

Kinetic, mechanistic and spectral investigations of ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin by alkaline diperiodatonickelate(IV) (stopped flow technique)

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Abstract

The kinetics of oxidation of ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin (HDC) by diperiodatonickelate(IV) (DPN) in aqueous alkaline medium at a constant ionic strength of 1.0 mol dm^{-3} was studied spectrophotometrically. The reaction between DPN and 4-hydroxycoumarin in alkaline medium exhibits 3:1 stoichiometry (DPN:HDC). The reaction is of first order in [DPN] and less than unit order in [HDC] and [alkali]. Periodate has no effect on the rate of reaction. The reaction rate increases with increase in ionic strength and decrease in dielectric constant of the medium. The main products were identified by spot test and spectral studies. A mechanism involving the DPN as the reactive species of the oxidant and a complex formation between 4-hydroxycoumarin and ruthenium(III) species has been proposed. The reaction constants involved in the different steps of mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed and thermodynamic quantities are also calculated.

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Keywords: Kinetics; Diperiodatonickelate(IV); Oxidation; 4-Hydroxycoumarin; Ruthenium(III)

1. Introduction

The use of diperiodatonickelate(IV) (DPN) as an oxidant in alkaline medium is new and restricted to a few cases [1–6] due to the fact of its limited solubility and stability in aqueous medium. Reduction of nickel(IV) complexes have been received a considerable attention in order to understand, the nature of intermediate oxidation states of nickel, such as nickel(III). Indeed, stable nickel(III) complexes are known [7–9]. Moreover, when nickel(IV) periodate is oxidant, it needs to be known which of the species is the active form of oxidant, since multiple equilibria between the different nickel(IV) species are involved.

Ruthenium(III) acts as an efficient catalyst in many redox reactions, particularly in an alkaline medium [10]. The catalysed mechanism can be quite complicated due to the

formation of different intermediate complexes, free radicals and different oxidation states of ruthenium. The uncatalysed reaction between 4-hydroxycoumarin and DPN in an alkaline medium has been studied previously [11]. A microscopic amount of ruthenium(III) is sufficient to catalyse the reaction and a variety of mechanisms are possible.

The biological importance of coumarin derivatives as anticoagulants, aflatoxins, mycotoxins and antibiotics has led to a considerable amount of synthetic work in the field of coumarin for their pharmacological evaluation. 4-Hydroxycoumarin (4-hydroxy-2H-1-benzopyran-2-one) (HDC) is used in the synthesis of pharmaceuticals especially for anticoagulants. It is used in manufacturing fluorescent dyes and rodenticides. The 4-hydroxycoumarin derivative, Mercamour [12], is a long oral anticoagulant. The anticoagulant activity is in the duration of 48–72 h. Ichikawa et al. [13] reported that 4-hydroxy-3-sulphonamidocoumarins are used as antibacterial and antitubercular agents. In earlier reports [4–7] on DPN oxidation, periodate had a re-

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tarding effect and order in the $[\text{OH}^-]$ was found to be less than unity in almost all the reactions and monoperiodatonickelate(IV) (MPN), is considered to be the active species. However, in the present study we have observed entirely different kinetic observations and diperiodatonickelate(IV) (DPN) itself is found to be active form of the oxidant. The literature survey reveals that there are no reports on mechanistic study of ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin by DPN. Thus, in order to explore the mechanism of oxidation by DPN in alkaline medium and to check the reactivity of hydroxy compounds towards DPN, we have selected 4-hydroxycoumarin as a substrate. The title reaction is studied to investigate the redox chemistry of the nickel(IV) in such media and to arrive at a plausible mechanism.

2. Experimental and methods

All chemicals used were of reagent grade. Double distilled water was used throughout the work. The solution of 4-hydroxycoumarin (M/s. S.S. Antibiotics Pvt. Ltd., Aurangabad, India) was prepared by dissolving appropriate amount of recrystallised sample (from aqueous acetone) in alkali. The solid complex nickel(IV) periodate was prepared by known method [14]. The purity of the complex was checked by its UV-vis spectrum, which shows a broad absorption band at 410 nm. Aqueous solution of DPN was obtained by dissolving the solid complex in 1.0 mol dm^{-3} KOH solution. The Ni(IV) in alkaline solution was estimated gravimetrically [15] after reducing it to Ni(II) and precipitating Ni(II) as its dimethyl glyoxime complex. Periodate solution was prepared by weighing out the required amount of a sample potassium periodate in hot water and was used after keeping for 24 h. Its concentration was ascertained [16] iodometrically at neutral pH maintained by a phosphate buffer. Ni(II) solution was prepared from nickel sulphate (Fischer). The ruthenium(III) solution was prepared by dissolving a known weight of RuCl_3 (s.d. fine-chem) in 0.20 mol dm^{-3} HCl. Mercury was added to the ruthenium(III) solution to reduce any Ru(IV) formed during the preparation of ruthenium(III) stock solution and was kept for a day. The ruthenium(III) concentration was assayed [17] by EDTA titration. Potassium hydroxide and potassium nitrate were employed to maintain required alkalinity and ionic strength, respectively. Since periodate is present in excess in the DPN complex, the possibility of 4-hydroxycoumarin oxidation by periodate in aqueous alkaline medium has been tested. The results indicated that the reaction between IO_4^- and 4-hydroxycoumarin is negligibly slow compared to the rate of reaction between DPN and 4-hydroxycoumarin under the experimental conditions.

Kinetic measurements were performed on a Hitachi 150-20 spectrophotometer. All kinetic runs were followed under pseudo-first-order conditions with the 4-hydroxycoumarin concentration in excess over that of the oxidant at $25 \pm 0.1^\circ\text{C}$,

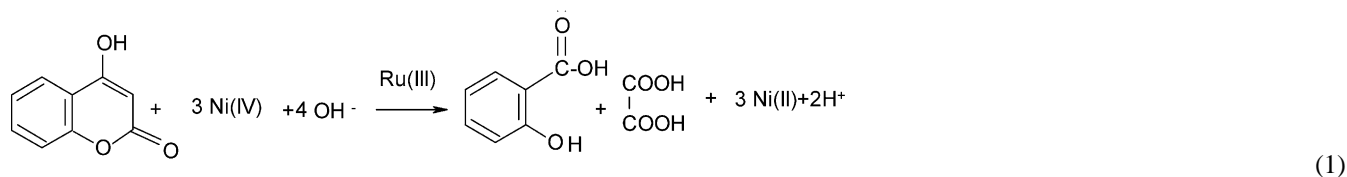
unless otherwise stated. The reaction was initiated by mixing thermally equilibrated solutions of DPN and 4-hydroxycoumarin which also contained a definite quantity of Ru(III), KOH, KNO_3 and IO_4^- . Here, the total concentration of hydroxide ion was calculated considering the KOH in DPN as well as the KOH additionally added. Similarly, the total metaperiodate concentration was calculated by considering the amount present in the DPN solution and that additionally added. The course of reaction was followed by measuring the absorbance of unreacted DPN in the reaction mixture in a 1 cm quartz cell located in the thermostatted compartment of a Hitachi 150-20 spectrophotometer, at its maximum absorption wavelength of 410 nm as a function of time. Earlier, it was verified that there is negligible interference from other species present in the reaction mixture at this wavelength. The obedience of Beer's law by DPN at 410 nm was verified earlier and the molar absorbance coefficient, ' ϵ ' was found to be $7500 \pm 375 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at this wavelength. The reaction was followed to more than 80% completion. The first-order rate constants, k_{obs} , were calculated from the slopes of $\log [\text{DPN}]$ versus time plots. The rate constants were reproducible to within $\pm 4\%$.

In view of the modest concentration of alkali used in the reaction medium, attention was also directed to the effect of the surface reaction vessel on the kinetics. Use of polythene or acrylic wares and quartz or polyacrylate cells gave the same results, indicating that the surface does not have any significant effect on reaction rates. Kinetic runs were also carried out in nitrogen 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 nitrogen 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. However, fresh solutions were, nevertheless, used while carrying out the kinetic study. Regression analysis of experimental data to obtain regression coefficient r , and the standard deviation S , of points from the regression line, was performed with the Microsoft Excel programme.

3. Results and discussion

3.1. Stoichiometry and product analysis

Different reaction mixtures with different sets of concentrations of reactants where [Ni(IV)] was in excess over 4-hydroxycoumarin at constant amount of ruthenium(III), ionic strength and alkali were kept for about 6 h at $25 \pm 0.1^\circ\text{C}$ in nitrogen atmosphere and in a closed vessel. The remaining [DPN] was assayed spectrophotometrically by measuring the absorbance at 410 nm. The results indicated the 3 mol of DPN is consumed by 1 mol 4-hydroxycoumarin as in Eq. (1)



The reaction product was extracted with ether and recrystallised from aqueous alcohol and the purity was checked by HPLC. This is identified as salicylic acid by its I.R. spectrum (KBr) from FT-IR—Spectrometer Nicolet Impact 410, which showed a band at (ν) 1701 cm^{-1} due to C=O and 3392 cm^{-1} due to phenolic OH. Salicylic acid was further characterised by ^1H NMR spectrum from NMR Spectrometer Bruker-F 300 MHz ($\text{CDCl}_3 + \text{DMSO}-d_6/\text{TMS}$) δ , 5.74 (s, 1H, phenolic OH, D_2O exchangeable), 7.27–7.82 (m, 4H, 4 aromatic protons), 11.5 (s, 1H, acidic OH, D_2O exchangeable). The other product oxalic acid, which is highly soluble in water, was identified by spot test [18] and nickel(II) sulphate was identified by spot test [19] and UV–vis spectrum. It was observed that the salicylic acid and oxalic acid do not undergo further oxidation under the present kinetic conditions.

3.2. Reaction order

As the diperiodatonickelate(IV) oxidation of 4-hydroxycoumarin in alkaline medium proceeds with a measurable rate in the absence of ruthenium(III), the catalysed reaction is understood to occur in parallel paths with contributions from both the catalysed and uncatalysed paths. Thus, the total rate constant (k_T) is equal to the sum

of the rate constants of the catalysed (k_C) and uncatalysed (k_U) reactions, so $k_C = k_T - k_U$. Hence, the reaction orders have been determined from the slopes of $\log k_C$ versus \log (concentration) plots by varying the concentrations of 4-hydroxycoumarin, ruthenium(III) and alkali, in turn, while keeping the others constant.

3.3. Effect of [diperiodatonickelate(IV)]

The oxidant, diperiodatonickelate(IV) concentration was varied in the range of 1.0×10^{-5} to $1.0 \times 10^{-4}\text{ mol dm}^{-3}$, as shown in Table 1. All kinetic runs exhibited identical characteristics. The linearity of plots of \log (Abs) versus time, ($r \geq 0.8763$, $S \leq 0.027$), for different initial concentrations of DPN indicates the order in [DPN] as unity (Fig. 1). This was also confirmed by varying [DPN], which did not show any change in pseudo-first-order rate constants, k_c (Table 1).

3.4. Effect of [4-hydroxycoumarin]

The substrate, 4-hydroxycoumarin, concentration was varied in the range of 3.0×10^{-4} to $3.5 \times 10^{-3}\text{ mol dm}^{-3}$ at 25°C , keeping all other reactant concentrations and conditions constant (Table 1). The k_c values increased with increase

Table 1

Effect of variation of [DPN], [Ru(III)], [HDC] and $[\text{OH}^-]$ on the ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin by diperiodatonickelate(IV) in aqueous alkaline medium at 25°C ; $[\text{IO}_4^-] = 1.0 \times 10^{-5}$, $I = 1.0\text{ mol dm}^{-3}$

10^3 [HDC] (mol dm^{-3})	10^4 [DPN] (mol dm^{-3})	10^5 [Ru(III)] (mol dm^{-3})	$[\text{OH}^-]$ (mol dm^{-3})	$10^2 k_T$ (s^{-1})	$10^3 k_U$ (s^{-1})	$10^2 k_C$ (s^{-1})	
						Expt.	Cal.
0.3	0.6	0.6	0.5	0.70	1.25	0.57	0.57
0.6	0.6	0.6	0.5	0.95	1.63	0.78	0.77
1.2	0.6	0.6	0.5	1.50	2.50	1.25	1.28
2.4	0.6	0.6	0.5	2.10	3.60	1.74	1.71
3.5	0.6	0.6	0.5	2.45	4.20	2.03	2.00
1.2	0.1	0.6	0.5	1.52	2.52	1.29	1.28
1.2	0.3	0.6	0.5	1.50	2.54	1.26	1.28
1.2	0.6	0.6	0.5	1.50	2.50	1.25	1.28
1.2	0.8	0.6	0.5	1.52	2.49	1.26	1.28
1.2	1.0	0.6	0.5	1.53	2.55	1.27	1.28
1.2	0.6	0.1	0.5	0.50	2.50	0.25	0.24
1.2	0.6	0.2	0.5	0.90	2.50	0.65	0.70
1.2	0.6	0.6	0.5	1.50	2.50	1.25	1.28
1.2	0.6	0.8	0.5	2.25	2.50	1.95	2.00
1.2	0.6	1.0	0.5	3.15	2.50	2.90	2.95
1.2	0.6	0.6	0.1	0.85	1.40	0.70	0.71
1.2	0.6	0.6	0.3	1.35	2.25	1.12	1.14
1.2	0.6	0.6	0.5	1.50	2.50	1.25	1.28
1.2	0.6	0.6	0.8	1.90	3.40	1.56	1.50
1.2	0.6	0.6	1.0	2.50	4.20	2.08	2.10

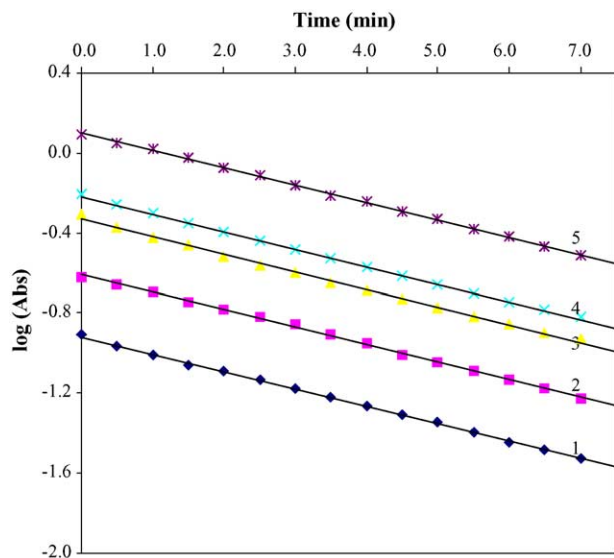


Fig. 1. First-order plots of Ru(III)-catalysed oxidation of 4-hydroxycoumarin by diperiodatonicelate(IV) in aqueous alkaline medium at 25 °C; 10^5 [DPN](mol dm⁻³), (1) 0.1, (2) 0.3, (3) 0.6, (4) 0.8, (5) 1.0 ([HDC]= 1.2×10^{-3} , [OH⁻]=0.5, [Ru(III)]= 6.0×10^{-5} and $I=1.0$ mol dm⁻³).

in concentration of 4-hydroxycoumarin indicating an apparent less than unit order dependence on substrate concentration. However, at lower concentration of 4-hydroxycoumarin, the reaction was first order in [HDC] and at high concentration of 4-hydroxycoumarin, the reaction was independent of [HDC]. The order in [HDC] changes from first order to zero order as the [HDC] varies.

3.5. Effect of [Ru(III)]

The ruthenium(III) concentrations was varied from 1.0×10^{-6} to 1.0×10^{-5} mol dm⁻³ range, at constant concentration of diperiodatonicelate(IV), 4-hydroxycoumarin, alkali and ionic strength. The order in [Ru(III)] was found to be unity from the linearity of the plots of $\log k_c$ versus \log [Ru(III)] ($r \geq 0.9997$, $S \leq 0.022$).

3.6. Effect of [alkali] and [periodate]

The effect of alkali on the reaction was studied at constant concentrations of 4-hydroxycoumarin and diperiodatonicelate(IV) (DPN) and at a constant ionic strength of 1.0 mol dm⁻³ at 25 °C. The rate constant increased with increase in [alkali] indicating an apparent less than unit order dependence on [alkali] as given in Table 1. Similar as in 4-hydroxycoumarin case, the order in alkali changes from first order to zero order as [alkali] varies. The effect of [IO₄⁻] was observed by varying the concentration from 1.0×10^{-5} to 1.0×10^{-4} mol dm⁻³, keeping all other reactants concentrations constant. It was found that the added periodate has no effect on the rate of reaction.

3.7. Effect of ionic strength and dielectric constant

The effect of ionic strength was studied by varying the potassium nitrate concentration from 0.5 to 2.0 mol dm⁻³ at constant concentrations of diperiodatonicelate(IV), ruthenium(III), 4-hydroxycoumarin and alkali. It was found that the rate constant increased with increase in concentration of KNO₃ and the plot of $\log k_c$ versus \sqrt{I} was linear with positive slope, which is given in Fig. 2 ($r \geq 0.9258$, $S \leq 0.009$). The relative permittivity (ϵ_T) effect was studied by varying the *t*-butanol–water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivities of the mixture of *t*-butanol–water were not successful. However, they were computed from the values of pure liquids [20]. The solvent did not react with the oxidant under the experimental conditions. The rate constant, k_c , increased with decrease in the dielectric constant of the medium. The plot of $\log k_c$ versus $1/\epsilon_T$ was linear with positive slope as shown in Fig. 2 ($r \geq 0.9553$, $S \leq 0.096$).

3.8. The effect of initially added products

The externally added products, such as the nickel sulphate, oxalic acid and salicylic acid did not have any significant effect on the rate of the reaction.

3.9. Polymerization study

To test the intervention of free radicals, the reaction mixture was mixed with acrylonitrile monomer and kept for 8 h under nitrogen atmosphere. On dilution with methanol, no precipitate of polymer was formed, indicating the absence of intervention of free radicals in the reaction.

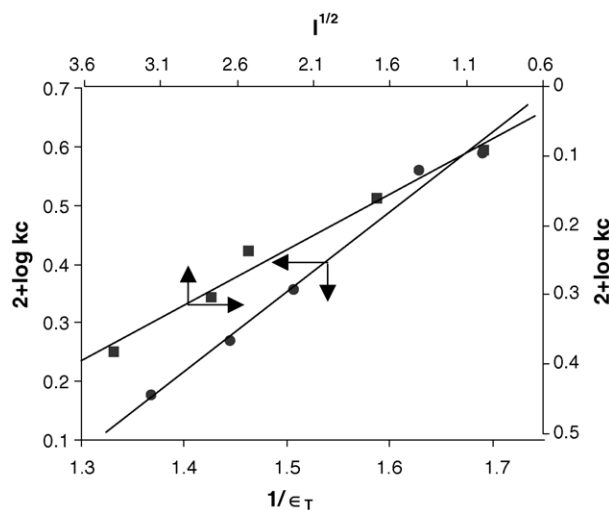


Fig. 2. Plots of $\log k_c$ vs. $I^{1/2}$ and $\log k_c$ vs. $1/\epsilon_T$.

Table 2

Thermodynamic activation parameters for the ruthenium(III)-catalysed oxidation of 4-hydroxycoumarin by alkaline diperiodatonickelate(IV) with respect to slow step of Scheme 1

Activation parameters	Values
E_a (kJ mol ⁻¹)	36.7 ± 1
ΔH^\ddagger (kJ mol ⁻¹)	34.7 ± 1
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-67.2 ± 1.5
ΔG^\ddagger (kJ mol ⁻¹)	46 ± 1

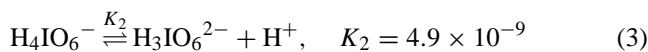
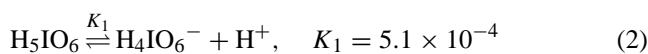
3.10. Effect of temperature

The rate of the reaction was measured at four different temperatures with varying [HDC] and [OH⁻], keeping other conditions constant. The rate of the reaction was found to increase with the increase of temperature. The rate constants, k , of the slow step of the reaction were obtained from slopes and the intercept of the plots of [Ru(III)]/ k_c versus 1/[HDC] ($r > 0.9769$, $S \leq 0.005$) and [Ru(III)]/ k_c versus 1/[OH⁻] ($r \geq 0.9986$, $S \leq 0.041$) for different temperatures. The values of $k \times 10^{-3}$ (dm³ mol⁻¹ s⁻¹) were 5.18, 6.91, 7.96 and 10.90 at 25, 30, 35 and 40 °C, respectively. The energy of activation corresponding to these constants were evaluated from the plot of log k versus 1/ T ($r \geq 0.9273$, $S \leq 0.004$) and other activation parameters of the reaction were calculated and are given in Table 2.

3.11. Mechanism

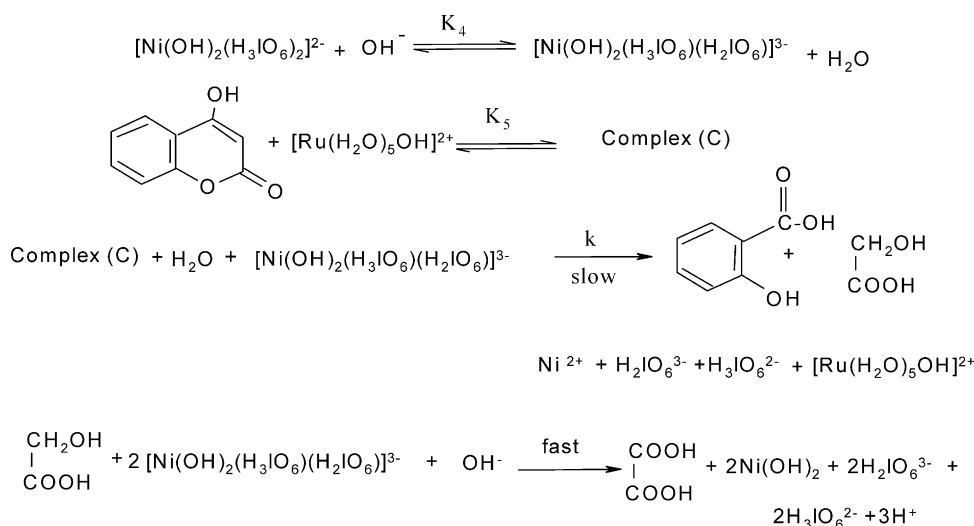
The water-soluble [8,9] nickel(IV) periodate complex is reported [5,6,21–24] to be [Ni(HIO₆)₂(OH)₂]⁶⁻. Although periodate is involved in multiple equilibria (2)–(4), which prevail to varying extents depending on the pH employed, under the strong alkaline conditions of the study (pH 13.3) the predominant form of periodate is expected to be H₃IO₆²⁻ and not HIO₆⁴⁻, which appears in present in the Ni(IV) complex [4–6,22,25]. On the contrary, in mild acidic and neutral

medium the predominant species of periodic acid is H₄IO₆⁻.



It is interesting to identify the probable ruthenium(III) chloride species in alkaline media. Electronic spectral studies [26] have confirmed that ruthenium(III) chloride exists in hydrated form as [Ru(H₂O)₆]³⁺. In the present study, it is quite probable that the [Ru(H₂O)₅OH]²⁺ species might assume the general form [Ru(III)(OH)_{*x*}]^{3-*x*}. The x -value would always be less than six because there are no definite reports of any hexahydroxy ruthenium species. The remainder of the coordination sphere would be filled by water molecules. Hence, under the conditions employed, e.g. [OH⁻] ≫ [Ru(III)], ruthenium(III) is mostly present as the hydroxylated species, [Ru(H₂O)₅OH]²⁺ [27].

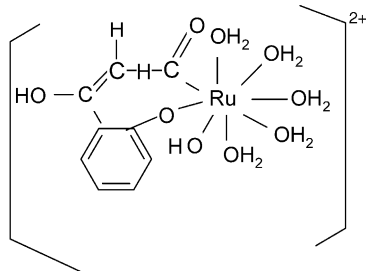
The reaction between DPN and 4-hydroxycoumarin in alkaline medium in the presence of ruthenium(III) presents a 3:1 stoichiometry of oxidant to reductant, with first-order dependence on both [DPN] and [ruthenium(III)] and an apparent order of less than unity in [OH⁻] and [HDC]. In most of the reports [4–7] on DPN oxidation, periodate had a retarding effect and order in the [OH⁻] was found to be less than unity and monoperiodatonickelate(IV) (MPN) is considered to be the active species. However, in the present kinetic study, different kinetic observations have been obtained, i.e., periodate has no effect on the rate of reaction and accordingly DPN itself is considered to be the active species of oxidant. The results indicate that the DPN combines with alkali to form a deprotonated form of DPN in equilibrium with the corresponding deprotonated species, as shown in Scheme 1. This is also supported by the observed fractional order in [OH⁻]. 4-Hydroxycoumarin reacts with



Scheme 1.

ruthenium(III) species to form a complex (C) which reacts with 1 mol of the deprotonated form of DPN in a slow step to give the products salicylic acid, glycolic acid and nickel(II) species with regeneration of catalyst, ruthenium(III). K_5 is the equilibrium constant comprising the equilibrium to bind 4-hydroxycoumarin to ruthenium(III). Further, the glycolic acid reacts with two more molecules of DPN species in a fast step to yield the products as given in Scheme 1. The formation of oxalic acid via glycolic acid is as per literature [28].

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



Spectral evidence for such a catalyst–substrate complex was obtained from the UV–vis spectra of 4-hydroxycoumarin ($1.2 \times 10^{-3} \text{ mol dm}^{-3}$) and mixture of ruthenium(III) ($6.0 \times 10^{-5} \text{ mol dm}^{-3}$) and 4-hydroxycoumarin ($1.2 \times 10^{-3} \text{ mol dm}^{-3}$). A hypsochromic shift about 6 nm, from 248 to 242 nm is observed together with hyperchromicity at 242 nm. Such a complex between a substrate and a catalyst has been observed in other studies [29].

The thermodynamic quantities for the first equilibrium step in Scheme 1 can be evaluated as follows: the substrate concentration was varied at four different temperatures and the value of K_4 was determined at each temperature. The values of K_4 ($\text{dm}^3 \text{ mol}^{-1}$) were obtained as 5.5, 7.0, 8.2 and 9.5 at 25, 30, 35 and 40 °C, respectively. A vant Hoff plot was made for the variation of K_4 with temperature [i.e., $\log K_4$ versus $1/T$ ($r \geq 0.9985$, $S \leq 0.036$)] and the values of the enthalpy of reaction, ΔH , entropy of reaction, ΔS , and free energy of reaction, ΔG , were calculated and tabulated in Table 3. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step are fairly slow and involves high activation energy [30]. In the presence of catalyst, the reaction appears to occur in parallel paths with contribution from the uncatalysed and catalysed 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. Scheme 1 leads

to rate law (5) as follows:

$$\text{Rate} = \frac{k K_4 K_5 [\text{HDC}] [\text{DPN}] [\text{OH}^-] [\text{Ru(III)}]}{(1 + K_5 [\text{Ru(III)}]) (1 + K_4 [\text{OH}^-]) \times (1 + K_4 [\text{DPN}]) (1 + K_5 [\text{HDC}])} \quad (5)$$

The terms $(1 + K_4 [\text{DPN}])$ and $(1 + K_5 [\text{Ru(III)}])$ in the denominator of Eq. (5) approximate to unity, in view of the low concentration of DPN and ruthenium(III) used, and therefore, Eq. (5) can be written as follows:

$$\begin{aligned} \frac{\text{Rate}}{[\text{DPN}]} &= k_C = k_T - k_U \\ &= \frac{k K_4 K_5 [\text{HDC}] [\text{Ru(III)}] [\text{OH}^-]}{1 + K_4 [\text{OH}^-] + K_5 [\text{HDC}] + K_4 K_5 [\text{OH}^-] [\text{HDC}]} \quad (6) \end{aligned}$$

Eq. (6) can be rearranged to Eq. (7), which is suitable for verification.

$$\begin{aligned} \frac{[\text{Ru(III)}]}{k_C} &= \frac{1}{k K_4 K_5 [\text{HDC}] [\text{OH}^-]} + \frac{1}{k K_5 [\text{HDC}]} \\ &+ \frac{1}{k K_4 [\text{OH}^-]} + \frac{1}{k} \quad (7) \end{aligned}$$

According to Eq. (7), the plots of $[\text{Ru(III)}]/k_C$ versus $1/[\text{HDC}]$ and $[\text{Ru(III)}]/k_C$ versus $1/[\text{OH}^-]$ ($r \geq 0.9994$, $S \leq 0.050$ and $r \geq 0.9986$, $S \leq 0.041$) are linear, with an intercept supporting the Ru(III)–4-hydroxycoumarin complex, which is verified (Fig. 3). From the slope and intercept of such plots, the values of K_4 , K_5 and k are calculated as $5.5 \pm 0.1 \text{ dm}^3 \text{ mol}^{-1}$, $1.0 \pm 0.05 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$ and $5.18 \pm 0.3 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The value obtained for K_4 is in agreement with previously reported [31]. The rate constants were evaluated over different experimental condi-

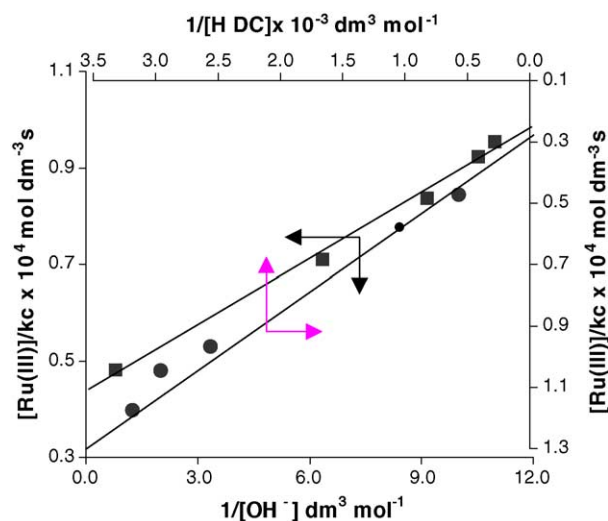


Fig. 3. Verification of rate law (6). Plots of $[\text{Ru(III)}]/k_C$ vs. $1/[\text{HDC}]$ and $[\text{Ru(III)}]/k_C$ vs. $1/[\text{OH}^-]$ (conditions as in Table 1).

Table 3
Thermodynamic quantities using K_4 values

Thermodynamic quantities	Values
ΔH (kJ mol^{-1})	22 ± 0.5
ΔS ($\text{JK}^{-1} \text{ mol}^{-1}$)	72 ± 2
ΔG (kJ mol^{-1})	1.2 ± 0.01

tions and there is a reasonable agreement between the calculated and experimental (Table 1) which fortifies the proposed mechanism. The effect of solvent on the reaction rate is described in detail in the literature [32]. In our present study, a plot of $\log k_c$ versus $1/\epsilon_T$ ($r \geq 0.984$, $s \leq 0.0053$) is linear with positive slope (Fig. 3), which is in accordance with the involvement of negative ions as given in Scheme 1.

The increase in the rate, with increasing ionic strength, is in the favour of a reaction between charged species of reactants, as presented in Scheme 1 of the proposed mechanism. The difference in the activation parameters for the catalysed (k_C) and uncatalysed (k_U) reaction explains the catalytic effect on the reaction. The catalyst, Ru(III), forms a complex with 4-hydroxycoumarin which can be reduced more easily than 4-hydroxycoumarin itself. Hence, the catalyst, Ru(III) lowers energy of activation. The negative value of ΔS^\ddagger indicates that the complex (C) is more ordered than the reactants. The observed modest enthalpy of activation and higher rate constant of the slow step indicate that the oxidation presumably occurs by inner-sphere mechanism. This conclusion is supported by earlier work [33].

4. Conclusions

Among various species of Ni(IV) in alkaline medium, in earlier reports the monoperiodatonickelate(IV) was the active species, whereas deprotonated form of diperiodateonickelate(IV) itself is considered to be the active species for the title reaction. 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.

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