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Os(VIII)/Ru(III) catalysed oxidation of aspirin drug by a new oxidant, diperiodatoargentate(III) in aqueous alkaline medium: A comparative kinetic study

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Abstract

The kinetics of Os(VIII) and Ru(III) catalysed oxidation of anti-pyretic drug, aspirin by diperiodatoargentate(III) (DPA) in alkaline medium at 298 K and a constant ionic strength of 0.10 mol dm^{-3} was studied spectrophotometrically. The oxidation products in both the cases are 1,4-benzoquinone2-carboxylate ion and Ag(I). The stoichiometry is the same in both the catalysed reactions i.e., [aspirin]:[DPA] = 1:2. The reaction is of first order in Os(VIII)/Ru(III) and [DPA] and has less than unit order in both [ASP] and [alkali]. The oxidation reaction in alkaline medium has been shown to proceed via a Os(VIII)/Ru(III)–aspirin complex, which further reacts with one molecule of DPA in a rate determining step followed by other fast steps to give the products. The main products were identified by spot test, IR, NMR and GC–MS. The reaction constants involved in the different steps of the mechanism are calculated. The catalytic constant (K_c) was also calculated for both catalysed reactions at different temperatures. From the plots of log K_c versus 1/T, values of activation parameters with respect to the catalyst have been evaluated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also determined. It has been observed that the catalytic efficiency for the present reaction is in the order of Os(VIII) > Ru(III). The probable active species of catalyst and oxidant have been identified.
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Keywords: Aspirin; Os(VIII) catalysis; Ru(III) catalysis; Diperiodatoargentate(III); Oxidation; Kinetics

1. Introduction

Aspirin (acetylsalicylic acid) (ASP) is a non-steroidal analgesic, anti-inflammatory and anti-pyretic agent. It is used in acute conditions such as headache, arthralgia, myalgia and other cases requiring mild analgesia. Aspirin is widely studied in medicine and several methods are suggested in literature for its determination [1].

Diperiodatoargentate(III) (DPA) is a powerful oxidizing agent in alkaline medium with the reduction potential [2.a] 1.74 V. It is widely used as a volumetric reagent for the determination of various organic and inorganic species [3]. Jayaprakash Rao et al. [4] have used DPA as an oxidizing agent for the kinetics of oxidation of various organic substrates. They normally found that order with respect to both oxidant and substrate was unity and [OH$^-$] was found to enhance the rate of reaction. It was also observed that they did not arrive the possible active species of DPA in alkali and on the other hand they proposed mechanisms by generalizing the DPA as $[Ag(HL)L]^{(x+1)-}$. However, Kumar et al. [5] put an effort to give an evidence for the reactive form of DPA in the large scale of alkaline pH. In the present investigation, we have obtained the evidence for the reactive species for DPA in alkaline medium.

In recent years, the use of transition metal ions such as osmium, ruthenium and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest [6]. The role of osmium (VIII) as a catalyst in some redox reactions has been reviewed [7]. Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and experimental conditions, it has been

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shown [8] that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. osmium(VIII) and ruthenium(III) catalysis in redox reactions involves several complexes, different oxidation states of osmium/ruthenium, etc. The uncatalysed reaction of oxidation of aspirin by DPA has been studied [9]. We have observed that osmium(VIII) and ruthenium(III) catalyse the oxidation of aspirin by DPA in alkaline medium in micro amounts. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanism, the title reaction is investigated in detail.

2. Experimental

2.1. Materials and reagents

All chemicals used were of reagent grade and double distilled water was used throughout the work. A solution of aspirin (M/s. S.S. Antibiotics Pvt. Ltd.,) was prepared by dissolving an appropriate amount of recrystallised sample in double distilled water. The purity of ASP sample was checked by comparing its IR spectrum with literature data and with its m.p.136 °C. The required concentration of ASP was used from its aqueous stock solution. The osmium (VIII) solution was prepared by dissolving OsO_4 (VIII) oxide (Johnson Matthey) in 0.50 mol dm^{-3} in NaOH. The concentration was ascertained [10] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce(IV) solution in an acidic medium. A standard stock solution of Ru(III) was prepared by dissolving $RuCl_3$ (S.D. Fine Chemicals) in 0.20 mol dm^{-3} HCl. The concentration was determined [11] by EDTA titration. KNO_3 and KOH (BDH) were used to maintain ionic strength and alkalinity of the reaction, respectively. Aqueous solution of $AgNO_3$ was used to study the product effect, Ag(I). A stock standard solution of IO_4^- was prepared by dissolving a known weight of KIO_4 (Riedel-de Haen) in hot water and used after keeping for 24 h. Its concentration was ascertained iodomettrically [12] at neutral pH maintained using phosphate buffer. The temperature was maintained constant to within ± 0.10 °C.

2.2. Preparation of DPA

DPA was prepared by oxidizing Ag(I) in presence of KIO_4 as described elsewhere [13]: the mixture of 28 g of KOH and 23 g of KIO_3 in 100 cm^3 of water along with 8.5 g $AgNO_3$ was heated just to boiling and 20 g of $K_2S_2O_8$ was added in several lots with stirring then allowed to cool. It was filtered through a medium porosity fritted glass filter and 40 g of NaOH was added slowly to the filtrate, whereupon a voluminous orange precipitate agglomerates. The precipitate is filtered as above and washed three to four times with cold water. The pure crystals were dissolved in 50 cm^3 water and warmed to 80 °C with constant stirring thereby some solid was dissolved to give a red solution. The resulting solution was filtered when it was hot and on cooling at room temperature, the orange crystals separated out and were recrystallised from water.

The complex was characterized from its U.V. spectrum, exhibited three peaks at 216, 255 and 362 nm. These spectral features were identical to those reported earlier for DPA [13]. The magnetic moment study revealed that the complex is diamagnetic. The compound prepared was analysed [14] for silver and periodate by acidifying a solution of the material with HCl, recovering and weighing the AgCl for Ag and titrating the iodine liberated when excess KI was added to the filtrate for IO_4^-. The aqueous solution of DPA was used for the required [DPA] in the reaction mixture. During the kinetics a constant concentration viz. 1×10^{-4} mol dm^{-3} of KIO_4 was used throughout the study unless otherwise stated. Thus, the possibility of oxidation of ASP by periodate was tested and found that there was no significant interference due to KIO_4 under experimental condition. Precaution was also taken to avoid the dissolution of O_2 and CO_2 in the solution by maintaining inert atmosphere with N_2 throughout the study.

2.3. Kinetic measurements

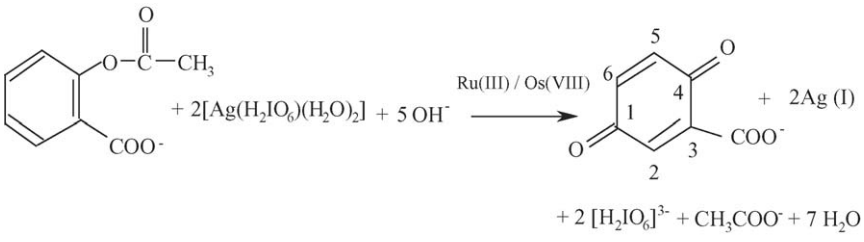
The kinetic measurements were performed on a Varian CARY 50 Bio UV–vis spectrophotometer. The kinetics was followed under pseudo first order condition where [ASP] > [DPA] at 25 ± 0.1 °C, unless specified. The reaction was initiated by mixing the DPA to ASP solution which also contained required concentration of KNO_3, KOH, catalyst (Ru(III) or Os(VIII)) and KIO_4. The progress of reaction was followed spectrophotometrically at 360 nm by monitoring decrease in absorbance due to DPA with the molar absorbancy index, 'ε' to be 13900 ± 100 dm^3 mol^{-1} cm^{-1}. 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 85% completion of reaction. The orders for various species were determined from the slopes of plots of log k_{obs} versus respective concentration of species except for [DPA] in which non variation of 'k_{obs}' 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

3.1. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of DPA to aspirin in presence constant amount of OH^-, KNO_3 and catalyst, were kept for 3 h in closed vessel under nitrogen atmosphere. The remaining concentration of DPA was estimated by spectrophotometrically at 415 nm. The results indicate that 1:2 stoichiometry for both the catalysts as given in Eq. (1).



(1)

The main reaction products were eluted with ether, which is identified as 1,4-benzoquinone2-carboxylate ion by spot test [15]. The nature of 1,4-benzoquinone2-carboxylate ion was confirmed by its IR spectrum which showed a C=O stretching at 1631 cm^{-1} indicating the presence of C=O group at 1,4-benzoquinone moiety, the band at 1580 cm^{-1} and also at 1362 cm^{-1} indicating the presence of COO^- group. The product was also characterized by NMR spectra ($CDCl_3$, δ ppm) chemical shift at 6.73 (s, 1H, C_2-H), 6.80 (s, 1H, C_5-H) 7.28 (s, 1H, C_6-H). It was further confirmed by its melting point 206 °C (lit. m.p. 205–207 °C). Further, 1,4-benzoquinone2-carboxylate ion was subjected to GC–mass spectral analysis. GC–MS data was obtained on a 17 A Shimadzu gas chromatograph with a QP-5050A shimadzu mass spectrometer using the EI ionization technique. The mass spectrum showed a molecular ion peak at 152 amu confirming 1,4-benzoquinone2-carboxylate ion. All other peaks observed in GC–MS can be interpreted in accordance with the observed structure of the product (Fig. 1). Potassium acetate was confirmed by spot test [16]. The formation of free Ag+ in solution was detected by adding KCl solution to the reaction mixture, which produced white turbidity due to the formation of AgCl. It was observed that 1,4-benzoquinone2-carboxylate ion does not undergo further oxidation under the present kinetic conditions for both the catalysts.

3.2. Reaction orders

As the diperiodatoargentate(III) oxidation of aspirin in alkaline medium proceeds with a measurable rate in the absence of Os(VIII) and Ru(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence, the reaction orders have been determined from the slopes of log k_C versus log(concentration) plots by varying the concentrations of aspirin, IO_4^-, OH^- and catalysts (Ru(III) and Os(VIII)), in turn, while keeping others constant. The DPA concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} and the linearity of the plots of log(absorbance) versus time up to 85% completion of the reaction indicates a reaction order of unity in [DPA]. This is also confirmed by varying of [DPA], which did not result in any change in the pseudo first order rate constants, k_C (Table 1 Ru(III)) (Table 2 Os(VIII)). The aspirin concentration was varied in the range 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3} at 25 °C while keeping other reactant concentrations and conditions constant for both the catalysts. The k_C values increased with the increase in concentration of aspirin indicating an apparent less than unit order dependence on [ASP] (Tables 1 and 2). The effect of alkali on the reaction has been studied in the range of 0.01–0.10 mol dm^{-3} at constant concentrations of aspirin, DPA, catalyst and a constant ionic strength of 0.10 mol dm^{-3}. The rate constants increased with increasing [alkali] and the order was found to be less than unity (Table 1 Ru(III)) (Table 2 Os (VIII)) in both the cases.

3.3. Effect of [periodate]

Periodate was varied from 0.5×10^{-5} to 5.0×10^{-5} at constant [DPA], [ASP], [catalyst] and ionic strength. It was observed that the rate constants decreased by increasing

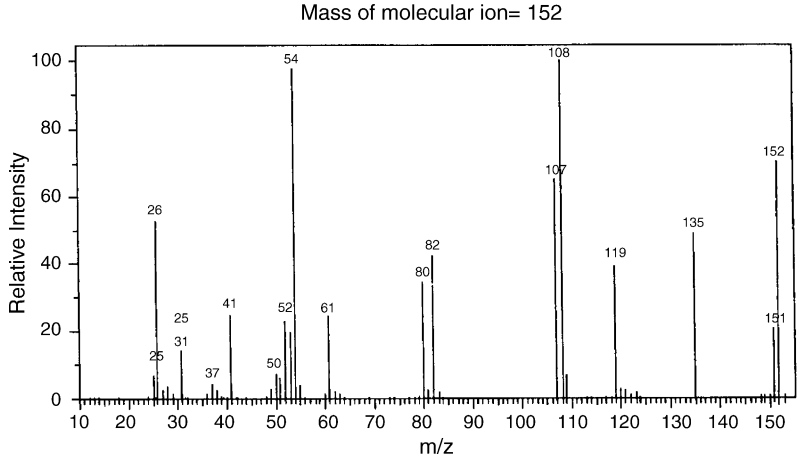


Fig. 1. GC–mass spectrum of 1,4-benzoquinone2-carboxylate ion with its molecular ion peak at 152 amu.

Table 1
Effect of [DPA], [ASP], [OH^-] and [IO_4^-] on the ruthenium(III) catalysed oxidation of aspirin by DPA(III) in alkaline medium at 25 °C, $I = 0.10\ mol\ dm^{-3}$

$[DPA] \times 10^5$ ($mol\ dm^{-3}$)	$[ASP] \times 10^4$ ($mol\ dm^{-3}$)	[OH^-] ($mol\ dm^{-3}$)	$[IO_4] \times 10^5$ ($mol\ dm^{-3}$)	10^6 [Ru(III)] ($mol\ dm^{-3}$)	$10^3\ k_T$ (s^{-1})	$10^4\ k_U$ (s^{-1})	$k_C \times 10^3$ (s^{-1})	
							Found	Calculated
1.0	3.0	0.05	1.0	5.0	1.81	6.25	1.21	1.21
3.0	3.0	0.05	1.0	5.0	1.84	6.14	1.19	1.21
5.0	3.0	0.05	1.0	5.0	1.85	6.24	1.22	1.21
8.0	3.0	0.05	1.0	5.0	1.83	6.24	1.20	1.21
10	3.0	0.05	1.0	5.0	1.83	6.28	1.20	1.21
3.0	1.0	0.05	1.0	5.0	1.09	6.01	0.49	0.51
3.0	3.0	0.05	1.0	5.0	1.81	6.14	1.19	1.21
3.0	5.0	0.05	1.0	5.0	2.25	6.48	1.61	1.66
3.0	8.0	0.05	1.0	5.0	2.72	7.08	2.02	2.11
3.0	10	0.05	1.0	5.0	2.98	7.65	2.20	2.32
3.0	3.0	0.01	1.0	5.0	1.19	5.87	0.60	0.60
3.0	3.0	0.03	1.0	5.0	1.61	6.09	1.00	1.03
3.0	3.0	0.05	1.0	5.0	1.81	6.14	1.19	1.21
3.0	3.0	0.08	1.0	5.0	2.01	6.85	1.32	1.31
3.0	3.0	0.10	1.0	5.0	2.18	7.24	1.46	1.38
3.0	3.0	0.05	0.5	5.0	2.15	7.65	1.38	1.39
3.0	3.0	0.05	0.8	5.0	2.00	6.97	1.30	1.27
3.0	3.0	0.05	1.0	5.0	1.81	6.14	1.19	1.21
3.0	3.0	0.05	3.0	5.0	1.40	6.07	0.80	0.79
3.0	3.0	0.05	5.0	5.0	1.19	6.01	0.59	0.59
3.0	3.0	0.05	1.0	1.0	0.82	6.14	0.20	0.19
3.0	3.0	0.05	1.0	3.0	1.32	6.14	0.71	0.72
3.0	3.0	0.05	1.0	5.0	1.81	6.14	1.19	1.21
3.0	3.0	0.05	1.0	8.0	2.49	6.14	1.88	1.86
3.0	3.0	0.05	1.0	10	3.02	6.14	2.40	2.43

Table 2
Effect of [DPA], [ASP], [OH^-] and [IO_4^-] on the osmium (VIII) catalysed oxidation of aspirin by DPA(III) in alkaline medium at 25 °C, $I = 0.10\ mol\ dm^{-3}$

$[DPA] \times 10^5$ ($mol\ dm^{-3}$)	$[ASP] \times 10^4$ ($mol\ dm^{-3}$)	[OH^-] ($mol\ dm^{-3}$)	$[IO_4] \times 10^5$ ($mol\ dm^{-3}$)	10^6 [Os(VIII)] ($mol\ dm^{-3}$)	$10^3\ k_T$ (s^{-1})	$10^4\ k_U$ (s^{-1})	$k_C \times 10^3$ (s^{-1})	
							Found	Calculated
1.0	3.0	0.05	1.0	5.0	2.11	6.25	1.49	1.49
3.0	3.0	0.05	1.0	5.0	2.11	6.14	1.50	1.49
5.0	3.0	0.05	1.0	5.0	2.21	6.24	1.58	1.49
8.0	3.0	0.05	1.0	5.0	2.18	6.24	1.50	1.49
10	3.0	0.05	1.0	5.0	2.10	6.28	1.48	1.49
3.0	1.0	0.05	1.0	5.0	1.24	6.01	0.64	0.64
3.0	3.0	0.05	1.0	5.0	2.11	6.14	1.50	1.49
3.0	5.0	0.05	1.0	5.0	2.65	6.48	2.00	2.03
3.0	8.0	0.05	1.0	5.0	3.21	7.08	2.51	2.54
3.0	10	0.05	1.0	5.0	3.61	7.65	2.85	2.78
3.0	3.0	0.01	1.0	5.0	1.40	5.87	0.83	0.83
3.0	3.0	0.03	1.0	5.0	1.89	6.09	1.30	1.31
3.0	3.0	0.05	1.0	5.0	2.11	6.14	1.50	1.49
3.0	3.0	0.08	1.0	5.0	2.25	6.85	1.60	1.61
3.0	3.0	0.10	1.0	5.0	2.34	7.24	1.67	1.65
3.0	3.0	0.05	0.5	5.0	2.42	7.65	1.65	1.66
3.0	3.0	0.05	0.8	5.0	2.25	6.97	1.55	1.55
3.0	3.0	0.05	1.0	5.0	2.11	6.14	1.50	1.49
3.0	3.0	0.05	3.0	5.0	1.66	6.07	1.05	1.05
3.0	3.0	0.05	5.0	5.0	1.42	6.01	0.82	0.82
3.0	3.0	0.05	1.0	1.0	0.94	6.14	0.32	0.31
3.0	3.0	0.05	1.0	3.0	1.54	6.14	0.93	0.92
3.0	3.0	0.05	1.0	5.0	2.11	6.14	1.50	1.49
3.0	3.0	0.05	1.0	8.0	3.24	6.14	2.63	2.61
3.0	3.0	0.05	1.0	10	3.96	6.14	3.30	3.34

$[IO_4^-]$ (Table 1 Ru(III)) (Table 2 Os (VIII)) in both the cases.

3.4. Effect of added products

Initially added products, Ag(I), potassium acetate and 1,4-benzoquinone2-carboxylate ion did not have any significant effect on the rate of reaction (for both catalysts).

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

The addition of KNO_3, to increase the ionic strength of the reaction, increased the rate of reaction at constant [DPA], [ASP], $[OH^-]$ $[IO_4^-]$ and [catalyst]; the plot of $\log k_{obs}$ versus $\sqrt{I}$ was found to be linear with positive slope for Ru(III) and Os(VIII) catalysis (Fig. 2).

Dielectric constant of the medium, '*D*' was varied by varying the *t*-butyl alcohol and water percentage. The decrease in dielectric constant of the reaction medium, increases the rate and the plot of $\log k_C$ versus $1/D$ was linear with positive slope for Ru(III) and Os(VIII) catalysis (Fig. 2).

3.6. Effect of temperature (T)

The influence of temperature on the rate of reaction was studied at 25, 30, 35 and 40 °C. The rate constants, (k), of the slow step of Scheme 1 were obtained from the Slopes and the intercept of the plots of [catalyst]/k_C versus 1/[ASP], [catalyst]/k_C versus 1/[OH] and [catalyst]/k_C versus $[H_3IO_6^{2-}]$ plots at four different temperatures. The values are given in Tables 3 and 4. 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 Tables 3 and 4.

3.7. Test for free radicals (polymerization study)

The intervention of free radicals was examined as follows, the reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1 h. Upon diluting the reaction mixture with methanol, no precipitate resulted, suggesting there is no participation of free radicals in the reaction for both Ru(III)/Os(VIII) catalysis.

3.8. Effect of [Ru(III)] and [Os(VIII)]

The [Ru(III)] and [Os(VIII)] concentrations was varied from 1.0×10^{-6} to 1.0×10^{-5} mol dm^{-3} range, at constant concentration of diperiodatoargentate(III), aspirin, alkali and ionic strength. The order in [Ru(III)] and [Os(VIII)] was found to be unity from the linearity of the plots of $\log k_C$ versus log[Ru(III)] and $\log k_C$ versus log[Os(VIII)].

3.9. Catalytic activity

It has been pointed out by Moelwyn-Hughes [17] that in presence of the catalyst, the uncatalysed and catalysed reactions

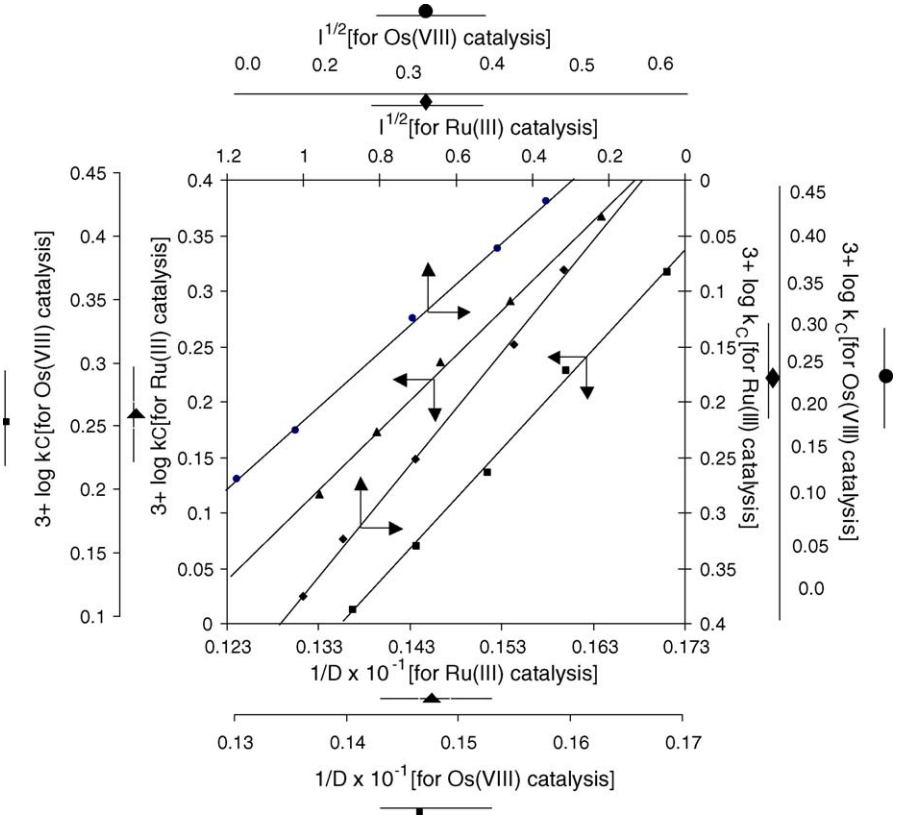


Fig. 2. Effect of ionic strength and dielectric constant of the medium on Os(VIII) and Ru(III) catalysed oxidation of aspirin by diperiodatoargentate(III) at 25 °C.

Table 3
Thermodynamic activation parameters for the Ru(III) catalysed oxidation of aspirin by DPA in alkaline medium with respect to the slow step of Scheme 1: (A) effect of temperature, (B) activation parameters (Scheme 1), (C) effect of temperature to calculate K_1, K_2 and K_3 for the oxidation of Aspirin by diperiodatoargentate(III) in alkaline medium, (D) thermodynamic quantities using K_1, K_2 and K_3

Temperature (K)	$10^{-2}\ k$ (dm^3 mol^{-1} s^{-1})
(A)	
298	7.62
303	7.92
308	8.21
313	8.46

Parameters	Values
(B)	
E_a (kJ mol^{-1})	5.2 ± 0.2
$\Delta H^{\#}$ (kJ mol^{-1})	3.0 ± 0.2
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−180 ± 12
$\Delta G^{\#}$ (kJ mol^{-1})	57 ± 2.0
log A	3.8 ± 0.2

Temperature (K)	K_1 (dm^3 mol^{-1})	$K_2 \times 10^4$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
(C)			
298	0.45 ± 0.01	7.29 ± 0.40	2.50 ± 0.08
303	0.65 ± 0.03	6.83 ± 0.30	3.68 ± 0.10
308	0.85 ± 0.04	5.53 ± 0.16	5.44 ± 0.20
313	1.14 ± 0.05	4.33 ± 0.20	8.40 ± 0.30

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
(D)			
ΔH (k J mol^{-1})	46.8 ± 2.0	−27.5 ± 0.8	62.3 ± 2.0
ΔS (J K^{-1} mol^{-1})	151 ± 8	−152 ± 10	274 ± 15
ΔG_{298} (k J mol^{-1})	1.9 ± 0.1	17.9 ± 0.9	−19.5 ± 0.4

[DPA] = 3.0×10^{-5}; [ASP] = 3.0×10^{-4}; [OH$^-$] = 0.05; [Ru(III)] = 5.0×10^{-6} mol dm^{-3}; [IO_4] = 1.0×10^{-5} mol dm^{-3}.

proceed simultaneously, so that

$$k_T = k_U - K_c[\text{catalyst}]^x \quad (2)$$

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)] or [Os(VIII)]. In the present investigations; x values for the standard run were found to be unity for Ru(III) and Os(VIII). Then the value of K_c is calculated using the equation,

$$K_c = \frac{k_T - k_U}{[\text{catalyst}]^x} = \frac{k_C}{[\text{catalyst}]^x} \quad (\text{where, } k_T - k_U = k_C) \quad (3)$$

The values of K_c were evaluated for both the catalysts 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 of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 5. The value of K_c for Ru(III) is 2.4×10^2 and Os(VIII) is 3.0×10^2 at 298 K. The values of K_c indicate that Os(VIII) is most efficient catalyst compared to Ru(III) in the oxidation of aspirin by DPA in alkaline medium.

4. Discussion

In the later period of 20th century the kinetics of oxidation of various organic and inorganic substrates have been studied by Ag(III) species which may be due to its strong versatile nature of two electrons oxidant. Among the various species of Ag(III), $Ag(OH)_4^-$, diperiodatoargentate(III) and ethylenebis (biguanide), (EBS), silver(III) are of maximum attention to the researchers due to their relative stability [18]. The stability of $Ag(OH)_4^-$ is very sensitive towards traces of dissolved oxygen and other impurities in the reaction medium whereupon it had not drawn much attention. However, the other two forms of Ag(III) [4,5,19] are considerably stable; the DPA is used in highly alkaline medium and EBS is used in highly acidic medium.

The literature survey [13] reveals that the water soluble diperiodatoargentate(III) (DPA) has a formula $[Ag(IO_6)_2]^{7-}$ with dsp^2 configuration of square planar structure, similar to diperiodatocopper(III) complex with two bidentate ligands, periodate to form a planar molecule. When the same molecule is used in alkaline medium, it is unlike to be existed as $[Ag(IO_6)_2]^{7-}$ as periodate is known to be in various protonated forms [20] depending on pH of the solution as given in following multiple equilibria (4)–(6).

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

Table 4
Thermodynamic activation parameters for the osmium(VIII) catalysed oxidation of Aspirin by DPA in aqueous alkaline medium with respect to the slow step of Scheme 1: (A) Effect of temperature, (B) activation parameters (Scheme 1), (C) effect of temperature to calculate K_1, K_2 and K_3 for the Os(VIII) catalysed Oxidation of aspirin by diperiodatoargentate(III) in alkaline medium, (D) thermodynamic quantities using K_1, K_2 and K_3

Temperature (K)	10^{-2} k (dm^3 mol^{-1} s^{-1})
(A)	
298	8.84
303	9.13
308	9.35
313	9.68

Parameters	Values
(B)	
E_a (kJ mol^{-1})	4.6 ± 0.2
$\Delta H^{\#}$ (kJ mol^{-1})	2.1 ± 0.05
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−181 ± 9.0
$\Delta G^{\#}$ (kJ mol^{-1})	56 ± 3.4
log A	3.7 ± 0.1

Temperature (K)	K_1 (dm^3 mol^{-1})	$K_2 \times 10^4$ (mol dm^{-3})	$K_3 \times 10^{-3}$ (dm^3 mol^{-1})
(C)			
298	0.58 ± 0.02	7.79 ± 0.40	2.46 ± 0.08
303	0.92 ± 0.01	6.25 ± 0.30	3.65 ± 0.10
308	1.23 ± 0.04	5.22 ± 0.16	5.20 ± 0.20
313	2.05 ± 0.08	3.83 ± 0.20	7.41 ± 0.30

Thermodynamic quantities	Values from K_1	Values from K_2	Values from K_3
(D)			
ΔH (kJ mol^{-1})	62.8 ± 2	−35.8 ± 0.8	56.8 ± 2.0
ΔS (J K^{-1} mol^{-1})	206 ± 8	−180 ± 10	255 ± 15
ΔG_{298} (kJ mol^{-1})	1.3 ± 0.1	17.7 ± 0.9	−19.4 ± 0.4

[DPA] = 3.0×10^{-5}; [ASP] = 3.0×10^{-4}; [OH$^-$] = 0.05; [Os(VIII)] = 5.0×10^{-6} mol dm^{-3}; [IO_4] = 1.0×10^{-5} mol dm^{-3}.

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

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

Periodic acid (H_5IO_6) exists in acid medium and also as $H_4IO^-_6$ at pH 7. Thus, under the present alkaline conditions, the main species are expected to be $H_3IO_6^{2-}$and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise [2.b]. On contrary, the authors [4] in their recent past studies have proposed the DPA as $[Ag(HL)_2]^{x-}$ in which '*L*' is a periodate with uncertain number of protons and 'HL' is a protonated periodate of uncertain number of protons. This can be ruled out by considering the alternative form [20] of IO_4^- at pH > 7 which is in the form $H_3IO_6^{2-}$ or $H_2IO_6^{3-}$. Hence, DPA could be as $[Ag(H_3IO_6)_2]^-$ or $[Ag(H_2IO_6)_2]^{3-}$ in alkaline medium. Therefore, under the present condition, diperiodatoargentate(III), may be depicted as $[Ag(H_3IO_6)_2]^-$. The similar speciation of periodate in alkali was proposed [21] for diperiodatonickelate(IV).

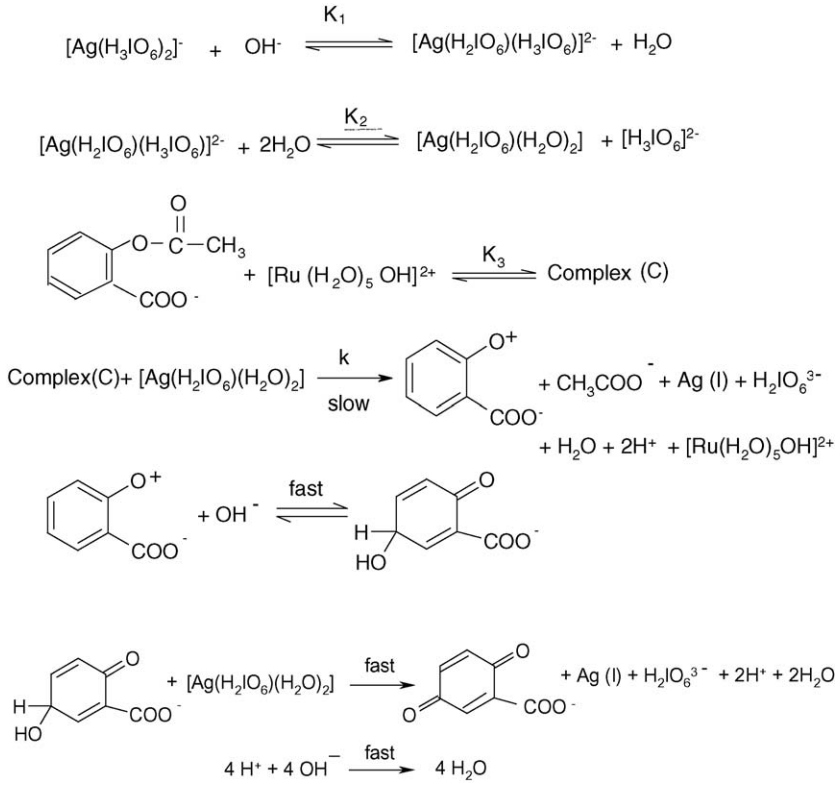
4.1. Ru(III) catalysis

It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies [22] have confirmed hat ruthenium chloride exists in hydrated form as $[Ru(H_2O)_5OH]^{2+}$. In the present study, it is quite probable

Table 5
Values of catalytic constant (K_c) at different temperatures and activation parameters calculated using K_c values

Temperature (K)	$10^{-2}K_c$ Ru(III)	$10^{-2}K_c$ Os(VIII)
298	2.38	3.00
303	3.30	4.10
308	4.28	5.22
313	5.16	6.28
E_a (kJ mol^{-1})	40.1	38.14
$\Delta H^{\#}$ (kJ mol^{-1})	37.6	35.7
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−73	−77
$\Delta G^{\#}$ (kJ mol^{-1})	59	58
log A	9.3	9.1

[DPA] = 3.0×10^{-5}; [ASP] = 3.0×10^{-4}; [OH$^-$] = 0.05 mol dm^{-3}; [IO_4] = 1.0×10^{-5} mol dm^{-3}; [Os(VIII)] = 5.0×10^{-6} mol dm^{-3}; [Ru(III)] = 5.0×10^{-6} mol dm^{-3}.



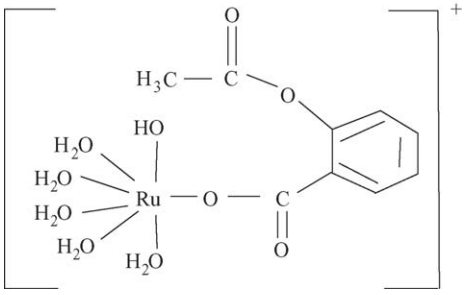
Scheme 1. Detailed scheme for the Ru(III) catalysed oxidation of aspirin by alkaline diperiodatoargentate(III).

that the $[Ru(III)(OH)_x]^{3-x}$, the x-value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, e.g., $[OH^-] \gg [Ru(III)]$, ruthenium(III) is mostly present as the hydroxylated species, $[Ru(H_2O)_5OH]^{2+}$ [23].

Since, the reaction was enhanced by $[OH^-]$, added periodate retarded the rate and first order dependency in [DPA] and catalyst (either Ru(III) or Os(VIII)) and fractional order in [ASP] and $[OH^-]$, the following Scheme 1 has been proposed by considering its ASP as anionic form of ASP in alkaline medium which also explains all other experimental observations.

In the prior equilibrium step 1, the $[OH^-]$ deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 1). It may be expected that lower Ag(III) periodate species such as monoperiodatoargentate(III)(MPA) is more important active species in the reaction than the DPA. The inverse fractional order in $[H_3IO_6]^{2-}$ might also be due to this reason. In the pre rate determining stage, the hydroxylated species of Ru(III) combines with a molecule of anionic form of ASP to give an intermediate complex, which further reacts with one mole of MPA in a rate determining step to give intermediate species of aspirin with regeneration of catalyst, ruthenium(III). This intermediate species further reacts with another molecule of MPA species in a fast step to give the products as given in Scheme 1.

The probable structure of the complex (C) is given below:



Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV–vis spectra of aspirin (3.0×10^{-4}), Ru(III) (5.0×10^{-6}, $[OH^-] = 0.05\ mol\ dm^{-3}$) and mixture of both. A hypsochromic shift of about 13 nm from 309 nm to 296 nm in the spectra of DPA was observed and hyperchromicity was observed at 296 nm. However, the Michelis-Menten plot proved the complex formation between catalyst and reductant, which explains less than unit order in [ASP]. The oxygen atom of carboxyl group of the ASP is involved in the formation of intermediate, as the molecular order in ASP and the absence of intervention of free radical redundant such a possibility. The rate law for the Scheme 1 could be derived as,

$$\text{Rate} = \frac{-\text{d[DPA]}}{\text{dt}} = \frac{kK_1K_2K_3[\text{DPA}][\text{ASP}][OH^-][\text{Ru(III)}]}{[H_3IO_6{}^{2-}] + K_1[OH^-][H_3IO_6{}^{2-}] + K_1K_2[OH^-] + K_1K_2K_3[OH^-][\text{ASP}]} \quad (7)$$

$$\frac{\text{Rate}}{[\text{DPA}]} = k_C = k_T - k_U = \frac{k\,K_1K_2K_3[\text{ASP}][\text{OH}^-][\text{Ru(III)}]}{[\text{H}_3\text{IO}_6{}^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6{}^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{ASP}]} \quad (8)$$

Eq. (8) can be rearranged to Eq. (9), which is suitable for verification.

$$\frac{[\text{Ru(III)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6{}^{2-}]}{kK_1K_2K_3[\text{ASP}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6{}^{2-}]}{kK_2K_3[\text{ASP}]} + \frac{1}{kK_3[\text{ASP}]} + \frac{1}{k} \quad (9)$$

The plots of $[\text{Ru(III)}]/k_C$ versus $[\text{H}_3\text{IO}_6]^{2-}$, $1/[\text{OH}^-]$ and $1/[\text{ASP}]$ were linear (Fig. 4); from the intercepts and slopes of such plots, the reaction constants K_1, K_2, K_3 and k were calculated as $(0.45 \pm 0.02)\,\text{dm}^3\,\text{mol}^{-1}$, $(7.16 \pm 0.10) \times 10^{-4}\,\text{mol}\,\text{dm}^{-3}$, $(2.61 \pm 0.14) \times 10^3\,\text{dm}^3\,\text{mol}^{-1}$, $(7.4 \pm 0.2) \times 10^2\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}$, 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 (Table 1), which fortifies the Scheme 1.

The thermodynamic quantities for the different equilibrium steps, in Scheme 1. can be evaluated as follows. The aspirin and hydroxide ion concentrations (Table 1) were varied at different temperatures. The plots of $[\text{Ru(III)}/k_C$ versus $1/[\text{ASP}]$ ($r \geq 0.9992$, $S \leq 0.00131$), $[\text{Ru(III)}]/k_C$ versus $[\text{H}_3\text{IO}_6{}^{2-}]$ ($r \geq 0.9991$, $S \leq 0.00132$), $[\text{Ru(III)}/k_C$ versus $1/[\text{OH}^-]$ ($r \geq 0.9994$, $S \leq 0.00087$) 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 $1/T$ ($r \geq 0.9992, S \leq 0.1104$] 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 3. A comparison of the latter values 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 reaction before the rate determining step is fairly slow and involves a high activation energy [24] In the same manner, K_2 and K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 3.

4.2. Os(VIII) catalysis: mechanism

Osmium(VIII) is known to form different complexes at different OH^- [25] concentrations, $[OsO_4(OH)_2]^{2-}$ and $[OsO_5(OH)]^{3-}$. At higher concentration of OH^-, $[OsO_5(OH)]^{3-}$ is significant. At lower concentrations of OH^-, as employed in the present study, and since the rate of oxidation increased with increase in $[OH^-]$, it is reasonable that $[OsO_4(OH)_2]^{2-}$ was operative and its formation is important in the reaction. To explain the observed orders the following Scheme 2 is proposed for osmium(VIII) catalysed reaction.

In the prior equilibrium step 1, the $[OH^-]$ deprotonates the DPA to give a deprotonated diperiodatoargentate(III); in the second step displacement of a ligand, periodate takes place to give free periodate which is evidenced by decrease in the rate with increase in [periodate] (Table 2). It may be expected that lower Ag(III) periodate species such as MPA is more important in the reaction than the DPA. The inverse fractional order in $[H_3IO_6]^{2-}$ might also be due to this reason. In the pre rate determining stage, the Os(VIII) species combines with a molecule of anionic

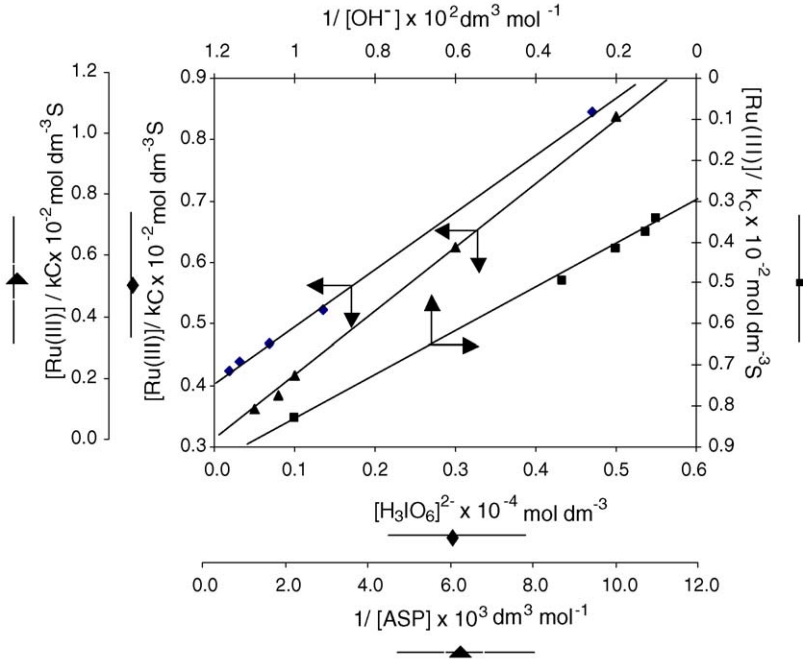
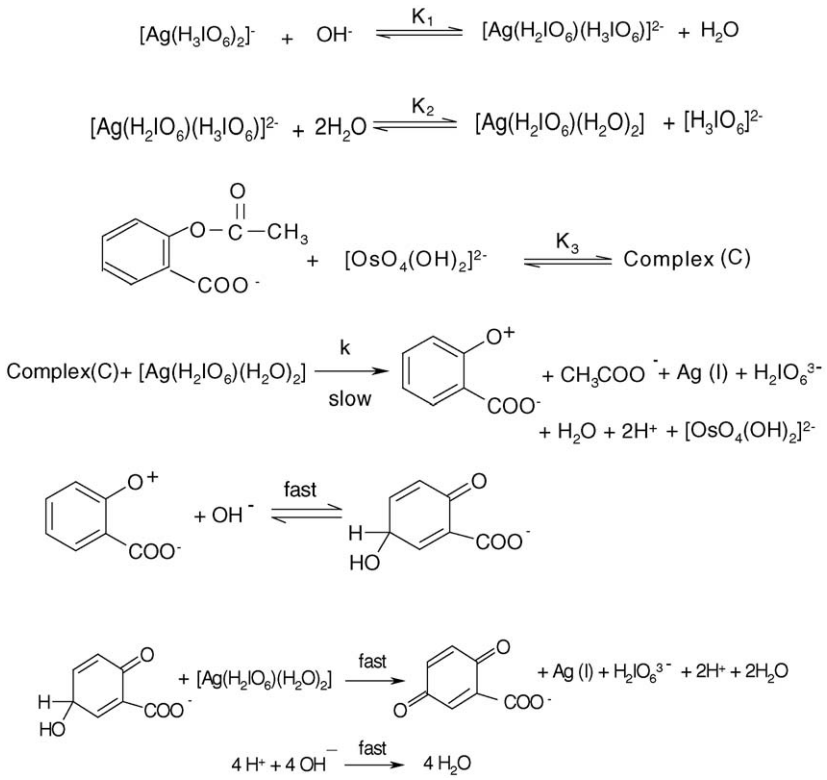


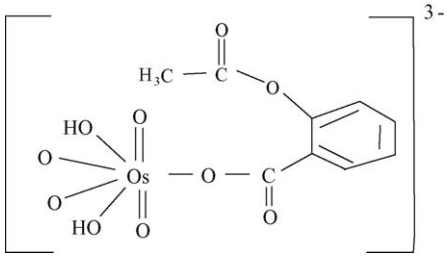
Fig. 3. Verification of rate law (6) of Ru(III) catalysed oxidation of aspirin by diperiodatoargentate(III) at 25 °C.



Scheme 2. Detailed scheme for the Os(VIII) catalysed oxidation of aspirin by alkaline diperiodatoargentate(III).

species of ASP to give an intermediate complex (C), which further reacts with one mole of MPA in a rate determining step to give intermediate species of aspirin and regeneration of catalyst, osmium(VIII). This Intermediate species further reacts with another molecule of MPA species in further fast step to give the products as given in Scheme 2.

The probable structure of the complex (C) is given below:



Spectroscopic evidence for the complex formation between catalyst and substrate was obtained from UV–vis spectra of aspirin (5.0×10^{-4}), Os(VIII) (5.0×10^{-6}, $[OH^-] = 0.05\ mol\ dm^{-3}$) and mixture of both. A hypsochromic shift of about 12 nm from 309 nm to 297 nm in the spectra of DPA was observed and hypochromicity was observed at 296 nm. However, the Michelis-Menten plot proved the complex formation between catalyst and reductant, which explains less than unit order in [ASP]. The oxygen atom of carboxyl group of the ASP is involved in the formation of intermediate, as the molecular order in ASP and the absence of intervention of free radical redundant such a possibility. The rate law for the Scheme 2 could be derived as,

$$\text{Rate} = \frac{-\text{d[DPA]}}{\text{dt}} = \frac{kK_1K_2K_3[\text{DPA}][\text{ASP}][\text{OH}^-][\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6{}^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6{}^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{ASP}]} \quad (10)$$

$$\frac{\text{Rate}}{[\text{DPA}]} = k_C = k_T - k_U = \frac{kK_1K_2K_3[\text{ASP}][\text{OH}^-][\text{Os(VIII)}]}{[\text{H}_3\text{IO}_6{}^{2-}] + K_1[\text{OH}^-][\text{H}_3\text{IO}_6{}^{2-}] + K_1K_2[\text{OH}^-] + K_1K_2K_3[\text{OH}^-][\text{ASP}]} \quad (11)$$

Eq. (11) can be rearranged to Eq. (12), which is suitable for verification.

$$\frac{[\text{Os(VIII)}]}{k_C} = \frac{[\text{H}_3\text{IO}_6{}^{2-}]}{k\,K_1K_2K_3[\text{ASP}][\text{OH}^-]} + \frac{[\text{H}_3\text{IO}_6{}^{2-}]}{k\,K_2K_3[\text{ASP}]} + \frac{1}{k\,K_3[\text{ASP}]} + \frac{1}{k} \quad (12)$$

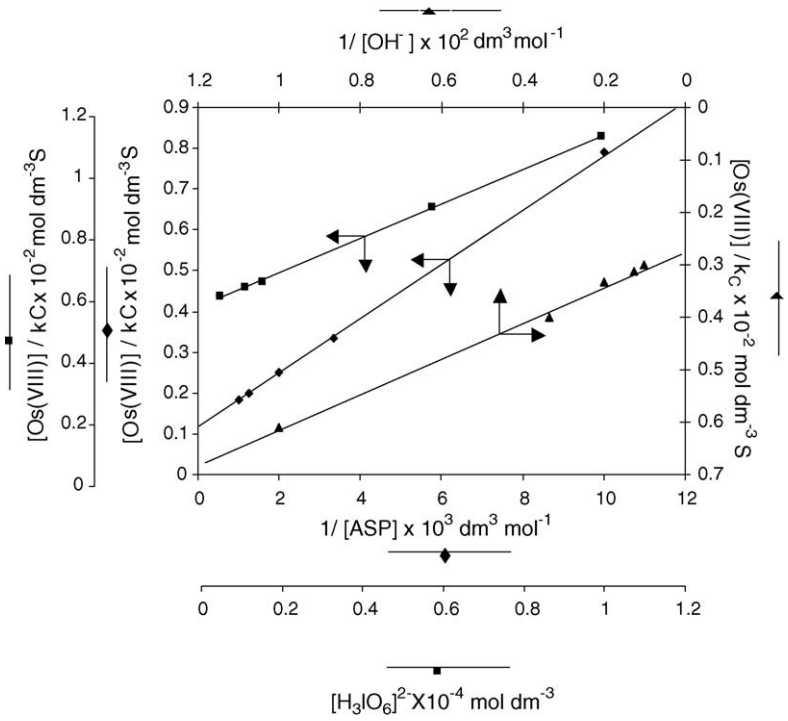


Fig. 4. Verification of rate law (9) of Os(VIII) catalysed oxidation of aspirin by diperiodatoargentate(III) at 25 °C.

The plots of $[Os(VIII)]/k_C$ versus $[H_3IO_6]^{2-}$, $1/[OH^-]$ and $1/[ASP]$ were linear (Fig. 4); from the intercepts and slopes of such plots, the reaction constants K_1, K_2, K_3 and k were calculated as $(0.58 \pm 0.02)\,dm^3\,mol^{-1}$, $(7.79 \pm 0.40) \times 10^{-4}\,mol\,dm^{-3}$, $(2.46 \pm 0.08) \times 10^3\,dm^3\,mol^{-1}$, $(8.84 \pm 0.40) \times 10^2\,dm^3\,mol^{-1}\,s^{-1}$, 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 2.

The thermodynamic quantities for the different equilibrium steps, in Scheme 2 can be evaluated as follows. The aspirin and hydroxide ion concentrations (Table 2) were varied at different temperatures. The plots of $[Os(VIII)/k_C$ versus $1/[ASP]$ ($r \geq 0.9994$, $S \leq 0.00136$), $[Os(VIII)]/k_C$ versus $[H_3IO_6{}^{2-}]$ ($r \geq 0.9990$, $S \leq 0.00132$), $[Os(VIII)/k_C$ versus $1/[OH^-]$ ($r \geq 0.9991$, $S \leq 0.00084$) should be linear as shown in Fig. 4. 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 $1/T$ ($r \geq 0.9981$, $S \leq 0.1101$)] 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 4. A comparison of the latter values 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 reaction before the rate determining step is fairly slow and involves a high activation energy [24] In the same manner, K_2 and K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 4.

The increase in the rate, with increasing ionic strength, is in the favor of a reaction between charged species of reactants, as presented in Schemes 1 and 2 of the proposed mechanism. The effect of solvent on the reaction rate is described in detail in the literature [26]. Increasing the content of *t*-butyl alcohol in the reaction medium leads to an increase in the rate of reaction (Fig. 2), which seems to be contrary to the expected interaction 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 low relative permittivity, which is less solvated than DPA at higher relative permittivity because of its larger size.

The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more ordered than the reactants [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]. The values of $\Delta H^{\#}$, $\Delta S^{\#}$, $\Delta G^{\#}$ and rate constant (k) indicate the order of reactivity of the catalysts as Ru(III) < Os(VIII) for the oxidation of aspirin by DPA. The Os(VIII) catalysed reaction, however, is reasonably fast in view of readiness of Os(VIII) to act across the –COO group and the Ru(III) catalysed reaction is slower probably owing to the less ability of the Ru(III) to act across the –COO group. The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst Ru(III) or Os(VIII) form the complex (C) with substrate which enhances the reducing property of the substrate than that without catalyst (Ru(III) or Os(VIII)). Further, the catalyst Ru(III)

or Os(VIII) modifies the reaction path by lowering the energy of activation.

5. Conclusion

The comparative study of Ru(III) and Os(VIII) catalysed oxidation of aspirin by Diperiodatoargentate(III) was studied. Oxidation products were identified. Among the various species of Ag(III) in alkaline medium, in earlier reports the diperiodatoargentate(III) was the active species, whereas deprotonated form of monoperiodatoargentate(III) itself is considered to be the active species for the title reaction. Active species of Ru(III) is found to be $[Ru(H_2O)_5OH]^{2+}$ and that of Os(VIII) is $[OsO_4(OH)_2]^{2-}$. Activation parameters were evaluated for both catalysed and uncatalysed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. Catalytic efficiency is Ru(III) < Os(VIII).

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References

[1] (a) S.M. Sultan, Analyst 112 (1987) 1331;
(b) J. Anwar, T.A. Awan, J. Chem. Soc. Pak. 12 (1990) 30.
[2] (a) B. Sethuram, Some Aspects of Electron Transfer Reactions Involving Organic Molecules, Allied Publishers (P) Ltd., New Delhi, 2003, p. 151;
(b) B. Sethuram, Some Aspects of Electron Transfer Reactions Involving Organic Molecules, Allied Publishers (P) Ltd., New Delhi, 2003, p. 78.
[3] (a) P.K. Jaiswal, K.L. Yadav, Talanta 17 (1970) 236;
(b) P.K. Jaiswal, Analyst 1 (1972) 503.
[4] (a) P. Jayaprakash Rao, B. Sethuram, T. Navaneeth Rao, React. Kinet. Catal. 29 (1985) 289;
(b) K. Venkata Krishna, P. Jayaprakash Rao, Ind. J. Chem. 37A (1998) 1106, references therein.
[5] (a) A. Kumar, P. Kumar, P. Ramamurthy, Polyhedron 18 (1999) 773;
(b) A. Kumar, P. Kumar, J. Phys. Org. Chem. 12 (1999) 79;
(c) A. Kumar, P. Vaishali, Ramamurthy, Int. J. Chem. Kinet. 32 (2000) 286.
[6] A.K. Das, Coord. Chem. Revs. 213 (2001) 307.
[7] (a) M.C. Agarwal, S.K. Upadhyay, J. Sci. Ind. Res. 42 (1983) 508;
(b) G.H. Hugar, S.T. Nandibewoor, Trans. Met. Chem. 19 (1994) 215.
[8] P. Veerasomaiah, K. Bal Reddy, B. Sethuram, T. Navaneeth Rao, Indian J. Chem. 26A (1987) 402.
[9] T.S. Kiran, S.T. Nandibewoor, J. Chem. Res. (2005) in press.
[10] O.C. Saxena, Microchem. J. 12 (1967) 609.
[11] (a) C.S. Reddy, T. Vijaykumar, Indian J. Chem. 34A (1995) 615;
(b) D.L. Kamble, R.B. Chougale, S.T. Nandibewoor, Indian J. Chem. 35A (1996) 865.
[12] G.P. Panigrahi, P.K. Misro, Indian J. Chem. 15A (1977) 1066.
[13] G.L. Cohen, G. Atkinson, Inorg. Chem. 3 (1964) 1741.
[14] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, fifth ed., Longmans Singapore Publishers Pte Ltd., Singapore, 1996, p. 467 and p. 391.
[15] F. Fiegl, Spot Tests in Organic Analysis, Elsevier, New York, 1975, p. 333.
[16] F. Fiegl, Spot Tests in Organic Analysis, Elsevier, New York, 1975, p. 455.
[17] E.A. Moelwyn-Hughes, Kinetics of Reaction in Solutions, Oxford University Press, London, 1947, pp. 297–299.
[18] L.J. Krishenbaum, L. Mrozowski, Inorg. Chem. 17 (1978) 3718.
[19] (a) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, John Wiley & Sons, New York, 1980, p. 974;
(b) R. Banerjee, K. Das, A. Das, S. Dasgupta, Inorg. Chem. 28 (1989) 585;
(c) R. Banerjee, R. Das, S. Mukhopadhyay, J. Chem. Soc. Dalton Trans. (1992) 1317.
[20] (a) C.E. Crouthumel, H.V. Meek, D.S. Martin, C.V. Banus, J. Am. Chem. Soc. 71 (1949) 3031;
(b) C.E. Crouthamel, A.M. Hayes, D.S. Martin, J. Am. Chem. Soc. 73 (1951) 82.
[21] (a) S. Bhattacharya, B. Saha, A. Datta, P. Banerjee, Coord. Chem. Rev. 47 (1988) 170;
(b) R.I. Haines, A. McAuley, Coord. Chem. Rev. 39 (1981) 77.
[22] (a) A.M. Balado, B.C. Galan, F.J.P.P. Martin, An. Quim. 88 (1992) 170;
(b) F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley Eastern, New York, 1996, p. 153.
[23] (a) D.L. Kamble, S.T. Nandibewoor, Oxid. Commun. 21 (1998) 396;
(b) S.M. Desai, N.N. Halligudi, S.T. Nandibewoor, Trans. Met. Chem. 27 (2002) 207;
(c) R.S. Shetter, S.T. Nandibewoor, J. Mol. Catal. A 234 (2005) 137;
(d) G.A. Hiremath, P.L. Timmanagoudar, S.T. Nandibewoor, React. Kinet. Catal. Lett. 63 (1998) 403.
[24] K.S. Rangappa, M.P. Raghavendra, D.S. Mahadevappa, D. Channegouda, J. Org. Chem. 63 (1998) 531.
[25] D.L. Kamble, S.T. Nandibewoor, J. Phys. Org. Chem. 11 (1998) 171.
[26] (a) E.A. Moelwyn-Hughes, Physical Chemistry, second ed., Pergamon Press, New York, 1961;
(b) E.S. Amis, Solvent Effects on Reaction Rates and Mechanisms, Academic Press, New York, 1966, p. 183.
[27] A. Weissberger, in: E.S. Lewis (Ed.), Investigation of Rates and Mechanism of Reactions in Techniques of Chemistry, vol. 4, Wiley, New York, 1974, p. 421.
[28] M. Martinez, M.A. Pitarque, R.V. Eldik, J. Chem. Soc. Dalton Trans. (1996) 2665.