Mechanism of allopurinol uncatalysed oxidation by DPC(III) in aqueous alkaline medium: A kinetics study

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Abstract: The kinetics of oxidation of allopurinol (ALO) by diperiodatocuprate (III) (DPC) in aqueous alkaline medium at a constant ionic strength of 0.02 mol dm^{-3} was studied spectrophotometrically. The reaction between DPC and allopurinol in alkaline medium exhibits 1:2 stoichiometry (ALO: DPC). Intervention of free radicals was observed in the reaction. Based on the observed orders and experimental evidences, a mechanism involving the diperiodatocuprate (III) (DPC) as the reactive oxidant species has been proposed. The products were identified by spot test and characterized by spectral studies. The reaction constants involved in the different steps of mechanism were calculated. The activation parameters with respect to slow step of the mechanism were computed and discussed. The thermodynamic quantities were also determined for different equilibrium steps.

Keywords: Kinetics, Oxidation, Allopurinol, Diperiodatocuprate(III), Thermodynamic parameters.

Introduction

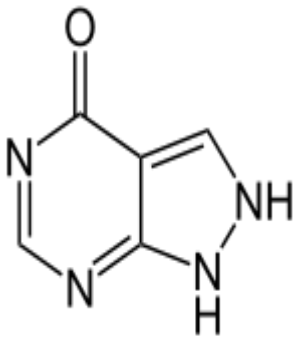
In recent years, the study of highest oxidation state of transition metal has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. Metal chelates, such as diperiodatocuprate (III)[1], Diperiodatoargentate (III)[2] 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 analysis of several organic compounds[4]. The kinetics of self decomposition of these complexes was studied in some details[5]. Copper (III) is shown to be 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 low stability in aqueous medium. DPC is versatile one electron oxidant for various organic compounds in alkaline medium and it is used as an analytical reagent[9]. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry[10].

Allopurinol its chemical name 4H - Pyrazole (3, 4) – pyramidine -4 - one. It is important to minor the concentration of purine metabolites in cell or body fluids to findout metabolic defects which are characterized by abnormal concentrations of the metabolites resulting in indicators of pathological conditions such as gout, hyperuricaemia, Lesch-Nyan disease, renal failure, diabetes, high blood pressure, kidney disease, and heart disease[11].

Copper (III) is involved in many biological electron transfer reactions[12]. They have also been used[13] in the differential titration of organic mixtures, in the estimation of chromium, calcium, and magnesium from their ores, and antimony, arsenic and tin from their alloys. Since multiple equilibria between different copper (III) species are involved, it would be interesting to know which of the species is the active oxidant.

In the earlier reports[14] on DPC oxidation, periodate had retarding effect and the order in [OH^-] was found to be less than unity in most of the reactions. However in the present study, we have observed entirely different kinetic behavior. A literature survey reveals that there are no reports on the oxidation of ALO by diperiodatocuprate(III). The present study deals with the title reaction to investigate the redox chemistry of DPC in alkaline media, to compute the thermodynamic quantities of various steps of Scheme 1 and to arrive at a plausible mechanism on the basis of kinetics and spectral studies.



Structure of allopurinol

Experimental

Material and Reagent

All Chemicals used were of reagent grade and double distilled water was used throughout the experiment. The copper (III) periodate complex was prepared[15, 16] and standardized by standard procedure[17]. The UV –vis spectrum with maximum absorption at 415nm was characteristic of the copper (III) complex. Solutions of ALO (S.D- media) and copper sulphate (BDH) were prepared by dissolving known amounts of the samples in the distilled water. Periodate solution was prepared and standardized by iodometrically[18]. Required alkalinity and ionic strength were maintained by KOH (BDH) and KNO_3 (Analar), respectively, in the reaction solution.

Kinetic studies

The kinetics was followed under pseudo-first order condition where [ALO] >[DPC] at 298±0.1K, unless specified using double beam spectrophotometer. The reaction was initiated by mixing the DPC to ALO solution which also contained required concentration of KNO_3, KOH and KIO_4. The progress of the reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbency index, 'ε' to be 6,231± 100 dm^3 mol^{-1} cm^{-1} (Literature ε = 6,230 [23]). It was verified that there is a negligible interference from other species present in the reaction mixture at this wavelength.

The pseudo first-order rate constants, 'k_{obs}' were determined from the log(absorbance) versus time plots. The plots were linear up to 80% completion of reaction under the range of [OH^-] used. The order for various species were determined from the slopes of plots of log k_{obs} versus respective concentration of species except for [DPC] in which non variation of 'k_{obs}' was observed as expected for the reaction condition. During the kinetics a constant concentration, viz. 5.0 x 10^{-5} mol dm^{-3} ofKIO_4 was used through out the study unless otherwise stated. Since periodate is present in excess in DPC, the possibility of oxidation of ALO by periodate in alkaline medium at 298 K was tested. The progress of the reaction was followed iodometrically. However, it was found that there was no significant reaction under the

experimental conditions employed compared to the DPC oxidation of ALO. The total concentration of periodate and OH^- were calculated by considering the amount present in the DPC solution and that additionally added. Kinetics runs were also carried out in N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. The spectral changes during the reaction are shown in Fig.1. It is evident from the figure that the concentration of DPC decreases at 415nm.

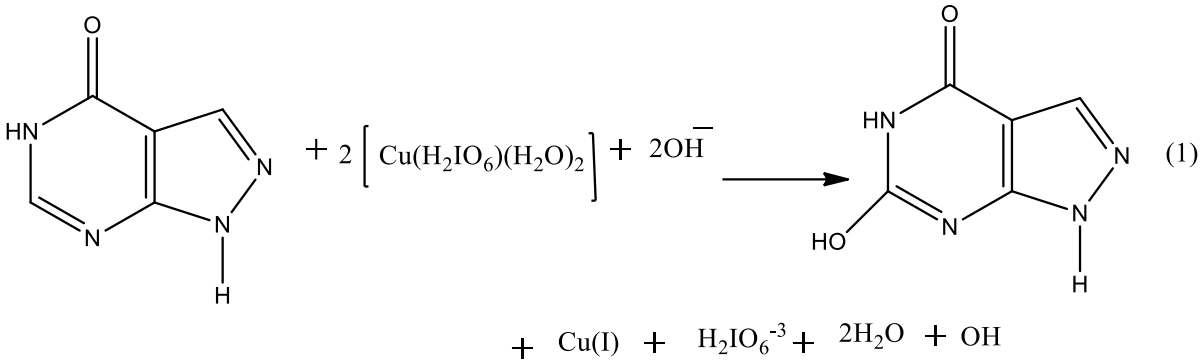
Preparation of DPC

The copper(III) periodate complex was prepared by standard procedure[19]. 3.54g, of copper sulphate and 9.0g of potassium hydroxide were added to about 250cm^3 of water. The order of additionis not important th mixture was shaken thoroughly and heated on a hot plate, in about 20 minutes the boiling mixture turned intense red and boiling was continued for another 20minutes, more for the completion of the reaction. The mixture was then cooled, filtered through sintered crucible (G_4) and diluted to 250 cm^3 persulphate used was just sufficient to oxidize copper (II) to copper (III) was therefore completely removed during boiling. If an excess of persulfate was used, boiling for long time was necessary for its complete decomposition. Existence of copper (III) complex was verifiedby its UV visible spectrum, which showed an absorption band with maximum absorption at 415nm. The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by thiocynate[20] method. The copper solution was prepared by dissolving the known amount of coppersulphate BDM in distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and used after 24 hours. Its concentration was ascertained iodometrically at neutral pH by phosphate buffer KOH & KNO_3 (BDH).

Results and Discussion

Stoichiometry and product analysis

Different sets of reaction mixtures containing excess of DPC to ALO in presence of constants amounts of OH^- and KNO_3 were kept for 6h in closed vessel under inert atmosphere. The remaining DPC concentration was estimated spectrophotometrically at 415 nm. The results, 1:2 stoichiometry, are as given in Eq. 1.



The main oxidation products were identified as 6,hydroxy–1–14–pyrazole [3,4 - d] pyrimidin –4 (5H) –one. The presence of Cu (I) was confirmed by UV-visible spectra.

Regression analysis of experimental data to obtain the regression coefficient r and standard deviation s from the regression line was performed using Microsoft Excel-2003.

Reaction Order

The reaction order were determined from the slope of log k_{obs} versus log [concentration] plots by varying the concentration of ALO, alkali in turn while keeping all other concentrations and conditions constant.

Effect of [Diperiodatocuprate(III)]

The oxidation of DPC concentration was varied in the range of 1.0 x 10^{-5} to 1.0 x 10^{-4} mol dm^{-3} and fairly constant k_{obs}value indicate that order with respect to [DPC] was unity (Table1). This was also confirmed by linearity of the plots of log [absorbance] versus time to 80% completion of reaction.

Effect of [Allopurinol]

The effect of ALO on the rate of reaction was studied at constant concentration of alkali, DPC and periodate at constant ionic strength of 0.01 mol dm^{-3}. The substrate ALO was varied in the range of 1.0 x 10^{-4} to 1.0 x 10^{-3} mol dm^{-3}. The k_{obs} values increased with increase in concentration of ALO. The apparent order with respect to [allopurinol] was found to be less than unity (Table1). This was also confirmed by the plots of k_{obs} versus [ALO] which is linear.

Effect of [alkali]

The effect of increase in concentration of alkali on the reaction was studied at constant concentration of ALO, DPC and periodate at constant ionic strength of 0.02 mol dm^{-3} at 298K. The rate of reaction is decreased with increase in alkali concentrations (Table 1), indicatingpositive fractional order dependence of rate on alkali concentration . This was also confirmed by the plots of k_{obs} versus [OH^-] which is linear.

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 reactants concentration constant. It was found that added periodate had retarding effect on the rate of reaction.

Effect of ionic strength (I) and dielectric constant of medium (D)

The addition of KNO_3 at constant [DPC], [ALO], [OH^-] and [IO_4^-] was found that increasing ionic strength of the reaction medium did not effect the rate of reaction.

Varying the t-butyl alcohol and water percentage varied dielectric constant of the medium 'D'. The D values were calculated from the equation $D = D_wV_w + D_BV_B$, where D_w and D_B are dielectric constants of pure water and t-butyl alcohol respectively and V_w and V_B are the volume fractions of components of water and t-butyl alcohol respectively in the total mixture. The decrease in dielectric constant of the reaction medium decreased the rate of reaction. The plot of log k_{obs}versus 1/D was linear with negative slope .

Effect of initially added products

The externally added product Cu(I), 6,hydroxy–1–14–pyrazole [3,4 - d] pyrimidin –4 (5H) –one , did not have any significant effect on the rate of reaction.

Polymerization study

The intervention of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer initially added, was kept for 2 hrs in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, which indicated the intervention of free radicals in the reaction [23]. The blank experiments of either DPC or allopurinol alone with acrylonitrile did not induce any polymerization under the same conditions as those induced for the reaction mixture. Initially, added acrylonitrile decreased the rate of reaction indicating free radical intervention, which is the case in earlier work[21, 22].

Effect of temperature

The kinetics was studied at six different temperatures (25, 30, 35 and 40 ^{0}C) under varying concentrations of ALO, alkali and periodate keeping all other conditions constant. The rate constants (k), of the slow step of the reaction mechanism were obtained from the slopes and intercepts of the plots of $1/k_{obs}$versus 1/[ALO]at four different temperatures and were used to calculate the activation parameters. The energy of activation corresponding to these constants was evaluated from the Arrhenius plot of log k versus 1/T and other activation parameters obtained are tabulated in Table **2.**

Discussion

The water soluble copper (III) periodate complex is reported to be $[Cu(HIO_6)_2\ (OH)_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range employed in the 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[23] depending on the pH of the solution.

Periodic acid exists as H_5IO_6 in acid medium and as $H_3IO_6^{2-}$ near pH 7. Hence, under alkaline conditions as employed in this study, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. Thus, at the pH employed in this study, the soluble copper (III) periodate complex might be $[Cu(OH)_2(H_3IO_6)_2]^{3-}$, a conclusion also supported by earlier work [24,25].

The reaction between the diperiodatocuprate (III) complex and allopurinol in alkaline medium has the stoichiometry 1:2 **(**ALO: DPC**)** with a first order dependence on [DPC] and an apparent order of less than unit order in [substrate], [alkali] and a negative fractional order dependence on [periodate]. No effect of added product was observed. Based on the experimental results, a mechanism is proposed for which all the observed orders in each constituent such as [oxidant], [reductant], $[OH^-]$ and $[IO4^-]$ may be well accommodated. In most report on DPC oxidation, periodate had a retarding effect and OH- had an increasing effect on the rate of reaction. However, in the present kinetic study, different kinetic results have been obtained. In this study OH^- had less than unit order and periodate retarded the rate of reaction with increase in alkalinity (Table 1) can be explained in terms of prevailing equilibrium of formation of $[Cu(OH)_2(H_3IO_6)]^{3-}$ from $[Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$ hydrolysis as given in the following Eq. 2.

$$[Cu(H_3IO_6)_2]^- + [OH^-] \underset{}{\overset{K}{\rightleftharpoons}} [Cu(H_2IO_6)(H_3IO_6)]^{2-} + H_2O \qquad (2)$$

Also, decrease in the rate of reaction with increase in $[H_3IO_6^{2-}]$ (Table1) Suggest that equilibrium of copper(III) periodate complex to form monoperiodatocuptrate(III) (MPC) species as given in Eq. 3 is established.

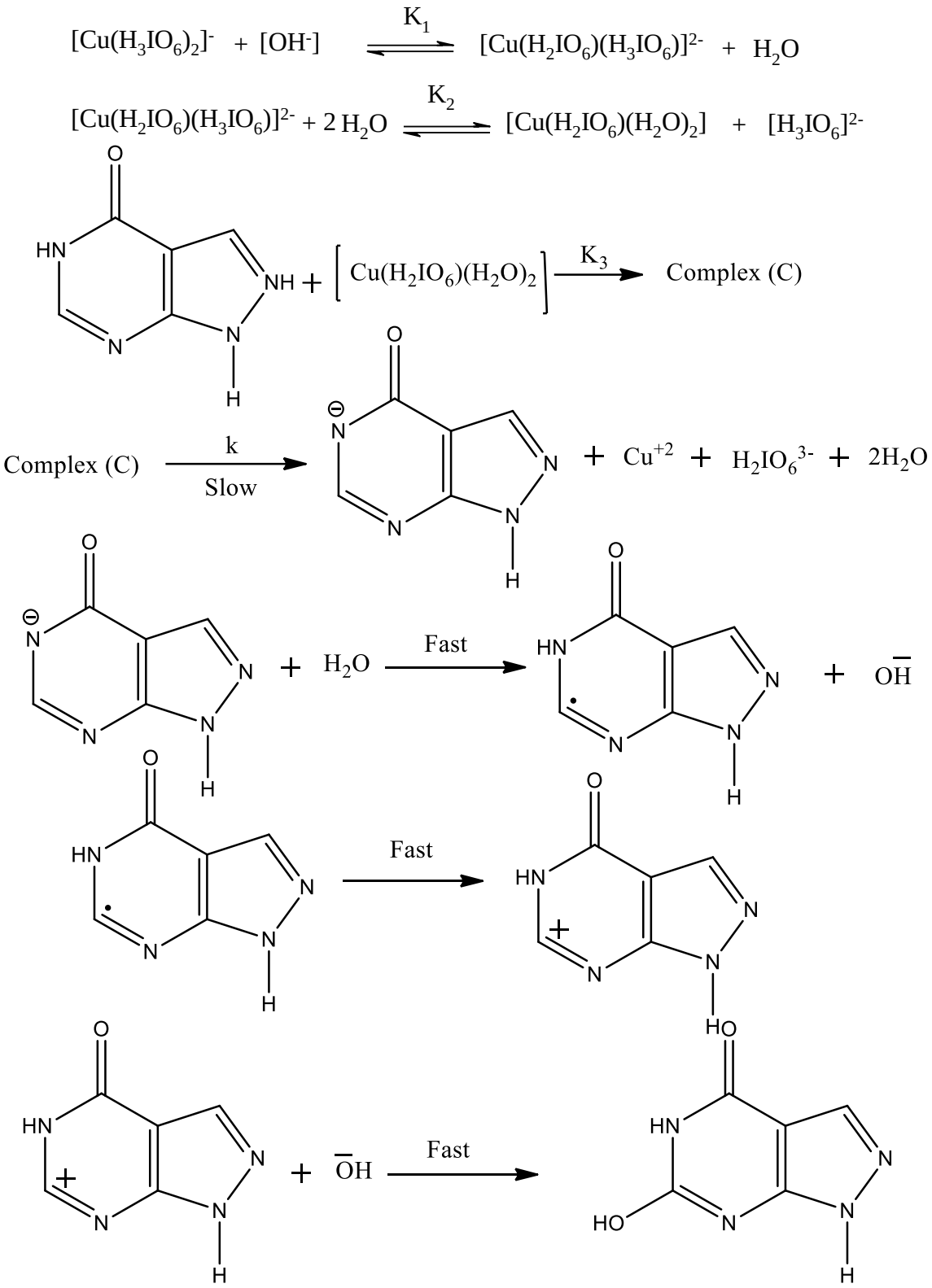
$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2\,H_2O \underset{}{\overset{K}{\rightleftharpoons}} [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6]^{2-} \qquad (3)$$

Such equilibria (2) and (3) have been well documented in the literature. It may be expected that a lower periodate complex such as monoperiodatocuptrate(III) (MPC) is more important in the reaction . The inverse fractional order in [$H_3IO_6^{2-}$] might also be due to this reason. Therefore, MPC might be the main reactive form of the oxidant.

The less than unit order in [ALO] presumably results from formation of a complex (C) decomposes slowly in a slow step to form a free radical allopurinol derived from. This free radical species further reactive with another molecule of MPC in a fast step to form the products such as given in Scheme 1.

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 the oxidant would afford a radical intermediate. A free radical scavenging experiment revealed such a possibility. This type of radical intermediate has also been observed in earlier work. A direct plot of k_{obs} versus [ALO] was drawn to characterize the parallel reaction if any along with interaction of oxidant and reductant. However, the plot of k_{obs} vs [ALO] was not linear. Thus, in Scheme 1, the parallel reaction and involvement of two molecules of allopurinol in the complex are excluded. The fractional order with respect to ALO presumably results from the complex formation between MPC and ALO prior to the slow step. Indeed it is to be noted that a plot of $1/k_{obs}$versus 1/ [ALO] was linear and shows an intercept in agreement with the complex formation which slowly decomposes to form the product. In the rate determining stage, this monoperiodatocuprate(III) (MPC) combines with molecule of allopurinol to give a complex (I) which decomposes in a slow step. All these results may be interpreted in the form of

Scheme 1



Scheme 1: Detailed scheme for the oxidation of allopurinol by alkaline DPC (III)

Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-visible spectra of allopurinol (5 x 10^{-4}), DPC (5 x 10^{-5}), [OH^-] = 0.002mol dm^{-3} and a mixture of both. A hypsochromic shift of about 8nm from 291 to 283 nm in the spectra of DPC was observed. The Michalis-Menten plot also proved the complex formation between DPC on [allopurinol]. Such a complex between an oxidant has been observed in other studies. Scheme 1 leads to the rate law (4)

$$\text{Rate} = -\frac{d[DPC]}{dt} = \frac{kK_1K_2K_3[DPC][ALO][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][ALO]} \quad (4)$$

$$K_{obs} = \frac{\text{Rate}}{[DPC]} = \frac{kK_1K_2K_3[ALO][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][ALO]} \quad (5)$$

This explains all the observed kinetic orders of different species. In eq. 6 the appearance of [ALO] term in both numerator and denominator explains the observed less than unit order in [allopurinol]. Similarly the appearance of [$H_3IO_6^{2-}$] and [OH-] in the denominator agree with the observed negative less than unit order [$H_3IO_6^{2-}$] and [OH^-], respectively. This explains all the observed kinetic orders of different species.

The rate law (5) can be rearranged into the following form which is suitable for verification.

$$\frac{1}{K_{obs}} = \frac{[H_3IO_6^{2-}]}{kK_1K_2K_3[OH^-]} + \frac{[H_3IO_6^{2-}]}{[H_3IO_6^{2-}]} + \frac{1}{kK_3[ALO]} + \frac{1}{k} \quad (6)$$

According to eqn (6), other conditions being constant, plot of $1/k_{obs}$versus 1/[ALO] ,$1/k_{obs}$versus$1/[OH^-]$ and $1/k_{obs}$versus$[H_3IO_6^{2-}]$ should be linear and are fond to be so (Fig 6a, 6b and 6c). The slopes and intercepts of such plots leads to the value of K_1, K_2, K_3 and k as 2.3 dm^3 mol^{-1}, 1.6 x 10^{-4} mol dm^{-3}, 2.2 x 10^3 dm^3 mol^{-1} and 0.60 x 10^{-2} s^{-1} respectively. The values of K_1 and $K_2$are in good agreement with

earlierliterature. These constants were used to calculate the rate constant and compared with the experimental k_{obs}values and found to be in reasonable agreement with each other which fortifies Scheme 1.

The negligible effect of ionic strength on the rate explains qualitatively the reaction between one negatively charged ion and neutral molecule, as seen in Scheme 1. The effect of solvent on the rate has been described in detail in the literature. Increasing the content of t-butyl alcohol in the reaction medium leads to an increased effect on the rate of reaction, which seems to be contrary to the expected reaction between neutral and anionic species in media of lower relative permittivity. However an increase in the rate of reaction with decreasing relative permittivity may be due to stabilization of the complex (C) at relative permittivity, which is less solvated than DPC at higher relative permittivity because of its larger size.

The thermodynamic quantities for the first, second and third equilibrium steps of Scheme 1 can be evaluated as follows: [ALO], $[OH^-]$ and $[IO_4]^-$ (Table 1) were varied at four different temperatures. The plot of $1/k_{obs}$versus 1/[AL0] $1/k_{obs}$versus $1/[OH^-]$ and $1/k_{obs}$versus$[H_3IO_6^{2-}]$ should be linear**.** From the slopes and intercepts, the values of K_1, K_2 and K_3were calculated at four different temperatures and these values are given in Table 2. The vant Hoff's plots were made for variation of K_1, K_2 and K_3 with temperatures (log K_1versus 1/T) (log K_2versus 1/T) and (log K_3versus 1/T) the values of enthalpy of reaction ΔH, entropy of reactionΔS and free energy of reaction ΔG, were calculated for the first second and third equilibrium steps. These values are given in Table 2. A comparison of the thermodynamic quantities of Scheme 1 with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the before rate determining step is fairly fast and involves low activation energy[26]. The values $\Delta H^{\#}$ and $\Delta S^{\#}$ were both favorable for electron transfer processes. The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactant[27]. The observed modest enthalpy of activation and a higher rate constant for the slow step indicates that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observations[28, 29]. The activation parameters for the oxidation of some amino acids by DPC are summarized in Table 2.

Conclusion

Among the various species of DPC in alkaline medium, MPC i.e., $[Cu(H_2IO_6)(H_2O)_2]$ is considered as active species for the title reaction. The results indicated that, the role of pH in the reaction medium is crucial. Rate constant of slow step and other equilibrium constants involved in the mechanism were evaluated and activation parameters with respect to slow step of reaction were computed. The overall mechanistic sequence described is consistent with product studies, mechanistic and kinetic studies.

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Appendix:

According to Scheme 1,

$$\text{Rate} = -\frac{d[DPC]}{dt} = k[C] = \frac{k_1 K_1 K_2 K_3 [DPC][ALO][OH^-]}{[H_3IO_6]^{2-}} \quad (a)$$

The total concentration of $[DPC]_T$ is given by,

$$[DPC]_T = [DPC]_f + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)H_2O)_2] + [C] \quad (b)$$

Where T and f refer to total and free concentration

$$[DPC]_f = \frac{[DPC]_T\ [H_3IO_6]^{2-}}{[H_3IO_6]^{2-} + K_1[H_3IO_6]^{2-}[OH^-] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][ALO]}$$

Similarly,

$$[ALO]_T = [ALO]_f + C$$

$$= [ALO]_f + \frac{K_1K_2K_3[DPC]_f[ALO]_f[OH^-]_f}{[H_3IO_6]^{2-}}$$

$$= [ALO]_f \left[1 + \frac{K_1K_2K_3[DPC]_f[OH^-]_f}{[H_3IO_6]^{2-}}\right]$$

In view of low concentration of [DPC] and $[H_3IO_6]^{2-}$ second term can be neglected

$$\left[ALO \right]_T = \left[ALO \right]_f \qquad (c)$$

Similarly,

$$[OH^-]_T = [OH^-]_f + [Cu(H_2IO_6)(H_3IO_6)]^{2-} + [Cu(H_2IO_6)(H_2O)_2]$$

$$= [OH^-]_f + K_1[OH^-][DPC] + \frac{K_1 K_2 [DPC]\,[OH^-]}{[H_3IO_6]^{2-}}$$

In view of low concentration of $[DPC]$ and $[H_3IO_6]^{2-}$ used ,

$$\left[OH^- \right]_T = \left[OH^- \right]_f \qquad (d)$$

Substituting the values of $[DPC]_f$, $[ALO]_f$ and $[OH^-]_f$ in eq (A1) and omitting subscripts, we get

$$k_{obs} = \frac{\text{Rate}}{[DPC]} = \frac{kK_1K_2K_3[ALO][OH^-]}{[H_3IO_6^{2-}] + K_1[OH^-][H_3IO_6^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][ALO]}$$

Table 1. Effect of [DPC], [ALO], $[OH^-]$ and $[IO_4^-]$ on the oxidation of allopurinol by DPC in alkaline medium at 298 K, I = 0.1 mol dm^{-3}

$[DPC]\times10^5$, mol dm^{-3}	$[ALO] \times 10^4$, mol dm^{-3}	$[OH^-]$, mol dm^{-3}	$[IO_4^-] \times 10^6$, mol dm^{-3}	$k_{obs} \times 10^3$	k_{cal}
1.0	5.0	0.05	1.0	3.0	5.0
3.0	5.0	0.05	1.0	3.0	5.0
5.0	5.0	0.05	1.0	2.9	4.9
8.0	5.0	0.05	1.0	2.1	4.9
10.0	5.0	0.05	1.0	3.0	5.0
5.0	1.0	0.05	1.0	1.2	1.1
5.0	3.0	0.05	1.0	3.0	2.7
5.0	5.0	0.05	1.0	3.9	3.0

5.0	8.0	0.05	1.0	5.4	4.9
5.0	10.0	0.05	1.0	6.0	4.8
5.0	5.0	0.01	1.0	2.8	2.5
5.0	5.0	0.03	1.0	3.6	3.5
5.0	5.0	0.05	1.0	4.0	5.0
5.0	5.0	0.08	1.0	4.2	5.3
5.0	5.0	0.1	1.0	4.5	5.6
5.0	5.0	0.05	0.5	4.3	3.4
5.0	5.0	0.05	0.8	4.1	3.0
5.0	5.0	0.05	1.0	4.0	2.8
5.0	5.0	0.05	3.0	3.0	2.5
5.0	5.0	0.05	5.0	2.4	2.0

Table 2. Thermodynamic activation parameters for the oxidation of allopurinol by DPC in aqueous alkaline medium with respect to the slow step of Scheme 1

(a) Effect of temperature

Temperature (K)	10^2k s^{-1}
288	0.1
298	0.2
308	1.0
318	1.8

(b) Activation Parameters (Scheme 1)

Parameters	Value
E_a (kJ mol^{-1})	62.81
$\Delta H^{\#}$(kJ mol^{-1})	59.24

$\Delta S^{\#}$ (JK^{-1} mol^{-1})	41.05
$\Delta G^{\#}$ (kJ mol^{-1})	78.20
log A	10.1

(c) Effect of temperature to calculate K_1, K_2 and K_3 for the oxidation of allopurinol by DPC in alkaline medium

Temperature (K)	K_1 (dm^3 mol^{-1})	K_2x10^4 (mol dm^{-3})	K_3x 10^{-3} (dm^3 mol^{-1})
288	2.1	1.9	2.13
298	3.2	2.1	2.65
308	3.0	3.9	1.81
318	4.3	4.1	1.12

(d) Thermodynamic quantities using K_1, K_2 and K_3

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
ΔH (kJ mol^{-1})	68.33	38.73	37.03

ΔS	(JK^{-1} mol^{-1})	183.4	87.50	120.4
ΔG	(kJ mol^{-1})	-0.68	14.03	-14.3

Fig 1. Spectroscopic changes occurring in the oxidation of ALO by DPC at 298K, [DPC] = 5.0 x 10^{-5}; [ALO] = 5.0 x 10^{-4}; [OH^-] = 0.50; and I = 0.5 mol dm^{-3} with scanningtime interval is 1min

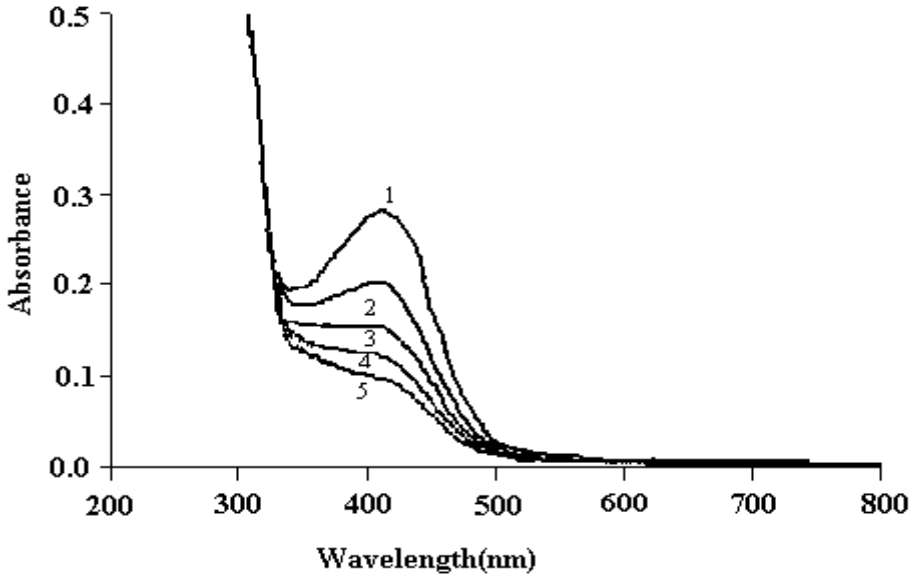

Fig 2: Verification of rate law (3) for the oxidation of ALO by DPC.

Fig 2(a). 1/k_{obs}versus 1/[ALO] at four different temperature (condition as in Table1)

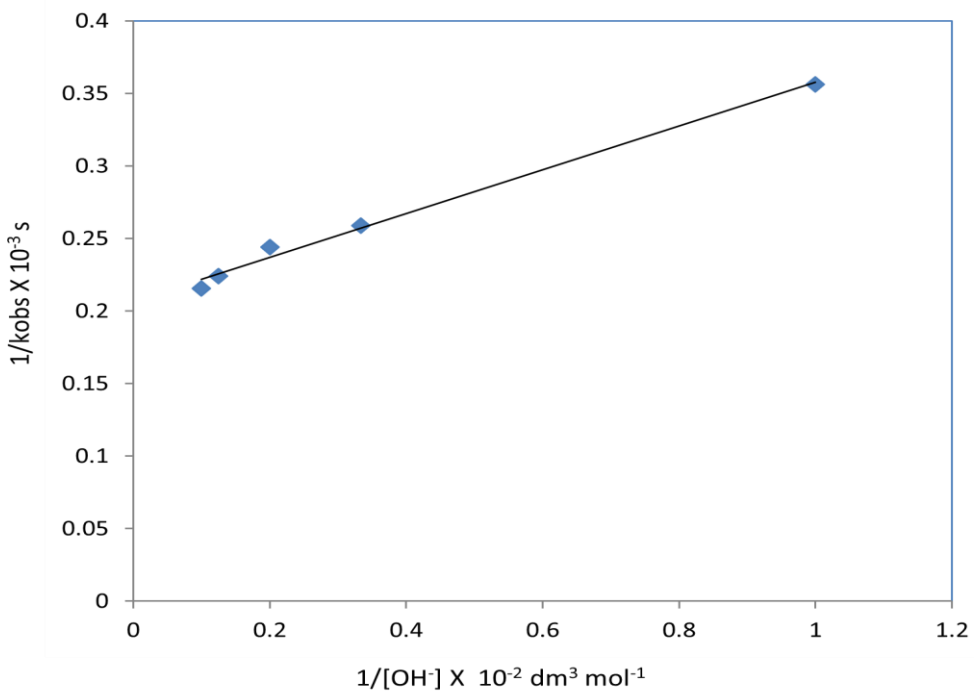

Fig 2(b). $1/k_{obs}$versus $1/[OH^-]$ at four different temperature (condition as in Table1)

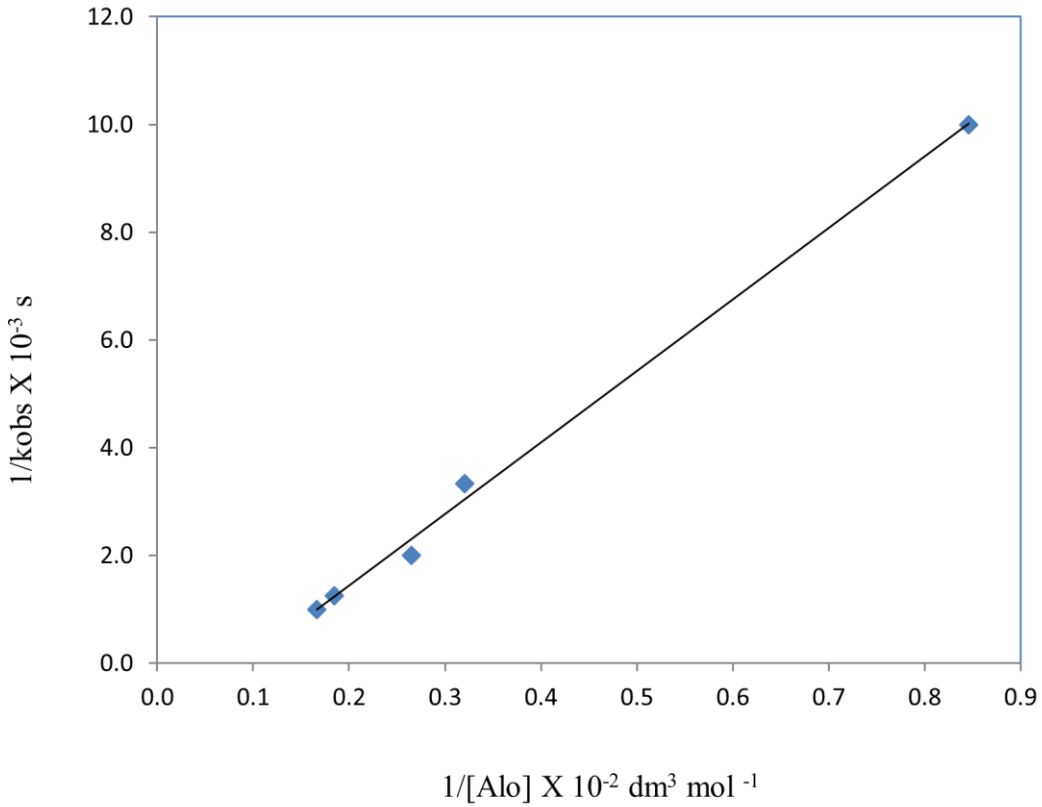

Fig 2(c). $1/k_{obs}$versus $[H_3IO_6]^{2-}$ at four different temperature (condition as in Table1)