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DETERMINATION OF THERMODYNAMIC PARAMETERS OF Ru(III) CATALYSED OXIDATION OF ALLOPURINOL BY Cu(III) PERIODATE COMPLEX IN ALKALINE MEDIUM: A KINETIC STUDY

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ABSTRACT

The kinetics of oxidation of the Allopurinol (ALP) by diperiodatocuprate (III) (DPC) was carried in presence of Ruthenium (III) 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] = 1:2. 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 [Ruthenium (III)] was unity. A mechanism involving the formation of a complex between ALP and Ruthenium (III) 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); Ru (III)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) catalyzed 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 behave as the active oxidant.

Allopurinol, its chemical name is 4H - Pyrazole (3, 4) – pyramidine -4 - one. is a radical sifting clinical drug and widely used in the treatment of hyperuricemia and chronic gout and it can be controlled either intravenously or orally.

It is important to monitor the concentration of purine metabolites in cell or body fluids to find out metabolic defects which are characterized by abnormal concentrations of the metabolites resulting in indications of pathological conditions such as gout, hyperuricaemia, Lesch-Nyan disease, renal failure, diabetes, high blood pressure, kidney disease, and heart disease.[11]

Transition metals are known to catalyze many oxidation-reduction reactions since they involve multiple oxidation states. In recent years the use of transition metal ions such as Ruthenium, Osmium, Palladium, Manganese, Chromium, Iridium, either alone or as binary mixtures, as catalysts in various red-ox processes has attracted considerable interest.[12] Ru(III) acts as catalyst in the oxidation of many organic and inorganic substrates.[13,14] Although the mechanism of catalysis depends on the nature of the substrate, oxidant and experimental conditions, it has been shown[15] that metal ions act as catalysts by one of several paths, such as the formation of complexes with reactants, oxidation of the substrate itself or the formation of free radicals. Ruthenium (III) catalysis in red-ox reactions involves different degrees of complexity, due to the formation of different intermediate complexes and different oxidation states of Ruthenium. We have observed that Ru (III) catalyzes the oxidation of Allopurinol by DPC in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst as well as 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 ALP sample was checked with its m.p. 312 ^{0}C (Lit. m.p. 314 ^{0}C). The required concentration of ALP was made from its stock solution. The Ru (III) solution was prepared by dissolving $RuCl_3$ (S D Fine Chem) in 0.20 mol dm^{-3} HCl. The concentration was determined by EDTA titration.[16] 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.[17] The aqueous solution of Copper (III) was standardized by iodometric titration and gravimetrically by thiocyanate method.[18] 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[19] at neutral pH maintained using phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of ALP 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 ALP. 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 [ALP] > [DPC] in catalysed reaction at 25 ± 0.1 ^{0}C, unless specified. The reaction in the presence of catalyst was initiated by mixing DPC to ALP solution which also contained required concentration of KNO_3, KOH, KIO_4 and Ru (III) 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 631 ± 100 dm^3 mol^{-1} cm^{-1} in catalysed 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.

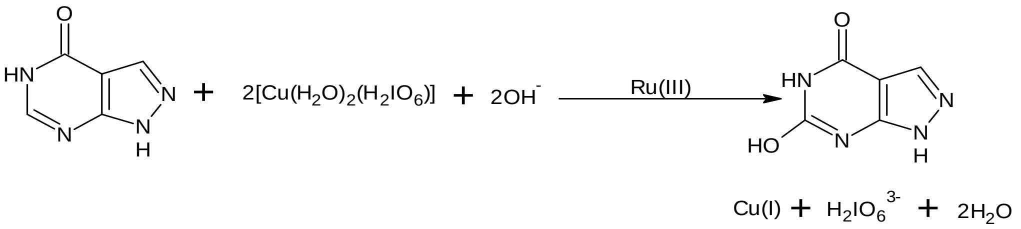
The pseudo first-order rate constant, ('k_C'), was determined from the log (absorbance) versus time plots. The plots were linear up to 80% completion of reaction Fig. 2. The orders for various species were determined from the slopes of plots of log (k_C) versus respective concentration of species except 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

3.1. Stoichiometry and product analysis

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



(1)

The main oxidation products were identified as 6-hydroxy–1,5–di hydro -4H-pyrazolo [3,4-d] pyrimidine –4–one. The presence of Cu (I) was confirmed by UV-visible spectra.

3.2. Reaction orders

As the diperiodatocuprate (III) oxidation of Allopurinol in alkaline medium proceeds with a measurable rate in the absence of Ru (III), the catalyzed reaction is understood to occur in parallel paths with contributions from both the catalyzed and uncatalyzed 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 ALP, alkali, periodate and Ru (III) catalyst in turn while keeping all other concentrations and conditions constant. The order in DPC was unity between the concentrations varied in the range of 1.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} at fixed ALP, KOH and KNO_3 concentrations in catalyzed 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] which did not result in any change in the rate constants, K_c (Table 1).

3.2 Effect of Allopurinol

The effect of ALP 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 catalyzed reaction. In case of catalyzed reaction the ALP concentration was varied in the range of 1.0 x 10^{-4} to 1.0 x 10^{-3} mol dm^{-3} at 25 ^{0}C while keeping other reactant concentrations and conditions constant. The K_c values increased with the increase in concentration of ALP indicating an apparent less than unit order dependence on [ALP] (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 ALP, DPC and periodate at a constant ionic strength of 0.01 mol dm^{-3} in Ru (III) catalyzed reaction. The rate constants decreased with increase in alkali concentration indicating negative fractional order dependence of rate on alkali concentration.

3.3. 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 added periodate had no effect on the rate of reaction (Table 1) in catalyzed conditions.

3.4. Effect of added products

The externally added products, aldehyde and copper (II) sulphate ($CuSO_4$) did not have any significant effect on the rate of the reaction.

3.5. 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 the cases of catalyzed conditions.

3.6. Test for free radicals (Polymerization study)

The involvement of free radicals, for catalyzed reactions was tested. The reaction mixture was mixed with acrylonitrile monomer initially added, and 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. The blank experiments of either DPC or ALP alone with acrylonitrile did not induce any polymerization under the same conditions. Initially added acrylonitrile decreased the rate of reaction, indicating free radical participation.

3.7. Effect of temperature

The influence of temperature on the rate of reaction was studied at 25, 30, 35 and 40 ^{0}C. The rate constants, (k_1), of the slow step of Scheme 1 were obtained from the slopes and the intercepts of the plots of [Ru (III)]/k_C versus 1/[ALP] 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 versus 1/T and are presented in Table 2.

3.8. Effect of [Ru (III)]

The [Ru (III)] 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), ALP, alkali and ionic strength. The order in [Ru (III)] was found to be unity from the linearity of the plots of K_C versus [Ru(III)].

3.9. Catalytic activity

It has been pointed out by Moelwyn-Hughes[20] that in presence of the catalyst, the uncatalyzed and catalyzed reaction proceed simultaneously, so that

$$K_T = K_U + K_C[Ru(III)]^X \tag{2}$$

Here K_T is the observed pseudo first order rate constant in the presence [Ru(III)] 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 [Ru(III)]. 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,

$$K_c = \frac{K_T - K_U}{[\mathrm{Ru(III)}]^x} = \frac{K_C}{[\mathrm{Ru(III)}]^x} \quad (\text{Where } K_T\text{-}K_U\text{=}K_C) \qquad (3)$$

The values of K_C were evaluated for [Ru (III)] 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[21] 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[22] (4)-(6) depending on the pH of the solution.

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

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

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

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.[23] 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.[24]

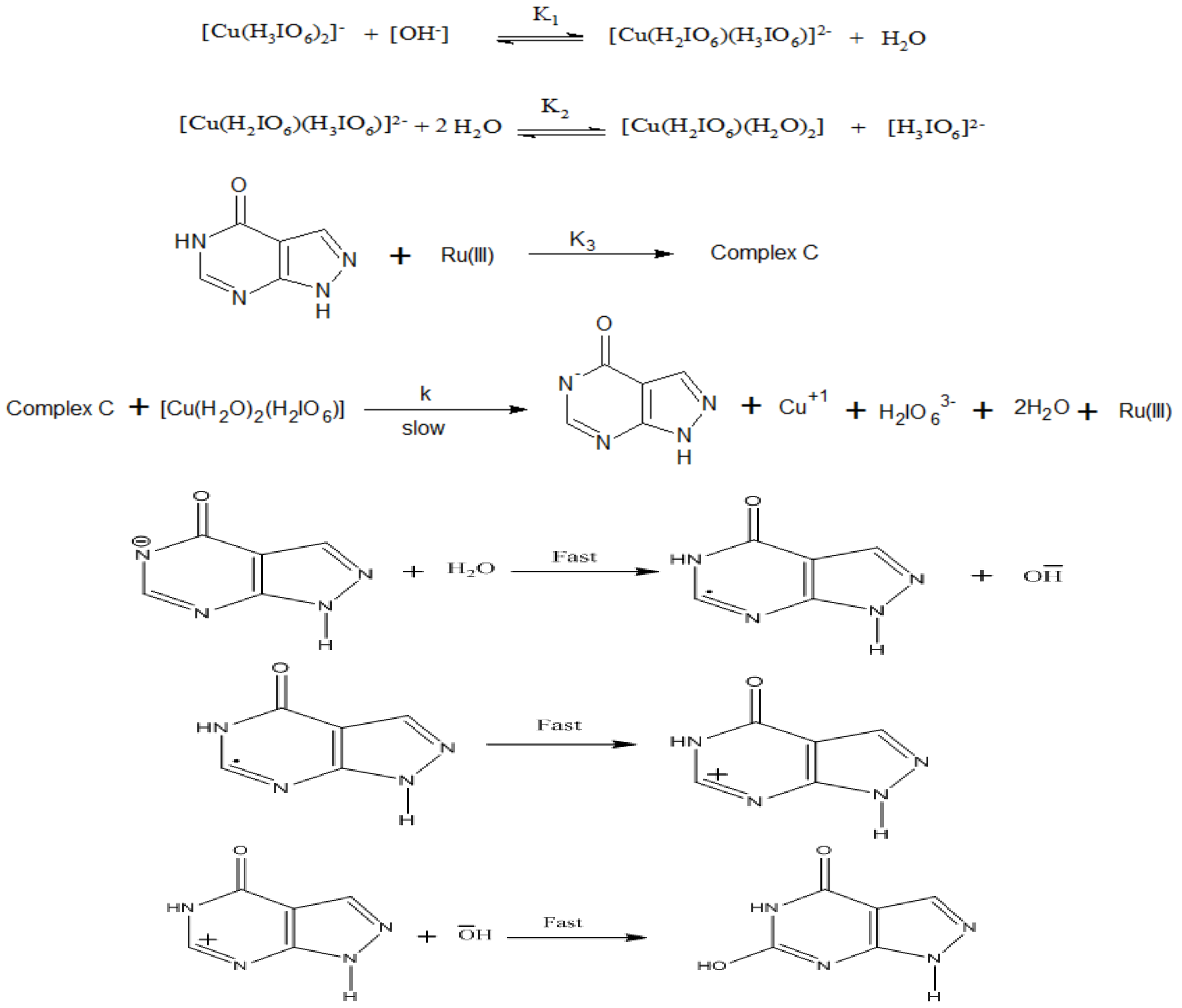
In most of the reports[25] on DPC oxidation, periodate retards and OH^- increases the rate of the reaction. However in the present kinetic study, entirely different kinetic observations have been obtained. In this study OH^- retards the rate of reaction and periodate shows no effect on the rate. The 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 hydrolysis of $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ as given below.

$$[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + H_2O \overset{K}{\rightleftharpoons} [Cu(OH)_2(H_3IO_6)_2]^{3-} + OH^- \qquad (7)$$

Because of this reaction and the observation that the k_C values are inversely related to the hydroxyl ion concentration with negative 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.

Mechanism

ALP reacts with Ru (III) active species to form a complex (C) which further reacts with one mole of DPC in a slow step to give the free radical of ALP, Cu (I) with regeneration of catalyst Ruthenium (III). Further this free radical of ALP reacts with one more molecule of DPC species in a fast step to yield the products as given in Scheme 1.



Scheme 1: Detailed Scheme for the Ru(III) catalysed oxidation of Allopurinol by alkaline diperiodatocuprate(III).

Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV-vis spectra of ALP (4.0×10^{-4}), Ru(III) (8.0×10^{-7}), $[OH^-]$ =0.004 mol dm^{-3}) and mixture of both. A hypsochromic shift of about 7 nm from 294 nm of ALP to 283 nm of mixture of Ru(III) and ALP and a hyperchromicity at 285 nm, was observed. The Lineweaver-Burk plot proved the complex formation between Ru (III) and ALP, which explains less than unit order in [ALP]. The rate law for Scheme 1 could be derived as,

$$\text{Rate} = \frac{-d[\text{DPC}]}{dt} = \frac{K_2K_1K_3[\text{ALP}][\text{Ru(III)}]}{[\text{OH}^-] + K_1 + K_3[\text{ALP}][\text{OH}^-] + K_1K_3[\text{ALP}]} \quad (8)$$

$$\frac{\text{Rate}}{[\text{DPC}]} = K_C = K_T - K_U = \frac{K_2K_1K_3[\text{ALP}][\text{Ru(III)}]}{[\text{OH}^-] + K_1 + K_3[\text{ALP}][\text{OH}^-] + K_1K_3[\text{ALP}]} \quad (9)$$

The rate law (9) can be rearranged to Eqn (10), which is suitable for verification

$$\frac{[\text{Ru(III)}]}{K_C} = \frac{[\text{OH}^-]}{K_2K_1K_3[\text{ALP}]} + \frac{1}{K_2K_3[\text{ALP}]} + \frac{[\text{OH}^-]}{K_2K_1} + \frac{1}{k} \quad (10)$$

According to Eq (10), the plots of [Ru(III)]/k_C versus 1/[ALP] and [Ru(III)]/k_C versus [OH$^-$] were linear (Fig. 3). From the intercepts and slopes of such plots, the reaction constants k, K_1 and K_2 were calculated as (3.3 ± 0.1) x 10^5 dm^3 mol^{-1} s^{-1}, (3.5 ± 0.2) x 10^2 dm^3 mol^{-1}, (1.6 ± 0.02) x 10^{-2} mol dm^{-3}, respectively. These constants were used to calculate the rate constants and compared with the experimental k_C values and found to be in reasonable agreement with each other, which fortifies the Scheme 1.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The ALP and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of [Ru (III)]/k_C versus 1/[ALP] ($r \geq 0.9996, s \leq 0.00134$), [Ru(III)]/$k_C$ versus [OH$^-$] ($r \geq 0.9994, s \leq 0.00086$), should be linear as shown in Fig. 3. From the slopes and intercepts, the values of K_1 are calculated at different temperatures. A van't Hoff's plot was made for the variation of K_1 with temperature [i.e. log K_1 versus 1/T ($r \geq 0.9992$, $s \leq 0.1106$)] and the values of the enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated. These values are also given in Table 2. The values of the catalytic constant *(K_C)* at different temperatures and activation parameters calculated using K_C values are also given in Table 3.

Negligible effect of ionic strength and dielectric constant in catalyzed reaction might be due to involvement of neutral species in the reaction (Scheme 1). The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants. 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.

The activation parameters evaluated for the catalysed reaction explain the catalytic effect on the reaction. The catalyst Ru (III) forms the complex (C) with ALP which enhances the reducing property of the substrate than that without catalyst. Further, the catalyst Ru (III) modifies the reaction path by lowering the energy of activation.

Table 1: Effect of [DPC], [ALP], $[IO_4]$, $[OH^-]$ and [Ru(III)] on the ruthenium(III) catalysed 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 [ALP] (mol dm^{-3})	10^5 $[IO_4]$ (mol dm^{-3})	10^2 $[OH^-]$ (mol dm^{-3})	10^7 [Ru(III)] (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	2.9	3.5	2.5	2.5
3.0	4.0	5.0	0.4	8.0	2.7	3.4	2.3	2.5
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.5
8.0	4.0	5.0	0.4	8.0	2.7	3.3	2.3	2.5
10.0	4.0	5.0	0.4	8.0	2.5	3.4	2.1	2.5
5.0	1.0	5.0	0.4	8.0	0.82	0.89	0.73	0.72
5.0	2.0	5.0	0.4	8.0	1.5	1.6	1.4	1.4
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	6.0	5.0	0.4	8.0	4.4	5.0	3.9	3.7
5.0	10.0	5.0	0.4	8.0	6.2	6.7	5.5	5.6
5.0	4.0	1.0	0.4	8.0	3.5	3.8	3.0	2.5
5.0	4.0	3.0	0.4	8.0	3.2	3.5	2.9	2.5
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.9	2.5
5.0	4.0	8.0	0.4	8.0	2.6	3.4	2.8	2.5
5.0	4.0	10.0	0.4	8.0	2.4	3.2	2.9	2.5
5.0	4.0	5.0	0.1	8.0	3.8	4.2	3.3	3.1
5.0	4.0	5.0	0.2	8.0	3.2	3.5	2.9	2.9
5.0	4.0	5.0	0.4	8.0	2.8	3.2	2.5	2.6
5.0	4.0	5.0	0.6	8.0	2.5	2.8	2.3	2.4
5.0	4.0	5.0	1.0	8.0	2.3	2.4	2.1	2.0
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 Ruthenium (III) catalyzed oxidation of Allopurinol by DPC in aqueous alkaline medium with respect to the slow step of Scheme 1.

(A) Temperature Effect

Temperature (K)	**10^{-5} k (dm^3 mol^{-1} s^{-1})**	**10^{2} K_1 (mol dm^{-3})**	**10^{-2} K_2 (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 1)

Activation parameters using k	**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_2

Thermodynamic quantities	**Values from K_1**	**Values from K_2**
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

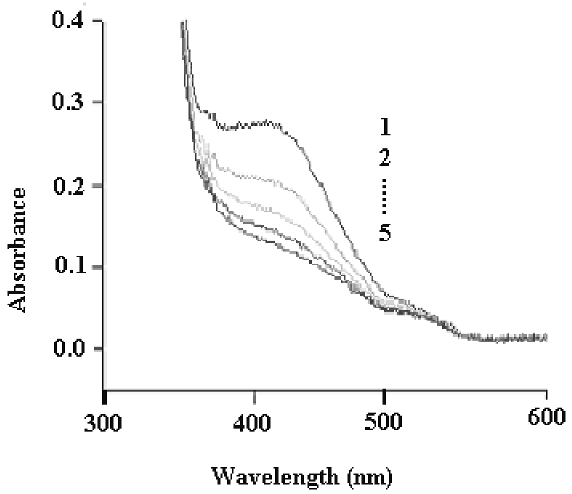


Fig. 1: Spectroscopic changes occurring in the oxidation of Allopurinol by diperiodatocuprate (III) at 25 ^{0}C, [DPC]= 5.0 x 10^{-5}, [ALP] = 4.0 x 10^{-4}, [OH$^-$]= 0.004 and I = 0.01 mol dm^{-3} with scanning time interval of: (1) 0.5, (2) 1.0, (3) 1.5, (4) 2.0 and (5) 2.5 minutes.

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

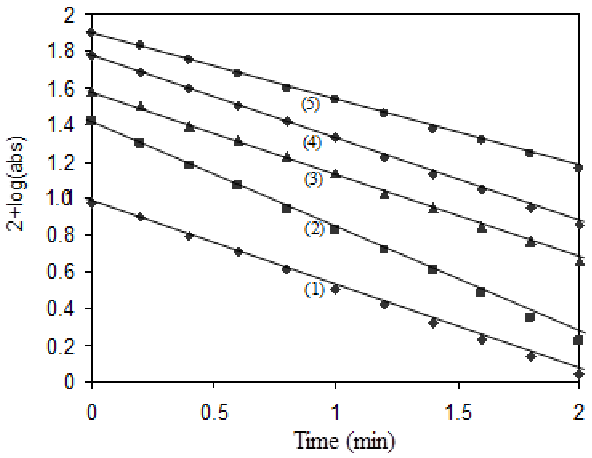


Fig. 2: First order plots for the oxidation of Ru(III) catalysed Allopurinol by diperiodatocuprate(III) in aqueous alkaline medium.[diperiodatocuprate(III)] X 10^5 (mol dm^{-3}).

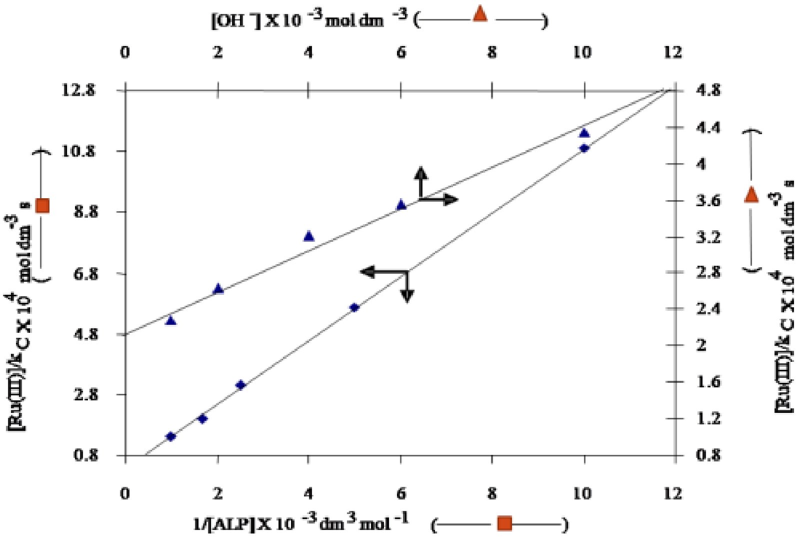


Fig. 3: Verification of rate law (11) in the form of (12) for the Ru(III) catalyzed oxidation of Allopurinol by diperiodatocuprate (III) at 25 ^{0}C.

4. CONCLUSION

The Ruthenium (III) catalyzed oxidation of ALP 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 Ru(III) is found to be $[Ru(OH)_2]^{+1}$. Activation parameters were evaluated for catalyzed reaction with respect to slow step of reaction (scheme 1). Catalytic constants and activation parameters with respect to catalyst were also computed.

REFERENCES

1. B. Reddy, B. Sethuram, T. Navaneeth Rao, Indian J. Chem., 1984; 23: 593.
2. A. Kumar, P. Kumar, P. Ramamurthy, Polyhedron. 1999; 18: 773.
3. R.S. Shettar, S.T. Nandibewoor, J. Mol. Cat. A 2005; 234: 137.
4. W. Niu, Y. Zhu, K. Hu, C. Tong, H. Yang, Int. J. Chem. Kinet. 1996; 28: 899.
5. G.I. Rozovoskii, A.K. Misyavichyus, A.Y. Prokopchik, Kinet. Catal., 1975; 16: 337.
6. M.G. Ramreddy, B. Sethuram, T. Navaneeth Rao, Indian J. Chem., 1978; 16: 313.
7. K.D. Karlin, Y. Gultneh, In, S.J. Lipard, (ed)., Progress in Inorganic Chemistry, wiley, New York, 1997; 220.
8. W.B. Tolman, Acc. Chem. Res., 1997; 30: 227.
9. Z. Kovat, Acta. Chim. Hung., 1960; 22: 313.
10. K.N. Kitajima, Y. Moro-oka, Chem. Rev., 1994; 94: 737.

11. L. D, Whitcombe, F. Davis, P.S Sharma, B.B Prasad, A Review. Electroanalysis, 2011; 23: 320.
12. Das, A.K. Coord. Chem. Rev., 2001; 213: 307–325.
13. Shivananda, K.N., Lakshmi, B., Jagdeesh, R.V., Puttaswamy, Mahendra, K.N, Appl. Catal. A, Gen., 2007; 326: 202–212.
14. Tandon, P.K., Mehrotra, A., Shrivastava, M., Dhusia, M., Singh, S.B.Transit. Met. Chem., 2007; 32: 991–999.
15. Singh, A.K., Srivastava, S., Srivastava, J., Srivastava, R., Singh, P. J. Mol. Catal. A Chem., 2007; **278:** 72–81.
16. O.C. Saxena, Microchem J., 1967; 12 : 609.
17. C.P. Murthy, B. Sethuram, T. Navaneeth Rao, Z. Phys. Chem., 1981; 262: 336.
18. G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denny, Vogel's Textbook of Quantitative Chemical Analysis, 5th edn., ELBS Longman., Essex UK, 1996: 455.
19. G.P. Panigrahi, P.K. Misro, Indian J. Chem., 1977; 15A: 1066.
20. K.B. Reddy, B. Sethuram, T. Navaneeth Rao, Z. Phys. Chem., 1987; 268: 706.
21. J.C. Bailar, H.J. Emeleus, S.R. Nyholm, A.F. Trotman-Dikenson, Comprehensive Inorganic Chemistry Pergamon press, Oxford, 1975: 1456.
22. B. Sethuram, Some Aspects of Electron Transfer Reactions Involving Organic Molecules, Allied Publishers (P) Ltd., New Delhi, 2003: 78.
23. T.S. Kiran, D.C. Hiremath, S.T. Nandibewoor, Z. Phys. Chem., 2007; 221: 501.
24. R. Chang, Physical Chemistry with Applications to Biological Systems, Macmillan, New York, 1981: 326.
25. S.A. Farokhi, S.T. Nandibewoor, Tetrahedron, 2003; 59: 7595.