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Osmium(VIII) catalysed and uncatalysed oxidation of aspirin drug by diperiodatocuprate(III) complex in aqueous alkaline medium: A mechanistic approach

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ABSTRACT

The kinetics of oxidation of a non-steroidal analgesic drug, aspirin (ASP) by diperiodatocuprate(III)(DPC) in the presence and absence of osmium(VIII) have been investigated at 298 K in alkaline medium at a constant ionic strength of 0.10 mol dm^{-3} spectrophotometrically. The reaction showed a first-order in [DPC] and less than unit order in [ASP] and [alkali] for both the osmium(VIII) catalysed and uncatalysed reactions. The order with respect to Os(VIII) concentration was unity. The effects of added products, ionic strength, periodate and dielectric constant have been studied. The stoichiometry of the reaction was found to be 1:4 (ASP:DPC) for both the cases. The main oxidation product of aspirin was identified by spot test, IR, NMR and GC–MS. The reaction constants involved in the different steps of the mechanisms were calculated for both reactions. Activation parameters with respect to slow step of the mechanisms were computed and discussed for both the cases. The thermodynamic quantities were also determined for both reactions. The catalytic constant (K_C) was also calculated for catalysed reaction at different temperatures and the corresponding activation parameters were determined.

1. Introduction

In recent years, the study of highest oxidation state transition metals has intrigued many researchers. Transition metals in a higher oxidation state can be stabilized by chelation with suitable polydentate ligands. Metal chelates such as diperiodatocuprate(III) [1], diperiodatoargentate(III) [2] and diperiodatonickelate(IV) [3] are good oxidants in a medium with an appropriate pH value. Periodate and tellurate complexes of copper in its trivalent state have been extensively used in the analysis of several organic compounds [4]. The kinetics of self-decomposition of these complexes was studied in some detail [5]. Copper(III) is an intermediate in the copper(II) catalysed oxidation of amino acids by peroxydisulphate [6]. The oxidation reaction usually involves the copper(II)–copper(I) couple and such aspects are detailed in different reviews [7,8]. The use of diperiodatocuprate(III) (DPC) as an oxidant in alkaline medium is new and restricted to a few cases due to its limited solubility and stability in aqueous medium. DPC is a versatile one-electron oxidant for various organic compounds in alkaline medium and its use as an analytical reagent is now well-recognized [9]. Copper complexes have occupied a major place in oxidation chemistry due to their abundance and relevance in biological chemistry. When the copper(III) periodate complex is the oxidant and multiple equilibria between different copper(III) species are involved, it would be interesting to know which of the species is the active oxidant.

Aspirin (acetylsalicylic acid) (ASP) is one among the most used drugs worldwide. It 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. It is widely studied in medicine and several methods are suggested in literature for its determination [10].

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 have attracted considerable interest [11]. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed [12]. Although the mechanism of catalysis depends on the nature of the substrate, oxidant and on experimental conditions, it has been shown [13] 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) catalysis in redox reactions involves several complexes, different oxidation states of osmium, etc. The literature survey reveals that there are no reports on the oxidative mechanism of aspirin by DPC. We have also observed that micro amounts of osmium(VIII) enhanced the rate of oxidation of aspirin by DPC. Such oxidation studies may throw some light on the mechanism of conversions of compounds in biological system. In view of the complexity of the title reaction,

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a detailed study of the reaction becomes important. Hence in order to understand the active species of copper(III) species and osmium(VIII), and to propose the appropriate mechanisms for both Os(VIII) catalysed and uncatalysed reactions, the title reaction was undertaken.

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., Aurangabad, India) was prepared by dissolving the 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. 135 °C (literature 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 (Johnson Matthey) in 0.50 mol dm^{-3} NaOH. The concentration was ascertained [14] by determining the unreacted $[Fe(CN)_6]^{4-}$ with standard Ce(IV) solution in an acidic medium. The copper(III) periodate complex was prepared by standard procedure [15,16]. The copper(III) complex was verified by its UV–Vis spectrum, which showed an absorption band with maximum at 415 nm. The aqueous solution of copper(III) was standardized by iodometric titration and gravimetrically by thiocyanate [17] method. The copper(II) was prepared by dissolving a known amount of copper sulphate (BDH) distilled water. Periodate solution was prepared by weighing out the required amount of sample in hot water and used after keeping it for 24 h to attain equilibrium. Its concentration was ascertained iodometrically [18] at neutral pH using phosphate buffer. Since periodate is present in excess in DPC, the possibility of oxidation of aspirin by periodate in alkaline medium at 25 °C was tested. The progress of the reaction was followed iodometrically. There was no significant reaction under the experimental conditions employed compared to the DPC oxidation of aspirin. KOH and KNO_3 (BDH, AR) were employed to maintain the required alkalinity and ionic strength respectively in reaction solutions.

2.2. Kinetic measurements

The kinetic measurements were performed on a Varian CARY 50 Bio UV–Vis spectrophotometer. The kinetics was followed under pseudo first-order conditions where [ASP] > [DPC] both in uncatalysed and catalysed reactions at 25 ± 0.1 °C, unless specified. In the absence of catalyst the reaction was initiated by mixing the DPC to ASP solution which also contained required concentration of KNO_3, KOH and KIO_4.The reaction in the presence of catalyst was initiated by mixing DPC to ASP solution which also contained required concentration of KNO_3, KOH, KIO_4 and Os(VIII). The progress of reaction was followed spectrophotometrically at 415 nm by monitoring the decrease in absorbance due to DPC with the molar absorbancy index, 'ε' taken as 6230 ± 100 dm^3 mol^{-1} cm^{-1} in both catalysed and uncatalysed reactions. 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_U or k_t), in both the cases were determined from the log(absorbance) versus time plots. The plots were linear up to 80% completion of reaction and the rate constants were reproducible within ±5%. Regression analysis of experimental data to obtain the regression coefficient, r and standard deviation, S was performed using Microsoft Excel-2003.

Kinetic runs were also carried out under N_2 atmosphere in order to understand the effect of dissolved oxygen on the rate of reaction. No significant difference in the results was obtained under a N_2 atmosphere and in the presence of air. In view of the ubiquitous contamination of carbonate in the basic medium, the effect of carbonate was also studied. Added carbonate had no effect on the reaction rates. The spectroscopic changes during the reaction are shown in Fig. 1. It is evident from the figure that the concentration of DPC decreases at 415 nm.

3. Results and discussion

3.1. Stoichiometry and product analysis

Reaction mixture containing different ratios of DPC to aspirin in the presence of 5.0×10^{-5} mol dm^{-3} KIO_4 (8.0×10^{-7} mol dm^{-3} osmium(VIII) for the catalysed reaction) were equilibrated at 298 K for 6 h in a closed vessel under nitrogen atmosphere. The remaining concentration of DPC was estimated spectrophotometrically at 415 nm. The results indicate four moles of diperiodatocuprate(III) consumed by one mole of aspirin as given in Scheme 1.

The main reaction products were extracted with ether, which was identified as 1,4-benzoquinone-2-carboxylate ion by spot test [19]. The nature of 1,4-benzoquinone-2-carboxylate ion was confirmed by its IR spectrum which showed a C=O stretching at 1632 cm^{-1} indicating the presence of C=O group at 1,4-benzoquinone moiety, the band at 1584 cm^{-1} and also at 1361 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 (d, 1H, C_6–H), 6.80 (d, 1H, C_5–H) 7.78 (s, 1H, C_3–H). It was further confirmed by its melting point 206 °C (literature m.p. 205–207 °C). Further, 1,4-benzoquinone-2-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 (Fig. 2) showed a molecular ion peak at 152 amu confirming 1,4-benzoquinone-2-carboxylate ion. All other peaks observed in GC–MS can be interpreted in accordance with the observed structure of the 1,4-benzoquinone-2-carboxylate ion. Another product, acetate was identified by spot test [19]. The product Cu(II) was identified by UV–Vis spectra. The reaction products do not undergo further oxidation under the present kinetic conditions.

3.2. Reaction orders

The kinetics of oxidation of aspirin by DPC was investigated at several initial concentrations of reactants in alkaline medium in

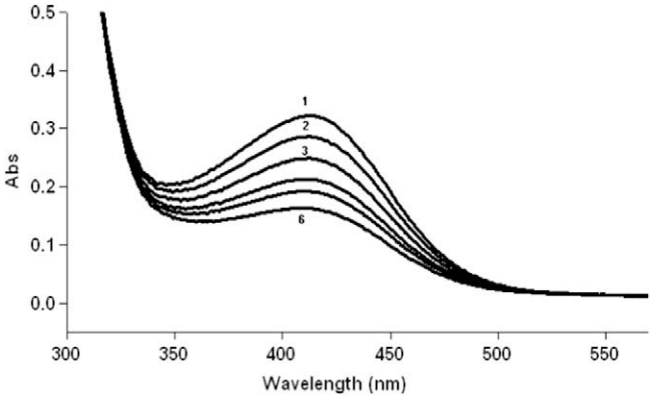
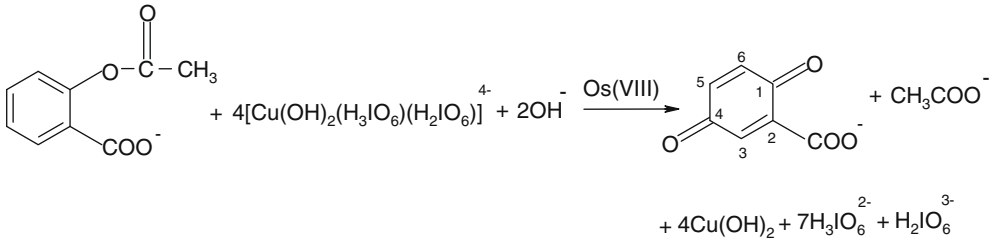


Fig. 1. Spectroscopic changes occurring in the oxidation of aspirin by diperiodatocuprate(III)] at 25 °C, [DPC] = 1.0×10^{-4}, [ASP] = 1.0×10^{-3}, [OH^-] = 0.05 and I = 0.10 mol dm^{-3} with scanning time interval = 1 min.



Scheme 1. Stoichiometry of the reaction.

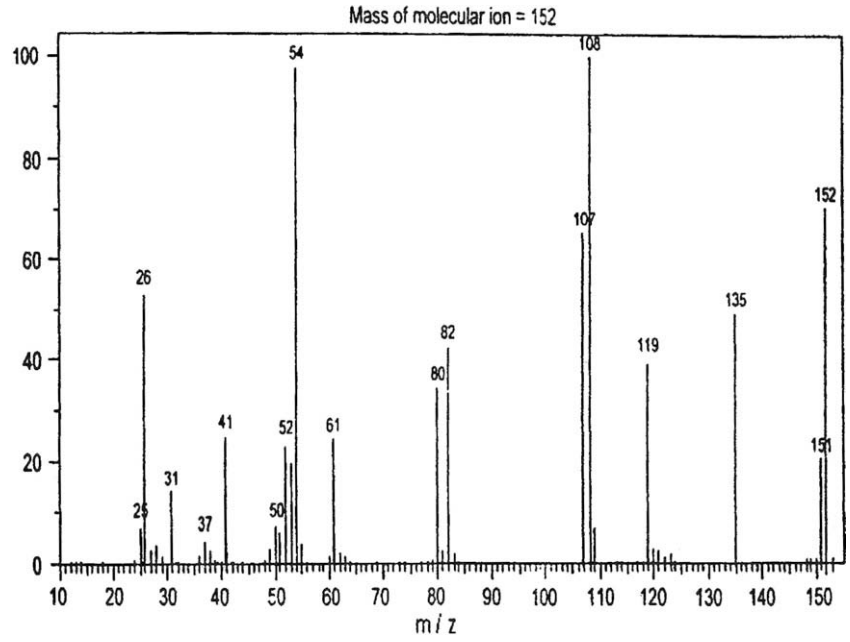


Fig. 2. GC–Mass Spectrum of 1,4-benzoquinone-2-carboxylate ion with its molecular ion peak at 152 amu.

the presence and absence of osmium(VIII). The reaction is understood to occur in parallel paths with contributions from both 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, OH^- and catalyst Os(VIII), in turn, while keeping all other concentrations and conditions constant.

3.3. Effect of [diperiodatocuprate(III)]

The oxidant DPC concentration was varied in the range of 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} at fixed aspirin, OH^- and IO_4^- for uncatalysed and catalysed reactions. The linearity of the plots of log [absorbance] versus time ($r \geqslant 0.983$, $S \leqslant 0.016$) up to 80% completion of the reaction (Fig. 3) indicates a first-order dependence of the reaction rate on [DPC]. The pseudo first-order rate constants remained unchanged with the variation of [DPC] (k_U (Table 1), k_C (Table 2; Os(VIII)). This confirms the unit order in [DPC] for both the reactions.

3.4. Effect of [aspirin]

The effect of aspirin on the rate of reaction was studied at constant concentrations of alkali, DPC and a constant ionic strength of 0.10 mol dm^{-3} uncatalysed reaction and at constant concentration

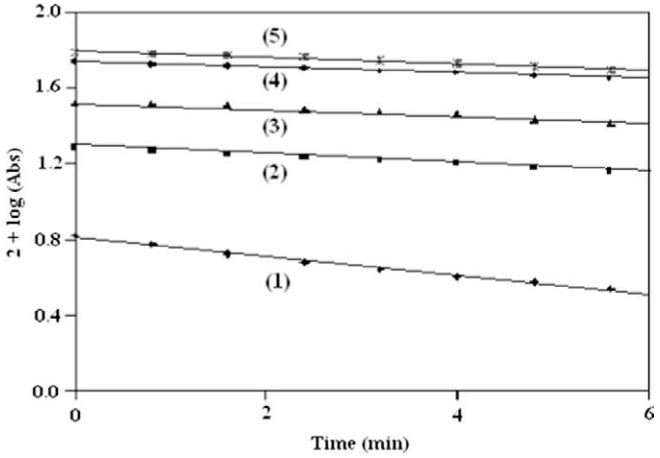


Fig. 3. First-order plots for the oxidation of aspirin by DPC in aqueous alkali medium at 298 K. [DPC] $\times 10^{-4}$; (1) 1.0; (2) 3.0; (3) 6.0; (4) 8.0; (5) 10.0 [ASP] = 1.0×10^{-3}, [OH^-] = 0.05 and I = 0.10 mol dm^{-3}.

of Os(VIII) in catalysed reaction. The substrate aspirin was varied in the range of 1.0×10^{-4} to 1.0×10^{-3} mol dm^{-3}. The k_U and k_C values increased with increase in concentration of aspirin indicating an apparent less than unit order dependence on [ASP] [order k_U = 0.50 and k_C = 0.68] under the conditions of experiment (Tables 1 and 2) ($r \geqslant 0.997$, $S \leqslant 0.009$). This is also confirmed in the plots of

Table 1
Effect of [DPC], [ASP], [OH^-] and [IO_4^-] on the oxidation of aspirin by DPC in alkaline medium at 25 °C, I = 0.10 mol dm^{-3}.

10^5 [DPC]	10^3 [ASP]	[OH^-]	10^5 [IO_4^-]	10^4 k_U (s^{-1})	
(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	Found	Calculated
1.0	1.0	0.05	1.0	9.43	9.49
3.0	1.0	0.05	1.0	9.41	9.49
6.0	1.0	0.05	1.0	9.44	9.49
8.0	1.0	0.05	1.0	9.45	9.49
10.0	1.0	0.05	1.0	9.45	9.49
10.0	0.1	0.05	1.0	3.00	3.10
10.0	0.3	0.05	1.0	6.03	6.18
10.0	0.6	0.05	1.0	7.98	8.23
10.0	0.8	0.05	1.0	9.02	8.97
10.0	1.0	0.05	1.0	9.43	9.49
10.0	1.0	0.01	1.0	5.2	5.22
10.0	1.0	0.03	1.0	8.63	8.35
10.0	1.0	0.05	1.0	9.43	9.49
10.0	1.0	0.08	1.0	1.01	1.02
10.0	1.0	0.1	1.0	1.05	1.05
10.0	1.0	0.05	1.0	9.43	9.49
10.0	1.0	0.05	2.0	9.45	9.49
10.0	1.0	0.05	5.0	9.46	9.49
10.0	1.0	0.05	7.0	9.47	9.49
10.0	1.0	0.05	10.0	9.47	9.49

k_U versus $[ASP]^{0.50}$ in which it is linear rather than the direct plot of log k_U versus [ASP] (Fig. 4) similarly catalysed reaction the plots of k_C versus $[ASP]^{0.68}$ in which it is linear rather than the direct plot of log k_C versus [ASP] (Fig. 5).

3.5. Effect of [alkali]

The effect of alkali on the reaction has been studied for both the cases in the range of 0.01– 0.1 mol dm^{-3} at constant concentrations of aspirin, DPC and a constant ionic strength of 0.10 mol dm^{-3} in uncatalysed reaction and at constant concentration of Os(VIII) in catalysed reaction. The rate constants increased

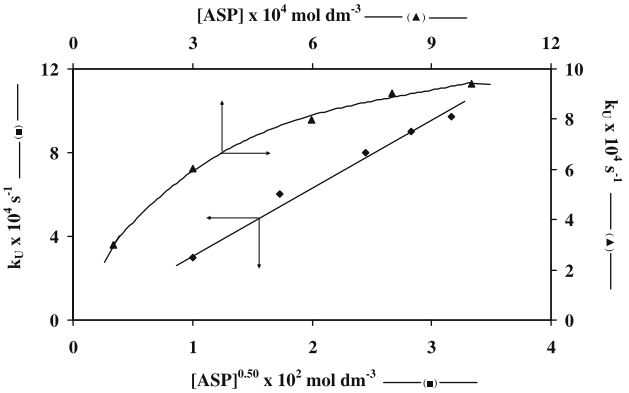


Fig. 4. Plot of k_U vs. $[ASP]^{0.50}$ and k_U vs. [ASP]. In case of oxidation of aspirin by DPC.

with increasing [alkali] and the order was found to be less than unity (Tables 1 and 2).

3.6. Effect of [periodate]

The effect of increasing concentration of periodate was studied by varying the periodate concentration from 1.0×10^{-5} to 1.0×10^{-4} mol dm^{-3} keeping all other reactants concentrations constant. The added periodate had no effect on the rate of reaction (Tables 1 and 2).

3.7. Effect of Ionic strength (I) and dielectric constant of the medium (D)

The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.1 to 1.0 mol dm^{-3} at constant concentrations of all other reactants. The rate was found to increase with increase in the ionic strength for both cases. A plot of log k_U or k_C versus $I^{1/2}$ is linear with positive slope (Figs. 6 and 7).

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

10^5 [DPC]	10^3 [ASP]	[OH^-]	10^5 [IO_4]	10^7 [Os(VIII)]	10^3 k_T	10^4 k_U	10^3 k_C (s^{-1})	
(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(mol dm^{-3})	(s^{-1})	(s^{-1})	Found	Calculated
1.0	1.0	0.05	1.0	8.0	6.21	9.43	5.26	5.26
3.0	1.0	0.05	1.0	8.0	6.20	9.41	5.25	5.26
6.0	1.0	0.05	1.0	8.0	6.24	9.44	5.29	5.26
8.0	1.0	0.05	1.0	8.0	6.23	9.45	5.28	5.26
10.0	1.0	0.05	1.0	8.0	6.23	9.45	5.28	5.26
10.0	0.1	0.05	1.0	8.0	1.02	3.00	0.70	0.71
10.0	0.3	0.05	1.0	8.0	2.73	6.03	2.12	2.06
10.0	0.6	0.05	1.0	8.0	4.14	7.98	3.34	3.50
10.0	0.8	0.05	1.0	8.0	5.14	9.02	4.24	4.46
10.0	1.0	0.05	1.0	8.0	6.21	9.43	5.26	5.26
10.0	1.0	0.01	1.0	8.0	1.90	5.20	1.38	1.39
10.0	1.0	0.03	1.0	8.0	4.58	8.63	3.71	3.59
10.0	1.0	0.05	1.0	8.0	6.21	9.43	5.26	5.27
10.0	1.0	0.08	1.0	8.0	7.77	10.1	6.76	6.97
10.0	1.0	0.1	1.0	8.0	9.09	10.50	8.07	8.09
10.0	1.0	0.05	1.0	8.0	6.21	9.43	5.26	5.26
10.0	1.0	0.05	2.0	8.0	6.31	9.45	5.36	5.26
10.0	1.0	0.05	5.0	8.0	6.54	9.46	5.59	5.26
10.0	1.0	0.05	7.0	8.0	6.71	9.47	5.76	5.26
10.0	1.0	0.05	10.0	8.0	6.86	9.47	5.91	5.26
10.0	1.0	0.05	1.0	3.0	2.85	9.43	1.91	1.90
10.0	1.0	0.05	1.0	5.0	4.05	9.43	3.11	3.08
10.0	1.0	0.05	1.0	8.0	6.21	9.43	5.26	5.26
10.0	1.0	0.05	1.0	20.0	13.5	9.43	12.60	12.40
10.0	1.0	0.05	1.0	30.0	18.4	9.43	17.5	17.3

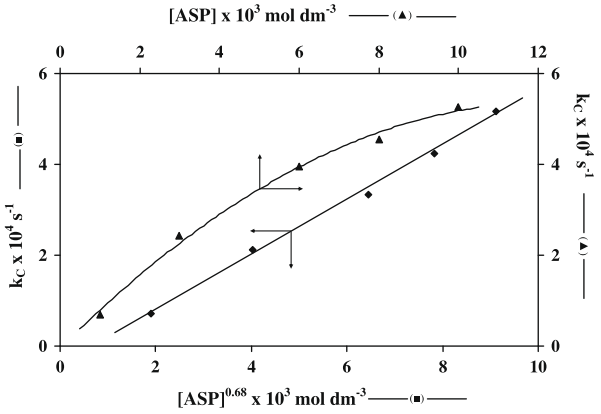


Fig. 5. Plot of k_C vs. $[ASP]^{0.68}$ and k_C vs. [ASP]. In case of Os(VIII) catalysed oxidation of aspirin by DPC.

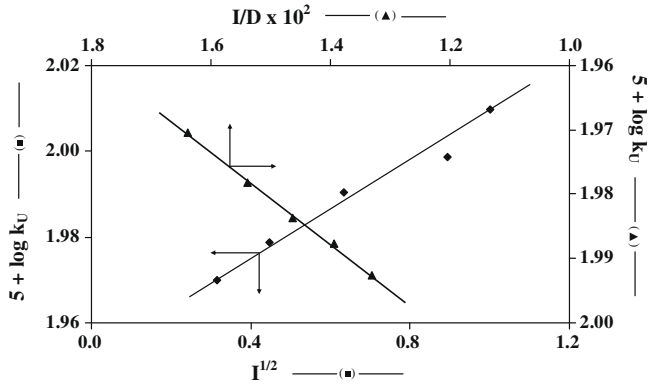


Fig. 6. Effect of ionic strength and dielectric constant of the medium on oxidation of aspirin by DPC in aqueous alkali medium at 298 K.

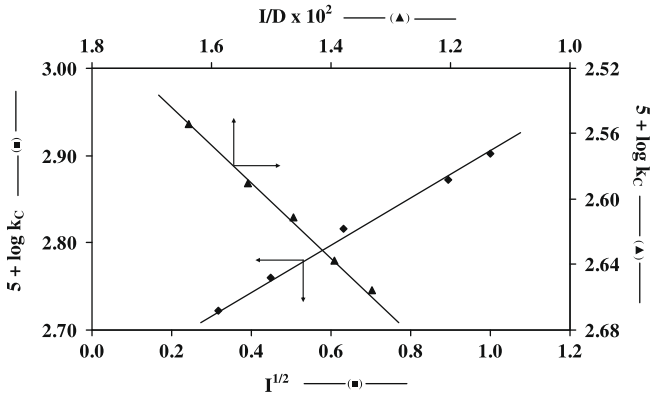


Fig. 7. Effect of ionic strength and dielectric constant of the medium on Os(VIII) catalysed oxidation of aspirin by DPC in aqueous alkali medium at 298 K.

Varying the *t*-butyl alcohol and water percentage varied the dielectric constant of the medium, '*D*'. The *D* values were calculated from the equation $D = D_wV_w + D_BV_B$, where D_w and D_B are dielectric constants of pure water and *t*-butyl alcohol, respectively, and V_w and V_B are the volume fractions of components water and *t*-butyl alcohol, respectively, in the total mixture. The decrease in dielectric constant of the reaction medium decreases the rate and the plot of log k_U or k_C versus I/D was liner with negative slope (Figs. 6 and 7) ($r \geqslant 0.9824$, $S \leqslant 0.006$).

3.8. Effect of added products

The initially added products, 1,4-benzoquinone-2-carboxylate and copper(II) ($CuSO_4$) did not have any significant effect on the rate of the reaction in both the case of uncatalysed and catalysed reactions.

3.9. Polymerization study

The involvement of free radicals in the reaction was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile monomer was initially added, was kept for 2 h in an inert atmosphere. On diluting the reaction mixture with methanol, a white precipitate was formed, indicating the involvement of free radicals in the reaction. The blank experiments of either DPC or aspirin alone with acrylonitrile did not induce any polymerization under the same conditions. Initially added acrylonitrile decreased the rate of reaction indicating free radical participation in presence and absence of Os(VIII).

3.10. Effect of [Os(VIII)]

The [Os(VIII)] concentrations was varied from 3.0×10^{-7} to 3.0×10^{-6} mol dm^{-3} range, at constant concentration of DPC, aspirin, alkali and ionic strength. The order in [Os(VIII)] (Table 2) was found to be unity from the linearity of the plot of k_C versus [Os(VIII)] ($r = 0.9725$).

3.11. Effect of temperature

The influence of temperature on the rate of reaction was studied for uncatalysed reaction at 25, 30, 35 and 40 °C. The rate constants (k_1), of the slow step of Scheme 2 were obtained from the slopes and the intercepts of the plots of $1/k_U$ versus 1/[ASP] and $1/k_U$ versus $1/[OH^-]$ plots at four different temperatures. The values are given in Table 3. The activation parameters for the rate determining step were obtained by the least square method of plot of log k_1 versus $1/T$ and are presented in Table 3.

The rate constants (k_2), of the slow step of Scheme 3 were obtained from the slopes and the intercepts of the plots of [Os(VIII)]/k_C versus 1/[ASP] and [Os(VIII)]/k_C versus $1/[OH^-]$ plots at four different temperatures. The values are given in Table 4. The activation parameters for the rate determining step were obtained by the least square method of plot of log k_2 versus $1/T$ and are presented in Table 4.

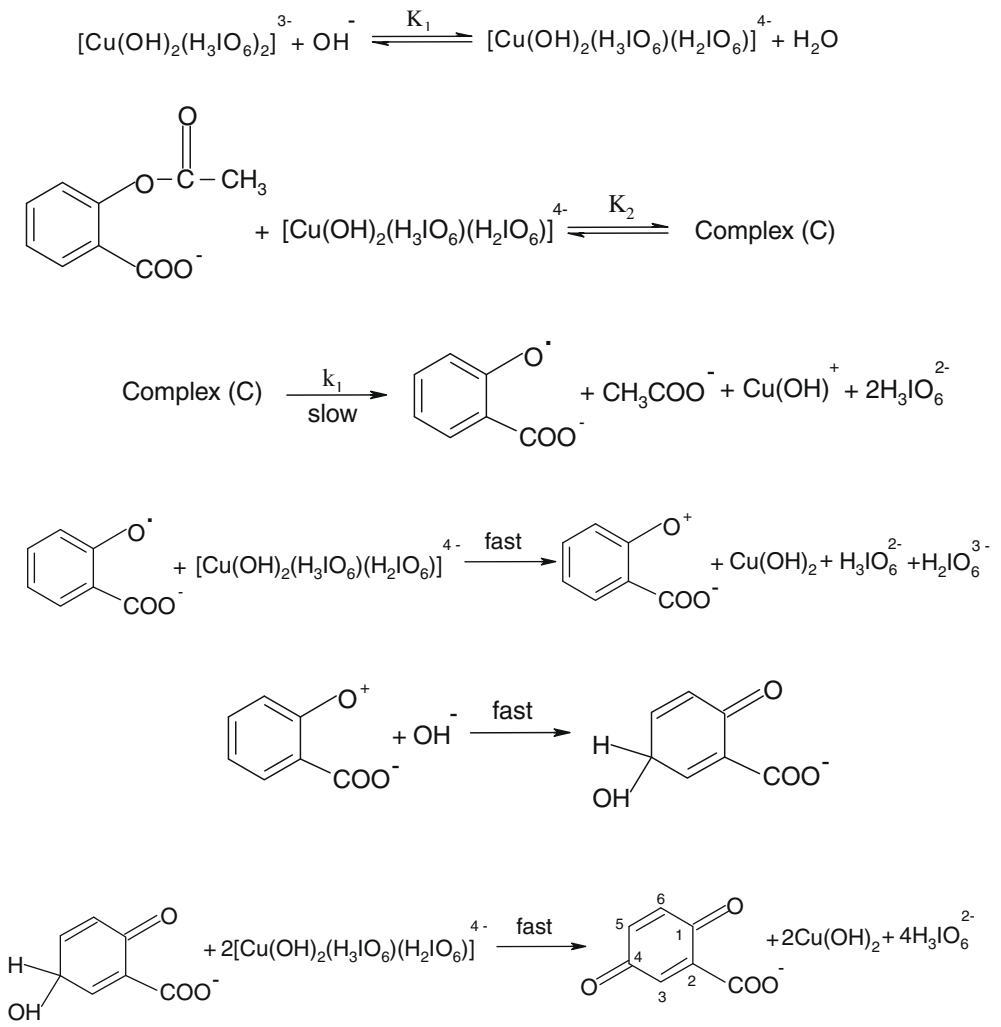
The water-soluble copper(III) periodate complex is reported [20] to be $[Cu(HIO_6)_2(OH)_2]^{7-}$. However, in aqueous alkaline medium at high pH as employed in this study, periodate is unlikely to exist as HIO_6^{4-} (as present in the complex) as is evident from its involvement in the multiple equilibria [21] (1)–(3) depending on the pH of the solution.

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+ \quad (1)$$

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

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

Periodic acid exists as H_5IO_6 and as $H_4IO_6^-$ around pH 7. Thus, under the conditions employed in alkaline medium, the main species are expected to be $H_3IO_6^{2-}$ and $H_2IO_6^{3-}$. At higher concentrations, periodate also tends to dimerise [9]. However, formation of this species is negligible under the conditions employed for this study. Hence, at the pH employed in this study, the soluble copper(III) periodate complex exists as diperiodatocuprate(III), $[Cu(H_3IO_6)_2(OH)_2]^{3-}$, a conclusion also supported by earlier work [22].



Scheme 2. Detailed scheme for the oxidation of aspirin by alkaline diperiodatocuprate(III).

4. Mechanism for uncatalysed reaction

The reaction between the aspirin and DPC complex in alkaline media has the stoichiometry of 1:4 with first-order dependence on the DPC concentration and apparently less than unit order in aspirin and alkali concentrations. In most of the reports [23] on DPC oxidation, periodate had retarding effect and OH^- had an a increasing effect on the rate of reaction and monoperiodatocuprate(III) is considered to be active species. However in the present kinetic study, entirely different kinetic observations have been obtained. The rate of reaction increased with increase in alkalinity (Table 1) and periodate had totally no effect on the rate of the reaction. Accordingly, the deprotonated form of DPC is considered to be the active species of copper(III). It is well known that aspirin exists in the anionic form in basic medium [24].

In the first equilibrium step the $[OH^-]$ deprotonates the DPC to give a deprotonated DPC. The less than unit order in [ASP] presumably results from formation of a complex (C) between the anionic form of aspirin and the active species of DPC. This complex (C) decomposes in a slow step to give a free radical of salicylate ion, acetate ion and copper(II). Such type anionic free radical is available in the literature [25]. This free radical species further reacts with three more moles of deprotonated DPC in further fast steps to form the products such as 1,4-benzoquinone-2-carboxylate ion, Cu(II) and periodate as given in Scheme 2.

Since Scheme 2 is in accordance with the generally well-accepted principle of noncomplementary 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 (see infra). This type of radical intermediate has also been observed in earlier work [26].

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

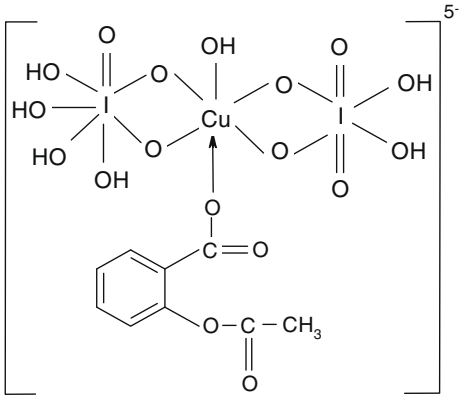


Table 3
Thermodynamic activation parameters for the oxidation of aspirin by DPC in alkaline medium with respect to the slow step of Scheme 2.

Temperature (K)		$10^3 k_1$ (s^{-1})
(A) Effect of temperature		
298		1.23
303		2.10
308		3.00
313		3.39
318		3.98
Parameters		**Values**
(B) Activation parameters (Scheme 2)		
Ea (kJ mol^{-1})		44.7 ± 2.0
$\Delta H^{\#}$ (kJ mol^{-1})		42.3 ± 2.1
$\Delta S^{\#}$ (J K^{-1} mol^{-1})		−158 ± 6
$\Delta G^{\#}$ (kJ mol^{-1})		89.3 ± 3.1
log *A*		5.0 ± 0.3
Temperature (K)	K_1 (dm^3 mol^{-1})	$10^{-4} K_2$ (dm^3 mol^{-1})
(C) Effect of temperature to calculate K_1 and K_2 for the oxidation of aspirin by diperiodatocuprate(III) in alkaline medium		
298	2.46	3.06
303	6.03	1.42
308	9.15	0.74
313	17.2	0.69
318	21.7	0.63
Thermodynamic quantities	**Values from K_1**	**Values from K_2**
(D) Thermodynamic quantities using K_1 and K_2		
ΔH (kJ mol^{-1})	86 ± 4	−61 ± 3
ΔS (J K^{-1} mol^{-1})	297 ± 20	−122 ± 15
ΔG_{298} (kJ mol^{-1})	−2.2 ± 0.5	−25 ± 1.5

[DPC] = 1.0×10^{-4}; [ASP] = 1.0×10^{-3}; [OH^-] = 0. 05; [IO_4^-] = 1.0×10^{-5} mol dm^{-3}.

Spectroscopic evidence for the complex (C) formation between oxidant and substrate was obtained from UV–Vis spectra of aspirin (1.0×10^{-3}), DPC (1.0×10^{-4}), [OH^-] (0.05 mol dm^{-3}) and a mixture of both. A bathochromic shift of about 4 nm from 242 to 246 nm in the spectra of ASP was observed. However, the Michaelis–Menten plot also proved the complex formation between DPC and aspirin, which explains the less than unit order dependence on [ASP]. Such a complex between a substrate and an oxidant has been observed in other studies [27].

The Scheme 2 leads to rate law (5)

$$\text{Rate} = \frac{-\mathrm{d}[\text{DPC}]}{\mathrm{dt}} = k_1[\text{C}] = k_1K_1K_2[\text{DPC}][\text{ASP}][\text{OH}^-] \quad (4)$$

$$\frac{\text{Rate}}{[\text{DPC}]} = k_\text{U} = \frac{k_1K_1K_2[\text{ASP}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1K_2[\text{ASP}][\text{OH}^-]} \quad (5)$$

The rate law (5) may be verified by rearranging it in the form of Eq. (6)

$$\frac{1}{k_\text{U}} = \frac{1}{k_1K_1K_2[\text{OH}^-][\text{ASP}]} + \frac{1}{k_1K_2[\text{ASP}]} + \frac{1}{k_1} \quad (6)$$

According to Eq. (6), the plots of $1/k_\text{U}$ versus $1/[\text{OH}^-]$ ($r \geqslant 0.998$, $S \leqslant 0.014$) and $1/k_\text{U}$ versus 1/[ASP] ($r \geqslant 0.997$, $S \leqslant 0.016$) should be linear which is the case as given in Fig. 8. From the slopes and intercepts of such plots, the reaction constants K_1, K_2 and k_1 were calculated as (2.46 ± 0.05) dm^3 mol^{-1}, $(3.06 \pm 0.12) \times 10^4$ dm^3 mol^{-1} and $(1.23 \pm 0.04) \times 10^{-3}$ s^{-1} respectively. The value of K_1 is in the neighborhood of earlier literature [27]. Using these constants the rate constants were calculated and the values agreed well with the experimental values (Table 1).

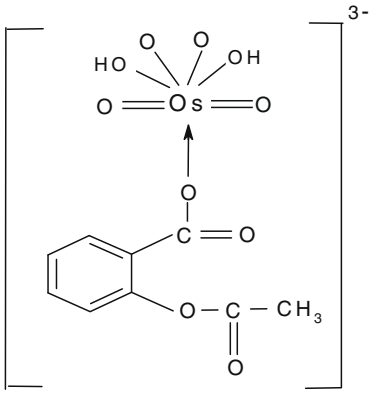
The thermodynamic quantities for the first and second equilibrium steps of Scheme 2 can be evaluated as follows. The [ASP] and [OH^-] (Table 1) were varied at four different temperatures. The plots of $1/k_\text{U}$ versus $1/[\text{OH}^-]$ and $1/k_\text{U}$ versus 1/[ASP] should be linear (Fig. 8). From the slopes and intercepts, the values of K_1 and K_2 were calculated at different temperatures and these values are given in Table 3. The van't Hoff's plots were made for variation of K_1 and K_2 with temperature ($\log K_1$ versus $1/T$ ($r \geqslant 0.9605$, $S \leqslant 0.005$), $\log K_2$ versus $1/T$ ($r \geqslant 0.994$, $S \leqslant 0.008$) and the values of enthalpy of reaction ΔH, entropy of reaction ΔS and free energy of reaction ΔG, were calculated for the first and second equilibrium steps. These values are given in Table 3. A comparison of the ΔH value (86 kJ mol^{-1}) from K_1 with that of $\Delta H^{\#}$ (42 kJ mol^{-1}) of rate limiting step supports that the reaction before the rate determining step is fairly slow as it involves high activation energy [28]. A high negative value of $\Delta S^{\#}$ (−158 J K^{-1} mol^{-1}) suggests that intermediate complex is more ordered than the reactants [29].

5. Mechanism for Os(VIII) catalysed reaction

Osmium(VIII) is known [30] to form different complexes at different OH^- 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 [30]. To explain all the observed orders, Scheme 3 is proposed for osmium(VIII) catalysed reaction.

The equilibrium step 1 and stoichiometry is same as in uncatalysed reaction. In second step anionic form of aspirin reacts with active species of osmium(VIII) to form a complex (C_1) in view of less than unit order in [ASP]. The complex (C_1) reacts with one mole of deprotonated DPC in a slow step to give a free radical of salicylate ion [25] acetate ion and copper(II) with regeneration of catalyst Os(VIII). This free radical species further reacts with three more moles of deprotonatad DPC in further fast steps to yield the products such as 1,4-benzoquinone-2-carboxylate ion, Cu(II) and periodate as given in Scheme 3.

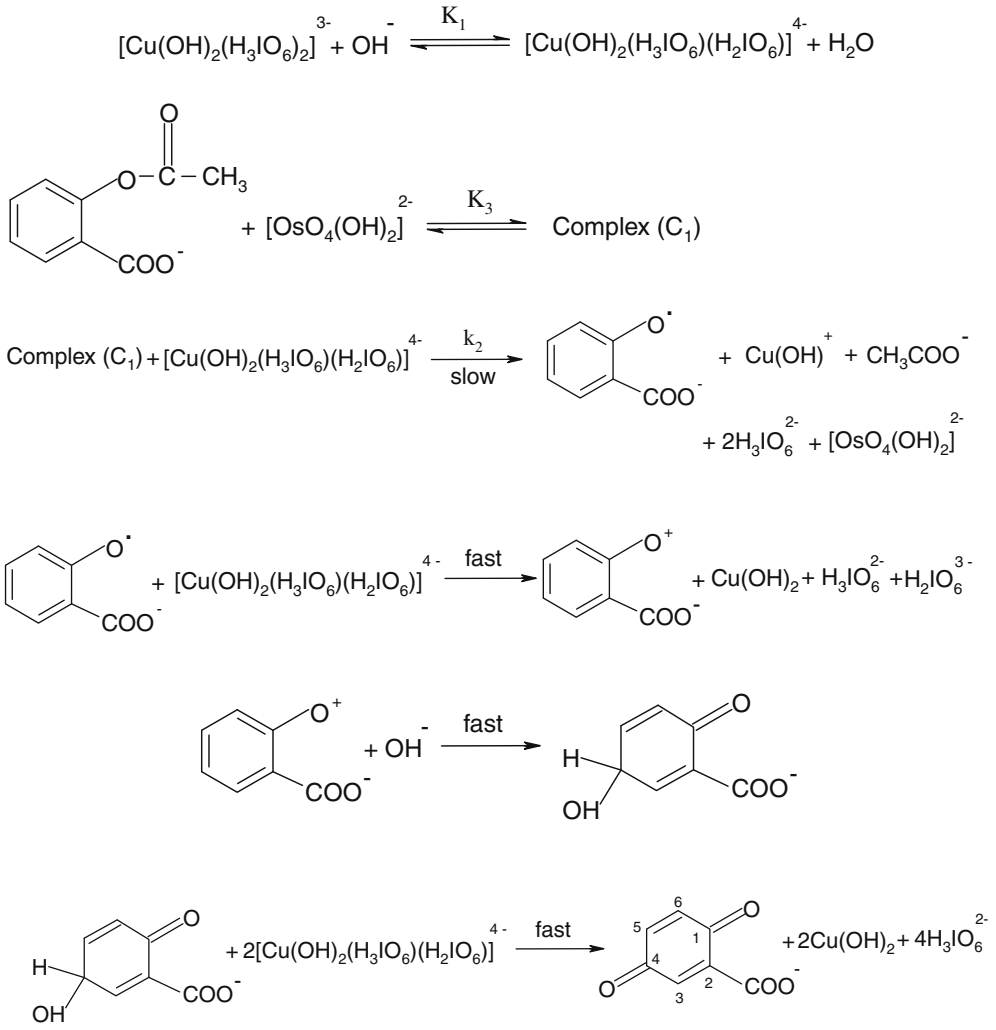
The probable structure of the complex (C_1) is given below:



Spectroscopic evidence for the complex (C_1) formation between osmium(VIII) and aspirin was obtained from UV–Vis spectra of aspirin (1.0×10^{-3}), Os(VIII) (8.0×10^{-7}), [OH^-] (0.05 mol dm^{-3}) and a mixture of both. A hypsochromic shift from 341 to 337 nm in the spectra of aspirin was observed. This is also evident from the plot of $1/k_\text{C}$ versus 1/[ASP], which shows a straight line with non-zero intercept. Such type of catalyst-substrate complex formation was also observed in other studies [31]. Scheme 3 leads to the rate law (8)

$$\text{Rate} = k_2[\text{C}_1][\text{DPC}] = k_2K_1K_3[\text{DPC}][\text{ASP}][\text{OH}^-]\text{Os(VIII)} \quad (7)$$

$$\frac{\text{Rate}}{[\text{DPC}]} = k_\text{C} = k_\text{T} - k_\text{U} = \frac{k_2K_1K_3[\text{ASP}][\text{OH}^-][\text{Os(VIII)}]}{1 + K_1[\text{OH}^-] + K_3[\text{ASP}] + K_1K_3[\text{ASP}][\text{OH}^-]} \quad (8)$$



Scheme 3. Detailed scheme for the Os(VIII) catalysed oxidation of aspirin by alkaline diperiodatocuprate(III).

The rate law (8) may be verified by rearranging it in the form of Eq. (9)

$$\frac{[\mathrm{Os(VIII)}]}{k_C} = \frac{1}{k_2K_1K_3[\mathrm{OH}][\mathrm{ASP}]} + \frac{1}{k_2K_3[\mathrm{ASP}]} + \frac{1}{k_2K_1[\mathrm{OH}^-]} + \frac{1}{k_2} \qquad (9)$$

According to Eq. (9), the plots of $[\mathrm{Os(VIII)}]/k_C$ versus $1/[\mathrm{OH}^-]$ and $[\mathrm{Os(VIII)}]/k_C$ versus $1/[\mathrm{ASP}]$ were linear (Fig. 9). From the intercepts and slopes of such plots, the reaction constants K_1, K_3, and k_2 were calculated as $(8.70 \pm 0.2)\ \mathrm{dm^3\ mol^{-1}}$, $(3.9 \pm 0.1) \times 10^2\ \mathrm{dm^3\ mol^{-1}}$, $(7.78 \pm 0.20) \times 10^4\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$, respectively. The value of K_1 is in the neighborhood of earlier literature [31]. 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 3.

The thermodynamic quantities for the different equilibrium steps, in Scheme 3 can be evaluated as follows. The aspirin and hydroxide ion concentrations (Table 2) were varied at different temperatures. The plots of $[\mathrm{Os(VIII)}]/k_C$ versus $1/[\mathrm{ASP}]$ ($r \geqslant 0.9988$, $S \leqslant 0.00132$) and $[\mathrm{Os(VIII)}]/k_C$ versus $1/[\mathrm{OH}^-]$ ($r \geqslant 0.9996$, $S \leqslant 0.00087$) should be linear as shown in Fig. 9. 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 $1/T$ ($r \geqslant 0.9984$, $S \leqslant 0.1105$)] 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 ΔH value (104 kJ mol^{-1}) from K_1 with that of $\Delta H^{\#}$ (10 kJ mol^{-1}) of rate limiting step supports that the reaction before the rate determining step is fairly slow as it involves high activation energy [28]. In the same manner, K_3 values were calculated at different temperatures and the corresponding values of thermodynamic quantities are given in Table 4.

5.1. Catalytic activity

Moelwyn-Hughes [32] pointed out that catalysed and uncatalysed reactions proceed simultaneously and the relationship is

$$k_T = k_U + K_C[\mathrm{catalyst}]^x$$

Here k_T is the observed pseudo first-order rate constant obtained in the presence of osmium(VIII) catalyst, k_U is that for the uncatalysed reaction, K_C is the catalytic constant and x is the order of the relation with respect to osmium(VIII) which is found to be unity in the present study. The value of K_C was calculated using the equation

$$K_C = (k_T - k_U)/[\mathrm{Os(VIII)}]^x = k_C/[\mathrm{Os(VIII)}]^x$$

The values of K_C were evaluated at different temperatures (298–318 K) and K_C was found to vary with temperature. A plot of $\log K_C$ versus $1/T$ was linear and the values of energy of activation and other thermodynamic parameters for the catalyst are tabulated in Table 5.

Table 4
Thermodynamic activation parameters for the Os(VIII) catalysed oxidation of aspirin by DPC in alkaline medium with respect to the slow step of Scheme 3.

Temperature (K)		$10^{-4}\ k_2$ (dm^3 mol^{-1} s^{-1})
(A) Effect of temperature		
298		7.78
303		8.12
308		8.68
313		9.83
318		10.4
Parameters		Values
(B) Activation parameters (Scheme 3)		
Ea (kJ mol^{-1})		12 ± 1
$\Delta H^{\#}$ (kJ mol^{-1})		10 ± 1
$\Delta S^{\#}$ (J K^{-1} mol^{-1})		−119 ± 8
$\Delta G^{\#}$ (kJ mol^{-1})		45 ± 2
log *A*		7.0 ± 0.3
Temperature (K)	K_1 (dm^3 mol^{-1})	$K_3 \times 10^{-2}$ (dm^3 mol^{-1})
(C) Effect of temperature to calculate K_1 and K_3 for the oxidation of aspirin by diperiodatocuprate(III) in alkaline medium		
298	8.70	3.9
303	34.5	3.4
308	58.0	3.0
313	106	2.8
318	132	2.4
Thermodynamic quantities	Values from K_1	Values from K_3
(D) Thermodynamic quantities using K_1 and K_3		
ΔH (kJ mol^{-1})	104 ± 08	−17 ± 0.8
ΔS (J K^{-1} mol^{-1})	372 ± 35	−10 ± 0.2
ΔG_{298} (kJ mol^{-1})	−3.5 ± 1.0	−15 ± 1.0

[DPC] = 1.0×10^{-4}; [ASP] = 1.0×10^{-3}; [OH$^-$] = 0.05; [IO_4^-] = 1.0×10^{-5}; [Os(VIII)] = 8.0×10^{-7}; I = 0.10 mol dm^{-3}.

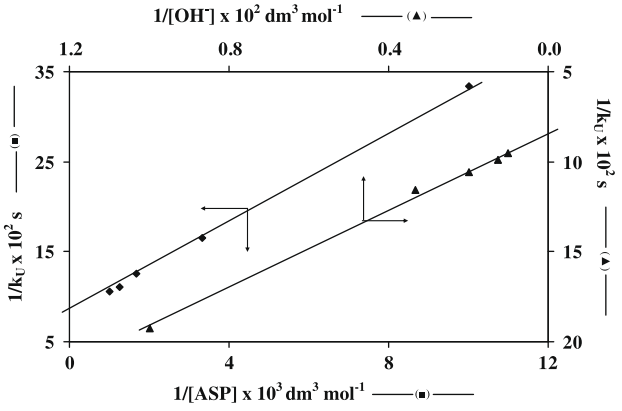


Fig. 8. Verification of rate law (6) for the oxidation of aspirin by diperiodatocuprate(III) at 298 K.

The increases in the rate, with increasing ionic strength, is in favor of reaction between charged species of reactants, as present in Schemes 2 and 3. The effect of solvent on the reaction rate is described in detail in the literature [33]. For the limiting case of a zero angle approach between two dipoles or anion dipole system, Amis [34] has shown that log k_{obs} versus $1/D$ gives a straight line, with a negative slope for a reaction between negative ion and a dipole or between two dipoles, while a positive slope is obtained for positive ion-dipole reactions. In the present investigations, plot of log k_U or k_C versus $1/D$ were linear with negative slopes, which supports the involvement of negative ions as in Schemes 2 and 3.

The negative value of $\Delta S^{\#}$ suggests that the intermediate complex is more order than the reactants [29]. The observed higher

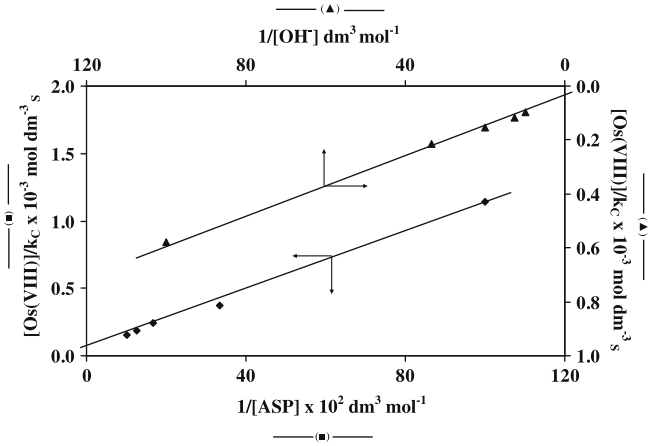


Fig. 9. Verification of rate law (9) of Os(VIII) catalysed oxidation of aspirin by diperiodatocuprate(III) at 298 K.

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

Temperature (K)	$K_C \times 10^{-3}$ (dm^3 mol^{-1} s^{-1})
298	4.47
303	8.25
308	12.6
313	17.4
318	21.2
Ea (kJ mol^{-1})	40.4 ± 2.1
$\Delta H^{\#}$ (kJ mol^{-1})	37.9 ± 1.5
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−47.4 ± 5.0
$\Delta G^{\#}$ (kJ mol^{-1})	52.0 ± 2.5
log *A*	10.7 ± 0.5

[DPC] = 1.0×10^{-4}; [ASP] = 1.0×10^{-3}; [OH$^-$] = 0.05 mol dm^{-3}; [IO_4^-] = 1.0×10^{-5} mol dm^{-3}; [Os(VIII)] = 8.0×10^{-7} mol dm^{-3}; I = 0.10 mol dm^{-3}.

rate constant for the slow step indicate that the oxidation presumably occurs via an inner-sphere mechanism. This conclusion is supported by earlier observation [35]. The activation parameters evaluated for the catalysed and uncatalysed reaction explain the catalytic effect on the reaction. The catalyst, Os(VIII) form the complex (C_1) with substrate which enhances the reducing property of the substrate than that without catalyst, Os(VIII). Further the catalyst Os(VIII) modifies the reaction path by lowering the energy of activation.

6. Conclusion

Among the various species of Cu(III) in alkaline medium, deprotonated form of diperiodatocuprate(III)(DPC)[$Cu(OH)_2(H_3IO_6)(H_2IO_6)$]$^{4-}$ is considered as the active species. The active species of osmium(VIII) is found to be $[OsO_4(OH)_2]^{2-}$. Thermodynamic quantities of individual steps in the mechanisms were evaluated. Activation parameters with respect to slow step were also computed. The overall sequence is consistent with the observed product, mechanistic and kinetic study.

Appendix A

According to Scheme 2

$$\text{Rate} = \frac{-\text{d[DPC]}}{\text{dt}} = k_1[\text{C}] = k_1K_1K_2[\text{DPC}][\text{ASP}][\text{OH}^-] \quad (\text{A.1})$$

The total concentration of DPC is given by (where T and f stands for total and free, respectively)

$$[DPC]_T = [DPC]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-} + [C]$$
$$= [DPC]_f\{1 + K_1[OH^-] + K_1K_2[ASP][OH^-]\}$$

Therefore,

$$[DPC]_f = \frac{[DPC]_T}{1 + K_1[OH^-] + K_1K_2[ASP][OH^-]} \quad (A.2)$$

Similarly,

$$[ASP]_T = [ASP]_f + [C]$$
$$[ASP]_f = \frac{[ASP]_T}{1 + K_1K_2[DPC][OH^-]}$$

In view of low concentration of [DPC] used,

$$[ASP]_f = [ASP]_T \quad (A.3)$$

Similarly,

$$[OH^-]_f = [OH^-]_T \quad (A.4)$$

Substituting Eqs. (A.2)–(A.4) in Eq. (A.1) and omitting T and f we get

$$\frac{\text{Rate}}{[DPC]} = k_U = \frac{k_1K_1K_2[ASP][OH^-]}{1 + K_1[OH^-] + K_1K_2[ASP][OH^-]}$$

Appendix B

According to Scheme 3

$$\text{Rate} = k_2[C_1][DPC]$$
$$= k_2K_1K_3[DPC][ASP][OH^-][Os(VIII)] \quad (B.1)$$

The total concentration of DPC is given by (subscripts T and f stands for total and free, respectively)

$$[DPC]_T = [DPC]_f + [Cu(OH)_2(H_3IO_6)(H_2IO_6)]^{4-}$$
$$= [DPC]_f + K_1[DPC][OH^-]$$
$$[DPC]_T = [DPC]_f(1 + K_1[OH^-])$$

Therefore,

$$[DPC]_f = \frac{[DPC]_T}{1 + K_1[OH^-]} \quad (B.2)$$

Similarly,

$$[ASP]_f = \frac{[ASP]_T}{1 + K_3[Os(VIII)]} \qquad [OH]_f = \frac{[OH]_T}{1 + K_3[DPC]}$$

In view of low concentration of [Os(VIII) and [DPC] used,

$$[ASP]_f = [ASP]_T \quad (B.3)$$
$$[OH^-]_f = [OH^-]_T \quad (B.4)$$

And,

$$[OS(VIII)]_T = [OS(VIII)]_f + [C_1] = [Os(VIII)_f](1 + K_3[ASP])$$
$$[OS(VIII)]_f = \frac{[Os(VIII)]_T}{1 + K_3[ASP]} \quad (B.5)$$

Substituting Eqs. (B.2)–(B.5) in Eq. (B.1) and omitting T and f we get

$$\frac{\text{Rate}}{[DPC]} = k_C = k_T - k_U = \frac{k_2K_1K_3[ASP][OH^-][Os(VIII)]}{1 + K_1[OH^-] + K_3[ASP] + K_1K_3[ASP][OH^-]}$$

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