A spectroscopic investigation of kinetics and mechanism of ruthenium(III)-catalyzed oxidation of N-(2-hydroxyethyl)phthalimide by cerium(IV) in aqueous sulphuric acid and sulphate media

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Abstract: The oxidation of N-(2-hydroxyethyl)phthalimide with cerium(IV) with a small amount of ruthenium(III) present as a catalyst has been studied by spectro-photometric means. The spectroscopic study has been carried out in aqueous $\text{H}_2\text{SO}_4$ and $\text{SO}_4^{2-}$ media at constant ionic strength of $I = 1.60 \text{ mol dm}^{-3}$. Stoichiometric analysis shows that one mole of NHEP reacts with two moles of cerium(IV). The oxidation products were identified by IR and GC–MS. Orders with respect to substrate, oxidant, ruthenium(III) and acid concentrations were determined. Increase in sulphuric acid concentration increases the rate. Effect of ionic strength and solvent polarity of the medium on the rate of the reaction was studied. The added product, cerium(III), has no significant effect on the rate of reaction. The active species of oxidant in sulphate medium and catalyst are $\text{CeSO}_4^{2+}$ and $\left[\text{Ru(H}_2\text{O})_6\right]^{3+}$. Based on the experimental results a suitable mechanism is proposed. The activation parameters and the thermodynamic quantities are also determined and discussed.

Subjects: Environmental Studies & Management; Food Science & Technology; Physical Sciences

Keywords: oxidation; cerium(IV); N-(2-hydroxyethyl)phthalimide; ruthenium(III) catalyst

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PUBLIC INTEREST STATEMENT
This paper demonstrates the kinetic study of oxidation of ruthenium(III)-catalysed oxidation of N-(2-Hydroxyethyl)phthalimide(NHEP) by cerium(IV) in aqueous $\text{H}_2\text{SO}_4$ and $\text{SO}_4^{2-}$ media spectrophotometrically. Thus, the study of NHEP becomes important because of its biological significance and selectivity towards the oxidants. There is a lack of literature on the oxidation of NHEP by cerium(IV) and its catalysis by ruthenium(III). The authors have observed that the slow cerium(IV) oxidation of NHEP is facilitated by micro amounts($10^{-6} \text{ mol dm}^{-3}$) of ruthenium(III) in sulphuric acid medium. Such studies are of much significance in understanding the mechanistic profile of NHEP in redox reactions, also to know the active species of cerium(IV) and ruthenium(III) catalyst, and to resolve the complexity of the reaction; a detailed study of the reaction becomes important.
1. Introduction
Cerium is the most abundant of the rare earths. The numerous commercial applications of cerium include metallurgy, glass and glass polishing ceramics, catalysts and in phosphors. Cerium is characterised chemically by varying two valence states, the +3 cerous state and +4 ceric states (Emsley, 2011). The cerous state closely resembles the other trivalent rare earths. Ceric salts are orange red or yellowish; cerous salts are usually white. The ceric state is the only non-trivalent rare earth ion stable at high acid concentration. It is therefore a strong oxidiser. Cerium (IV) is a well-known oxidant in acid media (Byadagi, Naik, Savanur, Nandibewoor, & Chimatadar, 2010; Thabaj, Chimatadar, & Nandibewoor, 2006), having the reduction potential (Day & Selbin, 1964) of the couple Ce(IV)/Ce(III) is 1.70 V. The oxidation of organic compounds by cerium(IV), in general seems to proceed via the formation of an intermediate complex (Yatsimerskii & Luzan, 1965). Among the inorganic substrates which serve as ligands for cerium(IV) are chloride, bromide and hypophosphite (Caroll & Thomas, 1966). In sulphuric acid and sulphate media, several sulphate complexes of cerium(IV) form (Bugaenko & Kuan-lin, 1963; Kharzeoua & Serebrennikou, 1967; Thabaj et al., 2006) but these have not been studied in-depth so far.

Phthalimide and its derivatives are important compounds in diverse fields. In medical field, they are used in the synthesis of compounds having anti-microbial activity, anti-androgen and other agents for treating tumour necrosis factor. Certain phthalimide derivatives are used as herbicides for reducing bacterial contamination. On the industrial side, they act like bleaching detergents, anion-exchange resin, antidepressants, heat-resistant polymer, flame retardant, etc., and also widely used in the production of pesticides, plastics, resins and surfactants (Balachandran, Lalitha, & Rajeswari, 2012). N-(2-hydroxyethyl)phthalimide (NHEP) is used in medicine, pharmacy, dyes and pesticides. The structure of NHEP is shown below.

Thus, the study of NHEP becomes important because of its biological significance and selectivity towards the oxidants. There is a lack of literature on the oxidation of NHEP by cerium(IV) and its catalysis by ruthenium(III). The authors have observed that the slow cerium(IV) oxidation of NHEP is facilitated by micro amounts($10^{-6}$ mol dm$^{-3}$) of ruthenium(III) in sulphuric acid medium. Such studies are of much significance in understanding the mechanistic profile of NHEP in redox reactions and provide an insight into the interaction of metal ions with the substrate and its mode of action in biological systems. Also to know the active species of cerium(IV) and ruthenium(III) catalyst, and to resolve the complexity of the reaction, a detailed study of the reaction becomes important. Hence, the present investigation is aimed to see the reactivity of NHEP towards cerium(IV) in presence of ruthenium(III) catalyst and to arrive at suitable mechanisms.

2. Experimental

2.1. Materials and methods
All reagents were of analytical reagent grade and millipore water was used throughout the work. NHEP was purchased from Sigma Chemical Company, St. Louis, USA. The stock solution of NHEP was prepared by dissolving an appropriate reagent grade and amount in millipore water. The required concentration of NHEP was obtained from its stock solution. The stock solution of cerium(IV) was prepared by dissolving known weight of cerium ammonium sulphate in 100 cm$^3$ of 1 mol dm$^{-3}$ H$_2$SO$_4$ solution. The volumetric flask is covered with silver aluminium foil. The solution was standardised with standard iron(II) ammonium sulphate (S.D. Fine-Chem Ltd) solution (Jeffery, Bassett, Mendham, & Denney, 1966) using ferroin as an indicator. The ruthenium(III) stock solution was prepared by dissolving a known weight of ruthenium(III) chloride (S.D. Fine-Chem Ltd) in 0.20 mol dm$^{-3}$ HCl solution. Mercury was added to the ruthenium(III) stock solution to reduce any ruthenium(IV) formed.
during the preparation of ruthenium(III) stock solution. The ruthenium(III) concentration was assayed by EDTA titration (Reddy & Vijay Kumar, 1995). The stock solutions were diluted as required before use. $\text{H}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4$ were employed to maintain the required acidity and ionic strength, respectively, in reaction solutions. The cerium(III) was prepared by dissolving an appropriate quantity of reagent grade and cerium(III) millipore water.

2.2. Kinetic studies

Kinetic measurement was carried out at $25 \pm 0.1^\circ\text{C}$ and at constant ionic strength, $I = 1.60 \text{ mol dm}^{-3}$. Reactions were initiated by mixing previously thermostatted solutions of cerium(IV) and NHEP which also contained the required amount of sodium sulphate and sulphuric acid. The kinetics was followed under pseudo-first-order conditions with NHEP in excess. Progress of reaction was followed by measuring the absorbance of cerium(IV) in the reaction mixture at 360 nm in a 1-cm cell placed in the thermostatted compartment of a Varian carry 50 Bio UV–vis spectrophotometer. At this wavelength, all other materials concerned have negligible absorbance. Application of Beer's law under the present experimental conditions had been verified between $1.0 \times 10^{-4}$ and $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ of cerium(IV) at 360 nm, and the extinction coefficient was found to be $\varepsilon = 3500 \pm 10 \text{ dm}^{-3} \text{ mol}^{-1} \text{ cm}^{-1}$. Kinetic runs followed more than 85% completion of the reaction. The pseudo-first-order rate constant, $k_{\text{obs}}$, was calculated from the plot log[Ce(IV)] vs. time. The rate constants were reproducible within ±5% and are the average of at least three independent kinetic runs (Table 1).

2.3. Stoichiometry and product analysis

Different sets of reaction mixtures containing varying ratios of cerium(IV) to NHEP in the presence of constant amount of H⁺, Ru(III), $\text{Na}_2\text{SO}_4$, and at constant ionic strength of 1.60 mol dm⁻³ were allowed to react for about 5 h at 25°C under nitrogen atmosphere in a closed vessel. The remaining concentration of cerium(IV) was assayed by measuring the absorbance at 360 nm. The results indicated that two moles of cerium(IV) reacted with one mole of NHEP as given in Equation (1).

\[ 2 \text{Ce}^{4+} + \text{NHEP} \rightarrow \text{Ce}^{3+} + \text{n}-\text{methylphthalimide} + \text{formic acid} + 2\text{H}^+ \] (1)

After the completion of the reaction, the reaction mixture was acidified, concentrated and extracted with ether. The products were identified as $n$-methylphthalimide and formic acid. The IR spectrum of $n$-methylphthalimide showed two bands at 1,777 and at 1,694 cm⁻¹ which correspond to carbonyl group stretching (Figure 1). The GC–MS analysis of $n$-methylphthalimide showed a molecular ion peak at 161 amu (Figure 2). The product, formic acid, was identified by spot test.
Table 1. Effect of [Ce(IV)], [NHEP] and [Ru(III)] on ruthenium(III)-catalysed Ce(IV) oxidation of NHEP in acid medium at 25°C, $I = 1.60 \text{ mol dm}^{-3}$

| [Ce(IV)] $\times 10^{-4}$ (mol dm$^{-3}$) | [NHEP] $\times 10^{-3}$ (mol dm$^{-3}$) | $[\text{H}_2\text{SO}_4]$ (mol dm$^{-3}$) | [Ru(III)] $\times 10^{-6}$ (mol dm$^{-3}$) | $k_{obs} \times 10^{-3}$ (s$^{-1}$) | SD |
|------------------------------------------|----------------------------------------|----------------------------------------|----------------------------------------|---------------------------------|----|
| 0.50                                     | 2.0                                    | 0.5                                    | 5.0                                    | 1.98                           | 0.015 |
| 1.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.10                           | 0.050 |
| 2.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.03                           | 0.025 |
| 3.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.22                           | 0.015 |
| 4.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.01                           | 0.038 |
| 5.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.10                           | 0.021 |
| 2.0                                      | 0.5                                    | 0.5                                    | 5.0                                    | 0.71                           | 0.020 |
| 2.0                                      | 1.0                                    | 0.5                                    | 5.0                                    | 1.22                           | 0.036 |
| 2.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.03                           | 0.025 |
| 2.0                                      | 3.0                                    | 0.5                                    | 5.0                                    | 2.46                           | 0.087 |
| 2.0                                      | 4.0                                    | 0.5                                    | 5.0                                    | 3.17                           | 0.031 |
| 2.0                                      | 5.0                                    | 0.5                                    | 5.0                                    | 3.87                           | 0.090 |
| 2.0                                      | 2.0                                    | 0.5                                    | 1.0                                    | 0.29                           | 0.020 |
| 2.0                                      | 2.0                                    | 0.5                                    | 2.0                                    | 0.55                           | 0.020 |
| 2.0                                      | 2.0                                    | 0.5                                    | 4.0                                    | 1.30                           | 0.035 |
| 2.0                                      | 2.0                                    | 0.5                                    | 5.0                                    | 2.03                           | 0.025 |
| 2.0                                      | 2.0                                    | 0.5                                    | 8.0                                    | 2.72                           | 0.012 |
| 2.0                                      | 2.0                                    | 0.5                                    | 10.0                                   | 3.25                           | 0.046 |

Figure 1. FT-IR spectrum of n-methylphthalimide, the product obtained during the oxidation of NHEP by cerium(IV) in aqueous sulphuric acid medium.
3. Results

3.1. Reaction order
The order with respect to each of the oxidant, reductant and acid was determined by the slopes of log $k_{obs}$ vs. log (concentration) plots. Here, orders were obtained by varying the concentrations of oxidant, reductant and acid in turn while keeping all other concentrations and conditions constant.

3.2. Effect of varying [cerium(IV)]
At constant concentrations of NHEP, Ru(III), acid and constant ionic strength, 1.60 mol dm$^{-3}$, the oxidant, cerium(IV) concentration varied in the concentration range of $0.50 \times 10^{-4}$–$5.0 \times 10^{-4}$ mol dm$^{-3}$. The fairly constant $k_{obs}$ values indicate that the order with respect to the [cerium(IV)] was unity. The pseudo-first-order plots were linear, over 75% completion of the reaction also indicates first order with respect to cerium(IV) concentrations.

3.3. Effect of varying [NHEP]
The substrate, NHEP concentration varied in the range of $0.50 \times 10^{-3}$–$5.0 \times 10^{-3}$ mol dm$^{-3}$, at constant concentrations of cerium(IV), acid and at constant ionic strength, $I = 1.60$ mol dm$^{-3}$, the $k_{obs}$ values increased with increase in the concentration of NHEP (Table 1). The apparent order in NHEP was found to be less than unity (0.71).

3.4. Effect of [ruthenium(III)]
The ruthenium(III) concentration varied from $1.0 \times 10^{-6}$ to $10.0 \times 10^{-6}$ mol dm$^{-3}$ range, at constant concentrations of cerium(IV), NHEP, acid and at constant ionic strength of 1.60 mol dm$^{-3}$. As the catalyst, ruthenium(III), concentration increases, the rate of reaction also increases (Table 1). The order in [Ru(III)] was found to be unity (Figure 3). The experimentally found rate law is:

$$\text{Rate} = [\text{Ce}^{4+}]^{1.0} [\text{Ru}(\text{III})]^{1.0} [\text{NHEP}]^{0.71} [\text{H}^+]^{0.81}$$

3.5. Effect of varying [H$_2$SO$_4$]
At fixed ionic strength, $I = 1.60$ mol dm$^{-3}$ and with other conditions remaining constant, the rate was found to increase with increasing acidity (Table 2). A constant amount of sulphuric acid, from the original cerium(IV) stock solution in all reaction mixtures apart from the varying sulphuric acid, enables formation of various sulphate complexes of cerium(IV). The in situ H$^+$ concentration in the reaction mixture was calculated using known ionisation constant (Bugaenko & Kuam-lin, 1963; Kharzeoua & Serebrennikou, 1967) of acid-sulphate as in an earlier study (Ya Kulba, Yu Yakovlev, & Mironov, 1965). The order with respect to H$^+$ ion concentration was fractional (0.81), found from a plot of log $k_{obs}$ vs. log (acid concentration)
$k_{\text{obs}}$ vs. log[H$^+$] (Figure 4). The fractional order with respect to H$^+$ ion concentration might have arisen due to its role of being involved in the formation of several cerium(IV) complexes in acid-sulphate media. Cerium(IV) is known to form several sulphate complexes in sulphuric acid-sulphate media (Ya Kulba et al., 1965) such as Ce(OH)$_3^+$, CeSO$_2^{4+}$, Ce(SO$_4$)$_2$, Ce(SO$_4$)$_2$HSO$_4$ and H$_3$Ce(SO$_4$)$_2$ as shown in equilibria (2)–(6):

$$\text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{Ce(OH)}^{3+} + \text{H}^+ \quad K_{\text{OH}}$$

$$\text{Ce}^{4+} + \text{SO}_2^{2-} \rightleftharpoons \text{Ce(SO}_4)_2^{2+} \quad K_1$$

$$\text{Ce(SO}_4)_2^{2+} + \text{SO}_2^{2-} \rightleftharpoons \text{Ce(SO}_4)_4^2 \quad K_2$$

$$\text{Ce(SO}_4)_4^2 \rightleftharpoons \text{Ce(SO}_4)_2^2 \rightleftharpoons \text{H}_3\text{Ce(SO}_4)_2$$

$$\text{Ce(SO}_4)_2^2 \rightleftharpoons \text{H}_3\text{Ce(SO}_4)_2$$

The Ce(OH)$^{3+}$ species may also be present in these solutions and its concentration varies with acidity. The total cerium(IV) is sum of the different species concentrations of Ce$^{4+}$, Ce(OH)$^{3+}$, CeSO$^{2+}$, Ce(SO$_4$)$_2$, H(Ce(SO$_4$)$_2$, and HCe(SO$_4$)$_2$, the complex having the cumulative equilibrium constants, $K_{\text{OH}}, K_1, K_2$, and $K_4$ as shown in Equation (7):

| $[\text{H}_2\text{SO}_4]$ (mol dm$^{-3}$) | $[\text{H}^+]$ (mol dm$^{-3}$) | $[\text{SO}_2^{2-}]$ (mol dm$^{-3}$) | $[\text{HSO}_4^-]$ (mol dm$^{-3}$) | $\alpha_0 \times 10^3$ | $\alpha_\text{OH}$ | $\alpha_1$ | $\alpha_2 \times 10^2$ | $\alpha_3 \times 10^3$ | $\alpha_4 \times 10^5$ | $k_{\text{obs}} \times 10^3$ (s$^{-1}$) |
|--------------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------|----------------|-------------|-----------------|-----------------|-----------------|-----------------|
| 0.05                                | 0.0210                        | 0.4543                        | 0.0789                        | 1.08                | 0.77          | 0.19        | 3.77            | 1.78            | 0.59            | 0.33            |
| 0.1                                 | 0.0483                        | 0.3738                        | 0.1517                        | 2.07                | 0.64          | 0.30        | 5.00            | 4.53            | 6.68            | 0.58            |
| 0.2                                 | 0.1268                        | 0.2598                        | 0.2732                        | 4.30                | 0.51          | 0.43        | 4.90            | 8.00            | 55.60           | 1.10            |
| 0.3                                 | 0.2435                        | 0.1765                        | 0.3565                        | 7.29                | 0.45          | 0.50        | 3.84            | 8.18            | 14.27           | 1.52            |
| 0.4                                 | 0.3922                        | 0.1253                        | 0.4077                        | 10.98               | 0.42          | 0.53        | 2.92            | 7.10            | 22.83           | 1.85            |
| 0.5                                 | 0.5609                        | 0.0943                        | 0.4390                        | 15.12               | 0.40          | 0.55        | 2.27            | 5.96            | 29.50           | 2.03            |

$\alpha_0, \alpha_\text{OH}, \alpha_1, \alpha_2, \alpha_3$ and $\alpha_4$ are the fractions of total Ce(IV) of the species Ce$^{4+}$, Ce(OH)$^{3+}$, CeSO$^{2+}$, Ce(SO$_4$)$_2$, Ce(SO$_4$)$_2$HSO$_4$ and H$_3$Ce(SO$_4$)$_2$ respectively.
where $\beta_1(=K_1) = 3.85 \times 10^2$, $\beta_2(=K_1K_2) = 1.69 \times 10^2$, $\beta_3(=K_1K_2K_3) = 1.01 \times 10^2$, $\beta_4(=K_1K_2K_3K_4) = 2.03 \times 10^2$ and KOH = 15.

The approximate concentrations of cerium sulphate complexes can be calculated from the concentrations of Ce$^{4+}$, H$^+$, HSO$_4^-$, SO$_4^{2-}$, from the equilibria and their constants (Kharzeoua & Serebrennikou, 1967). In Equation (7), the subscripts “t” and “f” stand for total and free, respectively. The formation of Ce(OH)$_2^{2+}$ occurs to a much smaller extent and is therefore neglected. The results of such calculation were utilised to draw (Figure 4), it is observed that of the concentration of different species, the variation of only CeSO$_2^{2+}$ with H$^+$ ion concentration showed any parallelism with the variation of rate with H$^+$ ion concentration. Hence, it is assumed that CeSO$_2^{2+}$ is the active species of cerium(IV).

3.6. Effect of varying ionic strength and dielectric constant

At constant concentrations of reactants and other condition constants, the ionic strength varied between 1.60 and 3.0 mol dm$^{-3}$ by varying the concentrations of sodium sulphate, the rate was found to increase with increase in the ionic strength. The plot of log $k_{obs}$ vs. $\sqrt{I}$ was found to be linear with positive slope (Figure 5). The effect of dielectric constant was studied by varying the acetic acid–water (v/v) content in the reaction mixture with all other conditions being maintained constant. On decreasing the dielectric constant of the reaction medium, an increase in the rate, and the plot of log $k_{obs}$ vs. $1/D$ was linear with positive slope (Figure 5).

3.7. Effect of added products

The effect of initially added product, cerium(III) sulphate has no significant effect on the rate of reaction.

3.8. Test for free radicals (polymerisation study)

The intervention of free radicals in the reaction was examined as follows: the reaction mixture, to which a known quantity of acrylonitrile scavenger had been initially added, was kept for 5 h under a nitrogen atmosphere. On diluting the reaction mixture with methanol, no precipitate resulted, indicating the absence of free radicals in the reaction (Thaboj et al., 2006).

![Figure 4. Effect of acid concentration on different cerium(IV) species and also on the rate constant.](image-url)
3.9. Effect of temperature

The rate constant was measured at three different temperatures, 25, 35 and 45°C by varying the substrate, NHEP and acid concentrations. The rate of reaction increased with increase in temperature. The rate constant, $k$, of the slow step of Scheme 1 was obtained from the intercept and slopes of the plots of $\text{Ru(III)}/k_{\text{obs}}$ vs. $1/[$NHEP$]$ at three different temperatures and the values are given in Table 3. The ionisation constant of ($K_5$) of the first step of Scheme 1 was evaluated from $(\text{Intercept})^2/(\text{slope})^2$ of the plot of $[\text{Ru(III)}]/k_{\text{obs}}$ vs. $1/[$H$^+]$ at three different temperatures. Similarly, the formation constant ($K_6$) of the complex of the second step of Scheme 1 was obtained from $(\text{Intercept})/(\text{slope})_1$ of the plot of $[\text{Ru(III)}]/k_{\text{obs}}$ vs. $1/[$NHEP$]$ at three different temperatures. The values of $K_5$ and $K_6$ at different temperatures are given in Table 3. van’t Hoff plot was drawn for the variation of $K_5$ and $K_6$

![van't Hoff plot](image_url)

Table 3. Activation parameters and thermodynamic quantities for the oxidation of NHEP by cerium(IV) in aqueous acid medium with respect to the slow step of Scheme 1

| Temperature (K) | $k$ (s$^{-1}$) | Parameters | Values |
|----------------|----------------|------------|--------|
| 298            | 2,813          | $E_a$ (kJ mol$^{-1}$) | $33 \pm 3$ |
| 308            | 4,559          | $\Delta H$° (kJ mol$^{-1}$) | $31 \pm 3$ |
| 318            | 6,545          | $\Delta S$° (J K$^{-1}$ mol$^{-1}$) | $-75 \pm 4$ |
|                |                | $\Delta G$° (kJ mol$^{-1}$) | $53 \pm 3$ |
|                |                | $\log A$    | $9.0 \pm 0.2$ |

| Temperature (K) | $K_5$ (dm$^3$ mol$^{-1}$) | $K_6$ (dm$^3$ mol$^{-1}$) |
|----------------|--------------------------|--------------------------|
| 298            | 1.405                     | 278.7                     |
| 308            | 1.683                     | 212.4                     |
| 318            | 2.243                     | 176.9                     |

| Thermodynamic quantities | Values from $K_5$ | Values from $K_6$ |
|--------------------------|--------------------|--------------------|
| $\Delta H$ (kJ mol$^{-1}$) | $18 \pm 3$        | $-17.9 \pm 3$     |
| $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | $64 \pm 4$       | $-13.5 \pm 3$     |
| $\Delta G$ (kJ mol$^{-1}$) | $-0.84 \pm 0.01$  | $-13.9 \pm 0.8$   |
with temperature i.e. (log \( K_5 \) vs. \( 1/T \) and log \( K_6 \) vs. \( 1/T \)). The values of enthalpy of reaction \( \Delta H \), entropy of reaction \( \Delta S \) and free energy of reaction \( \Delta G \), were calculated, and these values are given in Table 3. A comparison of these values obtained for the slow step shows that the reaction before the rate-determining step is fairly fast as it involves low activation energy (Chimatadar, Nandibewoor, Sambrani, & Raju, 1987; Lewis, 1974).

4. Discussion
The cerium(IV) oxidation of NHEP is slow in aqueous sulphuric acid. However, the oxidation occurs with reasonable rates in the presence of ruthenium(III) in aqueous sulphuric acid. The cerium(IV) oxidation of NHEP in presence of ruthenium(III) in aqueous sulphuric acid has a stoichiometry 2:1. In the presence of ruthenium(III), the order with respect to cerium(IV) and NHEP concentrations were found to be unity and less than unity, respectively. As the sulphuric acid concentration increased in the reaction mixture, the H\(^+\) ion concentration increased, hence rate of reaction also increased. The order with respect to H\(^+\) ion concentration was found to be less than unity. Similarly, as the catalyst ruthenium(III) concentration increases, the rate also increases with first-order dependence on ruthenium(III) concentration. As discussed in result section, cerium(IV) forms Ce(OH)\(^{3+}\) along with sulphate complexes in sulphuric acid and sulphate media. The potentiometric study indicates Ce(OH)\(^{3+}\) is the predominant active species of cerium(IV) in aqueous acid medium (Basavaiah, Ramakrishna, & Kumar, 2007; Offner & Skoog, 1966). In the presence of ruthenium(III), initially added products did not have any significant effect on the rate of reaction. By using all these results, a mechanism is proposed in the form of Scheme 1.

The mechanism (Scheme 1) involves combination of Ce(OH)\(^{3+}\) with acid to give Ce\(^{4+}\) species (Offner & Skoog, 1966) in a prior equilibrium step, which is also supported by the observed fractional order in [H\(^+\)]. NHEP combines with catalyst ruthenium(III) species to give a complex (C\(_1\)), which enhances the reducing property of the NHEP than without catalyst, Ru(III). Hence, the oxidant Ce(IV) easily reacts with complex in a slow step to give products with regeneration of catalyst.

The Michaelis–Menten plot (Figure 6) suggests the complex formation between substrate and catalyst. This type of complex found in the literature also (Cotton, Wilkinson, Murrillo, & Bochmann, 1999). From Scheme 1, the rate law (9) can be derived as follows:

\[
\text{Rate} = -\frac{d[\text{Ce(IV)}]}{dt} = k[\text{complex}][\text{Ce}^{4+}] \tag{8}
\]

(Or)

\[
\frac{\text{Rate}}{[\text{Ce(IV)}]} = \frac{k [\text{complex}][\text{Ru(III)}][\text{H}^+]}{1 + K_6[N\text{HEP}] + K_5[H^+] + K_4[\text{H}^+][N\text{HEP}]} = k_{\text{obs}} \tag{9}
\]

The rate law (9) can be rearranged in the form of Equation (10), which is suitable for verification:

\[
\frac{[\text{Ru(III)}]}{K_{\text{obs}}} = \frac{1}{k K_6[N\text{HEP}][\text{H}^+]} + \frac{1}{k K_5[H^+] + K_4[\text{H}^+][N\text{HEP}]} + \frac{1}{k} \tag{10}
\]

According to the Equation (10), the plots of [Ru(III)]/k\(_{\text{obs}}\) vs. 1/[NHEP] and [Ru(III)]/k\(_{\text{obs}}\) vs. 1/[H\(^+\)] should be linear, which are shown in Figure 6.

(1) From the 1st plot, i.e. [Ru(III)]/k\(_{\text{obs}}\) vs. 1/[NHEP]
Figure 6. Verification of rate law (9) in the form of Equation (10) for the ruthenium(III)-catalysed oxidation of NHEP by Ce(IV) in acid medium.

Scheme 1. Detailed mechanism for Ru(III) mediated oxidation of NHEP by cerium(IV).

\[
\text{Ce(OH)}^{3+} + \text{H}^+ \xrightleftharpoons[k_5]{K_5} \text{Ce}^{4+} + \text{H}_2\text{O}
\]

\[
\text{N}=\text{O} \quad \text{OH} \quad \text{[Ru(H}_2\text{O)}_6]^{3+} \text{K}_6 \xrightarrow{[\text{Complex}]}^{3+} (C_1)
\]

\[
\text{[Complex]}^{3+} (C_1) + 2\text{Ce}^{4+} \xrightarrow[k_{\text{slow}}]{\text{H}_2\text{O}} 2\text{Ce}^{3+} + \quad \text{N}=\text{O} \quad \text{CH}_3 + \frac{1}{\text{C}=\text{O}} + \quad \text{[Ru(H}_2\text{O)}_6]^{3+} + 2\text{H}^+
\]

\[
\text{(Slope)}_1 = \frac{1}{kK_5K_6[H^+]} + \frac{1}{kK_6}
\]

\[
\text{(Intercept)}_1 = \frac{1}{kK_5[H^+]} + \frac{1}{k}
\]

Therefore,
where $K_6$ is the formation constant for complex C1.

(2) From the 2nd plot, i.e. $[\text{Ru(III)}]/k_{\text{obs}}$ vs. $1/[\text{H}^+]$

\[
\frac{\text{Intercept}}{\text{(Slope)}_1} = k K_6
\]

(13)

Therefore,

\[
\frac{\text{Intercept}}{\text{(Slope)}_2} = K_5
\]

(16)

where $K_i$ is the ionisation constant of Ce$^{4+}$·H$^+$.

Substituting the values of $K_5$, $K_6$ and $[\text{H}^+]$ into Equation (11), we get the value of $k$, the rate constant with respect to the slow step of Scheme 1.

The active species involved in the mechanism can be understood as follows: the variation of the rate with acidity is shown in the result section, to parallel the trend of variation of concentrations of the CeSO$_2$$^+$ species with the acidity (Table 2, Figure 4). Hence, it is confirmed that sulphate complex of Ce(IV), CeSO$_2$$^+$ is the active species of oxidant. The ruthenium(III) catalyst is understood to be present in the aqueous acid medium mainly as Ru(H$_2$O)$_6^3$+. Ruthenium(III)-mediated oxidation of NHEP is greatly facilitated in sulphuric acid solution and the reason may be that cerium(IV) species such as CeSO$_2$$^+$ and ruthenium(III) species, Ru(H$_2$O)$_6^3$+ are actively involved. The mechanism of Scheme 1 will therefore involve the species as shown in Scheme 2.

Therefore, in terms of active species, rate law (9) takes in the form (17)

\[
\text{Rate} = \frac{k K_5 K_6 [\text{CeSO}_2^+][\text{NHEP}][\text{H}^+][\text{Ru(H}_2\text{O)}_6^3+]}{1 + K_6 [\text{NHEP}] + K_4 [\text{H}^+] + K_5 K_6 [\text{NHEP}][\text{H}^+]}
\]

(17)

But, Ce$^{4+}$ + SO$_2$$^-$ \[\rightarrow\] CeSO$_2$$^+$

$\beta_1 = \frac{[\text{Ce}^{4+}][\text{SO}_2^-]}{\text{CeSO}_2^+}$

(18)

CeSO$_2$$^+$ \[\rightarrow\] $\beta_1 [\text{Ce}^{4+}][\text{SO}_2^-]$  

For $[\text{Ce}^{4+}]$, from Equation (7), we have:

\[
[\text{Ce(IV)}]_t = \frac{[\text{Ce(IV)}]_0}{\left(1 + \frac{K_{\text{obs}}}{[\text{H}^+]} + \beta_1 [\text{SO}_2^-] + \beta_2 [\text{SO}_2^-]^2 + \beta_3 [\text{SO}_2^-]^3 [\text{H}^+] + \beta_4 [\text{SO}_2^-]^4 [\text{H}^+] + \beta_5 [\text{SO}_2^-]^5 [\text{H}^+]^2 \right)}
\]

(19)

Substituting Equation (19) in (18), we get:
Scheme 2. Detailed mechanism for Ru(III) mediated oxidation of NHEP by cerium(IV) in terms of active species.

\[
\begin{align*}
\text{Ce}^{4+} + \text{SO}_4^{2-} & \overset{K_7}{\rightleftharpoons} \text{CeSO}_4^{2+} \\
\text{Ru}(III) + 6\text{H}_2\text{O} & \overset{K_8}{\rightleftharpoons} [\text{Ru(H}_2\text{O)}_6]^{3+} \\
\text{CeSO}_4^{2+} + \text{H}^+ & \overset{K_9}{\rightleftharpoons} \text{CeSO}_4^{2+} + \text{H}^+ \\
[\text{Complex}]^{3+} & \overset{K_{10}}{\rightleftharpoons} \text{[Ru(H}_2\text{O)}_6]^{3+} \\
[\text{Complex}]^{3+} \cdot \text{CeSO}_4^{2+} + \text{H}^+ & \overset{k}{\text{slow} \text{H}_2\text{O}} \text{CeSO}_4^{2+} + \text{[Ru(H}_2\text{O)}_6]^{3+} + 2\text{H}^+ \\
\end{align*}
\]

\[
[\text{Ce(SO)}_4^{2+}] = \frac{\beta_1[\text{Ce}^{6+}][\text{SO}_4^{2+}]}{1 + \frac{\beta_1[\text{Ce}^{6+}][\text{SO}_4^{2+}]}{[\text{NHEP}] [\text{Ru(H}_2\text{O)}_6]^{3+} [\text{H}^+]}} \quad (20)
\]

Substituting Equation (20) in (17):

\[
\text{Rate} = \frac{k K_9 K_6 \beta_1[\text{Ce(IV)}][\text{SO}_4^{2+}][\text{NHEP}][\text{Ru(H}_2\text{O)}_6]^{3+}[\text{H}^+]}{1 + K_9[\text{NHEP}] + K_9[\text{H}^+] + K_9 K_6[\text{NHEP}][\text{H}^+]} \times \frac{1}{[A]}
\]

\[
\text{Rate} = \frac{k K_9 K_6 \beta_1[\text{Ce(IV)}][\text{SO}_4^{2+}][\text{NHEP}][\text{Ru(H}_2\text{O)}_6]^{3+}[\text{H}^+]}{1 + K_6[\text{NHEP}] + K_5[\text{H}^+] + K_5 K_6[\text{NHEP}][\text{H}^+]} \times \frac{1}{[A]}
\]

\[
\text{Rate} = \frac{k K_9 K_6 \beta_1[\text{Ce(IV)}][\text{SO}_4^{2+}][\text{NHEP}][\text{Ru(H}_2\text{O)}_6]^{3+}[\text{H}^+]}{1 + K_6[\text{NHEP}] + K_5[\text{H}^+] + K_5 K_6[\text{NHEP}][\text{H}^+]} \times \frac{1}{[A]}
\]

\[
[A] = \left(1 + \frac{K_{\text{Oh}}}{[\text{H}^+]} + \beta_1[\text{SO}_4^{2-}] + \beta_2[\text{SO}_4^{2-}]^2 + \beta_3[\text{SO}_4^{2-}]^3[\text{HSO}_4^-] + \beta_4[\text{SO}_4^{2-}]^4[\text{HSO}_4^-]^2[\text{H}^+] \right)
\]

The effect of ionic strength and dielectric constant of medium on the rate explains qualitatively the reaction between ions having the same charge, as seen in Scheme 1. The values of \(\Delta H^+\) and \(\Delta S^+\) were both favourable for electron transfer processes. The negative value of \(\Delta S^+\) indicates that complex \(C_1\) is more ordered than the reactants (Sinha & Mathur, 1971). The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as higher value of the rate constant of the slow step indicates that the oxidation presumably occur via an inner sphere mechanism. Ru(III) forms complex with substrate which enhances the reducing property of substrate than without catalyst. The catalyst Ru(III) modifies the reaction path by reducing the activation energy.
5. Conclusions
Spectroscopic investigation and oxidation of NHEP by Ce(IV) in presence of ruthenium(III) catalyst in aqueous sulphuric acid media have been made. The reaction between cerium(IV) and NHEP is slow in sulphuric acid at room temperature, but effectively enhanced by ruthenium(III). The role of hydrogen ion is crucial to the reaction. The main active species of cerium(IV) and ruthenium(III) are considered to be CeSO$_4$$^{2-}$ and [Ru(H$_2$O)$_6$]$^{3+}$, respectively. Rate constant of slow step and other equilibrium constants involved in the mechanism are evaluated and activation parameters with respect to slow step of reaction were computed. The description of the mechanism is consistent with all the experimental evidences.

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