are reported to suffer from ulcers, allergic dermatitis, lung cancer, renal insufficiency, and liver necrosis. Chromium pollution in groundwater as a result of leaching of Cr (VI) from spent solid and liquid wastes at chromium-based industries has currently become a serious problem at the global level [1]. The increased usage of chromium has led to great growth in chromium-based industries. This growth, however, has severely affected the ecoenvironment on one hand and has reduced the forest cover considerably on the other. Hexavalent chromium is the principal species in surface waters and aerobic soils. It forms a number of stable oxyacids and anions, including $HCrO_4^-$ (hydrochromate), $Cr_2O_7^{2-}$ (dichromate), and CrO_4^{2-} (chromate). The chromate ion has a large ionic potential and tetrahedral coordination and is both a strong acid and an oxidizing agent. Cr (VI) is not readily adsorbed to surfaces. Most of Cr (VI) salts are soluble in water, and hexavalent chromium is very mobile. Cr (VI) has a long residence time in surface water and groundwater. The high oxidizing potential, high solubility and ease of permeation of biological membranes make Cr (VI) more toxic than Cr (III) [1]. Various methods used for removal of Cr(VI) ions include chemical reduction and precipitation, reverse osmosis, ion exchange and adsorption on activated carbon or similar material [2]. But all these methods suffer from severe constraints, such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products that require safe disposal. Some of the treatment methods involve high operating and maintenance cost. The high cost of the chemical reagents and the problems of secondary pollution also make the above physico-chemical methods rather limited in application. There is, therefore, a need for some alternative technique, which is efficient and cost-effective. The process of heavy metal removal by biological materials is known as biosorption and the biological materials used are called biosorbents. Various biosorbents like bacteria, fungi, yeasts, agricultural byproducts, industrial wastes, etc have been used for biosorption. In this regard, considerable attention has been focused in recent years upon the field of biosorption for the removal of heavy metal ions from aqueous solutions [3]. Recently Park et al established that for chromium(VI) biosorption, chromium(VI) is first reduced to chromium(III) and then it is adsorbed as chromium(III) in the biosorbent [4]. The effective biosorbents contain hydroxyl & carboxyl groups [5]. Understanding of mechanism of chromium(VI) reduction to chromium(III) by some compound containing hydroxyl & carboxyl group is important in this context. In this respect mandelic acid is ideal one. The present investigations have been carried out in micro-heterogeneous systems to substantiate the proposed reaction mechanism as we did in many cases [6-12].

Bipyridine (bpy) is an efficient chelating agent to catalyse Cr(VI) oxidation reactions. Because of the structural similarity between 2,2'- bipyridine and picolinic acid that shows an extraordinary catalytic effect on chromic acid oxidation, the catalytic effect of 2,2'- bipyridine on these oxidations is of interest. Picolinic acid (PA) and bipyridine (bpy) are never co-oxidised along with the substrate [13-17]. It was reported by Rocek et al. [18,19] that the uncatalysed chromic acid oxidation of mandelic acid proceeds through a three electron transfer at the rate determining step, involving the simultaneous rupture of C—C and C—H bonds within a

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cyclic transition state. Among the α-hydroxy acids, mandelic acid is especially interesting because, in chromic acid oxidation, it experiences a 3e-transfer as the rate-determining step while most other α-hydroxy acids undergo 2e-transfer [20-24] under comparable conditions. A 2e-transfer process in the chromic acid oxidation of mandelic acid was proposed by Panigrahi et al. [25] Thus in the literature, there is a confusion regarding the behaviour of mandelic acid in chromic acid oxidation. We carry out a detailed investigation under different conditions, namely the uncatalysed reaction and catalysed reaction. The effects of anionic micelles on both the catalysed and bpy-catalysed reactions have been studied to substantiate the proposed reaction mechanism.

II. Experimental and Methods

A. Materials And Reagents

dl-mandelic acid (AR, SRL), $K_2Cr_2O_7$ (AR, BDH),sodium dodecyl sulphate, SDS (AR, SRL) and all other chemicals used were of highest purity available commercially. The solutions were prepared in doubly distilled water.

B. Procedure And Kinetic Measurements

Under the kinetic conditions, solutions of the oxidant and mixtures containing the known quantities of the substrate (s) (i.e.,dl-mandelic acid)(under the conditions [S] >> $[Cr(VI)]_T$),acid and the other necessary chemicals were separately thermo stated(± 0.1ºC).The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. Progress of the reaction was followed by monitoring the decay of oxidant [Cr(VI)] at 415nm at different time intervals with a UV-VIS spectrophotometer. Quartz cuvettes of path length 1cm were used. The observed pseudo-first-order rate constants [$k_{obs}(s^{-1})$] were determined from the linear part of the plots of $\ln(A_{415})$ versus time (t). Reproducible results giving first-order plots (co-relation co-efficient,r≥0.998) were obtained for each reaction run. A large excess (≥15-fold) of reductant was used in all kinetic runs. No interference due to other species at 415 nm was verified. Under the experimental conditions, the possibility of decomposition of the surfactants by Cr(VI) was investigated and the rate of decomposition in this path was found to be kinetically negligible.

C. Product Analysis And Stoichiometry

Product analysis was also carried out by the 2,4-dinitrophenylhydrazine (DNP) test [28]. The reaction product solution was treated with an excess of saturated Under the kinetic conditions ($[S]_T$>>$[Cr(VI)]_T$), dl-mandelic acid in both the bpy-catalysed and uncatalysed reactions yields carbon di oxide, benzaldehyde and benzoic acid and a very small amount of phenylglyoxylic acid. In the reaction mixture, benzaldehyde was detected and confirmed by a spot test [25] using the reagent solution prepared by dissolving 0.2 ml of 37% formaldehyde in 10 ml conc H_2SO_4. The product was extracted in a non-aquous solvent like dichloromethane. One drop of the non-aquous final test solution containing the oxidized product of dl-mandelic acid was treated with two drops of the reagent solution in a spot plate. After a few minutes, the colour of the resultant solution appeared red, which indicated the presence of benzaldehyde. The same observation was noted using an authentic sample of benzaldehyde.

Product was also analysed by the 2,4-dinitrophenylhydrazine (DNP) test [28]. The reaction product solution was treated with an excess of saturated solution of 2,4-dinitrophenylhydrazine in dil HCL medium.The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried and recrystalised from ethanol. The melting point of DNP derivative was found to be somewhat less than the melting point (239ºC) of the DNP derivative of authentic benzaldehyde. The slight lowering of the melting point was due to the presence of the DNP derivative of phenylglyoxylic acid produced as a byproduct in a small amount. Thus the product analysis agreed with the reports of Rocek et al. Moreover phenylglyoxylic acid was detected and confirmed by spot tests [27] using a reagent solution subjected to esterification by treating with ethyl alcohol and conc. H_2SO_4. 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 conc. H_2SO_4 and treated with two drops of thiophen solution. A characteristic red colour appeared within fifteen minutes. A similar observation was noted by using an sample of phenylglyoxylic acid.

In the reaction mixture, benzoic acid was detected and confirmed by a sot test [27]. The product was extracted into anonaquous solvent like benzene. One drop of the benzene solution was treated with a colourless saturated solution of Rhodamine B and an intense pink colour appeared. This colour was intensified when shaken with an aquous solution of uranyl salts. The same identification was noted by using an authentic sample of benzoic acid.

Carbon dioxide was detected qualitatively [29] under the kinetic conditions, by purging di nitrogen through the reaction solution and passing out coming gas through a narrow tube containing $Ca(OH)_2$.

Thus the Stoichiometry of the reaction is:

$$2C_6H_5CH(OH)CO_2H + 2HCrO_4^- + 8H^+ \rightarrow C_6H_5CO_2H + C_6H_5CHO + 2CO_2 + 2Cr(III) + 7H_2O \quad (1)$$

III. Results and Discussion

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

Under the experimental conditions, [mandelic acid]$_T$>>[bpy]$_T$>>$[Cr(VI)]_T$, the rate of disappearance of Cr(VI) shows a first -order dependence on Cr(VI) both in the presence and absence of bipyridine (bpy). This first-order dependence on Cr(VI) is also observed in the presence of surfactant SDS. From the linear plot of $\log[Cr(VI)]_T$ versus time(t) the pseudo first-order rate constants (k_{obs}) have been calculated.

B. Dependence on [bpy]T

The plots of k_{obs} versus $[bpy]_T$ are linear (r>0.99) with positive intercepts measuring the contribution of the relatively slower uncatalysed path (see fig2). The pseudo first-order rate constants ($k_{obs(u)}$) directly measured in the absence of bpy under the same conditions agree well with those obtained from the intercepts of the plots of k_{obs} versus $[bpy]_T$.

C. Dependence on $[S]_T$ i.e. [mandelic acid]$_T$

From the plot of k_{obs} versus [mandelic acid]$_T$ (see fig3), it has been established that both the catalysed and uncatalysed paths show a first-order dependence on $[S]_T$,i.e.

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

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

The above first-order dependence on $[S]_T$ is also maintained in the presence of surfactant SDS.

D. Dependence on $[H^+]$

The acid dependence patterns for the uncatalysed and catalysed paths are the different (see fig4). From the experimental fit, the observations are:

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

$$k_{obs(c)} = k_{obs(T)} - k_{obs(u)} = k_{H(c)}[H^+]^0 \quad (5)$$

A similar dependence pattern is also observed in the presence of SDS with enhanced rate constants (see fig 6).

E. Test For Acrylonitrile Polymerisation

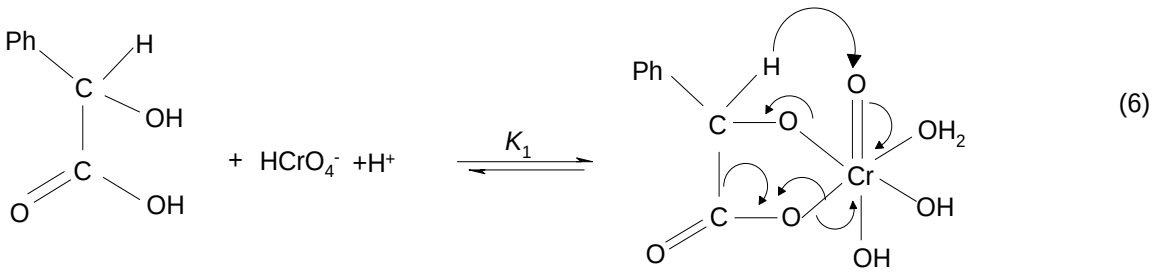
Under the experimental conditions, the polymerization of added acrylonitrile was indicated under a nitrogen atmosphere. This indicates the generation of free radicals during the course of reaction.

F. Mechanism And Interpretation

Discussion of the mechanism of the reaction can be divided in two parts: (i) uncatalysed path and (ii) catalysed path.

i. Reaction Mechanism For The Uncatalysed Chromic Acid Oxidation Of Dl-Mandelic Acid

The kinetics of the chromic acid oxidation of different α-hydroxy acids,including mandelic acid (MA), have been studied by different groups [18-24]. Of these α-hydroxy acids, mandelic acid is unique because it releases CO_2 as a product, indicating C—C bond rupture in its chromic acid oxidation.Besides the CO_2, it also produces C_6H_5CHO and C_6H_5COOH as the main products. These findings have been explained by considering a Cr(VI)—MA complex to be formed in a rapid pre-equilibrium step by the 3e-transfer in a single step within the cyclic transition state (see Scheme 1). This leads to the simultaneous rupture of C—H and C—C bond within the transition state [18,19]. Interestingly, for most of the other α-hydroxy acids, their chromic acid oxidation occurs via a 2e-transfer in the rate-determining step within the cyclic trasition state, giving rise to a keto acid [20-24].



$$Ph—\dot{C}=O + Cr(VI) \longrightarrow PhCOOH + Cr(V) \quad (8)$$

$$2Cr(V) \longrightarrow Cr(VI) + Cr(IV) \quad (9)$$

$$PhCH(OH)COOH + Cr(IV) \longrightarrow Ph\dot{C}HOH + CO_2 + Cr(III) \quad (10)$$

$$PhCHOH + Cr(VI) \longrightarrow PhCHO + Cr(V) \quad (11)$$

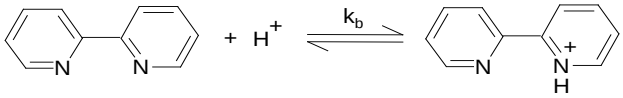
Scheme 1 Chromic acid oxidation of DL-mandelic acid.

gThe redox decomposition of the complex Cr(VI)—MA can be occurred in two parallel payhways, i.e. an acid-catalysed ($k_{H(u)}$ path) and an acid-independent path ($k_{o(u)}$ path).The acid-catalysed path is kinetically preferred. This is because the protonated complex favours electron flow towards Cr(VI) in the transition state. The 3e-transfer in a single step produces the radical C_6H_5CO which reacts subsequently with Cr(VI) in a faster step to give C_6H_5COOH and Cr(V). Mandelic acid is relatively stable [18,19] towards Cr(V) oxidation and it allows the accumulation of Cr(V) that subsequently undergoes disproportionation in a biomolecular process to generate Cr(VI) and Cr(IV). The substrate is then oxidized by Cr (IV) through C—C bond splitting to give CO_2. Here it may be pointed out that the 2e oxidation of mandelic acid without decarboxylation by Cr(IV) or Cr(V), leading to phenylglyoxylic acid under the experimental conditions, makes only a minor contribution to the total reaction.

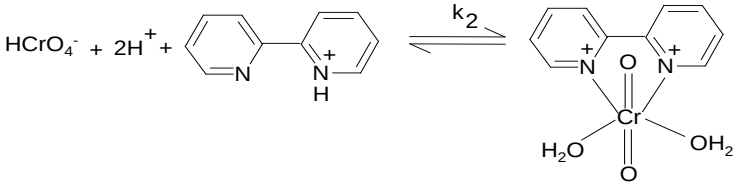
$$C_6H_5CH(OH)COOH + Cr(IV) \rightarrow C_6H_5COCOOH + 2H^+ + Cr(VI) \quad (12)$$

ii. Reaction Mechanism For The Bpy-Assisted Chromic Acid Oxidation Of Mandelic Acid

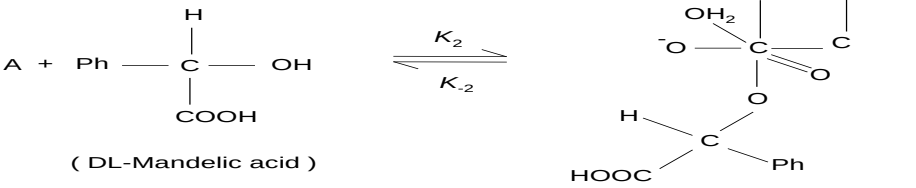
The findings for the bpy-assisted reaction can be explained by considering the reaction mechanism outlined in scheme 2. Cr(VI)—bpy complex is the active oxidant [3,16,24, 30-32]. In the next step, the Cr(VI)—bpy complex reacts with the substrate to form ternary complexe.. This ternary complexes undergo redox decomposition through 3e-transfer within the cyclic transition state in the rate determining step involving simultaneous rupture of C—C and C—H bonds to benzoyl radical, carbon dioxide and the Cr(III)—bpy complex . Subsequently, benzoyl radical reacts in faster steps as outlined in the case of the uncatalysed path.



(13)

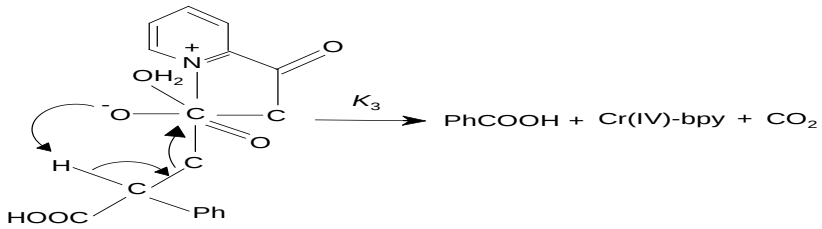


[A] (14)



(DL-Mandelic acid)

[B] (15)



[C] (16)

G. *Effect of SDS*

SDS (Sodium dodecyl sulphate, arepresentative anionic surfactant) accelerates both the uncatalysed and catalysed path. The rate acceleration is due to the preferential partitioning of the positively charged Cr(VI)—bpy complex by electrostatic attraction and the neutral substrate in the micellar surface (i.e. Stern layer) through H-bonding and ion-dipole interaction.Thus SDS allows the reaction to proceed in both aqueous and micellar interphases. The observed rate acceleration is due to the favoured reaction in the micellar phase where both the active oxidant and the substrate are preferentially accumulated. The plot of $k_{obs(T)}$ vs $[SDS]_T$ shows a continuous increase up to the concentration of SDS used for the bpy-catalysed reaction . An increase in $[SDS]_T$ increase the micellar counter ions (i.e. Na^+) which may displace H^+ and Ox^{+2} ions (A) out of micellar surface.

$$2Na^+_W + Ox^{2+}_M \rightleftharpoons 2Na^+_M + Ox^{2+}w \quad (17)$$

$$Na^+_W + H^+_M \rightleftharpoons Na^+_M + H^+_W \quad (18)$$

The above equilibria lead to decrease the value of $[H_M]^+$ and $[O_xM]^{2+}$ (A) to inhibit the rate process. These two effects are opposite in nature to determine the rate of reaction. In such bpy-catalysed path, the former effect (solubilisation effect) is greater than the later effect (i.e. counter ion effect) up to the used SDS concentration.

IV. Conclusions

The Cr(VI)—bpy complex, acationic species, has been found to act as the active oxidant in the bpy-assisted path.In this path, the Cr(VI)—bpy complex experiences nucleophilic attack by the dl-mandelic acid to form a ternary complex which subsequently undergoes redox decomposition involving a three- electron transfer, leading to oxidative decarboxylation through C—C bond cleavage along with the C—H bond cleavage. Benzoyl radical, CO_2 and Cr(III)—bpy complex are produced in this rate determining step. Benzoyl radical is subsequently oxidized to benzoic acid in the fast step. The reaction have been carried out in aquous micellar media. The effect of anionic surfactant, SDS on both the catalysed and uncatalysed paths have been studied. SDS accelerates the reaction rate for both paths but in different ways.

V. Acknowledgements

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VI. References

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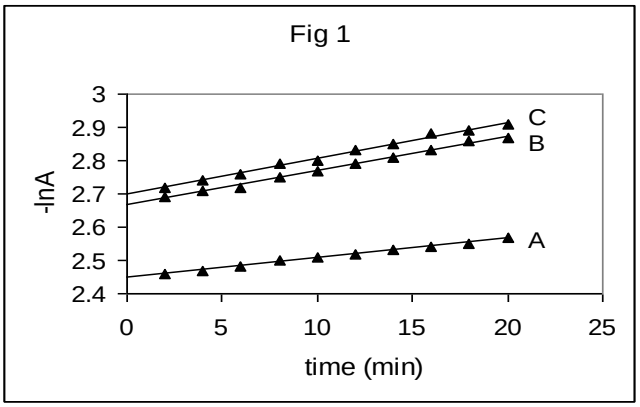
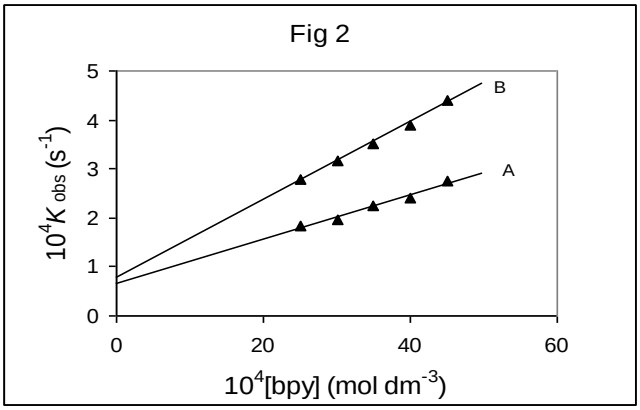
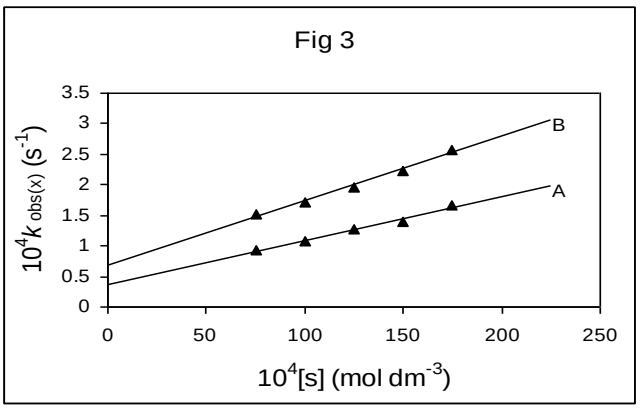
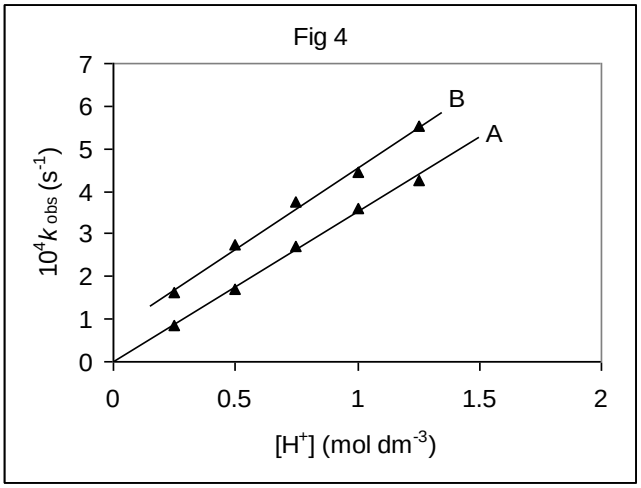
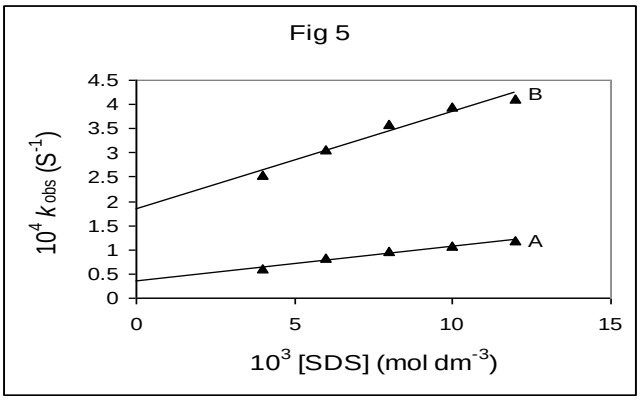
FIGURES

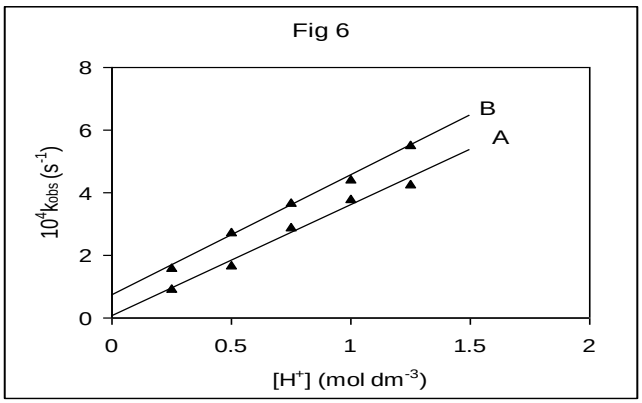












Legends to the Figures

***Fig.* 1** -Dependence of absorbance of Cr(VI) on time (min) for the oxidation of dl-mandelic acid at 25°C. $[Cr(VI)]_T$ = 5×10^{-4}mol dm^{-3}.[dl-mandelic acid]$_T$ = 75×10-4mol dm-3,[H2SO4] =.50(M). A ([bpy]T = 0 mol dm-3, $[SDS]_T$ = 0 mol dm-3 **),**B ([bpy] = 30×10^{-4} dm^{-3}), $[SDS]_T$ = 0 mol dm^{-3}), C ([bpy] = 25 mol dm^{-3} , $[SDS]_T$ = 4×10^{-3} mol dm^{-3}).

Fig. 2 -Dependence of $k_{obs(x)}$ on $[bpy]_T$for the chromium(VI) oxidation of dl-mandelic acid at 30°C. $[Cr(VI)]_T$ = 5×10^{-4}mol dm^{-3}, $[H_2SO_4]$ = 0.5 (M), x = u or c. A 25° C, B 45° C.

Fig 3 -Dependence of k_{obs} on [dl-mandelic acid]for the chromium(VI) oxidation of dl-mandelic acid at

25°C.$[Cr(VI)]_T = 5\times10^{-4}$mol dm^{-3}, $[H_2SO_4]$ = 0.5 (M). A $[bpy]_T$ = 0 mol dm^{-3}, B $[bpy]_T$ = 25×10^{-4}mol dm^{-3} .

Fig. 4 -Dependence of $[H^+]$ on k_{obs} for the chromium(VI) oxidation of dl-mandelic acid at 25°C. A $[bpy]_T$ = 0 mol dm^{-3} , B [bpy] = 25×10^{-4}mol dm^{-3} . $[Cr(VI)]_T = 5\times10^{-4}$mol dm^{-3}, $[dl\text{-mandelic acid}]_T = 75\times10^{-4}$mol dm^{-3}, $[H_2SO_4]$ =0.5 mol dm^{-3}.

Fig. 5 -Dependence of $[SDS]_T$ on k_{obs} for the chromium(VI) oxidation of dl-mandelic acid at 25°C.$[Cr(VI)]= 5\times10^{-4}$mol dm^{-3}, $[dl\text{-mandelic acid}]_T=75\times10^{-4}$mol dm^{-3}, $[H_2SO_4]$= 0.5 mol dm^{-3}. A $[bpy]_T$ = 0 mol dm^{-3} , B $[bpy]_T$ = 25 mol dm^{-3}.

Fig. 6-Dependence of $[H^+]$ on k_{obs} for the chromium(VI) oxidation of dl-mandelic acid at 25°C. .$[Cr(VI)]= 5\times10^{-4}$mol dm^{-3}, [dl-mandelic acid]=75×10^{-4}mol dm^{-3},$[H_2SO_4]$ = 0.5 (M) . A ([bpy] = 0 mol dm^{-3}, [SDS] = 4×10^{-3} mol dm^{-3}) , B ([bpy] = 25×10^{-4} mol dm^{-3} , [SDS] = 4×10^{-3} mol dm^{-3}).