

Kinetic and mechanistic studies of oxidation of chloramphenicol by sodium metaperiodate using Rh(III)-chloride as homogeneous catalyst

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The kinetics of oxidation of an antibiotic drug, chloramphenicol (CHP) by NaIO_4 in the presence of Rh(III) catalyst has been investigated in alkaline medium at 35 °C. The reaction shows first order kinetics with respect to $[\text{IO}_4^-]$ and $[\text{Rh(III)}]$. The fractional positive order kinetics in $[\text{OH}^-]$ and $[\text{CHP}]$ throughout their variations are observed. Ionic strength and dielectric constant of the medium show no effects on the reaction rates. No effect of $[\text{Cl}^-]$ is observed in the presence of Rh(III) chloride. The values of rate constants observed at four different temperatures have been utilized to calculate various activation parameters. The species IO_4^- and $[\text{RhCl}_3(\text{H}_2\text{O})_2\text{OH}]$ are proposed as the reactive species of NaIO_4 and Rh(III) respectively in alkaline medium. On the basis of kinetic results, spectroscopic information and activation parameters, a suitable mechanism and rate law for the oxidation of CHP has been proposed.

Keywords: Kinetics, Reaction mechanism, Oxidation, Rhenium, Chloramphenicol

In alkaline media, sodium metaperiodate is a less potent oxidant than in acid media. In alkaline medium, periodate is known to exist as different species involving multiple equilibria¹. Since it is widely employed as a diol cleaving agent², it is necessary to ascertain the active form of oxidant in the reaction. Sodium metaperiodate is a powerful oxidizing agent used for various catalysed^{3,4} and uncatalysed^{5,6} oxidations of dimethyl sulfoxide, N-methylaniline, L-arginine and hexacyanoferrate(II) in alkaline/acid medium.

Chloramphenicol (CHP) is effective against a wide variety of gram positive and gram negative bacteria, including mostly anaerobic microorganisms. It is considered a prototypical broad spectrum antibiotic, alongside the tetracyclines. In recent years, the platinum group metal ions including Ru(III), Os(VIII), Ir(III), Pd(II) and Rh(III) have been widely used as catalysts due to their strong catalytic influences in various reactions. Several reports are available on kinetics of oxidation of CHP by various oxidant such as chloramine-T⁷, cerium(IV)⁸, hexacyanoferrate(III)⁹ using Ru(III) as catalyst. The use of Ir(III) chloride as a non-toxic and homogeneous catalyst has been reported¹⁰. The coordination chemistry of Rh(III)¹¹ has drawn considerable attention due to its chemical reactivity, antitumor activity, electronic structure and catalytic functions of its complexes with potential industrial application. It is also reported that Rh(III) forms

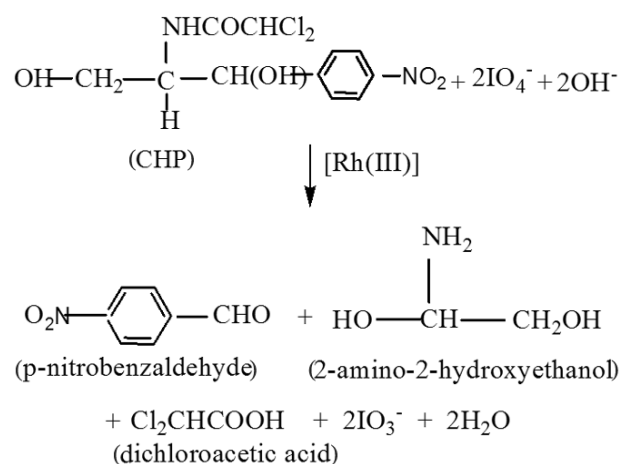
complexes with nitrogen donor ligands¹², viz., ethylene diamine, pyridine, 2,2'-bipyridine and 1, 10-phenanthroline, which are reported to have antibacterial and antitumor activities. Recently, the use of chloro complex of Rh(III) as homogeneous catalyst has been reported for the oxidation of reducing sugars by N-bromoacetamide¹³ and N-bromosuccinimide¹⁴ in acid medium. A report is available on catalytic activity of palladium(II) and osmium(VIII) on the oxidation of CHP by copper(III) periodate complex in aqueous alkaline medium¹⁵. From the kinetic and mechanistic point of view, literature survey revealed that till date the role of Rh(III) catalyst on the oxidation of CHP by periodate has not been examined. The objectives of the present study are to ascertain the influence of the oxidant, substrate and the medium on the reaction kinetics, explore the catalytic activity of Rh(III) on the oxidation of CHP by NaIO_4 , identify the oxidation products during the course of reaction and ascertain the various reactive species of catalysts and oxidant, and also elucidate a plausible mechanism and appropriate rate law.

Materials and Methods

All the standard solutions were prepared in doubly distilled water. All chemicals used were of A.R. grade. The solution of CHP (Sisco Chem) was prepared by dissolving known amount of the samples in distilled water. An aqueous solution of NaIO_4

(E. Merck) was prepared by dissolving a weighed amount in doubly distilled water. The solution of Rh(III) chloride (Loba) was prepared by dissolving 1 g of the sample in hydrochloric acid of known strength. The strength of Rh(III) chloride (RhCl_3) was 3.80×10^{-3} M in which the molar strength of HCl was maintained at 3 M. All the reagents used were of highest purity available. The reaction mixture containing appropriate amounts of all reactants, i.e., NaIO_4 , Rh(III)-chloride, NaOH and water except substrate (CHP) was taken in a reaction vessel and placed in a thermostatic bath at constant temperature (35°C) with an accuracy of $\pm 0.1^\circ\text{C}$. A freshly prepared solution of CHP was also kept in the same thermostatic bath at the same temperature. When both the solutions had acquired the temperature of bath, a measured amount of CHP solution was pipetted out and mixed in a conical flask containing the reaction mixture. As soon as the CHP solution was mixed with the reaction mixture, the reaction was initiated. To know the actual progress of the reaction, 5 mL of the reaction mixture was taken out and poured into a conical flask containing 5 mL of KI (4%) solution and 5 mL of HClO_4 solution and the unconsumed NaIO_4 was ascertained iodometrically against standard hypo solution using starch as indicator.

Various sets of experiments were performed with different $[\text{NaIO}_4]:[\text{CHP}]$ ratios under kinetic conditions for 72 h. Determination of unconsumed NaIO_4 revealed that for the oxidation of 1 mol of CHP, 2 mol of NaIO_4 were required. Accordingly, the following stoichiometric equation can be formulated:



Results and Discussion

Kinetics of oxidation of CHP by alkaline solution of NaIO_4 in presence of Rh(III) chloride as

homogeneous catalyst were studied at constant temperature 35°C . The initial rate, i.e., $(-dc/dt)$ of the reaction in each kinetic run was calculated by the slope of the tangent drawn at fixed concentration of the oxidant and pseudo first-order rate constant (k_1) was calculated as $k_1 = \frac{(-dc/dt)}{[\text{NaIO}_4]}$

The rate of the reaction increased in the same proportion in which the concentration of NaIO_4 increased, which indicates that the order of reaction with respect to $[\text{IO}_4^-]$ is unity throughout its ten-fold variation from 0.50×10^{-4} to 5.00×10^{-4} M at constant concentration of all other reactants. This result is further verified by the linear plots passing through the origin in the plots of $-dc/dt$ versus $[\text{NaIO}_4]$ in the oxidation of CHP (Fig. 1). In order to study the effect of $[\text{CHP}]$ on the rate of reaction, its concentration was varied in the range from 0.50×10^{-3} to 5.00×10^{-3} M at 35°C . The data presented in Fig. 2 shows fractional positive order dependence of CHP on the rate of reaction.

The order of reaction with respect to OH^- was investigated by varying the concentration of NaOH from $(5.00-50.00) \times 10^{-2}$ M. The reaction showed fractional positive order in $[\text{OH}^-]$ (Fig. 3). The effect of catalyst on the rate of the reaction was studied at constant concentration of all other reactants. The rate constants obtained was found to increase with the increase in $[\text{Rh(III)}]$ in direct proportion. The order in $[\text{Rh(III)}]$ was found to be unity from the linearity of

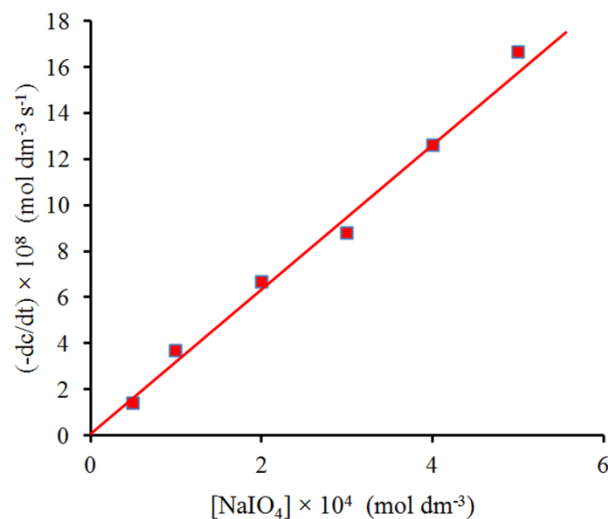


Fig. 1 – Plot between $-dc/dt$ and $[\text{NaIO}_4]$ at 35°C . $\{[\text{CHP}] = 1.00 \times 10^{-3}$ M, $[\text{RhCl}_3] = 3.78 \times 10^{-6}$ M, $[\text{NaOH}] = 10.00 \times 10^{-2}$ M, $[\text{KCl}] = 4.00 \times 10^{-2}$ M, $\mu = 0.70$ M $\}$.

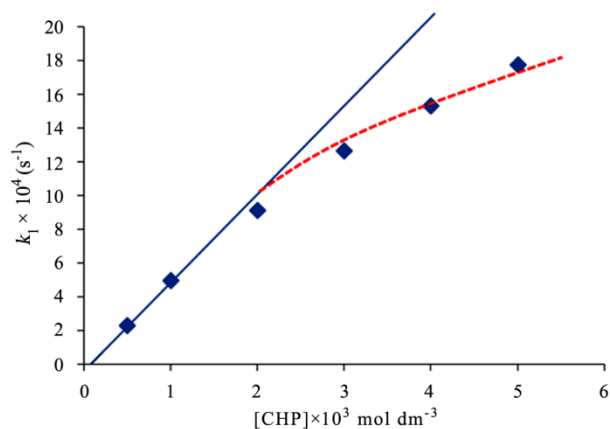


Fig. 2 – Plot between k_1 and $[\text{CHP}]$ at 35 °C. $\{[\text{NaIO}_4] = 1.00 \times 10^{-4} \text{ M}, [\text{RhCl}_3] = 3.78 \times 10^{-6} \text{ M}, [\text{NaOH}] = 10.00 \times 10^{-2} \text{ M}, [\text{KCl}] = 4.00 \times 10^{-2} \text{ M}, \mu = 0.70 \text{ M}\}$.

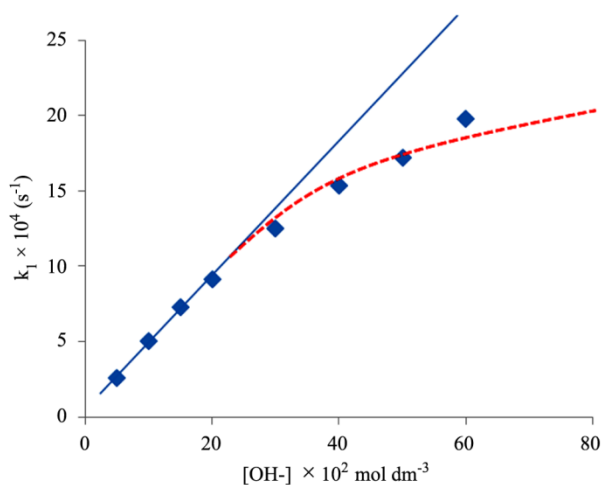


Fig. 3 – Plot between k_1 and $[\text{OH}^-]$ at 35 °C. $\{[\text{NaIO}_4] = 1.00 \times 10^{-4} \text{ M}, [\text{CHP}] = 1.00 \times 10^{-3} \text{ M}, [\text{RhCl}_3] = 3.78 \times 10^{-6} \text{ M}, [\text{KCl}] = 4.00 \times 10^{-2} \text{ M}, \mu = 0.70 \text{ M}\}$.

the plot of k_1 versus $[\text{Rh(III)}]$ (Fig. 4). Change in dielectric constant, ionic strength of the medium and $[\text{Cl}^-]$ had negligible effect on the rate of the reaction. The value of k was found to vary at different temperatures. From the linear plot of $\log k$ versus $1/T$, the activation energy ($E_a = 38.68 \text{ kJ mol}^{-1}$) was computed, and along with the rate constant, k_r ($1.15 \times 10^5 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$) the other activation parameters such as ΔH^\ddagger ($36.07 \text{ kJ mol}^{-1}$), ΔS^\ddagger ($-31.52 \text{ J K}^{-1} \text{ mol}^{-1}$), ΔG^\ddagger ($45.74 \text{ kJ mol}^{-1}$), and A ($3.55 \times 10^{11} \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$) were calculated.

Wasmuth and co-workers¹⁶ have reported that there are different forms of periodic acids with the change in pH from 1 to 13.6. According to them, at pH = 1, 75% of periodate remains in the form of H_5IO_6^- and at

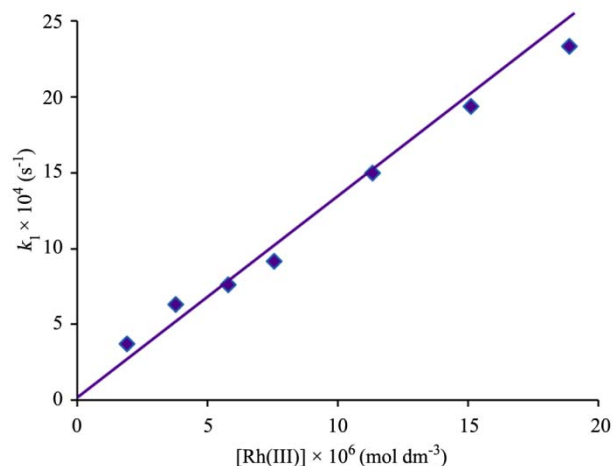
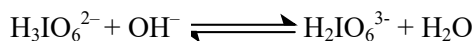


Fig. 4 – Plot between k_1 and $[\text{Rh(III)}]$ at 35 °C. $\{[\text{NaIO}_4] = 1.00 \times 10^{-4} \text{ M}, [\text{CHP}] = 1.00 \times 10^{-3} \text{ M}, [\text{NaOH}] = 10.00 \times 10^{-2} \text{ M}, [\text{KCl}] = 4.00 \times 10^{-2} \text{ M}, \mu = 0.70 \text{ M}\}$.

pH = 6.5, 97% is in the form of IO_4^- and 3% as H_4IO_6^- . At pH = 10.2, 100% periodate is in the form of $\text{H}_3\text{IO}_6^{2-}$ and at pH = 13.6, it is 100% in the form of $\text{H}_2\text{IO}_6^{3-}$. Herein, the study has been made for Rh(III) catalyzed oxidation of CHP in alkaline medium. Throughout the study, the pH of the solution was maintained either at ~13 or above. As per available literature¹⁶ and the spectrum for periodate solution alone (Fig. 5 (curve)), where a single peak was observed, it can be concluded that 100% of periodate is present in the form of $\text{H}_3\text{IO}_6^{2-}$ in the reaction under investigation. The study on the effect of variation of $[\text{OH}^-]$ on the rate of oxidation of CHP showed that there was a positive effect of $[\text{OH}^-]$ on the rate of reaction. Keeping in view the positive effect of $[\text{OH}^-]$ on the rate of oxidation, the existence of the following equilibrium is proposed in the reaction under investigation.



UV-vis spectra for the solutions of IO_4^- alone and for the solutions of IO_4^- with two different concentration of OH^- showed that there is substantial increase in absorbance (from 0.23 to 0.29 and 0.37) with the increase in $[\text{OH}^-]$ (Fig. 5 (curves 1-3)). This increase in absorbance with the increase in $[\text{OH}^-]$ may be due to increased formation of $[\text{H}_2\text{IO}_6^{3-}]$ according to the above mentioned equilibrium.

On the basis of the above, $\text{H}_2\text{IO}_6^{3-}$ is proposed to be the reactive species of NaIO_4 in alkaline medium in the oxidation of CHP in the presence of the chloro complex of Rh(III) as homogeneous catalyst.

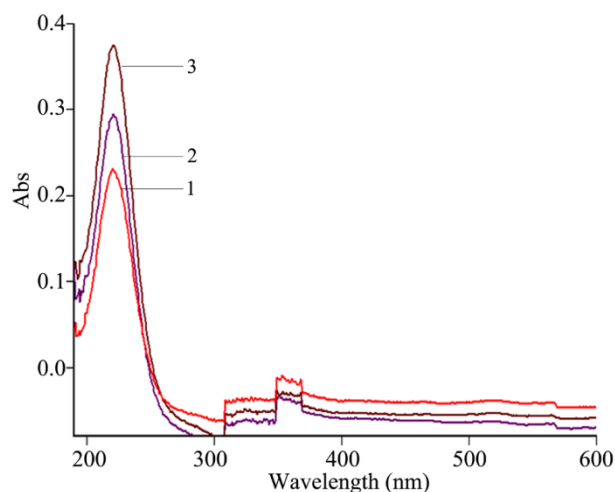


Fig. 5 – Absorption spectra of reaction solutions containing IO_3^- and OH^- at room temperature. {(1) $[\text{NaIO}_4] = 2.00 \times 10^{-5} \text{ M}$; (2) $[\text{NaIO}_4] = 2.00 \times 10^{-5} \text{ M}$, $[\text{OH}^-] = 10.00 \times 10^{-4} \text{ M}$; (3) $[\text{NaIO}_4] = 2.00 \times 10^{-5} \text{ M}$, $[\text{OH}^-] = 30.00 \times 10^{-4} \text{ M}$ }.

It is reported that Rh(III) forms a variety of complexes such as $[\text{RhCl}]^{2+}$, $[\text{RhCl}]^+$, RhCl_3 , $[\text{RhCl}_4]^-$, $[\text{RhCl}_4]^{2-}$ and $[\text{RhCl}_6]^{3-}$ in the presence of HCl ^{17,18}. In view of the literature reported^{19,20}, between the two species, $[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{RhCl}_6]^{3-}$, there are clearly several intermediates. The stock solution of Rh(III) chloride prepared in 3 M HCl ($3.79 \times 10^{-3} \text{ M}$) was further diluted with the doubly distilled water and the concentration of the catalyst Rh(III) chloride in each kinetic run was fixed in the order of 10^{-9} . From the observed kinetic data and the reported literature, it may be presumed that Rh(III) chloride is generated from $[\text{RhCl}_3(\text{H}_2\text{O})_3]$. This assumption is supported by the nil effect of $[\text{Cl}^-]$ on the rate of oxidation and also by the spectral evidence. In the present study, the effect of OH^- is of fractional positive order, hence absorbance spectra for different solutions of Rh(III) chloride with varying concentration of OH^- were recorded. On the basis of observed kinetic order with respect to $[\text{OH}^-]$ and also on the basis of spectra observed for $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ solution alone and for $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ solutions with two different concentrations of OH^- (where an increase in absorbance from 0.26 to 0.35 and 0.39 respectively was noted for $[\text{OH}^-] = 1.00 \times 10^{-3} \text{ M}$ and $4.00 \times 10^{-3} \text{ M}$) (Fig. 6 (curves 1-3)), the equilibrium (I) in Scheme 1 is proposed to exist in the reaction under investigation.

Of the two species, i. e., $[\text{RhCl}_3(\text{H}_2\text{O})_3]$ and $[\text{RhCl}_3(\text{H}_2\text{O})_2(\text{OH})]$, the species $[\text{RhCl}_3(\text{H}_2\text{O})_2(\text{OH})]^-$ can be considered as the reactive species of

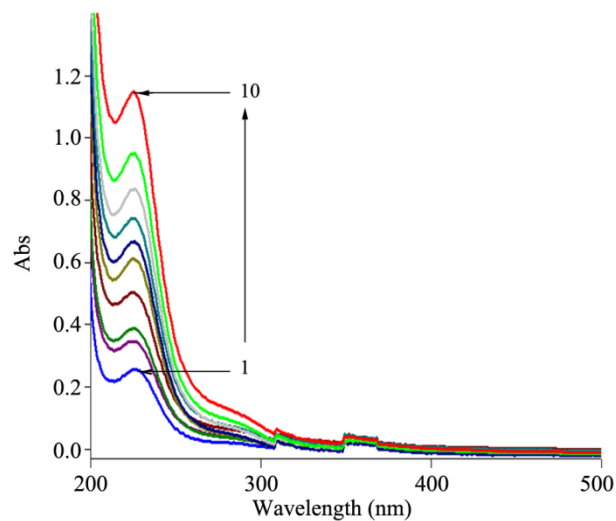


Fig. 6 – Absorption spectra of reaction solutions containing Rh(III), OH^- , NaIO_4 and CHP at room temperature. {(1) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$; (2) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 1.00 \times 10^{-3} \text{ M}$; (3) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$; (4) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 5.00 \times 10^{-4} \text{ M}$; (5) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$; (6) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 1.00 \times 10^{-5} \text{ M}$; (7) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 3.00 \times 10^{-5} \text{ M}$; (8) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 6.00 \times 10^{-5} \text{ M}$; (9) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 8.00 \times 10^{-5} \text{ M}$; (10) $[\text{Rh}(\text{III})] = 7.56 \times 10^{-6} \text{ M}$, $[\text{OH}^-] = 4.00 \times 10^{-3} \text{ M}$, $[\text{CHP}] = 10.00 \times 10^{-4} \text{ M}$, $[\text{NaIO}_4] = 12.00 \times 10^{-5} \text{ M}$ }.

Rh(III) chloride in alkaline medium because only with this reactive species the positive-order in $[\text{OH}^-]$ can be explained satisfactorily and a suitable rate law can be derived.

On the basis of the observed kinetic data, an effort was made to investigate the possibility of formation of a complex between CHP and the reactive form of Rh(III) chloride. Absorbance spectra of solutions containing Rh(III) chloride, NaOH , NaIO_4 and CHP were recorded. The increase in absorbance from 0.26 to 0.35 and 0.39, on addition of $[\text{OH}^-] = 1.00 \times 10^{-3} \text{ M}$ and $4.00 \times 10^{-3} \text{ M}$ indicates formation of a complex $[\text{RhCl}_3(\text{H}_2\text{O})_2\text{OH}]^-$ (Scheme 1). When two different concentrations of CHP ($[\text{CHP}] = 5.00 \times 10^{-4} \text{ M}$ and $10.00 \times 10^{-4} \text{ M}$) were added to the solution of Rh(III) and OH^- , it was found that there is an increase in absorbance from 0.39 to 0.50 and 0.61 respectively with a slight shift in λ_{max} value towards longer wavelength, i. e., from 224 to 224.67 and 225 nm (Fig. 6 (curves 3-5)). This increase in absorbance with the increase in $[\text{CHP}]$ is due to more and more formation of a complex between Rh(III) chloride, i.e.,

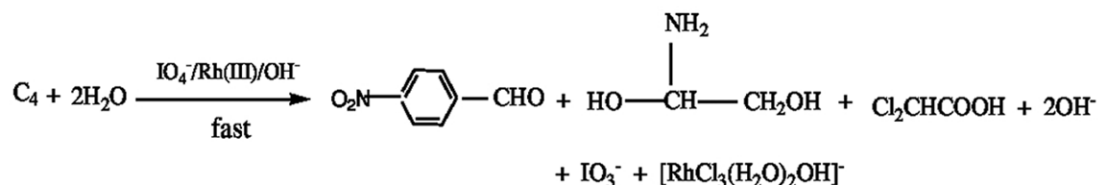
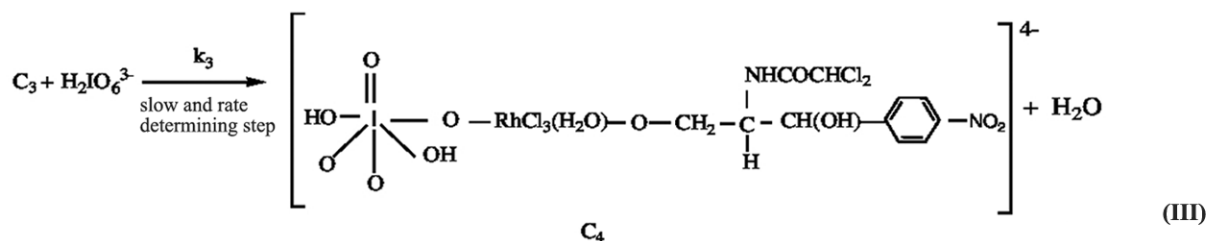
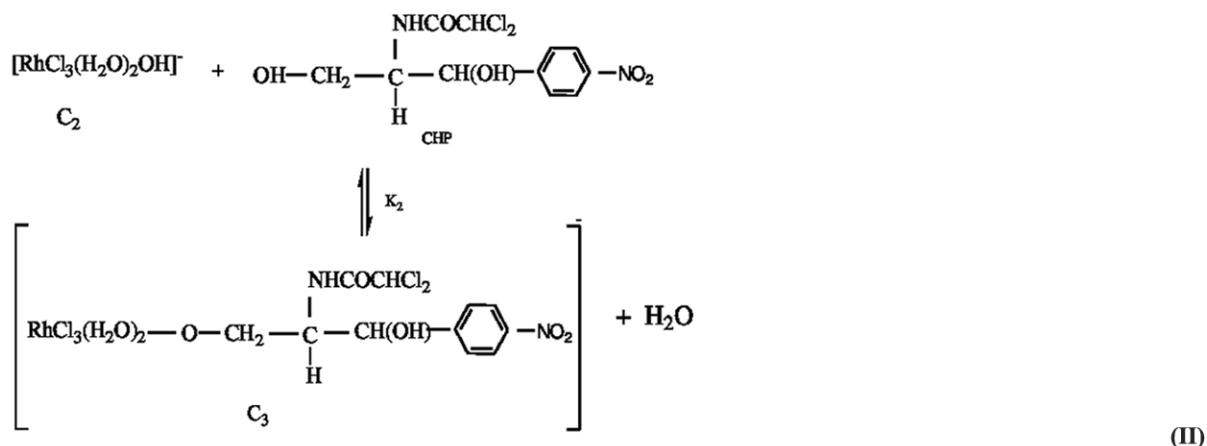
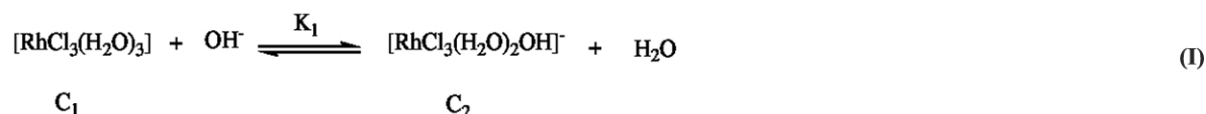
C₂ and CHP, according to the equilibrium (II) in Scheme 1.

Further, when increasing concentrations of IO₄⁻ ((1.00 to 12.00) × 10⁻⁵ M) were added to the solution of Rh(III), OH⁻ and CHP, there was an increase in absorbance from 0.61 to 1.15 with a slight shift in λ_{max} value towards longer wavelength, that is, from 225 to 226 nm (Fig. 6 (curves 5–10)). This indicates that reactive form of IO₄⁻ combines with the complex (C₃) to form a new complex (C₄). The formation of this 1:1 complex, (C₄) is supported by Job's plot (1/ΔA versus 1/[IO₄⁻]), where a straight line with positive intercept on y-axis was obtained.

Taking into consideration the observed kinetic orders with respect to reactants involved, spectrophotometric evidence collected for the formation of complexes during the course of reaction, effect of dielectric constant of the medium on the rate of oxidation and also the negative entropy of activation, the most probable mechanism is proposed for the Rh(III)-catalysed oxidation of CHP by NaIO₄ in alkaline medium (Scheme 1).

On the basis of the above proposed reaction scheme, the rate of reaction in terms of decrease in the concentration of IO₄⁻ can be written as,

$$\text{rate} = -\frac{d[\text{IO}_4^-]}{dt} = 2k_3 [\text{H}_2\text{IO}_6^{3-}] [\text{C}_3] \quad \dots (1)$$



Scheme 1

where one mole of CHP is oxidized by 2 moles of NaIO_4 .

On applying the law of chemical equilibrium to equilibrium (I) and (II), we get Eqs (2) and (3) respectively.

$$[C_2] = K_1 [C_1][\text{OH}^-] \quad \dots(2)$$

$$[C_3] = K_2 [C_2][\text{CHP}] \quad \dots(3)$$

Equations (2) and (3) will give Eq. (4)

$$[C_3] = K_1 K_2 [C_1][\text{OH}^-][\text{CHP}] \quad \dots(4)$$

On substituting the value of C_3 from Eq. (4) to Eq. (1), we get Eq. (5)

$$\text{rate} = 2k_3 K_1 K_2 [\text{H}_2\text{IO}_6^{3-}] [C_1][\text{OH}^-][\text{CHP}] \quad \dots(5)$$

According to Scheme 1, the total concentration of Rh(III), i.e., $[\text{Rh(III)}]_T$ at any time in the reaction can be shown as Eq. (6)

$$[\text{Rh(III)}]_T = [C_1] + [C_2] + [C_3] \quad \dots(6)$$

Equation (7) based on Eqs (2), (4) and (6) is as follows

$$[C_1] = \frac{[\text{Rh(III)}]_T}{1 + K_2 [\text{OH}^-] + K_1 K_2 [\text{CHP}][\text{OH}^-]} \quad \dots(7)$$

On substituting the value of $[C_1]$ from Eq. (7) to Eq. (5), we get Eq. (8).

$$\begin{aligned} \text{rate} &= -\frac{d[\text{IO}_4^-]}{dt} \\ &= \frac{2k_3 K_1 K_2 [\text{H}_2\text{IO}_6^{3-}][\text{OH}^-][\text{CHP}][\text{Rh(III)}]_T}{1 + K_2 [\text{OH}^-] + K_1 K_2 [\text{CHP}][\text{OH}^-]} \quad \dots(8) \end{aligned}$$

Under the condition, $1 + K_1 K_2 [\text{CHP}][\text{OH}^-] \gg K_1 [\text{OH}^-]$, above equation will take the shape of Eq. (9),

$$\begin{aligned} \text{rate} &= -\frac{d[\text{IO}_4^-]}{dt} \\ &= \frac{2k_3 K_1 K_2 [\text{H}_2\text{IO}_6^{3-}][\text{OH}^-][\text{CHP}][\text{Rh(III)}]_T}{1 + K_1 K_2 [\text{CHP}][\text{OH}^-]} \quad \dots(9) \end{aligned}$$

The rate law (9) derived on the basis of proposed Scheme 1 is in close agreement with the kinetic information obtained experimentally about the effect

of $[\text{IO}_4^-]$, $[\text{CHP}]$, $[\text{Rh(III)}]_T$ and $[\text{OH}^-]$ on the rate of oxidation of CHP. Equation (9) can also be written as

$$\frac{1}{\text{rate}} = \frac{1 + K_1 K_2 [\text{CHP}][\text{OH}^-]}{2k_3 K_1 K_2 [\text{H}_2\text{IO}_6^{3-}][\text{OH}^-][\text{CHP}][\text{Rh(III)}]_T} \quad \dots(10)$$

$$\frac{[\text{H}_2\text{IO}_6^{3-}][\text{Rh(III)}]_T}{\text{rate}} = \frac{1}{2k_3 K_1 K_2 [\text{OH}^-][\text{CHP}]} + \frac{1}{2K_3} \quad \dots(11)$$

According to Eq. (11), when $[\text{H}_2\text{IO}_6^{3-}][\text{Rh(III)}]_T / \text{rate}$ is plotted against $1/[\text{OH}^-]$ and $1/[\text{CHP}]$ straight lines with positive intercepts on Y-axis were obtained (Supplementary data, Figs S1 & S2). This clearly shows that with respect to $[\text{OH}^-]$ and $[\text{CHP}]$, the order is fractional positive. From the slopes and intercepts of straight lines, the value of $2k_3 K_1 K_2$ and $K_1 K_2$ were calculated as $0.15 \times 10^7 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$ and $1.20 \times 10^3 \text{ mol}^{-2} \text{ dm}^6$ respectively, from which the rates of reaction were calculated for the variations of $[\text{OH}^-]$ and $[\text{CHP}]$ and were found to be very close to the experimental rates (Table 1). This proves the validity of rate law (9) and the proposed mechanism.

For the reaction between ions of unlike sign there is generally an entropy increase going from reactants to activated complex and for ions of like sign, there is an entropy decrease²¹. In the present study on oxidation of CHP by alkaline solution of NaIO_4 in the presence of Rh(III) chloride as homogeneous catalyst, the entropy of activation was found to be $-31.52 \text{ J K}^{-1} \text{ mol}^{-1}$. The observed negative entropy of activation clearly supports the interaction between the species C_3 and $\text{H}_2\text{IO}_6^{3-}$, leading to the formation of most reactive activated complex, (C_4), (step III) as shown in the proposed reaction mechanism.

Experimental kinetic data for the variation of $[\text{CHP}]$, $[\text{Rh(III)}]$ and $[\text{OH}^-]$ were analyzed for multiple regression analysis, and the equation of fitted model was obtained in the form of Eq. (12).

$$\begin{aligned} \ln k_1 &= 4.81786 + 0.903513 \times \ln [\text{Rh(III)}] \\ &\quad + 0.809139 \times \ln [\text{CHP}] + 0.775351 \times \ln [\text{OH}^-] \quad \dots(12) \end{aligned}$$

On the basis of Eq. (12), the rates for the variation of $[\text{CHP}]$, $[\text{Rh(III)}]$ and $[\text{OH}^-]$ were calculated and found in close agreement with the experimental rates

Table 1 – Experimental and calculated values of the reaction rate for the variations of [CHP], [OH⁻] and [Rh(III)] in Rh(III)-catalysed oxidation of CHP by NaIO₄ at 35 °C

[CHP] × 10 ³ (M)	[OH ⁻] × 10 ² (M)	[Rh(III)] × 10 ⁶ (M)	-dc/dt × 10 ⁸ (M s ⁻¹)		
			Expt.	Eq. (9)	Multiple regression analysis
0.50	10.00	3.78	2.33	2.66	2.96
1.00	10.00	3.78	5.00	5.06	5.19
2.00	10.00	3.78	9.16	9.14	9.10
3.00	10.00	3.78	12.66	12.50	12.64
4.00	10.00	3.78	15.33	15.32	15.95
5.00	10.00	3.78	17.77	17.72	19.11
1.00	5.00	3.78	2.60	2.66	3.03
1.00	10.00	3.78	5.00	5.06	5.19
1.00	15.00	3.78	7.30	7.20	7.12
1.00	20.00	3.78	9.16	9.14	8.89
1.00	30.00	3.78	12.50	12.50	12.18
1.00	40.00	3.78	15.33	15.32	15.22
1.00	50.00	3.78	17.22	17.72	18.10
1.00	60.00	3.78	20.00	19.77	20.85
1.00	10.00	1.89	3.70	2.53	2.78
1.00	10.00	3.78	6.30	5.06	5.20
1.00	10.00	5.80	7.60	7.76	7.65
1.00	10.00	7.56	9.20	10.12	9.72
1.00	10.00	11.34	15.00	15.18	14.02
1.00	10.00	15.12	19.40	20.25	18.19
1.00	10.00	18.90	23.33	25.31	22.25

and the rates calculated on the basis of rate law (9) (Table 1).

In conclusion, CHP as such, IO₄⁻ and [RhCl₃(H₂O)₂(OH)]⁻ are the respective reactive species of CHP, NaIO₄ and Rh(III) chloride in alkaline medium. In the rate determining step, the most reactive activated complex, (C₄), is formed by the interaction of reactive species of IO₄⁻ and the complex (C₃), in alkaline medium. The observed negative entropy of activation clearly supports the interaction between the two similarly charged species, C₃ and H₂IO₆³⁻, leading to the formation of most reactive activated complex, (C₄), in the proposed reaction scheme. On the basis of observed positive effect of [OH⁻] on the rate of reaction, it may be concluded that IO₄⁻ is reactive species of NaIO₄. The existence of the complex species C₄ is supported by the spectral data. A significant increase on the rate and pseudo first-order rate constant is observed on increasing the temperature.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_57A\(04\)477-484_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_57A(04)477-484_SupplData.pdf).

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