



Kinetic and mechanistic study of Ru(III) catalysed oxidation of anti-cholinergic drug hyoscinebutylbromide by diperiodatocuprate(III) in aqueous alkaline medium

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Hyoscine butyl bromide (HBB) is an anti-cholinergic and anti-muscarinic drug used to treat pain and discomfort caused by abdominal cramps etc. It is semi-synthetic derivative alkaloid hyoscyamine having a broad spectrum of activity. Hence the Ru(III) catalyzed the oxidation of hyoscine butyl bromide drug by diperiodatocuprate(III) (DPC) in aqueous alkaline medium was investigated and monitored spectrophotometrically ($\lambda_{\text{max}} = 415 \text{ nm}$) at a constant ionic strength of 0.1 mol dm^{-3} and 301 K. The reaction shows 1:2 stoichiometry between HBB and DPC. The reaction is of the first order in [DPC] and [Ru(III)] and less than unit order in [HBB] and [alkali], periodate has a retarding effect on the reaction rate. The ionic strength, dielectric constant of the medium and added products has no significant effect on the rate of the reaction but Ru(III) increases the reaction rate. The main oxidation products of HBB were identified by spectral studies. The active forms of catalyst and oxidant were detected as Ru(III), $[\text{Cu}(\text{H}_2\text{IO}_6)(\text{H}_2\text{O})_2]$ respectively. The rate law and reaction mechanism was proposed. The equilibrium constants and rate constants were calculated. The activation parameters were deliberated for catalyzed and uncatalyzed reactions.

Keywords: Hyoscine butyl bromide, DPC(III), Ru(III), oxidation, kinetics, mechanism.

Introduction

Chemical kinetics gives information about mechanism, selection of suitable catalyst, rate of reaction, etc., also by selecting optimum conditions for chemical reactions one can get maximum yield. Kinetic study is essential for the chemical and pharmaceutical industries. Titrimetric, stopped-flow technique, flash photolysis, spectrophotometric and cyclic voltammetric methods are used to study the kinetics of various chemical reactions. Presently, in this paper, we are reporting oxidation of hyoscinebutylbromide in the absence and presence of Ru(III) catalyst by diperiodatocuprate(III) in aqueous alkaline medium by spectrophotometric method. Tropane alkaloids act as anti-cholinergic, antispasmodic and anti-muscarinic agents belong to the class of natural compounds. They are able to decrease saliva and gastrointestinal tract secretions widely used in preoperative procedures also decrease motility of smooth muscles in the treatment of bladder spasm. They are used as stimulators in curing diseases

like colic, cystitis belongs to respiratory system also antidotes in organophosphorus compounds¹.

The reductant hyoscinebutylbromide is a quaternary ammonium white, crystalline powder soluble in water which shows an anticholinergic agent² also antispasmodic in treating peptic ulcer, gastritis, dysmenorrhoea, discomfort caused by abdominal cramps and various disorders of the gastrointestinal tracts³ and urinary tracts⁴. Its chemical name is [(7(S)-(1 α ,2 β ,4 β ,5 α ,7 β))-9-butyl-7-(3-hydroxy-1-oxo-2-phenylpropoxy)-9-methyl-3-oxa-9-azonitricyclo [3.3.1.0(2,4)] nonane bromide⁴. It melts at about 139–141°C⁵. The hyoscine butylbromide is also known as scopolamine butyl bromide, butyl scopolamine having empirical formula $\text{C}_{21}\text{H}_{30}\text{BrNO}_4$ and its molecular weight is 440.4 g mol^{-1} (360.1 g mol^{-1} without bromide atom) (Fig. 1). It showed extensive decomposition under base hydrolytic conditions also degradation by oxidant has been reported⁶.

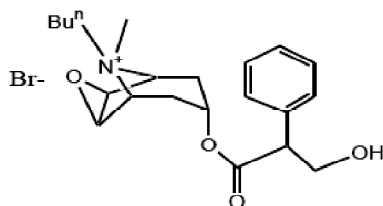


Fig. 1. Chemical structure of HBB.

Metal chelates such as diperiodatocuprate(III), diperiodatoargentate(III) and diperiodatonickelate(IV) are act as good oxidants⁷⁻⁹ in a medium with appropriate pH value. The substance DPC is a flexible one electron oxidant¹⁰, soluble and stable in aqueous medium and has multiple equilibrium between different Cu(III) species. Cu(III) has been investigated as a reactive intermediate in some biological reactions¹¹, electron transfer reactions¹² also identified as an analytical reagent^{13,14}. Transition metal ions such as osmium, iridium, and ruthenium were used as a catalyst in many redox reactions^{15,17}. Various researchers have studied the oxidation of drugs iosartan¹⁸, isoniazid¹⁹, chloramphenicol²⁰, sulfacetamide²¹, fluoroquinolone²², etc. by diperiodatocuprate(III) and Ru(III) catalyzed the oxidation of drug pentoxifyline²³, and anti-cholinergic drug atropinesulfatemonohydrate²⁴ by diperiodatocuprate(III). However, the mechanism differs for different reactions depend on the nature of substrate, oxidant and experimental conditions²⁵. The literature survey reveals that a considerable amount of work has been done on a determination of hyoscyne butylbromide in pharmaceutical preparations²⁶ but no information available on the kinetics and Ru(III) catalyzed the oxidation of HBB by DPC(III) in aqueous alkaline medium from the mechanistic viewpoint.

So there was a need for understanding and elucidate kinetic model also find (i) thermodynamic parameters, (ii) various reactive species and (iii) oxidation products.

Results and discussion

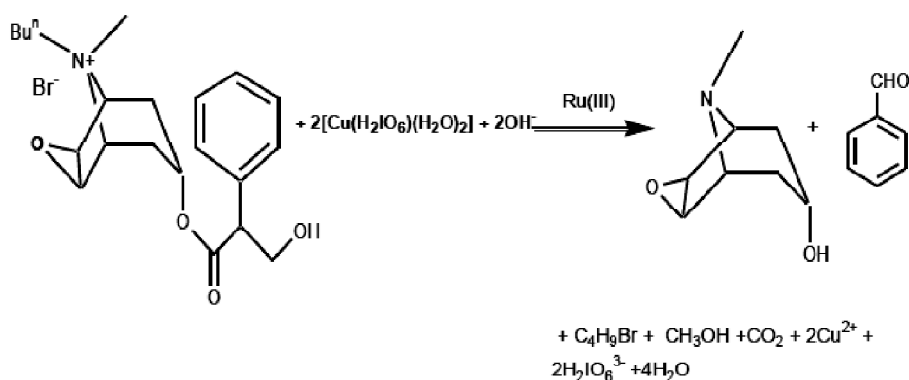
Stoichiometry:

Different sets of reaction mixtures containing various ratios of HBB to DPC in the presence of constant amounts of OH⁻ and KNO₃ were kept overnight in a flask. The unreacted [DPC] was estimated by spectrophotometer. The results indicated 1:2 stoichiometry as given in the Scheme 1.

Product analysis:

The reaction mixture of HBB with excess amount of DPC [in the presence of constant amount of OH⁻, KIO₄, KNO₃ and Ru(III)] was kept in a vessel under nitrogen atmosphere for 6 h to ensure the completion of reaction. The reaction mixture was acidified, concentrated and extracted with ether. The ethereal layer was subjected to column chromatography using hexane and ethyl acetate. The main oxidation product was found as scopine(C₈H₁₃NO₂) identified by melting point 76°C (75–76°C), FTIR, GC-MS and ¹H NMR studies. The other byproducts benzaldehyde methanol, butylbromide and carbon dioxide also detected.

The ¹H NMR (D₂O, 400 MHz) spectral analysis of scopine showed chemical shift a singlet for -OH at 8.432 ppm, singlet for the proton (attached to C₃) adjacent to -OH at 5.220 ppm, multiplets for the protons of -CH (C₁,C₇) at 5.287 ppm, (C₅,C₆) are observed in the range of 5.118–5.194 ppm, multiplets of methyl proton attached to nitrogen appear at 5.237, singlet for the protons -CH₂ (C₂,C₄) showed at 1.891 ppm.



Scheme 1. Stoichiometry of Ru(III) catalyzed oxidation of HBB by DPC in aqueous alkaline medium.

The IR spectrum of scopine showed a broad band at 3425 cm^{-1} assigned to -OH stretching, aliphatic stretching -CH at 2926 cm^{-1} and N-CH₃ at 2854 cm^{-1} . The scopine had molecular weight of 155.19 g mol^{-1} (exact mass 155.09 g/mol).

The GC-MS spectrum of scopine showed the molecular ion peak at 155 amu. Another product benzaldehyde was confirmed by hydrazone derivative³⁵, methyl alcohol, confirmed by sodium test³⁶ and CO₂ was qualitatively detected by bubbling nitrogen gas through the acidified reaction mixture and passing the gas to limewater. The presence of Cu(II) was confirmed by UV-Visible spectra.

Reaction order:

The oxidation of HBB by DPC(III) in aqueous alkaline medium proceeds slowly in the absence of Ru(III). The almost similar color changes observed in both catalyzed and

uncatalyzed reactions indicate that they progress in the same paths. Rate constants of catalyzed reaction was calculated by the equation, $k_C = k_T - k_U$. Since, the total rate constant (k_T) is the sum of the rate constants of the catalyzed (k_C) and uncatalyzed (k_U) reactions. Lastly, the reaction orders have been determined from the slopes of $\log k_C$ verses \log [concentration] plots by varying the concentrations of HBB, Ru(III), KIO₄ and KOH as mentioned in the Table 1.

Effect of variation of oxidant concentration:

The concentration of oxidant DPC(III) was varied in the range of 2×10^{-6} to 2.0×10^{-5} mol dm^{-3} at constant concentration of HBB, OH⁻, IO₄⁻ and Ru(III) catalyst. All sets of kinetic runs have given similar nature. The constant value k_C indicate that order with respect to DPC concentration was unity. The linearity of plots of \log [DPC] verses time ($r > 0.999$,

Table 1. Effect of variation of [DPC], [HBB], [Ru(III)], [IO₄⁻] and [OH⁻] on the Ru(III) catalyzed oxidation of HBB by DPC in aqueous alkaline medium at 28°C; $I = 0.1 \text{ mol dm}^{-3}$

[DPC] 10 ⁵ (mol dm ⁻³)	[HBB] 10 ⁴ (mol dm ⁻³)	[OH ⁻] (mol dm ⁻³)	[Ru(III)] 10 ⁸ (mol dm ⁻³)	[IO ₄ ⁻] 10 ⁵ (mol dm ³)	k_T 10 ³ (min ⁻¹)	k_U 10 ⁴ (min ⁻¹)	k_C 10 ³ (min ⁻¹)	
							Expt. ^a	Calcd. ^b
0.2	1.0	0.2	1.0	1.0	1.23	2.41	0.99	0.99
0.5	1.0	0.2	1.0	1.0	1.22	2.42	0.98	0.99
1.0	1.0	0.2	1.0	1.0	1.23	2.40	0.99	0.99
1.5	1.0	0.2	1.0	1.0	1.22	2.41	0.98	0.99
2.0	1.0	0.2	1.0	1.0	1.21	2.42	0.97	0.99
1.0	0.2	0.2	1.0	1.0	0.38	0.3	0.35	0.27
1.0	0.5	0.2	1.0	1.0	0.73	0.8	0.65	0.59
1.0	1.0	0.2	1.0	1.0	1.23	2.4	0.9	0.99
1.0	1.5	0.2	1.0	1.0	1.75	5.0	1.25	1.28
1.0	2.0	0.2	1.0	1.0	2.01	6.3	1.38	1.49
1.0	1.0	0.05	1.0	1.0	0.68	1.3	0.55	0.64
1.0	1.0	0.1	1.0	1.0	0.93	1.8	0.75	0.77
1.0	1.0	0.2	1.0	1.0	1.23	2.4	0.99	0.87
1.0	1.0	0.3	1.0	1.0	1.55	4.0	1.15	0.97
1.0	1.0	0.5	1.0	1.0	1.67	4.6	1.21	0.11
1.0	1.0	0.2	0.2	1.0	0.45	2.4	0.21	0.19
1.0	1.0	0.2	0.5	1.0	0.76	2.4	0.52	0.49
1.0	1.0	0.2	1.0	1.0	1.23	2.4	0.99	0.87
1.0	1.0	0.2	1.5	1.0	1.99	2.4	1.75	1.51
1.0	1.0	0.2	2.0	1.0	2.36	2.4	2.12	1.98
1.0	1.0	0.2	1.0	0.2	1.6	3.6	1.24	1.10
1.0	1.0	0.2	1.0	0.5	1.38	2.8	1.10	0.92
1.0	1.0	0.2	1.0	1.0	1.23	2.4	0.99	0.87
1.0	1.0	0.2	1.0	1.5	0.94	1.2	0.82	0.82
1.0	1.0	0.2	1.0	2.0	0.81	0.3	0.78	0.78

^aExperimental. ^bCalculated.

$S < 0.015$) for different initial concentration of DPC indicate the order in [DPC] as unity. This was also confirmed by varying [DPC], which did not show any change in pseudo-first order rate constant, k_C (Table 1).

Effect of reductant concentration on reaction rate:

The concentration of HBB was varied in the range of 2.0×10^{-4} to 2.0×10^{-3} mol dm⁻³ at 28°C, keeping all other reactant concentrations constant (Table 1). The k_C values increased with increasing concentrations of HBB indicating less than unit order dependence on [HBB] (Table 1 and Fig. 2).

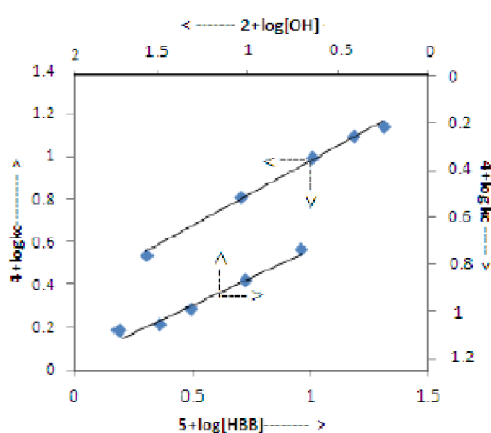


Fig. 2. Order with respect to HBB and OH⁻.

Effect of variation of catalyst concentration:

The concentration of catalyst Ru(III) was varied in the range of 2.0×10^{-9} to 2.0×10^{-8} mol dm⁻³, at constant concentration of DPC, HBB, KOH, KIO₄ and KNO₃. The order in [Ru(III)] was found to be unity (Table 1). As the catalyst concentration increases the rate of the reaction also increases.

Effect of variation of alkali and periodate concentration:

The concentration of KOH was varied in the range of 0.05 to 0.5 mol dm⁻³ at constant concentrations of HBB, DPC and constant ionic strength of 0.1 mol dm⁻³ at 28°C. The rate constant increased with increase in [KOH] indicating less than unit order dependence on [alkali].

The effect of [IO₄⁻] was observed by varying the concentration from 2×10^{-6} to 2×10^{-5} mol dm⁻³ range, keeping all other reactant concentrations constant. It was found that the rate constants decreased with an increase in KIO₄ concentration indicating less than zero order dependence on con-

centration of KIO₄ (Table 1 and Fig. 2).

Effect of ionic strength and dielectric constant:

Ionic strength was varied between 0.02 to 0.2 mol dm⁻³ by the addition of KNO₃ at constant [DPC], [HBB], [OH⁻] and [IO₄⁻]. Similarly, dielectric constant of the medium, D , was varied by adding dimethyl sulfoxide (DMSO) in the range of 5 to 25%. It was found that ionic strength and dielectric constant of the medium have no significant effect on the rate of reaction there by indicating insensitive nature of reaction to ionic strength and dielectric constant of the medium (Fig. 3 and Table 2).

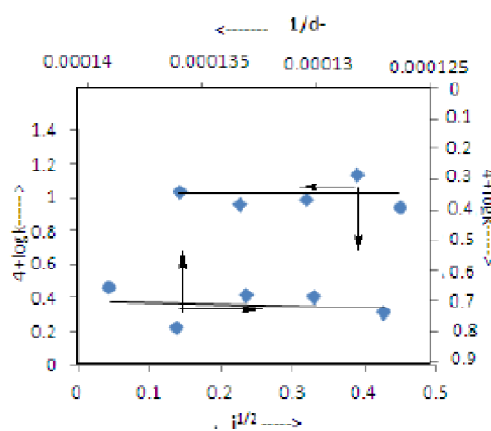


Fig. 3. Plots of $\log k_C$ vs $i^{1/2}$ and $\log k_C$ vs $1/d$.

Table 2. Effect of ionic strength and dielectric constant

$4 + \log k$	$1/d$	$4 + \log k$	$i^{1/2}$
0.7403	0.000127	1.041	0.141
0.6902	0.000130	0.973	0.223
0.6857	0.000133	0.995	0.316
0.7958	0.000136	1.152	0.387
0.6627	0.000139	0.954	0.447

The effect of initially added product:

The externally added product Cu(II) in the range 1.0×10^{-4} to 1.0×10^{-3} mol dm⁻³ did not have any significant effect on the rate of reaction. Thus, from the above observed results, the experimentally investigated rate equation for the title reaction is written as;

$$\text{Rate} = k_{\text{obs}} [\text{DPC}]^{1.0} [\text{HBB}]^{0.605} [\text{OH}^-]^{0.356} [\text{Ru(III)}]^{1.0} [\text{H}_3\text{IO}_6^{2-}]^{-0.2031} \text{ mol L}^{-1} \text{ min}^{-1}$$

The experimentally determined order with respect to re-

ductant and verified by plotting graphs of rate constants (k_C) vs [HBB] and $[HBB]^{0.605}$ as shown in the Fig. 4. The better linearity of the plot for rate constants vs $[HBB]^{0.605}$ indicate estimated order for reductant is in good agreement with experimental findings (Fig. 4). Similarly the experimentally determined order with respect to alkali and was verified by plotting graphs of rate constants (k_C) vs [OH] and $[OH]^{0.3566}$ as shown in the Fig. 5. The better linearity of the plot for rate constants vs $[OH]^{0.3566}$ indicate estimated order for alkali is in good agreement with experimental findings (Fig. 5).

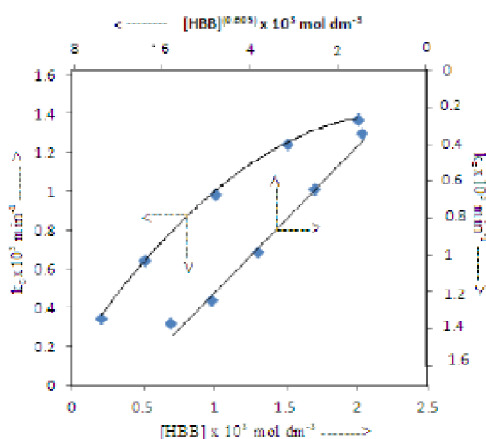


Fig. 4. Plots of k_C vs [HBB] and k_C vs $[HBB]^{0.605}$.

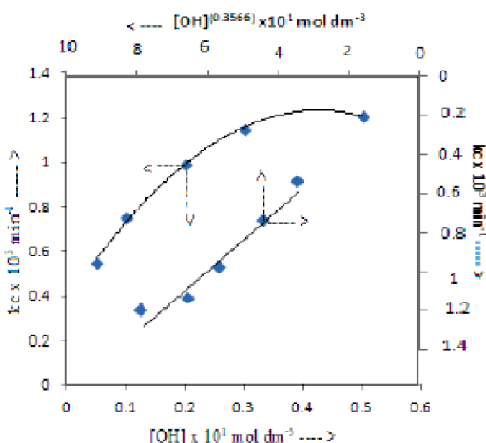


Fig. 5. Plots of k_C vs [OH] mol dm^{-3} and k_C vs $[OH]^{0.3566}$ mol dm^{-3} .

Polymerization study:

The reaction mixture was mixed with acrylonitrile monomer and kept for overnight in a flask. On dilution with methanol, no precipitate was formed, indicating the absence of intervention of free radicals in the reaction.

Effect of temperature:

The temperature effect on rate constants for both catalysed and uncatalysed reactions were studied at 28, 35, 40 and 45°C. The rate constants increased with an increase in temperature for both the reactions, indicating endothermic nature of oxidation. The plots of $4 + \log k_C$ and $4 + \log k_U$ versus $1/T$ yield straight line (Fig. 6) and the values of activation parameters viz. enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger) and Gibb's free energy (ΔG^\ddagger) are evaluated from the slopes of the plots by using the Eyring equation³⁷⁻³⁹ and are tabulated in Table 3 and thermodynamic quantities for different equilibrium steps in Scheme 2 calculated and shown in Table 4.

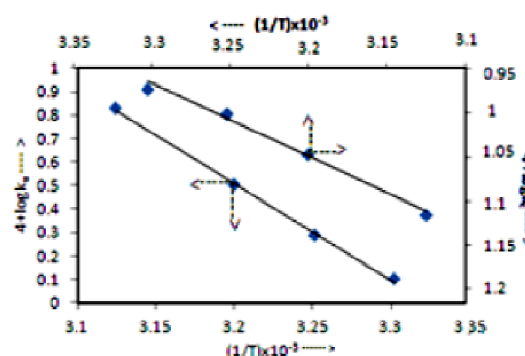


Fig. 6. Plot of $\log k$ vs $1/T$ for catalyzed and uncatalyzed reactions.

Parameters \rightarrow	ΔE^\ddagger	ΔH^\ddagger	ΔS^\ddagger	$\log A$	ΔG^\ddagger
Nature of reaction \downarrow	(kJ/mol)	(kJ/mol)	(JK mol ⁻¹)		(kJ/mol)
Uncatalyzed	59.24	56.74	143.20	6.65	43.05
Catalyzed	21.06	18.56	19.18	0.64	-5.75

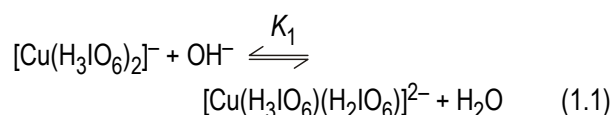
Catalyst activity:

According to Moelwyn-Hughes⁴⁰ the uncatalysed and catalysed reaction proceed simultaneously in presence of catalyst, so that $k_T = k_U + k_C[\text{Ru(III)}]x$, where k_T , is the observed pseudo-first order rate constant in the presence of Ru(III) catalyst; k_U , is the pseudo-first order rate constant for uncatalyzed; k_C , the catalytic constant and x is 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. $K_C = (k_T - k_U)/[\text{Ru(III)}]x = k_C/[\text{Ru(III)}]$ (where $k_C = k_T - k_U$). The value of k_C was calculated for Ru(III) catalyst at 28°C.

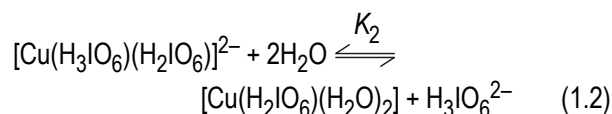
Table 4. Effect of temperature on Ru(III) catalyzed oxidation of HBB bydiperiodatocuprate(III) in aqueous alkaline medium

Effect of temp. on first, second and third equilibrium step of Scheme 2				Thermodynamic quantities with respect to first, second and third step of Scheme 2					Rate consts with respect to slow step of Scheme 2		
Temp. (K)	K_1 (10^{-3}) $\text{dm}^3 \text{mol}^{-1}$	K_2 mol dm^{-3}	K_3 (10^3) dm^3	Temp. (K)	ΔE^\ddagger (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔS^\ddagger ($\text{JK}^{-1} \text{mol}^{-1}$)	log A	ΔG^\ddagger (kJ/mol)	Temp. (K)	$k \times 10^5$ (min^{-1})
301	0.56	0.27	0.49							301	3.083
308	1.12	0.54	0.33	308	97.53	95.03	272.11	13.67	-81.18	308	4.46
313	2.24	1.08	0.16	313	0.09	-2.406	-39.31	-0.05	11.83	313	7.23
318	4.48	2.11	0.08	318	96.25	93.75	281.31	16.38	-84.58	318	9.763

The increase in alkali concentration has increased the rate. This finding clearly explains the formation of $[\text{Cu}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{2-}$ as shown in the following equilibrium;



The retarding effect of periodate on reaction. Rate suggests the formation of monoperoiodatocuprate(III) (MPC) species form $[\text{Cu}(\text{H}_3\text{IO}_6)(\text{H}_2\text{IO}_6)]^{2-}$.



The above stated equilibriums (1.1) and (1.2) have been reported by many researchers⁴¹. Copper(III) periodate in alkaline medium exhibits three forms⁴³ among them monoperoiodatocuprate(III) MPC is considered as a reactive species. Less than zero order in periodate is also due to the formation of MPC as given in equilibrium (1.2).

Based on the experimental results, a mechanism (Scheme 2) was proposed for which all the observed orders in $[\text{DPC}]$, $[\text{HBB}]$, $[\text{OH}^-]$, $[\text{Ru}(\text{III})]$ and $[\text{IO}_4^-]$. Less than unit order in HBB presumably results from the formation of a complex C, between the Ru(III) species and HBB. Spectroscopic evidence for the complex formation between Ru(III) and hyoscine butylbromide was obtained from UV-Vis spectra of hyoscinebutylbromide, Ru(III) separately in presence of alkali and a mixture of both in the same medium. A bathochromic shift of about 7 nm from 248 nm to 255 nm in the spectra of HBB was observed. The Michaelis-Menten plot (Fig. 8) also proved the complex formation between catalyst and reductant, which explains the less than unit order dependence on $[\text{HBB}]$. Such type of complex between a substrate and a catalyst has been observed in other studies⁴².

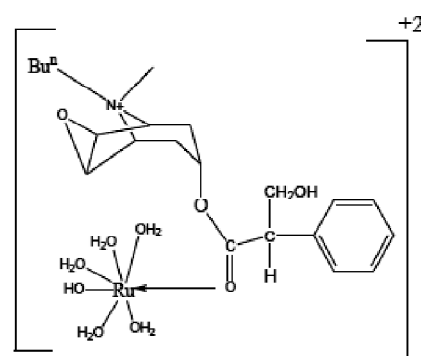


Fig. 7. The probable structure of complex.

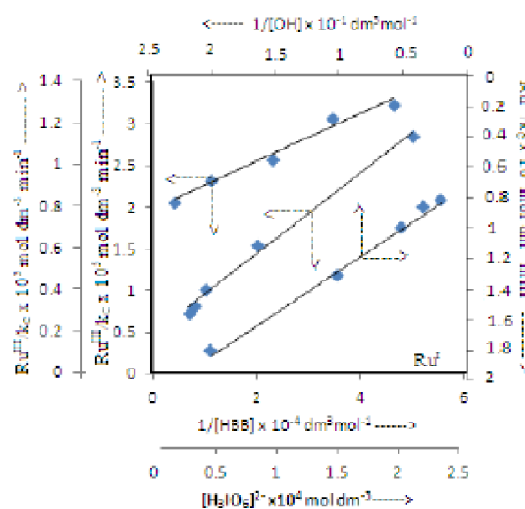


Fig. 8. Verification of rate law of Ru(III) catalyzed oxidation of HBB by DPC(III) in aqueous alkaline medium at 301 K.

The HBB-Ru(III) complex generated (Fig. 1) reacts immediately with one mole of MPC in slow step to form water soluble, colourless, crystalline compound scopine with intermediate compound. Thus, generated intermediate compound reacts one mole of MPC in a fast step leads to by product

benzaldehyde and methyl alcohol. With the help of Scheme 2 following rate law was derived;

$$\frac{\text{Rate}}{[\text{DPC}]} = k_C = k_T - k_U \quad (1.3)$$

$$k_C = \frac{kK_1K_2K_3[\text{HBB}][\text{OH}^-][\text{Ru(III)}]}{[\text{H}_3\text{IO}_6^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{HBB}][\text{OH}^-]} \quad (1.4)$$

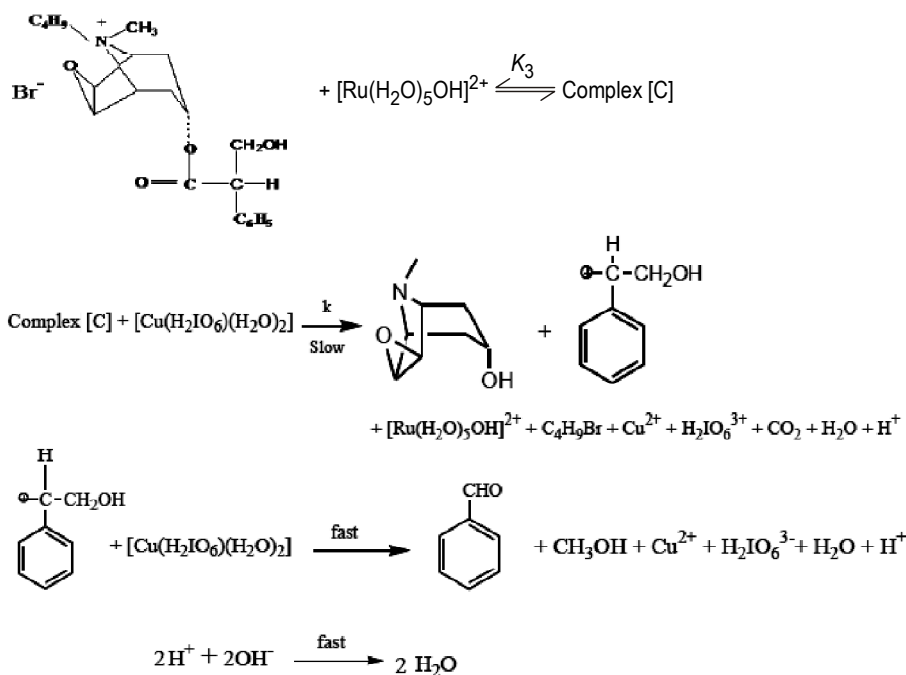
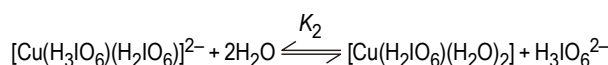
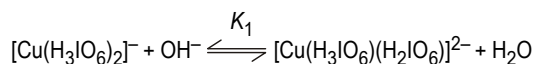
The rate law can be rearranged into the following form which is opposite for verification;

$$\frac{[\text{Ru(III)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_1K_2K_3[\text{HBB}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6^{2-}]}{kK_2K_3[\text{HBB}]} + \frac{1}{kK_3[\text{HBB}]} + \frac{1}{k} \quad (1.5)$$

According to above equation, the plots of $[\text{Ru(III)}]/k_C$ versus $1/[\text{OH}^-]$, $[\text{Ru(III)}]/k_C$ versus $[\text{H}_3\text{IO}_6^{2-}]$ and $[\text{Ru(III)}]/k_C$ versus $1/[\text{HBB}]$, were linear as in Fig. 8. From the slopes and intercepts of such plots, the equilibrium constants K_1 , K_2 , K_3 and k were calculated as $0.5573 \pm 0.07 \text{ dm}^3 \text{ mol}^{-1}$, $0.2714 \pm 0.06 \text{ mol dm}^{-3}$, $4.736 \pm 0.02 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $3.083 \pm 0.04 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ min}^{-1}$. The value of K_2 was in good agreement with earlier work²⁹. These constants were used to calculate the rate constants over different experimental conditions, when compared with the experimental k_C values, they were found to be in reasonable agreement with each other (Table 1), which supports Scheme 2.

Negligible effect of ionic strength and dielectric constant might be due to involvement of neutral and positively charged ions in the reaction as shown in the mechanism. Arrhenius activation energy E_a for uncatalysed and catalysed reactions were found 59.24 and 21.06 kJ/mol (Table 3) respectively. This suggests that Ru(III) has played significant role in re-

Mechanism:



Scheme 2. Detailed scheme of Ru(III) catalyzed oxidation of HBB by DPC.

ducing energy barrier. The moderate ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger values are favorable for electron transfer reaction. The higher value of ΔS^\ddagger for uncatalyzed reaction indicate the formation of less ordered intermediates where as smaller value of ΔS^\ddagger for catalyzed reaction suggests that the intermediate complex is more ordered but less than the reactants⁴⁴. 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.

Experimental

Materials and methods:

All chemicals and materials were of analytical grade and all solutions were freshly prepared in double distilled water throughout the work. The stock solution of HBB (CID Co. Chemical Industries Development, Giza, Egypt) was prepared by dissolving appropriate amount of the sample in double distilled water, the purity was checked by comparing it with its melting point 140°C and required concentration was obtained from stock solution. The DPC(III) was prepared^{27,29} and standardized by the standard procedure³⁰. The UV-Vis spectrum with maximum absorption at 415 nm verified the existence of copper(III) complex. All other reagents, namely KOH, KNO₃, CuSO₄, KIO₄ and acrylonitrile were of analAR grade. The Ru(III) solution was prepared by dissolving a known weight of RuCl₃ (sd Fine-Chem.) in HCl (0.2 mol dm⁻³). Formation of Ru(IV) in stock solution Ru(III) was prevented by adding mercury, which was set aside for 24 h. The Ru(III) concentration was then assayed by EDTA titration^{31,32}. Potassium hydroxide and potassium nitrate were employed to maintain required alkalinity and ionic strength respectively. Periodate solution was prepared by dissolving required amount of sample in double distilled water. Its concentration was determined iodometrically^{33,34} at 1 M sodium phosphate buffer solution. Kinetics measurements were performed on a UV3000+ spectrophotometer (Labindia make). A QP-2010S Shimadzu gas chromatograph mass spectrometer, Nicolet 5700-FT-IR soectrineter (Thermo, USA), NMR spectrophotometer (Bruker, Model, Av 400 Proton frequency 400 MHz, SAIF, Indian Institue of Science, Bangalore) were used to obtain GC-MS, IR and ¹H and ¹³C NMR spectra respectively. Elico pH meter model LI 120 was used for pH measurements.

Kinetic measurements:

All kinetics runs were followed under pseudo-first order conditions with the HBB concentration in excess over that of

DPC at 28±0.1°C. The reaction was initiated by mixing solutions of DPC and HBB which also contained a definite quantity of KOH, KNO₃ and KIO₄ in a thermostat (Temp. Instru- ment and Equipments (I) PVT. Ltd. cat no: T190B, Sr. no. 1452) for uncatalyzed reaction and for catalyzed reaction same procedure is followed in presence of definite quantity of Ru(III). The total [OH⁻] was also calculated considering the KOH in DPC as well as KOH additionally added. The progress of reaction was followed by measuring the absorbance of unreacted DPC(III) in the reaction mixture in 1 cm quartz cell (OPTIGLASS Limited UK (Q)) using UV3000+ spectrophotometer at its maximum absorbance of 415 nm as a function of time. It was also verified that there is a negligible interference from other species present in the reaction mixture at this wavelength. The Beer's law was verified for DPC at 415 nm and the molar absorbance coefficient, ϵ , was found to be 6250±25 dm³ mol⁻¹ cm⁻¹. The reaction was followed to more than 90% completion. The first order rate constants, k_{obs} , were calculated from slopes of log [DPC] versus time plots for both catalyzed and uncatalyzed reactions. The rate constants were reproducible to within ±5% further standard deviation and regression coefficient for all the plots were performed using Microsoft office Excel 2007 program. Kinetic runs were also carried out in nitrogen atmosphere.

Conclusions

Monoperiodatocuprate(III) is considered to be the active species of the Cu(III) in aqueous alkaline medium for the title reaction. The active species of ruthenium is understood to be as [Ru(H₂O)₅(OH)]²⁺. The activation parameters evaluated for the catalyzed and uncatalyzed reactions explain the catalytic effect of Ru(III) on the reaction. The Ru(III) catalyst alters the reaction path by lowering the energy of activation. The catalyzed path is more ordered than the uncatalyzed path.

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