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Oxidation of procainamide by diperiodatocuprate(III) complex in aqueous alkaline medium: a comparative kinetic study

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ABSTRACT

A comparative study of uncatalysed and ruthenium(III) catalyzed oxidation of procainamide(PAH) was carried out spectrophotometrically using diperiodatocuprate(III) in aqueous alkali. Stoichiometry observed was 1:2 (PAH: DPC). The reaction was of first order in both catalyzed and uncatalyzed cases, with respect to [DPC] & [Ru(III)], less than unit order in [PAH] and [alkali]. Negative fraction in [periodate]. Other kinetic parameters viz., ionic strength, dielectric constant, temperature effect and intervention of free radical were also studied. The main oxidation products were characterized by different techniques. The activation parameters with respect to slow step of the mechanism, also the thermodynamic quantities were determined.

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Diperiodatocuprate(III); oxidation; procainamide; ruthenium(III) catalyst; thermodynamic parameters

Introduction

In the latest past^[1,2], the study of maximum oxidation state of transition metals has attracted several scientists. Some relatively stable copper(III) complexes have been prepared namely, the periodate, guanidine and tellurate complexes are good oxidants in a medium with an appropriate pH value. Copper complexes have occupied a vital place in oxidation chemistry due to their abundance and wide applications in biological chemistry.^[3] Diperiodatocuprate (III) (DPC) is a versatile one-electron oxidant and its oxidation study is revealing in view of its partial solubility and stability in aqueous medium. Its usefulness as an analytical reagent is present well familiar.^[4] The oxidation reaction usually involves the copper(II)-copper(I) and such aspects are dealt in different reviews.^[5] The Cu^{3+}/Cu^{2+} reduction potential is -1.18 V in alkaline solution.^[5] When copper(III) periodate complex acts as an oxidant, many equilibrium steps between different copper(III) species are involved and it would be interesting to know about the active oxidants. The kinetics of self-decomposition of these complexes was also studied in detail.^[2]

Ruthenium(III) (Ru(III)) acts as an efficient catalyst in the several oxidations of many organic and inorganic substrates & it has gain attention in recent years owing to catalytic applications in various technologies.^[6] Ruthenium(III) catalysis in redox reactions contains different steps of complexity, due to the formation of different reaction intermediate complexes and the different oxidation states of ruthenium.^[7] An ideal catalyst is the one which shows a good catalytic effect at a negligible concentration range; hence, a micro (10⁻⁶ mol dm⁻³) quantity of the ruthenium(III) is used to study the catalytic

effect. The rate became tenfold faster than the uncatalysed reaction in this concentration range of the catalyst.

Procainamide [PAH] used for the treatment of cardiac arrhythmias, especially to treat certain types of irregular heartbeats (ventricular tachycardia).^[8] Procainamide hydrochloride (salt form of procainmide) is a group 1A cardiac antiarrhythmic drug, is p-amino-N-{2-(diethylamino)ethyl}-benzamide monohydrochloride. Procainamide's major active metabolite is N-acetylprocainmide (NAPA), which is approximately equipotent with the parent drug as an antiarrhythmic agent.^[9] The structure of procainamide is shown below



Procainmaide is also used as a chromatography resin, because it binds protein.^[10] It is structurally similar to procaine, but in place of an ester group, procainamide contains an amide group. Because of this substitution procainamide exhibits a longer half-life time than procaine.

Literature survey revealed that some work on oxidation of PAH by various oxidants have been carried out^[11], there is a lack of literature on the oxidation of this PAH by DPC and its catalysis by ruthenium(III). In view of the pharmaceutical importance of PAH and oxidation of procainamide by DPC, there was a need for understanding the mechanistic profile. Hence, the present investigation is aimed to find out the reactivity of PAH towards DPC in both uncatalyzed and ruthenium(III) catalyzed reactions, to identify the reactive species of DPC,

Table 1. Effect of Variation of Diperiodatocuprate(III), Procainamide, OH^- and Periodate on the Oxidation of Procainamide by Diperiodatocuprate(III) in Aqueous Alkaline Medium at 25°C and $I = 0.20 \text{ mol dm}^{-3}$.

$\begin{array}{l} \text{[DPC]}\times10^{5} \\ \text{(mol dm}^{-3}) \end{array}$	$[PAH] imes 10^4$ (mol dm ⁻³)	[OH ⁻] (mol dm ⁻³)	$[10_4^{-}] \times 10^4$ (mol dm ⁻³)	$k_{\rm U} imes 10^{-3}$ (s ⁻¹)
1.0	5.0	0.10	5.0	3.378
3.0	5.0	0.10	5.0	3.570
5.0	5.0	0.10	5.0	3.735
7.0	5.0	0.10	5.0	3.865
10.0	5.0	0.10	5.0	3.654
5.0	1.0	0.10	5.0	1.036
5.0	3.0	0.10	5.0	2.457
5.0	5.0	0.10	5.0	3.735
5.0	7.0	0.10	5.0	4.717
5.0	10.0	0.10	5.0	5.736
5.0	5.0	0.05	5.0	2.732
5.0	5.0	0.08	5.0	3.316
5.0	5.0	0.10	5.0	3.735
5.0	5.0	0.30	5.0	4.507
5.0	5.0	0.50	5.0	5.121
5.0	5.0	0.10	1.0	5.827
5.0	5.0	0.10	3.0	4.479
5.0	5.0	0.10	5.0	3.735
5.0	5.0	0.10	7.0	3.278
5.0	5.0	0.10	10.0	2.663

ruthenium(III) to propose suitable mechanisms, to design kinetic rate laws and to deduce the thermodynamic parameters.

Experimental section

Materials and reagents

PAH & RuCl₃ was purchased from Sigma Chemical Company, St. Louis, USA and was used without any further purification. KIO₄, KNO₃ & KOH was purchased from Himedia lab chemicals, India. Stock solution of PAH was prepared by dissolving a proper amount in millipore water, Ru(III) solution was prepared by dissolving RuCl₃ in $0.20 \text{ mol } \text{dm}^{-3}$ HCl. The concentration was examined via EDTA titration.^[12] KIO₄ was prepared by dissolving a known weight of KIO₄ (Himedia) in hot water and was used after one day. Its concentration was determined iodometrically^[13] and neutral pH was maintained using phosphate buffer. The ionic strength was maintained by addition of KNO3 solution and the pH value was controlled with KOH solution. The copper(III) periodate complex was prepared^[14] and standardized by using standard methods.^[15] Other chemical reagents which were used were of analytical/ reagent grade, and millipore water (resistivity of millipore water is $20M\Omega$) was used throughout the experimentation. The concentration of DPC was tested by measuring the absorbance at 415 nm.

Equipments and spectral measurements

• Equipped with a 1 cm quartz cell, a Peltier Accessory (temperature control) attached to a Varian CARY 50 Bio UV-vis. spectrophotometer (Varian, Victoria-3170, Australia) was used for kinetic measurements.

- A Shimadzu 17A gaschromatograph with a Shimadzu QP-5050A mass spectrometerusing the electron ionization (EI) technique, a Nicolet 5700 FT-IR spectrometer (ThermoElectron Corporation, Madison, WI, USA) were used for product analysis.
- Measurement of pH was conducted using an Elico model LI120 pH meter.

Kinetic measurements

Reactions were carried out by the oxidation of PAH by DPC followed under pseudo first order conditions where [PAH] >>> [DPC] in both uncatalyzed and ruthenium(III) catalyzed $(\gg10 \text{ fold excess})$ reactions at room temperature. The kinetic reactions and measurements were followed by our previous lab work.^[5] UV-vis spectral changes observed during the oxidation reaction in the absence and presence of Ru(III) was shown in (Figure S1). In the both cases the pseudo-first order rate constants ($k_{\rm U}$ and $k_{\rm C}$) were obtained from the plots of log(Absorbance) versus time (Figure S1). The pseudo-first order plots were linear over three half-lives. The rate constants, $k_{\rm U}$ and $k_{\rm C}$ values are shown in Tables 1 and 2. As the Figure 1 shows that the spectral changes observed during both uncatalyzed and catalyzed reactions at standard condition. From Figure 1 the concentration of DPC decreases slowly at 415 nm. During the kinetics, a constant concentration viz. 5.0×10^{-5} mol dm⁻³ of KIO₄ was used throughout the study.

Results and discussion

Stoichiometry and product analysis

The results indicated 1:2 stoichiometry, i.e., one mole of PAH consumes two moles of DPC species according to eq (1):



After the completion of the reaction, the reaction mixture was acidified, concentrated and extracted with ether. The major products were identified as 4-aminobenzoic acid and (E)-ethene-1, 2-diamine, which was separated by column chromatography by using hexane: ethyl acetate as eluent.

The GC-MS analysis of 4-aminobenzoic acid showed a base peak at 120 amu and molecular ion peak at 137 amu (Figure 2). The IR spectrum of 4-aminobenzoic acid showed a sharp band at 1672 cm^{-1} which corresponds to carbonyl group stretching. The bands at 3366 cm^{-1} and 3465 cm^{-1} are due to symmetric and asymmetric stretching of $-\text{NH}_2$ group (Figure S2). The ¹H NMR spectral analysis of 4-aminobenzoic acid exhibited a doublet at 6.54 ppm is due to aromatic protons. One more doublet of aromatic protons resonated at 7.59 ppm (Figure S3). The ¹³C NMR spectral

Table 2. Effect of Variation of Diperiodatocuprate(III), Procainamide, OH⁻ and Periodate on the Ruthenium(III) Catalysed Oxidation of Procainamide by Diperiodatocuprate(III) in Aqueous Alkaline Medium at 25°C and $I = 0.20 \text{ mol dm}^{-3}$.

$[DPC] \times 10^5$	$[PAH] \times 10^4$	[OH ⁻]	$[IO_4^{-}] \times 10^4$	$[Ru(III)] \times 10^{6}$	$k_{\rm T} \times 10^2$	$k_{\rm U} \times 10^3$	$k_{\rm C} \times 10^2$
(moi dm ⁻²)	(moi dm -)	(moi dm -)	(moi dm -)	(moi dm -)	(S ⁻¹)	(S ⁻)	(5)
1.0	5.0	0.10	5.0	8.0	1.294	3.378	0.956
3.0	5.0	0.10	5.0	8.0	1.351	3.570	0.994
5.0	5.0	0.10	5.0	8.0	1.386	3.735	1.013
7.0	5.0	0.10	5.0	8.0	1.215	3.865	0.829
10.0	5.0	0.10	5.0	8.0	1.395	3.654	1.029
5.0	1.0	0.10	5.0	8.0	0.334	1.036	0.231
5.0	3.0	0.10	5.0	8.0	1.032	2.457	0.787
5.0	5.0	0.10	5.0	8.0	1.387	3.735	1.013
5.0	7.0	0.10	5.0	8.0	1.817	4.925	1.325
5.0	10.0	0.10	5.0	8.0	2.345	6.356	1.709
5.0	5.0	0.05	5.0	8.0	0.811	2.732	0.538
5.0	5.0	0.08	5.0	8.0	1.204	3.116	0.892
5.0	5.0	0.10	5.0	8.0	1.386	3.735	1.033
5.0	5.0	0.30	5.0	8.0	1.561	4.507	1.112
5.0	5.0	0.50	5.0	8.0	1.963	5.410	1.422
5.0	5.0	0.10	1.0	8.0	2.756	0.582	2.174
5.0	5.0	0.10	3.0	8.0	1.825	0.448	1.377
5.0	5.0	0.10	5.0	8.0	1.386	0.373	1.013
5.0	5.0	0.10	7.0	8.0	1.301	0.327	0.974
5.0	5.0	0.10	10.0	8.0	0.983	0.286	0.697
5.0	5.0	0.10	5.0	0.0	-	3.735	-
5.0	5.0	0.10	5.0	2.0	0.578	3.735	0.205
5.0	5.0	0.10	5.0	5.0	0.807	3.735	0.434
5.0	5.0	0.10	5.0	8.0	1.386	3.735	1.013
5.0	5.0	0.10	5.0	10.0	1.543	3.735	1.169
5.0	5.0	0.10	5.0	20.0	2.533	3.735	2.160



Figure 1. UV-vis spectral changes during the oxidation of procainamide by alkaline diperiodatocuprate(III) at 25° C, [DPC] = 5.0 x 10^{-5} , [PAH] = 5.0 x 10^{-4} , [OH] = 0.10, and I = 0.20 mol dm⁻³ with scanning time interval of 1.0 min.

analysis of 4-aminobenzoic acid exhibited a peak 167 ppm is due to carboxylic acid carbon. A signal at 153 ppm is attributed to aromatic carbon adjacent to $-NH_2$ carbon a peak at 131 ppm is due to aromatic carbons, one more peak at 116.854 ppm is attributed to aromatic carbon adjacent to carboxylic group and remaining two aromatic carbons resonated at 112.52 ppm (Figure S4). Another product (E)-ethene-1, 2-diamine was confirmed by its GC-MS spectrum which showed a molecular ion peak at 58 amu (Figure S5). It was observed that the oxidation products do not undergo further oxidation under the prevailing kinetic conditions

Reaction orders

From the slopes of log (rate) versus log (concentration) plots by varying the [PAH], $[OH^-]$, $[KIO_4]$ and Ru(III) in turn

whereas keeping others constant, the reaction orders have been determined.

Evaluation of pseudo first order rate constants

Concentration of oxidant was varied from 1.0×10^{-5} - 10.0×10^{-4} mol dm⁻³. The pseudo- first order rate constants ($k_{\rm U}$ and $k_{\rm C}$) were almost constant in the both cases, showing that first order dependence with respect to DPC concentration. This was also confirmed by Figure S1, the plots were linear over three half-lives for different initial DPC concentrations (Table 1 and 2).

Effect of concentration of procainamide

The concentration range of PAH was varied 1.0×10^{-4} – 10.0×10^{-3} mol dm⁻³ at a constant concentration of DPC, OH⁻, KIO₄ and a constant ionic strength of 0.20 mol dm⁻³ in the uncatalyzed reaction and with a constant concentration of Ru(III) in the catalyzed reaction. The $k_{\rm U}$ (Table 1) and $k_{\rm C}$ (Table 2) values increased with the increase in [PAH] at constant temperature in both cases. The order with respect to [PAH] was less than unity. This was also confirmed by the plots of $k_{\rm U}$ versus [PAH]^{0.75} (Figure S6A) and $k_{\rm C}$ versus [PAH] ^{0.85} (Figure S6B). These were linear rather than the direct plot of $k_{\rm U}$ versus [PAH] and $k_{\rm C}$ versus [PAH].

Effect of [Alkali]

The effect of alkali was studied for both cases in the concentration range 0.05–0.5mol dm⁻³at keeping the constant concentrations of DPC, PAH, KIO₄ and ionic strength in the



Figure 2. GC-MS spectrum of the product, p-aminobenzoic acid showed base peak at 120 amu and molecular ion peak at 137 amu.

uncatalyzed reaction and with a constant concentration of Ru(III) in the catalyzed reaction. From Table 1 and 2, shows that the rate constants increased with the increase in [alkali] and less than unity, i.e., 0.25 & 0.33 order was observed in the uncatalysed & catalyzed reaction.

Effect of [Periodate]

At constant concentrations of DPC, PAH, OH^- and ionic strength in uncatalyzed and with constant concentration of Ru(III) in catalyzed reaction, the effect of periodate was studied for both the cases in the range of 1.0×10^{-4} – 10.0×10^{-3} mol dm⁻³. The experimental results indicated that the $k_{\rm U}$ and $k_{\rm C}$ values decreased with increase in [IO₄⁻¹] (Table 1 and 2) indicates the retarding effect of periodate on the rate of reaction. The order with respect to IO₄⁻⁻ was negative fractional i.e., - 0.32 in uncatalyzed and -0.47 in Ru(III) catalyzed reaction. The retarding effect of periodate indicates the existence of dissociation equilibrium for DPC species, through which the diperiodato complex dissociates to give a monoperiodato species.

Effect of [Ruthenium(III)]

Ruthenium(III) concentration was varied from 2.0×10^{-6} - 2.0×10^{-5} mol dm⁻³, at constant concentrations of DPC, PAH, KIO₄, OH⁻ and at constant ionic strength. As the concentration of ruthenium(III) increases, the rate of reaction also increases (Table 2). The order with respect to ruthenium(III) concentration was found to be unity from the linearity of the plot of $k_{\rm C}$ versus [Ru(III)] (Figure S7).

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

The ionic strength was varied by varying the KNO₃ concentration between 0.10 to 0.90 mol dm⁻³ in the absence and in the presence of catalyst, at constant concentrations of reactants and with other conditions constant. The rate was found to decrease with increase in ionic strength and a plot of log $k_{\rm U}$ or $k_{\rm C}$ versus $I^{-1/2}$ was linear with negative slope (Figures S8 and S9) indicates that there is no significant effect on the rate of reaction in the both cases. The effect of dielectric constant was studied by varying the t-butyl alcohol-water (v/v) percentage composition from 0-30%. It was found that rate of reaction increased with decreasing dielectric constant of the medium and the plot of log $k_{\rm U}$ or $k_{\rm C}$ versus 1/D was linear with a negative slope (Figure S8 and S9).

Effect of initially added products

The initially added products, in the absence and presence of catalyst, 4-aminobenzoic acid and (E)-ethene-1, 2-diamine did not have any significant effect on the rate of reaction.

Test for free radicals (polymerization study)

For both the uncatalyzed and catalyzed reactions, the intervention of the free radicals in the reaction was examined by using acrylonitrile monomer.

Free radical test: the reaction mixture, to which a known quantity of acrylonitrile monomer (scavenger) had been added initially, was kept in an inert atmosphere for 5h at room temperature and diluting the reaction mixture with methanol, there is no precipitate was observed, indicating that, absence of free radicals in the reaction.

Table 3. Activation Parameters and Thermodynamic Quantities for the Oxidation of PAH by DPC(III) in Aqueous Alkaline Medium With Respect to the Slow Step of Scheme 1.

(A) Effect of Temperature and Activation Parameters					
Temperature(K)	$k_1 imes 10^2$ (dm ³ mol ⁻¹ s ⁻¹)	Parameters	Values		
288	0.32	$E_{\rm a}(\rm kJmol^{-1})$	52 ± 3		
298	1.06	$\Delta H^{\ddagger}(kJmol^{-1})$	50 ± 3		
308	1.72	ΔS^{\ddagger} (JK ⁻¹ mol ⁻¹)	-115 ± 4		
318	2.69	$\Delta G^{\ddagger}(kJmol^{-1})$	84 ± 4		
		log A	7 ± 0.1		
(B) Effect of Temperature on F	irst, Second and Third Equilibrium Step o	of Scheme 1			
Temperature (K)	$K_1 (\mathrm{dm^3 \ mol^{-1}})$	$K_2 \times 10^4 (\rm dm^3 mol^{-1})$	$K_3 \times 10^3 (\rm dm^3 mol^{-1})$		
288	2.04	13.8	2.13		
298	3.26	9.84	3.19		
308	4.07	5.04	4.87		
318	7.57	3.72	7.43		
(C) Thermodynamic Quantities	With Respect to K_1 , K_2 and K_3				
Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3		
$\Delta H(kJmol^{-1})$	32	35	32		
$\Delta S(JK^{-1} \text{ mol}^{-1})$	115	176	174		
ΔG_{298} (kJmol ⁻¹)	-3	17	-20		

Table 4. Activation Parameters and Thermodynamic Quantities for the Ru(III) Catalysed Oxidation of PAH by DPC(III) in Aqueous Alkaline Medium With Respect to the Slow Step of Scheme 2.

(A) Effect of Temperature and Activation Parameters					
Temperature(K)	k_2 \times $10^{\text{-5}}$ ($dm^3~mol^{-1}~s^{-1}$)	Parameters	Values		
288	0.73	$E_{\rm a}({\rm kJmol}^{-1})$	35±3		
298	1.23	ΔH^{\ddagger} (kJmol ⁻¹)	31±3		
308	1.84	ΔS^{\ddagger} (JK ⁻¹ mol ⁻¹)	-61 ± 4		
318	2.80	$\Delta G^{\ddagger}(kJmol^{-1})$	50 ± 3		
		log A	10 ± 0.2		
(B) Effect of Temperature on Fir	st, Second and Third Equilibrium Step o	f Scheme 2			
Temperature (K)	$K_1 (\mathrm{dm^3 \ mol^{-1}})$	$K_2 \times 10^4 (\rm dm^3 mol^{-1})$	$K_3 \times 10^{-3} (\text{dm}^3 \text{ mol}^{-1})$		
288	2.58	14.7	0.49		
298	3.10	8.24	0.70		
308	3.69	4.92	1.13		
318	7.87	4.07	1.52		
(C) Thermodynamic Quantities W	With Respect to K_1 , K_2 and K_3				
Thermodynamic Quantities	Values from K_1	Values from K_2	Values from K_3		
$\Delta H(kJmol^{-1})$	27	-33	30		
$\Delta S(JK^{-1} \text{ mol}^{-1})$	99	-171	154		
ΔG_{298} (kJmol ⁻¹)	-3	18	-16		

Experimental rate

Thus, from the observed results, the experimental rate laws for both the uncatalysed and Ru(III) catalyzed reactions are:

Rate =
$$k_{\rm C}[{\rm DPC}]^{1.0}[{\rm PAH}]^{0.75}[{\rm OH}^{-}]^{0.25}[{\rm IO}_{4}^{-}]^{-0.32}$$

for uncatalysed reaction

Rate
$$= k_{\rm C} [{\rm DPC}]^{1.0} [{\rm PAH}]^{0.85} [{\rm OH}^{-}]^{0.33} [{\rm Ru}({\rm III})]^{1.0} [{\rm IO}_{4}^{-}]^{-0.47}$$

for catalysed reaction

Catalytic activity

For catalytic activity & catalytic constant $K_{\rm C}$, were studied & followed by our previous lab work [5]. The value of catalytic constant $K_{\rm C}$ was calculated at 25 °C and the value is 4.75 x 10^{3} at $25 \,^{\circ}$ C.

Effect of temperature

The kinetics were studied at four different temperatures 15, 25, 35 and 45 °C. The rate of reaction increased with increase in temperature. The rate constants $(k_1 \text{ and } k_2)$ of the slow steps of Schemes 1 and 2 were obtained from the intercepts of the plots of $1/k_{\rm U}$ versus $1/[{\rm PAH}]$ for uncatalysed reaction and [Ru(III)]/k_C versus 1/[PAH] for catalysed reaction at the four different temperatures (Tables 3 and 4). For both the uncatalyzed and catalyzed reactions the activation parameters (Tables 3 and 4) for the rate determining step were calculated by using Eyring equation.^[16]

The copper(III) periodate complex is known to exist as a crystalline diamagnetic, and dsp² configuration with a square planar structure, and plane formed by one edge from each of the two periodate octahedral molecules. The water soluble copper(III) periodate complex was reported^[17] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in an aqueous alkaline medium and at a high pH range, as employed in the present study, periodate is unlikely to exist as HIO₆⁴⁻ (as present in the complex) as is evident from its involvement in the multiple equilibria^[18] (2)-(4) depending on the pH of the solution:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \tag{2}$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+$$
(3)

6 🕢 M. D. METI ET AL.

$$H_3IO_6^{2-} \rightleftharpoons H_2IO_6^{3-} + H^+ \tag{4}$$

Periodic acid exists as H_5IO_6 in an acid medium and as $H_4IO_6^-$ around pH 7.0. 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. 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), $[Cu(H_2IO_6)(H_3IO_6)]^2$, a conclusion is also supported by literature.^[19]

Mechanism for uncatalyzed reaction

On the basis of above all experimental results, a plausible reaction mechanism has been proposed which also explains all other experimental observations as shown in Scheme 1. Copper(III) periodate in alkaline medium into three forms as diperiodatocuprate(III)(DPC), monoperiodatocuprate(III) (MPC) and tetrahydroxo cuprate(III) have been proposed by.^[19] The latter one is ruled out as its equilibrium constant is 8.0×10^{-11} at 40 °C. Monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex, because in the present study, in view of the negative and less than unit order in periodate concentration. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III) periodate complexes are possible as in the following equations:

$$[Cu(H_{3}IO_{6})_{2}]^{-} + OH^{-} \rightleftharpoons [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2-} + H_{2}O \quad (5)$$

$$[Cu(H_2IO_6)(H_3IO_6)]^{2-} + 2H_2O \rightleftharpoons [Cu(H_2IO_6)(H_2O)_2] + [H_3IO_6^{2-}]$$
(6)

The inverse fractional order in $[IO_4]$ might also be due to this reason. In this study the less than unit order in PAH presumably results from formation of a complex (C_1) between the oxidant and PAH prior to the formation of the products. K_3 is the composite equilibrium constant comprising the equilibrium to bind PAH to MPC species to form a complex (C_1) . Then this complex (C_1) undergoes decomposition in a slow step to give 4-aminobenzoic acid, intermediof N^1, N^1 -diethylethane-1,2-diamine, Cu(II) ate and periodate. In a subsequent fast step this intermediate of N¹,N¹-diethylethane-1,2-diamine reacts with another molecule of MPC species and decomposes to give (E)-ethene-1,2-diamine with elimination of ethane as a by products. All these results were proposed in a detailed mechanistic Scheme 1 and are shown below.

Since Scheme 1 is in accordance with the generally wellaccepted 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. A free radical scavenging experiment revealed such a possibility. Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV-vis spectra of DPC $(5.0 \times 10^{-5} \text{ mol dm}^{-3})$, PAH $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$, [OH⁻] (0.1 mol dm⁻³) and a mixture of both in which a hypsochromic shift of 4 nm from 278 to 274 nm was observed in the spectra of DPC to mixture of DPC and PAH. Michaelis – Menten plot proved the complex formation between oxidant and substrate, which explains less than unit order in [PAH].

$$\begin{bmatrix} Cu(H_{3}IO_{6})_{2}\end{bmatrix}^{2} + OH^{2} \xrightarrow{K_{1}} [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2^{2}} + H_{2}O \\ [Cu(H_{2}IO_{6})(H_{3}IO_{6})]^{2^{2}} + 2H_{2}O \xrightarrow{K_{2}} [Cu(H_{2}IO_{6})(H_{2}O)_{2}] + [H_{3}IO_{6}]^{2^{2}} \\ \xrightarrow{(CH_{3})} CH_{3} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}] \xrightarrow{K_{3}} Complex (C_{1}) \\ \xrightarrow{(CH_{3})} H_{2} \xrightarrow{(CH_{3})} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}] \xrightarrow{(CH_{3})} CH_{3} \\ + [H_{2}IO_{6}^{3^{2}}] + Cu^{2^{4}} + H_{2}O \\ \xrightarrow{(CH_{3})} H_{2} \xrightarrow{(CH_{3})} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}] \xrightarrow{(H_{2})} H_{2} \xrightarrow{(CH_{3})} + [H_{2}IO_{6}^{3^{2}}] + Cu^{2^{4}} + H_{2}O \\ \xrightarrow{(CH_{3})} H_{2} \xrightarrow{(CH_{3})} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}] \xrightarrow{(H_{2})} \xrightarrow{(H_{2})} H_{2} \xrightarrow{(CH_{3})} + [Cu(H_{2}IO_{6})(H_{2}O)_{2}] \xrightarrow{(H_{2})} \xrightarrow{(H_{2})} H_{2} \xrightarrow{(H_{2})} \xrightarrow{(H_$$

$$+ 2C_2H_6 + [H_2IO_6^{3-}] + Cu^{2+} + 2OH$$

Scheme 1. Detailed Scheme for the oxidation of procainamide by alkaline diperiodatocuprate(III).

Scheme 1 leads to the rate law (7)

$$Rate = -\frac{d[DPC]}{[dt]} = \frac{k_1 K_1 K_2 K_3 [PAH] [Cu(H_3 IO_6)_2]^- [OH^-]}{[H_3 IO_6]^{2-} + K_1 [OH^-] [H_3 IO_6^{2-}] + K_1 K_2 (OH^-]} + K_1 K_2 K_3 [PAH] [OH^-]}$$
(7)
$$k_U = \frac{Rate}{DPC} = \frac{k_1 K_1 K_2 K_3 [PAH] [OH^-]}{[H_3 IO_6]^{2-} + K_1 [OH^-] [H_3 IO_6^{2-}] + K_1 K_2 [OH^-]} + K_1 K_2 K_3 [PAH] [OH^-]}$$
(8)

which explains all the observed kinetic orders of different species. The rate law (8) is rearranged into the following form, which is suitable for verification

$$\frac{1}{k_{\rm U}} = \frac{[{\rm H}_3 {\rm IO}_6^{2-}]}{k_1 K_1 K_2 K_3 [{\rm PAH}] [{\rm OH}^-]} + \frac{[{\rm H}_3 {\rm IO}_6^{2-}]}{k_1 K_2 K_3 [{\rm PAH}]} + \frac{1}{k_1 K_3 [{\rm PAH}]} + \frac{1}{k_1}$$

$$+ \frac{1}{k_1}$$
(9)

According to eq. (9), other conditions being constant, plots of $1/k_{\rm U}$ versus $1/[{\rm PAH}]$, $1/k_{\rm U}$ versus $1/[{\rm OH}^-]$ and $1/k_{\rm U}$ versus $[{\rm H}_3{\rm IO}_6^{2^-}]$ should be linear and are found to be so (Figure 3). The slopes and intercepts of such plots lead to the values of K_1 , K_2 , K_3 and k_1 (Table 3). The values of K_1 and K_2 are in good agreement with the literature.^[5] The equilibrium constant K_1 is far greater than K_2 which may be attributed to the greater tendency of DPC to undergo hydrolysis compared to the dissociation of hydrolyzed species in alkaline medium.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1 can be evaluated as follows. The [PAH], [OH⁻] and [H₃IO₆²⁻] (Table 1) were varied at four different temperatures. The plots of $1/k_{\rm U}$ versus 1/[PAH], $1/k_{\rm U}$ versus $1/[OH^-]$ and $1/k_{\rm U}$ versus $[H_3IO_6^{2-}]$ should be linear and are found to be so (Figure 3). From the slopes and intercepts, the values of K_1 , K_2 and K_3 were calculated at different temperatures (Table 3B). A van't Hoff plot was made for the variation of K_1 , K_2 and K_3 with temperature $(\log K_1 \text{ versus } 1/T, \log K_2 \text{ versus } 1/T \text{ and, } \log K_3 \text{ versus } 1/T).$ The values of enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in Table 3C. A comparison of the ΔH value (32 k J mol⁻¹) from K_1 of first step with that of ΔH^{\ddagger} (50 k J mol⁻¹) obtained for rate determining step shows that the reaction before the rate determining step is fairly fast as it involves low activation energy.^[20] A high negative values of ΔS^{\ddagger} (-115 J K⁻¹ mol⁻¹) suggests that intermediate complex (C_1) is more ordered than the reactants.^[21]

Mechanism for ruthenium(III) catalyzed reaction

Ruthenium(III) chloride acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium.^[22] In the present study it is quite probable that the $[Ru(H_2O)_5OH]^{2+}$ species might assume the general form $[Ru(III)(OH)_x]^{3-x}$. The x value is always less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination



Figure 3. Verification of rate law (13) for the oxidation of procainamide by diperiodatocuprate(III). Plots of (A): 1/ $k_{\rm U}$ versus 1/[PAH]; (B): 1/ $k_{\rm U}$ versus 1/[OH⁻], (C): 1/ $k_{\rm U}$ versus [H₃IO₆]²⁻, at four different temperatures (conditions as in Table 1).

sphere would be filled by water molecules. Hence, under the conditions employed, e.g., $[OH^-] \gg [Ru(III)]$, ruthenium(III) is mostly present^[23] as hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$.

In the present study, in view of the negative less than unit order of periodateon the rate of reaction, monoperiodatocuprate(III) MPC is considered to be the active species of copper(III) periodate complex. The results of increase in the rate with increase in alkali concentration and decrease in the rate with increase in periodate concentration suggest that equilibria of different copper(III)



Scheme 2. Detailed Scheme for ruthenium(III) catalysed oxidation of procainamide by alkaline diperiodatocuprate(III).

periodatecomplexes are possible as already shown in Equations (9) and (10).

The ruthenium(III) species then reacts with procainamide to give a complex C_2 , Then this complex (C_2) which further reacts with one mole of MPC in a slow step to give 4-aminobenzoic acid, intermediate of N¹,N¹-diethylethane-1,2diamine, Cu(II) and periodate with regeneration of catalyst, ruthenium(III).In a subsequent fast step this intermediate of N¹,N¹-diethylethane-1,2-diamine reacts with another molecule of MPC species and decomposes to give (E)-ethene-1,2-diamine with elimination of ethane as a by products.All these results were proposed in a detailed mechanistic Scheme 2 as shown below.

Spectroscopic evidence for the complex formation between Ru(III) and PAH was obtained from UV-vis spectra of [PAH] $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$, [Ru(III)] $(8.0 \times 10^{-6} \text{ mol dm}^{-3})$, [OH⁻] $(0.1 \text{ mol dm}^{-3})$ and a mixture of both in which a hypsochromic shift of 5 nm from 273 to 278 nm was observed in the spectra of Ru(III) to mixture of Ru(III) and PAH. Michaelis – Menten plot proved the complex formation between a catalyst and substrate, which explains less than unit order in [PAH].

From Scheme 2, the rate law (10) can be derived.

$$Rate = \frac{-d[DPC]}{[dt]}$$

= $\frac{k_2 K_1 K_2 K_3 [PAH] [Cu(H_3 IO_6)_2]^- [OH^-] [Ru(III)]}{[H_3 IO_6^{2-}] + K_1 [OH^-] [H_3 IO_6^{2-}] + K_1 K_2 [OH^-] + K_1 K_2 K_3 [PAH] [OH^-]}$ (10)

$$k_{\rm C} = \frac{\text{Rate}}{\text{DPC}} = k_{\rm C} = k_{\rm T} - k_{\rm U}$$

=
$$\frac{k_2 K_1 K_2 K_3 [\text{PAH}] [\text{Ru}(\text{III})] [\text{OH}^-]}{[\text{H}_3 \text{IO}_6^{-1}] + K_1 K_2 [\text{OH}^-] + K_1 K_2 K_3 [\text{PAH}] [\text{OH}^-]}$$
(11)

Equation (11) can be rearranged to the following form (12) and is used for verification.

$$\frac{[\mathrm{Ru}(\mathrm{III})]}{k_{\mathrm{C}}} = \frac{[\mathrm{H}_{3}\mathrm{IO}_{6}^{2-}]}{k_{2}K_{1}K_{2}K_{3}[\mathrm{PAH}][\mathrm{OH}^{-}]} + \frac{[\mathrm{H}_{3}\mathrm{IO}_{6}^{2-}]}{k_{2}K_{2}K_{3}[\mathrm{PAH}]} + \frac{[\mathrm{H}_{3}\mathrm{IO}_{6}^{2-}]}{k_{2}K_{3}[\mathrm{PAH}]} + \frac{1}{k_{2}}$$
(12)

According to equation (12), other conditions being constant, plots of $[Ru(III)]/k_C$ versus 1/[PAH], $[Ru(III)]/k_C$ versus $1/[OH^-]$ and $[Ru(III)]/k_C$ versus $[H_3IO_6]^{2-}$ should be linear and are found to be so (Figure 4). The slopes and intercepts of such plots lead to the values of K_1 , K_2 , K_3 and k_2 (Table 4).

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The [PAH], [OH⁻] and $[H_3IO_6^{2^-}]$ (Table 2) were varied at four different temperatures. The plots of $[Ru(III)]/k_C$ versus 1/ [PAH], $[Ru(III)]/k_C$ versus 1/[OH⁻], $[Ru(III)]/k_C$ versus [H₃IO₆²⁻] should be linear and are found to be so (Figure 4). From the slopes and intercepts, the values of K_1K_2 and K_3 were calculated at different temperatures (Table 4B). van't Hoff plot was made for the variation of K_1 , K_2 and K_3 with temperatures (log K_1 versus 1/T, log K_2 versus 1/T and log K_3



Figure 4. Verification of rate law (16) for the Ru(III) catalyzed oxidation of procainamide by diperiodatocuprate(III). Plots of (A): [Ru(III)]/ $k_{\rm C}$ versus 1/[PAH], (B): [Ru(III)]/ $k_{\rm C}$ versus 1/[OH⁻], (C): [Ru(III)]/ $k_{\rm C}$ versus [H₃IO₆]²⁻, at four different temperatures (Conditions as in Table2).

versus 1/*T*). The values of enthalpy of reaction ΔH , entropy of reaction ΔS and free energy of reaction ΔG were calculated for the first, second and third equilibrium steps. These values are given in Table 4C. The negative values of ΔS^{\ddagger} (-61 JK⁻¹ mol⁻¹) suggests that the intermediate complex (C₂) is more ordered than the reactants.^[21] The observed modest enthalpy of activation and higher rate constants for the slow step indicate that the oxidation presumably occurred via an inner sphere mechanism. This conclusion is supported by literature.^[24,25] The activation parameters evaluated for the catalysed and uncatalysed reactions explain the catalytic effect on the reaction. The catalyst Ru(III) forms the complex (C_2) with substrate, which enhances the reducing property of substrate than that without catalyst. Further, the catalyst Ru(III) modifies the reaction path by lowering energy of activation. It is also interesting to note that the transient species involved in both uncatalysed and Ru(III) catalysed reactions is different but leads to formation of same products.

The decrease in the rate, with increasing ionic strength, is contrary to a reaction between neutral and charged species of reactants, as presented in Schemes 1 and 2. This might be due to the presence of different ions and use of high ionic strength in the reaction medium. The effect of solvent on the reaction rate has been described in detail in the literature.^[20] For the limiting case of a zero angle approach between two dipoles or anion-dipole system^[20], has shown that a plot of log $k_{\rm U}$ or $k_{\rm C}$ versus 1/D gives a straight line, with a negative slope for a reaction between a negative ion and a dipole or two dipoles, and with a positive slope for positive ion and dipole interaction. In the present study, the plot observed had a negative slope as shown in (Figures S8 and S9, which supports the involvement of negative ions as given in Scheme 1 and 2.

The catalyst ruthenium(III) forms the complex with PAH, which shows a greater reducing property than PAH itself. Hence, the catalyst, Ru(III), lowers the energy, i.e., it provides an alternative pathway with lower activation parameters for the reaction. The difference in the activation energies evaluated for the catalyzed ($E_a = 35 \text{ kJ mol}^{-1}$) and uncatalyzed ($E_a = 52 \text{ kJ mol}^{-1}$) reaction explains the catalytic effect on the reaction.

Conclusions

A comparative study of uncatalysed and ruthenium(III) catalysed oxidation of PAH by DPC in alkaline medium has been studied. The active species of Ru(III) is found to be $[Ru(H_2O)_5OH]^{2+}$. The reaction rates are about five - fold faster than the uncatalysed reaction. It becomes apparent that, in carrying out this reaction, the role of reaction medium is crucial. Activation parameters were evaluated for both catalysed and uncatalysed reactions. The overall sequence described here is consistent with all experimental conditions including the product, spectral, mechanistic and kinetic studies.

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