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CATALYSED OXIDATION OF ALLOPURINOL BY DIPERIODATOCUPRATE (III) PERIODATE COMPLEX IN AQUEOUS ALKALINE MEDIUM: A KINETIC APPROACH

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ABSTRACT

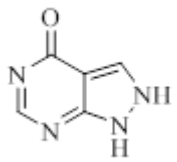
The kinetics of oxidation of the Allopurinol (ALP) by diperiodatocuprate(III) (DPC) was carried in presence of Osmium(VIII) catalyst in alkaline medium at constant ionic strength of 0.01 mol dm^{-3} spectrophotometrically. The involvement of free radicals was observed in the reactions. The stoichiometry is, [ALP]:[DPC] = 1:1. The reaction was first order in [DPC] and has positive fractional order in [OH^-] and negative fractional order in the catalyzed cases. The order in [Osmium (VIII)] was unity. A mechanism involving the formation of a complex between ALP and Osmium (VIII) in case of catalysed reaction was proposed. The reaction constants involved in the different steps of the mechanisms were calculated for reactions. The catalytic constant (Kc) was also calculated for catalysed reaction at different temperatures. The activation parameters with respect to slow step of the mechanisms were computed and discussed. The thermodynamic quantities were also determined for catalyzed reactions.

KEYWORDS: Allopurinol; Diperiodatocuprate (III); Os (VIII) catalysis; Oxidation; Kinetics.

1. INTRODUCTION

In recent years, the study of highest oxidation state transition metals has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable Polydentate ligands. Metal chelates, such as diperiodatocuprate (III)[1], diperiodatoargentate (III)[2] and diperiodatonickelate (IV)[3] are good oxidants in a medium with an appropriate pH value. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds.[4] The kinetics of self-decomposition of these complexes was studied in some detail.[5] Copper (III) is an intermediate in the copper(II) catalysed oxidation of amino acids by peroxydisulphate.[6] The oxidation reaction usually involves the copper(II)-copper(I) couple and such aspects are detailed in different reviews.[7,8] The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well recognized.[9] Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry.[10] When the copper(III) periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

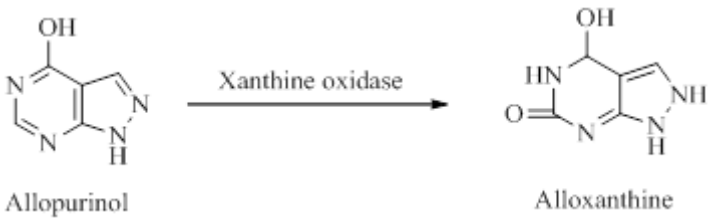
Allopurinol (4-hydroxypyrazolo[11,12] pyrimidine) (AP) as shown in Scheme 1, is a radical shifting clinical drug and widely used in the treatment of hyperuricemia and chronic gout and it can be controlled either intravenously or orally. The bioavailability is about 67 to 90% with a peak plasma concentration arising within one hour; the volume of distribution is approximately 1.62/kg.[4] It is additionally used in the novel therapeutic strategy for the treatment of human heart failure.[13] AP is greatly used to reduce the gout, hyperuricemia, Lesh-Nyan, renal failure, kidney disease, heart disease, high blood pressure and diabetes.[14]



Scheme 1. Chemical structure of allopurinol.

It is frequently used in patients with severe gout, although, optimization of allopurinol dosage by measuring oxypurinol serum levels might be necessary. Another indication for therapeutic

drug monitoring (TDM) is to verify a patient's adherence to the use of allopurinol, which in general is reported to be a point of concern. Usually drugs containing allopurinol (ALO) (daily dose 100-300 mg) are used. ALO (structural analogue to HYP and XO inhibitor) is preferentially oxidized to oxypurinol (OXY), which is excreted in the urine together with HYP and XAN as more soluble products compared to UA. From a medical point of view, it is necessary to monitor these substances, because, for instance, at a higher dosage of ALO, there is a danger of xanthine nephropathy caused by accumulation of natural purines. Allopurinol is a structural isomer of hypoxanthine (a naturally occurring purine in the body) and acts to inhibit xanthine oxidase. In the presence of xanthine oxidase, allopurinol will be converted to alloxanthine as shown in Scheme 2, after that the formation of uric acid from xanthine and hypoxanthine will be inhibited.[15]



Allopurinol Alloxanthine

Scheme 2. Inhibition of uric acid production.

Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation state. The use of transition metal ions such as Osmium, ruthenium and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest.[15] The role of Osmium (VIII) as a catalyst in some redox reactions has been reviewed.[16] Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and experimental conditions, it has been shown[17] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. In earlier report[18], it has been observed that Os(VIII) forms a complex with substrate, which gets oxidized by the oxidant to form a Os(VII) intermediate followed by the rapid reaction of Os(VII) with one more mole of oxidant to regenerate Os(VIII). In another report,[19] It has been observed that Oxidant-substrate complex reacts with Os (VIII) to forms a Os(VI) which on regenerated by reacting with oxidant in fast step to regenerate Os(VIII). In some other reports[20], it is observed that Os (VIII) forms complex with substrate is oxidized by the oxidant with the regeneration of Os (VIII). Hence understanding the role of Os (VIII) in catalyzed reaction is importance. Osmium (VIII) catalysis in redox reactions involves several

complexes, different oxidation states of Osmium, etc. We have observed that Osmium (VIII) catalyses the oxidation of AP by DPC in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanisms, the title reaction is investigated in detail in view of various mechanistic possibilities. An understanding of mechanism allows chemistry to be interpreted and hence understood and predicted.

2. EXPERIMENTAL

2.1. Materials and reagents

All chemicals were of reagent grade and double distilled water was used throughout the work. A solution of Allopurinol (S.D FINE CHEM.) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The purity of the AP sample was checked with its m.p. 302 ^{0}C (Lit. m.p. 300 ^{0}C). The required concentration of AP was made from its stock solution. The Osmium (VIII) solution was prepared by dissolving OsO_4 oxide (JOHNSON MATTHEY) in 0.50 mol dm^{-3} NaOH. The concentration was ascertained[21] by determining the unreacted $[Fe(CN)_6]4^-$ with standard Ce(IV) solution in an acidic medium. KNO_3 and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. The copper (III) periodate complex was prepared by standard procedure.[22] The aqueous solution of copper (III) was standardized by iodometric titration and gravimetrically by thiocyanate method.[23] The copper(II) solutions were prepared by dissolving a known amount of copper sulphate (BDH) in distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and used after keeping it for 24 h. Its concentration was ascertained iodometrically[24] at neutral pH maintained using phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of AP by periodate in alkaline medium at 25^{0}C was tested. The progress of the reaction was followed iodometrically. There was no significant reaction under the experimental conditions employed compared to the DPC oxidation of AP. The pH of the medium in the solution was measured by (ELICO (LI613) pH meter.

2.2. Kinetics

The kinetic measurements were performed on a Varian CARY 50 Bio UV–vis spectrophotometer. The kinetics was followed under pseudo first-order condition where [AP] > [DPC] in catalyzed reaction at 25 ± 0.1 ^{0}C, unless specified. In the absence of catalyst the reaction was initiated by mixing the DPC to AP solution which also contained required

concentration of KNO_3, KOH and KIO_4. The reaction in the presence of catalyst was initiated by mixing DPC to AP solution which also contained required concentration of KNO_3, KOH, KIO_4 and Os (VIII) catalyst. The progress of reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbency index, 'ε' taken as 6230 ± 100 dm^3 mol^{-1} cm^{-1} in catalyzed reactions. It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The spectroscopic changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of DPC in terms of absorbance of DPC decreases at 415 nm.

The pseudo first-order rate constants, (k_C'), in catalysed case were determined from the log (absorbance) versus time plots. The plots were linear up to 80% completion of reaction (Fig. 2 for catalysed). The orders for various species were determined from the slopes of plots of log (k_C) versus respective concentration of species except for [DPC] in which non-variation of 'k_C' was observed as expected to the reaction condition. The rate constants were reproducible to within ±5%. Regression analysis of experimental data to obtain regression coefficient r and the standard deviation s, of points from the regression line, was performed with the Microsoft office Excel-2003 programme.

3. RESULTS AND DISCUSSION

Table 1. Effect of [DPC], [AP], [IO_4], [OH^-] and [Os(VIII)] on the Osmium(VIII) catalyzed oxidation of allopurinol by DPC in alkaline medium at 25 ^{0}C, I=0.01 mol dm^{-3}.

10^5[DPC] (mol dm^{-3})	10^4 [AP] (mol dm^{-3})	10^5[IO_4] (mol dm^{-3})	10^2 [OH^-] (mol dm^{-3})	10^7 [Os(VIII)] (mol dm^{-3})	10^2 k_T (s^{-1})	10^3 k_U (s^{-1})	10^2 k_C (s^{-1})	
							Found	Calculated
1.0	4.0	5.0	0.4	8.0	6.5	4.0	6.1	6.2
3.0	4.0	5.0	0.4	8.0	6.7	4.0	6.3	6.2
5.0	4.0	5.0	0.4	8.0	6.8	4.1	6.3	6.2
8.0	4.0	5.0	0.4	8.0	6.7	3.9	6.2	6.2
10.0	4.0	5.0	0.4	8.0	6.6	4.1	6.2	6.2
5.0	1.0	5.0	0.4	8.0	0.8	1.1	0.7	0.71
5.0	2.0	5.0	0.4	8.0	1.5	3.1	1.2	1.4
5.0	4.0	5.0	0.4	8.0	2.8	3.7	2.4	2.6
5.0	6.0	5.0	0.4	8.0	4.2	5.4	3.6	3.7
5.0	10.0	5.0	0.4	8.0	5.4	6.0	4.8	5.6
5.0	4.0	1.0	0.4	8.0	4.9	4.8	4.4	4.5
5.0	4.0	3.0	0.4	8.0	4.4	4.4	3.9	3.5
5.0	4.0	5.0	0.4	8.0	3.7	3.7	3.3	3.5
5.0	4.0	8.0	0.4	8.0	3.0	3.0	2.7	3.4
5.0	4.0	10.0	0.4	8.0	2.6	2.6	2.3	2.4
5.0	4.0	5.0	0.1	8.0	2.8	2.8	2.5	3.1
5.0	4.0	5.0	0.2	8.0	3.4	3.4	3.0	2.9

5.0	4.0	5.0	0.4	8.0	3.7	3.7	3.3	3.4
5.0	4.0	5.0	0.6	8.0	4.4	4.4	3.9	3.4
5.0	4.0	5.0	1.0	8.0	4.7	4.7	4.2	4.0
5.0	4.0	5.0	0.4	5.0	1.5	3.2	1.2	1.3
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	4.0	5.0	0.4	10	3.4	3.2	3.1	3.3
5.0	4.0	5.0	0.4	30	8.6	3.2	8.3	8.4
5.0	4.0	5.0	0.4	50	14.0	3.2	14.0	14.5

Table 2. Thermodynamic activation parameters for the Osmium(VIII) catalysed oxidation of allopurinol by DPC in aqueous alkaline medium with respect to the slow step of Scheme 3. (A) Temperature Effect.

Temperature (K)	$10^{-5}\,k_2$ ($dm^3\,mol^{-1}\,s^{-1}$)	$10^{2}\,K_1$ ($mol\,dm^{-3}$)	$10^{-2}\,K_3$ ($dm^3\,mol^{-1}$)
298	3.3	1.6	3.4
303	3.8	1.4	3.9
308	4.7	0.8	5.8
313	5.7	0.5	6.6

(B) Activation parameters (Scheme 2).

Activation parameters using k_2	Values
$\Delta H^{\#}$ ($kJ\,mol^{-1}$)	25.2 ± 0.4
$\Delta S^{\#}$ ($JK^{-1}\,mol^{-1}$)	-56.5 ± 5
$\Delta G^{\#}$ ($kJ\,mol^{-1}$)	42.5 ± 2
log A	10.3 ± 0.4

(C) Thermodynamic quantities using K_1 and K_3.

Thermodynamic quantities	Values from K_1	Values from K_3
ΔH ($kJ\,mol^{-1}$)	-55.0 ± 3.0	36.3 ± 2.0
ΔS ($JK^{-1}\,mol^{-1}$)	-218 ± 20	170 ± 18
ΔG_{298} ($kJ\,mol^{-1}$)	11.6 ± 0.1	-15.6 ± 0.9

Table 3. Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C Values.

Temperature	$10^{-2}\,K_C$
298	2.5
303	3.5
308	4.3
313	5.3
Ea ($kJ\,mol^{-1}$)	37.8
$\Delta H^{\#}$ ($kJ\,mol^{-1}$)	35.2
$\Delta S^{\#}$ ($kJ^{-1}\,mol^{-1}$)	-159.6
$\Delta G^{\#}$ ($kJ\,mol^{-1}$)	84.1
log A	5.0

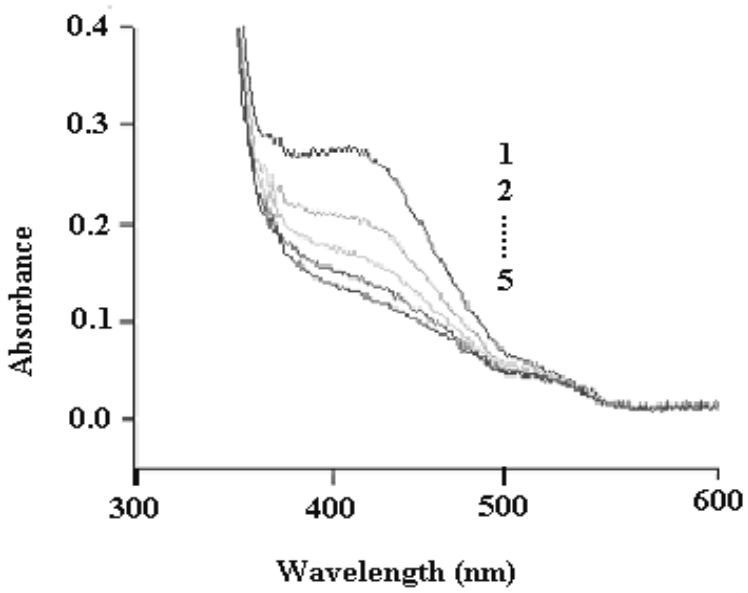
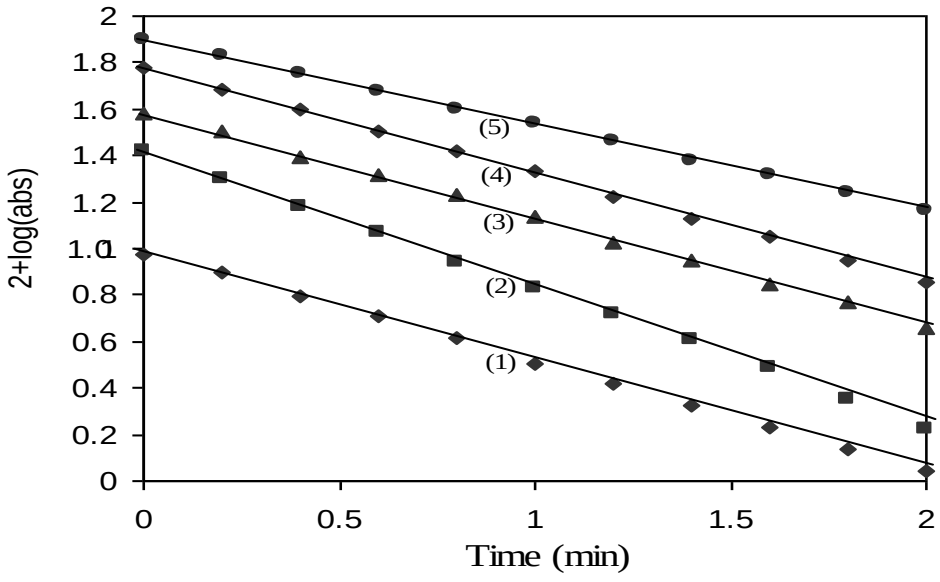


Fig. 1. Spectroscopic changes occurring in the oxidation of allopurinol by diperiodatocuprate(III) at 25 ^{0}C, [DPC]= 5.0 x 10^{-5}, [AP] = 4.0 x 10^{-4}, [OH^-]= 0.004 and I = 0.01 mol dm^{-3} with scanning time interval of: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0 and (5) 2.5 minutes.

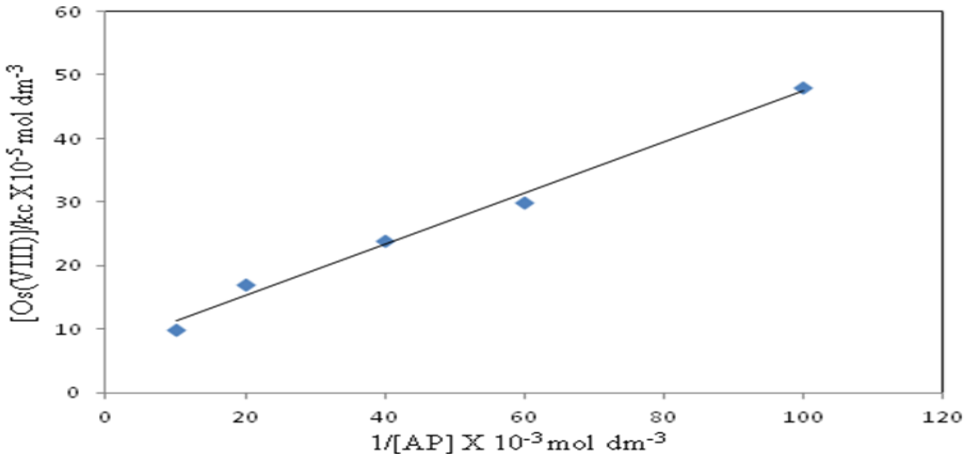
Fig. 2. First order plots for the oxidation of Os(VIII) catalysed allopurinol by diperiodatocuprate(III) in aqueous alkaline medium.

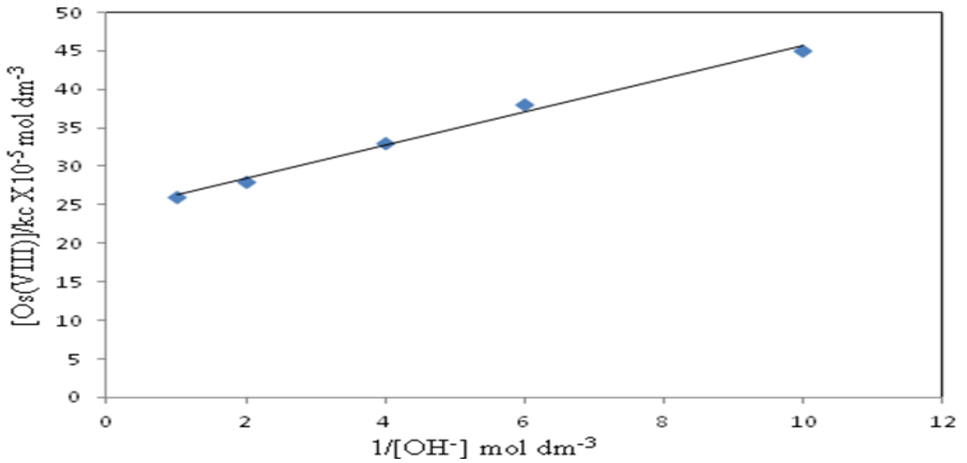
[diperiodatocuprate(III)] X 10^{5} (mol dm^{-3})

1) 1.0 2) 3.0 3) 5.0 4) 8.0 5) 10.0

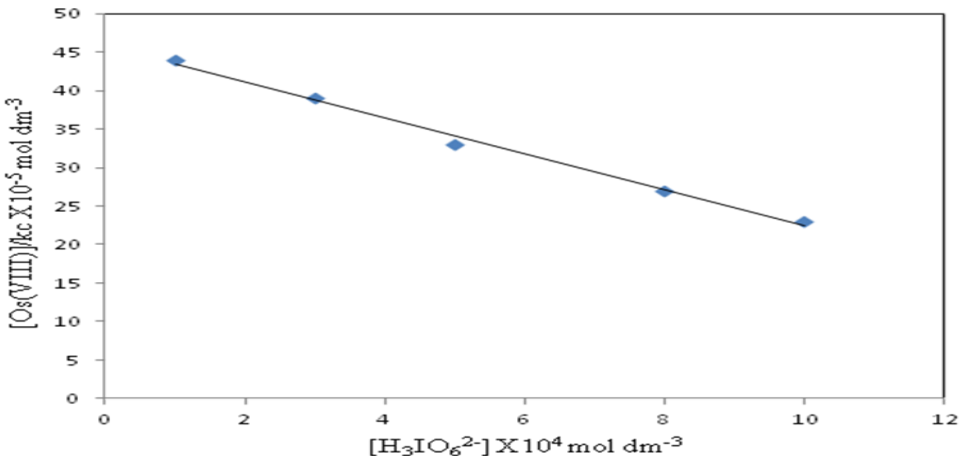


(A)





(B)

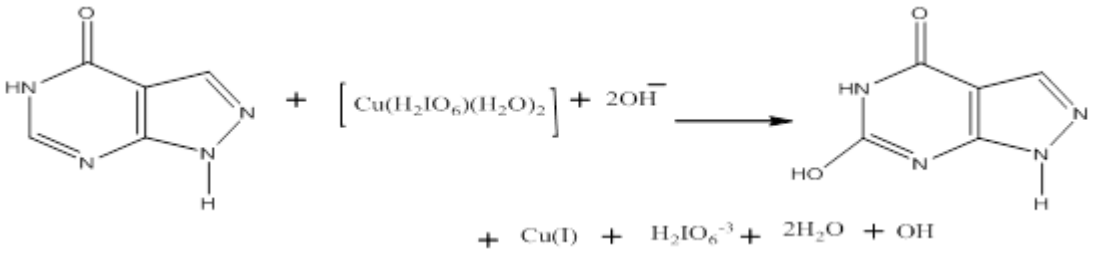


(C)

Fig. 3. Verification of rate law (A) Plot of [Os(VIII)]/kc vs 1/[AP] at room temperature, (B) plot of Plot of [Os(VIII)]/kc vs 1/[OH^-] and (C) plot of Plot of [Os(VIII)]/kc vs [$H_3IO_6^{2-}$] (As in condition Table 1).

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPC to AP in the presence of constant amount of OH^-, KNO_3 and KIO_4 in uncatalysed reaction and a constant amount of Os(VIII) in catalyzed reaction were kept for 2 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated by spectrophotometrically at 415 nm. The results indicate that 1:1 stoichiometry as given in Eqn (1).



The stoichiometric ratio in both the cases suggests that the main product was 6-hydroxy-4-oxo-4,7dihydro1-4pyrazole (3,4d) pyrimidium-7-ium. The metal product, Cu(II) was identified by UV-vis spectra. The reaction product did not undergo further oxidation under the present kinetic conditions.

3.2. Reaction orders

As the diperiodatocuprate(III) oxidation of allopurinol in alkaline medium proceeds with a measurable rate in the absence of Os(VIII), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence the reaction orders have been determined from the slopes of log k_C versus log (concentration) plots by varying the concentrations of AP, alkali, periodate and Os(VIII) catalyst in turn while keeping all other concentrations and conditions constant. The order in DPC was unity between the concentrations was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed AP, KOH and KNO_3 in both the cases uncatalysed and catalysed reactions. Linearity of the plots of log [absorbance] versus time up to 80% completion of the reaction indicates a reaction order of unity in [DPC]. This was also confirmed by varying [DPC], did not result in any change in rate constants, k_C (Table 1). The effect of AP on the rate of reaction was studied at constant concentrations of alkali, DPC and periodate at a constant ionic strength of 0.01 mol dm^{-3} in the case of catalysed reaction. In case of catalysed reaction the AP concentration was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at 25 ^{0}C while keeping other reactant concentrations and conditions constant.

The k_C and k_U values increased with the increase in concentration of AP indicating an evident less than unit order dependence on [AP] (Table 1). The effect of alkali on the reaction has been studied in the range of 0.001 to 0.01 mol dm^{-3} at constant concentrations of AP, DPC and periodate at a constant ionic strength of 0.01 mol dm^{-3} in at concentration of Os(VIII) in catalysed reaction. The rate constants increased with increase in alkali concentration (Table 1), indicating positive fractional order dependence of rate on alkali concentration.

3.3. Effect of allopurinol

The effect of allopurinol on the rate of reaction Os(VIII) catalysed, was studied at constant concentrations of alkali, DPC and Perodate at constant ionic strength. In case of catalyzed reaction the allopurinol concentration was varied in the range of 1.0 X 10^{-4} to 1.0 X 10^{-3} mol dm^{-3}. The kc values increased with the increase in concentration of allopurinol indicating an apparent less than unit order dependence on [AP] (Table 1).

3.4. Effect of Alkali

The effect of alkali on the reaction has been studied in case in the range of 0.001 to 0.01 mol dm^{-3} at constant concentration of allopurinol, DPC and periodate at a constant ionic strength of 0.01 mol $dm^{-3}$and at constant concentration of Os(VIII). The rate constants increased with increase in alkali concentration (Table 1), indicating positive fractional order dependence of rate on alkali concentration.

3.5. Effect of periodate

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} keeping all other reactant concentrations constant. The rate constant decrease with increase the periodate concentration had negative fractional order (Table 1) in catalysed reactions.

3.6. Effect of ionic strength (I) and dielectric constant (D)

It was found that ionic strength (using KNO_3) and dielectric constant of the medium (using t-butyl alcohol and H_2O) had no significant effect on the rate of reaction in catalysed reactions.

3.7. Test for free radicals (Polymerization study)

The involvement of free radicals, for catalysed reactions was tested. The reaction mixture was mixed with acrylonitrile monomer initially added, was kept for 2 h in an inert atmosphere**.** On diluting the reaction mixture with methanol, a white precipitate was formed,

indicating the involvement of free radicals in catalysed reactions. The blank experiments of either DPC or AP alone with acrylonitrile did not induce any polymerization under the same conditions. Initially added acrylonitrile decreased the rate of reaction, indicating free radical participation.

3.9. Effect of temperature

The influence of temperature on the rate of reaction was studied for catalysed reaction at 25, 30, 35 and 40 ^{0}C. The rate constants, (kc), of the slow step of Scheme 3 were obtained from the slopes and the intercepts of the plots of [Os(VIII)]/k_C versus 1/[AP] plots at four different temperatures. The values are given in Table 1. The activation parameters for the rate determining step were obtained by the least square method of plot of log k_2 versus 1/T and are presented in Table 2.

4.0. Effect of [Os(VIII)]

The [Os(VIII)] concentration was varied from 5.0 x 10^{-7} to 5.0 x 10^{-6} mol dm^{-3} range, at constant concentration of diperiodatocuprate(III), AP, alkali and ionic strength. The order in [Os(VIII)] was found to be unity from the linearity of the plots of k_C versus [Os(VIII)].

4.1. Catalytic activity

It has been pointed out by Moelwyn-Hughes[25] that in presence of the catalyst, the uncatalysed and catalysed reaction proceed simultaneously, so that,

$$k_T = k_U + K_C\,[Os(VIII)]^x \qquad (2)$$

Here k_T is the observed pseudo first order rate constant in the presence [Os(VIII)] catalyst, k_U the pseudo first–order rate constant for the uncatalysed reaction, K_C the catalytic constant and 'x' the order of the reaction with respect to [Os(VIII)]. In the present investigations, x values for the standard run were found to be unity. Then the value of K_C is calculated using the equation,

$$K_C = \frac{k_T - k_U}{[Os(VIII)]^x} = \frac{k_C}{[Os(VIII)]^x} \qquad (\text{where, } k_T - k_U = k_C) \qquad (3)$$

The values of K_C were evaluated for [Os(VIII)] catalyst at different temperatures and found to vary at different temperatures. Further, plots of log K_C versus 1/T were linear and the

values of energy activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 3.

The water-soluble copper (III) periodate complex is reported[26] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in aqueous alkaline medium at high pH as employed in this study, periodate is unlikely to exist as HIO_6^{4-} (as present in the complex) as is evident from its involvement in the multiple equilibria[27] (4)-(6) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad (4)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+ \quad (5)$$

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \quad (6)$$

Periodic acid exists as H_5IO_6 and as $H_4IO_6^-$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise.[28] However, formation of this species is negligible under the conditions employed for this study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)_2(OH)_2]^{2-}$, a conclusion also supported by earlier work.[29]

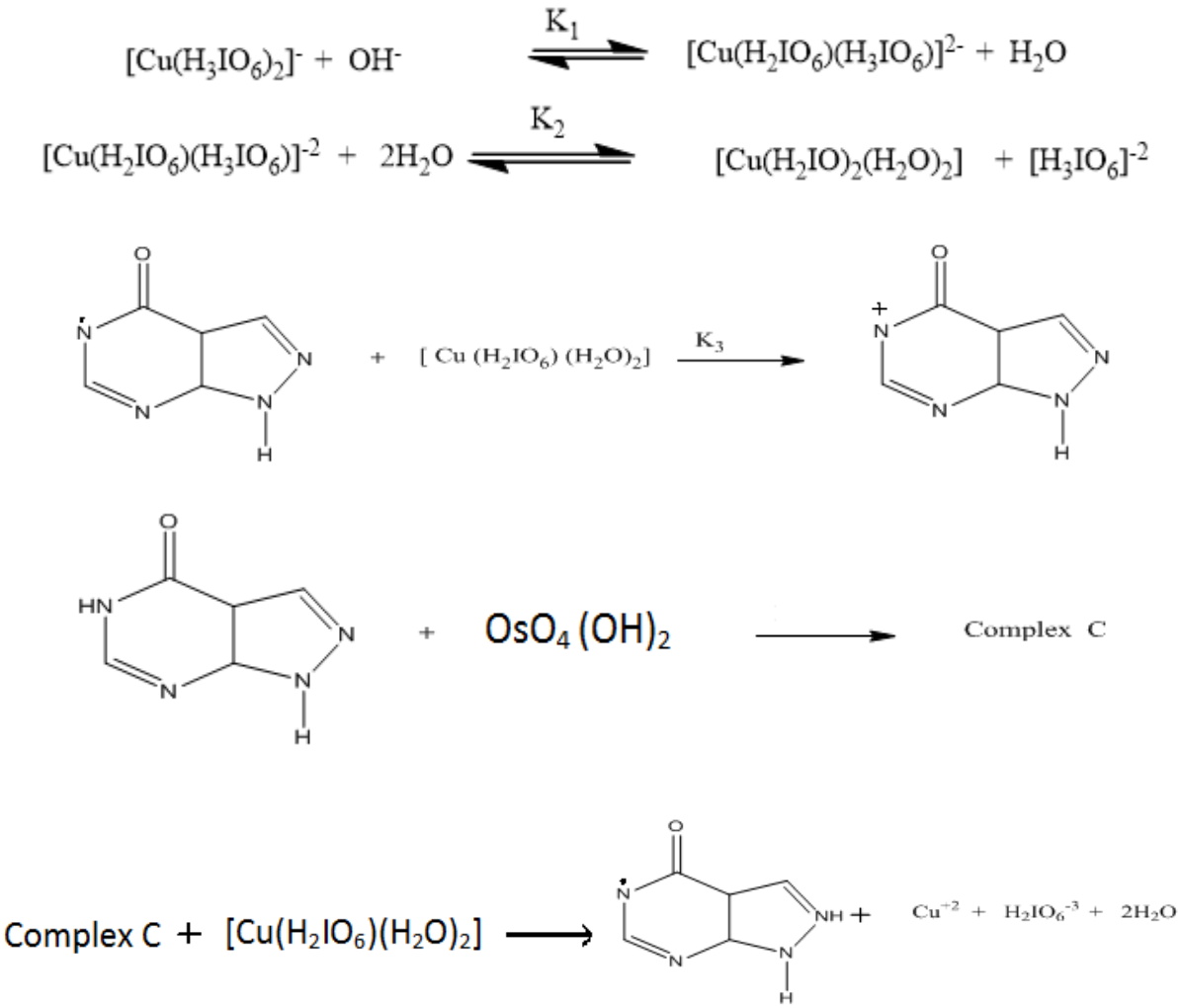
In most of the reports[29] on DPC oxidation, periodate retards and OH^- increases the rate of the reaction. However in the present kinetic study, entirely different kinetic observations have been obtained. In this study OH^- retards the rate of reaction and periodate shows no effect on the rate. The result of decrease in rate of reaction with increase in alkalinity (Table 1) can be explained in terms of a prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)_2)]^{3-}$ from $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ hydrolysis as given below.

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O \overset{K_1}{\rightleftharpoons} [Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^-$$

Because of this reaction and the observation that the k_U or k_C values are inversely related to the hydroxyl ion concentration with fractional order in OH concentration, the main oxidant species is likely to be $[Cu(OH)_2(H_3IO_6)_2]^{3-}$ and its formation by the above equilibrium is important in the present study.

4.2. Catalysed Mechanism

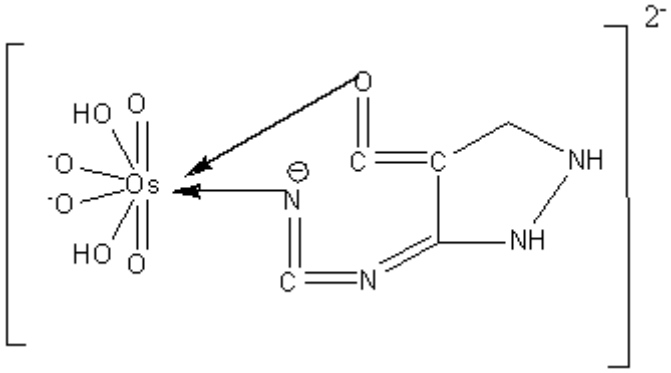
The [AP] reacts with Os(VIII) active species to form a complex (C) which further reacts with one mol of DPC in a slow step to give the free radical of allopurinol, Cu(II) with regeneration of catalyst. Further this free radical of allopurinol reacts with one more molecule of DPC species in a fast step to yield the products as given Scheme 3.



Scheme 3. Detailed Scheme for the oxidation of allopurinol by alkaline diperiodatocuprate(III).

Since, Scheme 1 is in accordance with the generally well-accepted principle of non-complementary oxidations taking place in sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. The free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work.[30]

The probable structure of the complex is given by,



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of AP = (4.0 x 10^{-4}), DPC = (5.0 x 10^{-5}), [OH^-] = 0.004 (mol dm^{-3}) and a mixture of both. A hypsochromic shift of about 9 nm from 246 nm of AP to 237 nm of mixture of DPC and AP and a hyperchromicity at 237 nm, was observed. A Lineweaver-Burk plot also indicated the complex formation between DPC and AP, which explains the less than unit order dependence on [AP]. Such a type of complex between a substrate and an oxidant has been observed in other studies.[31]

The rate law for Scheme 3 could be derived as,

$$k_C = \frac{\text{Rate}}{[\text{DPC}]} = \frac{kK_1K_2K_3[\text{ALO}][OH^-][\text{Os(VIII)}]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\text{ALO}]} \quad (7)$$

$$\frac{\text{Os(VIII)}}{k_C} = \frac{[H_3IO_6^{2-}]}{kK_1K_2K_3[OH^-][\text{ALO}]} + \frac{[H_3IO_6^{2-}]}{kK_2K_3[\text{ALO}]} + \frac{1}{kK_3[\text{ALO}]} + \frac{1}{k} \quad (8)$$

The rate law (7) can be rearranged to Eqn (8), which is suitable for verification.

According to equation (8), the plots of [Os(VIII)]/kc versus 1/[AP] [OH^-], [Os(VIII)]/kc versus 1/[OH^-] and [Os(VIII)]/kc versus [IO_4] were linear (Fig. IIIa, IIIb and IIIC). From the slopes and intercepts of such plots, the reaction constants K_1, K_2, K3 and k were calculated as (1.6 ± 0.02) x 10^{-2} mol dm^{-3}, (3.5 ± 0.2) x 10^2 dm^3 mol^{-1} and (3.3 ± 0.1) x 10^5 s^{-1} respectively. These constants were used to calculate the rate constants and compared with the experimental kc values and found to be in reasonable agreement with each other, which fortifies the scheme 3.

The thermodynamic quantities for the first and second equilibrium steps of Scheme 3 can be evaluated as follows. The [AP], [OH^-] and [IO_4^-] (Table 1) were varied at four different temperatures. The plots of [Os(VIII)]/kc versus 1/[AP] [OH^-], [Os(VIII)]/kc versus 1/[OH^-] and [Os(VIII)]/kc versus [IO_4] should be linear (Fig. 3). From the slopes and intercepts, the values of K_1 and K_2, K_3 and k were calculated at different temperatures and these values are given in Table 2. The Vant Hoff's plots were made for variation of K_1 and K_2 and K_3 with temperature and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated for the first and second and third equilibrium steps. These values are given in Table 2. A comparison of ΔH value (36.3 ± 2) from K_2 with that of $\Delta H^{\#}$ (25.2 ±0. 2) of rate limiting step supports that the second step of Scheme 3 is fairly fast since it involves low activation energy.[32]

The moderate values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron transfer processes. The value of $\Delta S^{\#}$ within the range for a radical reaction has been ascribed[33] to the nature of electron pairing and impairing processes and to the loss of degrees of freedom upon the formation of rigid transition state. The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations.[34] A high negative value of $\Delta S^{\#}$ (-184 JK^{-1} mol^{-1}) suggests that intermediate complex is more ordered than the reactants.[35]

Negligible effect of ionic strength and dielectric constant in uncatalysed and catalysed reaction might be due to involvement of neutral species in the reaction (Schemes 3). The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants.[35] The observed modest enthalpy of activation and a higher rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation.[34]

4. CONCLUSION

The comparative study of uncatalysed and Osmium(VIII) catalysed oxidation of AP by diperiodatocuprate(III) was studied. Oxidation products were identified. Among the various species of Cu(III) in alkaline medium, protonated DPC is considered to be the active species for the title reaction. Active species of Os(VIII) is found to be $[OsO_4(OH)_2]^{2-}$. Activation parameters were evaluated for catalyzed reactions with respect to slow step of reaction

schemes. Catalytic constants and activation parameters with respect to catalyst were also computed.

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