

Osmium(VIII)/ruthenium(III) Catalysis of periodate oxidation of acetaldehyde in aqueous alkaline medium

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Received 23 September 1996; revised 26 August 1997; accepted 1 September 1997

ABSTRACT: Os(VIII) and Ru(III) catalysis of the periodate oxidation of acetaldehyde in aqueous alkaline medium was investigated. The catalytic efficiency is Ru(III) < Os(VIII). The product of oxidation in both cases is acetate and IO₃⁻. The stoichiometry is the same in both catalyzed reactions, i.e. [IO₄⁻]:[CH₃CHO] = 1:1. Probable mechanisms are proposed and discussed. The reaction constants involved in the mechanisms are derived. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: acetaldehyde; oxidation; periodate; osmium (VIII) catalysis; ruthenium (III) catalysis

INTRODUCTION

Periodate is widely employed as a diol cleaving reagent.¹ Periodate is a less potent oxidant in alkaline than in acidic media. In an alkaline medium, periodate is known to exist as different species involving multiple equilibria² and it is necessary to know the active form of oxidant in the reaction.

Acetaldehyde is used in the manufacture of acetic acid, which is employed as a solvent in some mechanistic studies. It is also used in the preparation of phenolic resins in the manufacture of dyes and rubber. The oxidation of acetaldehyde by variety of oxidants³ such as bromine, chromium(VI), iron(III), cerium(IV), permanganate, chloramine-T and peroxodisulfate has been studied.

In recent years, the use of transition metal ions such as osmium, ruthenium and iridium, either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest. The role of osmium(VIII) as a catalyst in some redox reactions has been reviewed.⁴ Although the mechanism of catalysis depends on the nature of the substrate, the oxidant and other experimental conditions, it has been shown⁵ that metal ions act as catalysts by one of these different paths such as the formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. Osmium(VIII) and ruthenium(III) catalysis in redox reactions involves several complexes, different oxidation states of osmium/ruthenium, etc. We have observed that osmium(VIII) and ruthenium(III) catalyse the oxidation of acetaldehyde by periodate in alkaline medium and the

study of the reactions is reported here with a discussion of the mechanisms.

EXPERIMENTAL

Reagent grade chemicals were used. Doubly distilled water was used throughout. A 30–35% solution of acetaldehyde (S.D. Fine Chemicals) was distilled using a 1.3 m fractionating column and collected at 30–32 °C in ice-cold water, then standardized⁶ by mixing a known volume of solution with hydroxylamine hydrochloride in 90% methanol and titrating the liberated hydrochloric acid against standard alkali solution. A stock standard solution of IO₄⁻ was prepared by dissolving a known weight of KIO₄ (Riedel-de Haën) in hot water and used after keeping for 24 h. Its concentration was ascertained iodometrically⁷ at neutral pH maintained using phosphate buffer. A stock standard solution of Os(VIII) was prepared by dissolving OsO₄ (Johnson Matthey) in 0.50 mol dm⁻³ NaOH. The concentration was ascertained⁸ by determining the unreacted [Fe(CN)₆]⁴⁻ with standard Ce(IV) solution in an acidic medium. A stock standard solution of Ru(III) was prepared by dissolving RuCl₃ (S.D. Fine Chemicals) in 0.20 mol dm⁻³ HCl. The concentration was determined⁹ by EDTA titration.

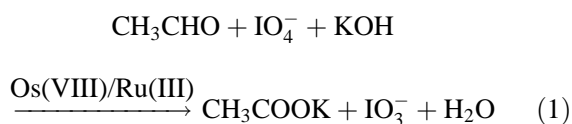
KIO₃ (Reechem) was used to prepare an iodate solution. Distilled and appropriately diluted acetic acid was neutralized with alkali and the resulting salt solution was used to study the effect of acetate ion on the reaction. KOH and KCl (AnalaR, BDH) were employed to maintain the required alkalinity and ionic strength, respectively. The temperature was maintained constant to within ±0.10 °C.

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Kinetic Measurements. Kinetic runs were initiated by mixing the previously thermostated reactant solutions of IO_4^- , CH_3CHO [which also contained the required amount of Os(VIII) or Ru(III)], KOH and KCl. Aliquots of the reaction mixture were removed by pipette at regular time intervals and poured into an iodine flask containing 5% KI and a suitable amount of 5% KH_2PO_4 , just sufficient to neutralize the alkali and to bring the pH of solution to 5–5.5. The liberated iodine was titrated⁷ against $\text{Na}_2\text{S}_2\text{O}_3$ solution using starch as an indicator. Under these conditions, iodate had no effect on the added iodide and the IO_4^- was quantitatively reduced to IO_3^- . Kinetic runs were carried under second-order conditions at $25 \pm 0.10^\circ \text{C}$ unless stated otherwise.

The apparent second-order rate constant, k_s , was obtained from plots of $1/(a-x)$ versus time from runs involving equivalent concentrations of reactants, where a and x are the initial concentration of IO_4^- and amount reacted at time t , respectively. The initial rates were obtained from the slopes of concentration versus time graphs in the initial stages of the reactions by the plane mirror method. The rates were reproducible to within $\pm 6\%$.

Stoichiometry and product analysis. Different sets of reactions containing excess IO_4^- over CH_3CHO with constant concentrations of Os(VIII) or Ru(III) and OH^- were kept for 24 h at 298 K and then analyzed. The unreacted oxidant was assayed iodometrically as mentioned earlier.⁷ Other product acetate was found by a spot test.¹⁰ There was no perceptible reaction between periodate and acetate in alkaline medium under the conditions employed. The results showed 1:1 stoichiometry according to the equation



RESULTS

Osmium(VIII) catalysis

The reaction orders were obtained from log–log plots of initial rates versus concentration. The reaction was carried out varying the concentration of oxidant, reductant, catalyst and alkali in turn while keeping all other conditions constant (Tables 1 and 2). The Os(VIII)-catalyzed oxidation of acetaldehyde by IO_4^- was shown to be nearly second order as the plot of $1/[\text{IO}_4^-]$ versus time was linear beyond two half-lives of completion of the reaction when $[\text{CH}_3\text{CHO}] = [\text{IO}_4^-]$. However, when $[\text{CH}_3\text{CHO}] \neq [\text{IO}_4^-]$ while varying the CH_3CHO and IO_4^- concentrations, it was found that the k_s values were not constant. Under such conditions, the log–log plots of

initial rates versus concentrations of CH_3CHO and IO_4^- showed that the order in $[\text{CH}_3\text{CHO}]$ was less than unity (≈ 0.8) whereas the order in $[\text{IO}_4^-]$ was nearly unity over the range of concentrations studied (Tables 1 and 2). Hence initial rates were given for variation of acetaldehyde and periodate. For variation of the alkali and catalyst, second-order rate constants ($a = b$) and initial rates were determined (Table 2). The order in alkali concentration was found to be less than unity and that in $[\text{Os(VIII)}]$ was unity over the range of concentrations studied (Table 2).

Initially added products, acetate and iodate, in the concentration range $1.0 \times 10^{-2} - 1.0 \times 10^{-3} \text{ mol dm}^{-3}$, did not have any significant effect on the reaction rate. The ionic strength of the medium was varied from 1.0×10^{-2} to $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ with KCl at constant concentrations of oxidant, reductant, alkali and catalyst. The results showed that ionic strength has no effect on the reaction rate. The dielectric constant (D) of the reaction medium was varied by varying the content of *tert*-butanol (its earlier found inertness towards oxidant was confirmed). The results showed that the plot of $\log k_s$ versus $1/D$ was linear with a positive slope. The dielectric constants were calculated from values of pure liquids as given earlier.¹¹

Test for free radicals

To test for free radicals, the reaction mixture containing acrylonitrile was kept for 24 h in an inert atmosphere. On dilution with methanol no precipitate resulted, indicating the absence of intervention of free radicals in the reaction.

Table 1. Effect of variation of [periodate] and [acetaldehyde] on osmium(VIII)-catalyzed oxidation of acetaldehyde by periodate in aqueous alkaline medium at 25°C , with $[\text{OH}^-] = 0.05$, $[\text{Os(VIII)}] = 2.0 \times 10^{-6}$ and $l = 0.06 \text{ mol dm}^{-3}$ (error $\pm 6\%$)

$[\text{IO}_4^-] \times 10^3$ (mol dm^{-3})	$[\text{CH}_3\text{CHO}] \times 10^3$ (mol dm^{-3})	Rate $\times 10^7$ ($\text{mol dm}^{-3} \text{ s}^{-1}$)	
		Exptl	Calcd ^a
0.30	1.00	1.16	1.09
0.60	1.00	2.33	2.16
0.80	1.00	3.03	2.90
1.00	1.00	3.80	3.63
2.00	1.00	6.89	7.26
3.00	1.00	9.08	10.96
1.00	0.50	2.00	1.96
1.00	0.80	2.80	2.99
1.00	1.00	3.80	3.63
1.00	2.00	6.73	6.30
1.00	3.00	8.80	8.35
1.00	5.00	12.20	11.28

^a Calculation of rate constants are on the basis of rate law (5) using $K_1 = 24.8 \pm 0.5 \text{ dm}^3 \text{ mol}^{-1}$, $K_3 = 325 \pm 12 \text{ dm}^3 \text{ mol}^{-1}$ and $k_1 = 1.19 \times 10^3 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Table 2. Effect of variation of [alkali] and [osmium(VIII)] on osmium(VIII)-catalyzed oxidation of acetaldehyde by periodate in aqueous alkaline medium at 25 °C, with $[\text{IO}_4^-] = 1.0 \times 10^{-3}$, $[\text{CH}_3\text{CHO}] = 1.0 \times 10^{-3}$ and $l = 0.06 \text{ mol dm}^{-3}$ (error $\pm 6\%$)

$[\text{OH}^-] \times 10^1$ (mol dm^{-3})	$[\text{Os(VIII)}] \times 10^6$ (mol dm^{-3})	Rate $\times 10^7$ ($\text{mol dm}^{-3} \text{ s}^{-1}$)		Rate constant, k_s ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)
		Exptl	Calcd	
0.20	2.00	2.29	1.09	0.15
0.50	2.00	3.80	3.63	0.45
0.70	2.00	4.10	4.06	0.54
1.00	2.00	4.43	4.46	0.69
1.50	2.00	4.90	4.85	1.00
2.00	2.00	5.51	5.83	1.10
0.50	1.00	1.73	1.81	0.25
0.50	2.00	3.80	3.63	0.45
0.50	3.00	4.66	5.45	0.69
0.50	4.00	9.01	9.08	1.19
0.50	5.00	12.01	12.71	2.41
0.50	10.00	18.00	18.16	3.05

The rate constants (k_1) of the slow step of Scheme 1 (see Discussion) were obtained from intercept of $[\text{Os(VIII)}]/[\text{IO}_4^-]/\text{rate}$ versus $[\text{CH}_3\text{CHO}]^{-1}$ plots at four different temperatures and were used for the calculation of activation parameters. The values of k_1 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) are 1.19×10^3 , 1.30×10^3 , 1.46×10^3 and 1.68×10^3 at 298, 302, 308 and 315 K, respectively. These data led to values of ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger of $15 \pm 1 \text{ kJ mol}^{-1}$, $54 \pm 3 \text{ kJ mol}^{-1}$ and $-137 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

Ruthenium(III) catalysis

The Ru(III)-catalyzed oxidation of CH_3CHO by IO_4^- was followed by varying the concentrations of oxidant, substrate, alkali, ruthenium(III) and KCl; one at a time while all the others were kept constant (Tables 3 and 4). The order in IO_4^- concentration was found to be zero,

Table 3. Effect of variation of [periodate] and [acetaldehyde] on ruthenium(III)-catalyzed oxidation of acetaldehyde by periodate in aqueous alkaline medium at 25 °C, with $[\text{OH}^-] = 0.10$, $[\text{Ru(III)}] = 5.0 \times 10^{-6}$ and $l = 0.11 \text{ mol dm}^{-3}$ (error $\pm 6\%$)

$[\text{IO}_4^-] \times 10^3$ (mol dm^{-3})	$[\text{CH}_3\text{CHO}] \times 10^3$ (mol dm^{-3})	$k_0 \times 10^7$ ($\text{mol dm}^{-3} \text{ s}^{-1}$)	
		Exptl	Calcd
0.30	1.00	10.32	10.50
0.50	1.00	10.46	10.50
0.80	1.00	10.43	10.60
1.00	1.00	10.45	10.50
1.50	1.00	10.50	10.50
2.00	1.00	10.24	10.50
1.00	0.50	04.91	05.23
1.00	0.80	08.12	08.37
1.00	1.00	10.46	10.50
1.00	2.00	21.00	21.00
1.00	3.00	28.83	30.00
1.00	5.00	51.33	51.75

since the initial rates were independent of the initial concentration of IO_4^- and the concentration versus time plots were linear and parallel. The order in $[\text{CH}_3\text{CHO}]$ was found to be nearly unity from the plot of $\log k_0$ (zero-order rate constant) versus $\log [\text{CH}_3\text{CHO}]$ over the range of concentrations studied. The order in Ru(III) was unity whereas the order in [alkali] was less than unity {concentrations as given in Table 4}.

Initial addition of products (iodate and acetate) and ionic strength did not have any significant effect on the reaction. Regarding the effect of dielectric constant on the reaction, it was found that the plot of $\log k_0$ versus $1/D$ was linear with a negative slope. The test for free radicals was negative.

The rate constants (k_2) of the slow step of Scheme 1 were obtained from intercept of $[\text{CH}_3\text{CHO}]/[\text{Ru(III)}]/\text{rate}$ versus $[\text{OH}^-]^{-1}$ plots at four different temperatures. The values of k_2 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) are 2.77×10^2 , 5.0×10^2 , 8.33×10^2 and 18.18×10^2 at 298, 304, 308

Table 4. Effect of variation of [alkali] and [ruthenium(III)] on ruthenium(III)-catalyzed oxidation of acetaldehyde by periodate in aqueous alkaline medium at 25 °C, with $[\text{IO}_4^-] = 1.0 \times 10^{-3}$, $[\text{CH}_3\text{CHO}] = 1.0 \times 10^{-3}$ and $l = 0.11 \text{ mol dm}^{-3}$ (error $\pm 6\%$)

$[\text{OH}^-] \times 10^1$ (mol dm^{-3})	$[\text{Ru(III)}] \times 10^6$ (mol dm^{-3})	$k_0 \times 10^7$ ($\text{mol dm}^{-3} \text{ s}^{-1}$)	
		Exptl.	Calcd.
0.10	5.00	03.30	03.33
0.30	5.00	06.88	06.70
0.50	5.00	08.41	08.46
0.70	5.00	09.00	09.50
0.90	5.00	10.41	10.25
1.00	5.00	10.46	10.50
1.00	1.00	02.24	02.10
1.00	1.50	03.30	03.14
1.00	2.00	04.33	04.20
1.00	3.00	05.92	06.30
1.00	5.00	10.46	10.50
1.00	10.00	19.66	21.01

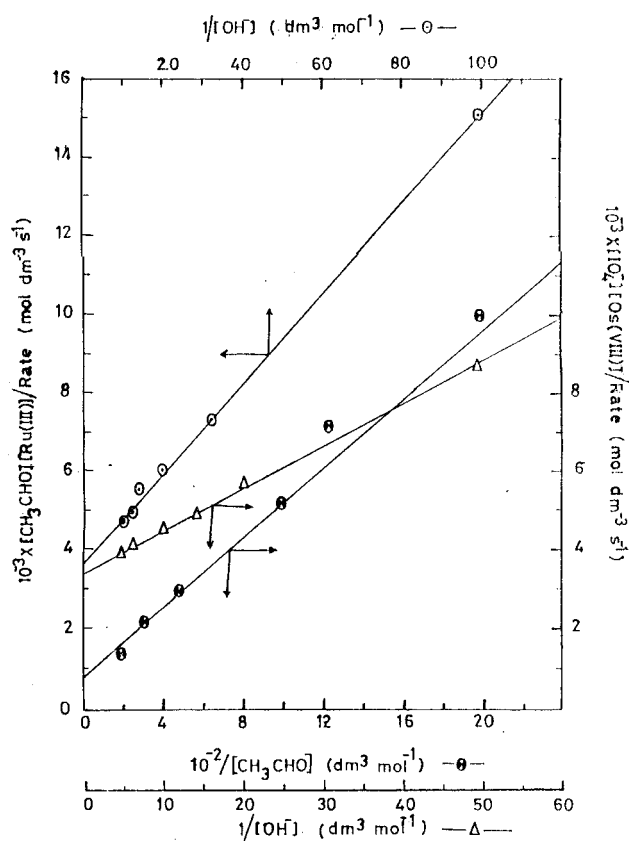


Figure 1. Verification of rate laws (5) and (6). Conditions as given in Tables 1–4

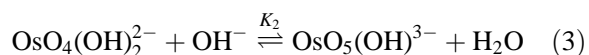
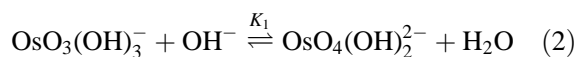
and 313 K, respectively. These data led to values of ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger of the slow step of $100 \pm 4 \text{ kJ mol}^{-1}$, $56 \pm 2 \text{ kJ mol}^{-1}$ and $147 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively.

DISCUSSION

Osmium (VIII)-catalyzed reaction

The reaction has 1:1 stoichiometry and acetate and IO_3^- are the main products of the reaction. The order in $[\text{IO}_4^-]$ and $[\text{Os(VIII)}]$ is unity and that in $[\text{CH}_3\text{CHO}]$ and $[\text{OH}^-]$ is fractional (Tables 1 and 2). The uncatalyzed reaction is very slow under the experimental conditions used.

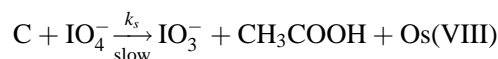
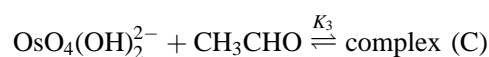
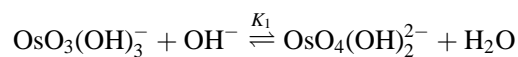
Osmium(VIII) is known to form different complexes at different OH^- concentrations, as shown in equations (2) and (3), where the equilibrium constants K_1 and K_2 have values of 24 and $6.8 \text{ dm}^3 \text{ mol}^{-1}$ respectively.¹²



At higher concentration of OH^- i.e. $>0.15 \text{ mol dm}^{-3}$, equilibrium (3) is significant. At lower concentrations of OH^- , as employed in the present study, and since the rate of oxidation increased with increase in $[\text{OH}^-]$, it is

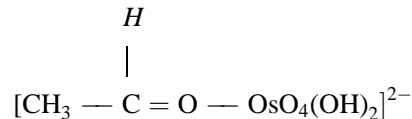
reasonable to assume that equilibrium (2) was operative. The main osmium(VIII) species is likely to be $\text{OsO}_4(\text{OH})_2^{2-}$ and its formation by equilibrium (2) is of importance in the reaction. This conclusion is in agreement with earlier work.^{4,13}

The results of our study on the osmium(VIII)-catalyzed reaction suggest the formation of a complex between the catalyst and substrate followed by its reaction with IO_4^- in the rate-determining step to give the products. Attempts to obtain UV-visible spectral evidence for the intermediate complex of CH_3CHO and Os(VIII) were not successful. However, the interaction may be weak and such complex formation between the catalyst and substrate has also been observed in earlier studies.⁴ The evidence for complex formation is restricted to kinetic data. The order of less than unity in [acetaldehyde] reveals the possibility of the involvement of complex formation between the substrate and catalyst in the reaction system in the pre-equilibrium step. All the experimental results are in agreement with Scheme 1.



Scheme 1.

The probable structure of complex (C) may be



Scheme 1 leads to the following rate law:

$$\text{rate} = \frac{k_s K_1 K_3 [\text{Os(VIII)}][\text{IO}_4^-][\text{CH}_3\text{CHO}][\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1 K_3 [\text{CH}_3\text{CHO}][\text{OH}^-]} \quad (4)$$

For verification of this rate law, it is necessary to rearrange equation (4) to

$$\frac{[\text{Os(VIII)}][\text{IO}_4^-]}{\text{rate}} = \frac{1}{k_s K_1 K_3 [\text{OH}^-][\text{CH}_3\text{CHO}]} + \frac{1}{k_s K_3 [\text{CH}_3\text{CHO}]} + \frac{1}{k_s} \quad (5)$$

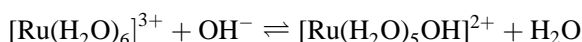
From the slopes and intercepts of the linear plots of the left-hand side of equation (5) versus $1/[\text{CH}_3\text{CHO}]$ and $1/[\text{OH}^-]$, the values of K_1 , K_3 and k_s at 298 K were calculated to be $24.8 \pm 0.5 \text{ dm}^3 \text{ mol}^{-1}$, $325 \pm 12 \text{ dm}^3 \text{ mol}^{-1}$ and $1.19 \times 10^3 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively (Fig. 1). The value of K_1 was found to be in good agreement with that reported earlier.¹³ These values of K_1 , K_3 and k_s were utilized for the calculation of rates under various experimental conditions and were found to be in reasonable agreement with the experimental rates (Table 1).

The negligibly small effect of ionic strength on the reaction is consistent with reaction between neutral and charged species as in Scheme 1. The effect of dielectric constant on the reaction is also as expected for a reaction between an ion and a neutral molecule.¹⁴ The sizeable negative value of the entropy of activation indicates complex formation during the reaction.

Ruthenium(III)-catalyzed reaction

In the ruthenium(III)-catalyzed reaction, the order in $[\text{CH}_3\text{CHO}]$ and $[\text{Ru(III)}]$ is unity in each and that in $[\text{IO}_4^-]$ is zero, unlike the case with Os(VIII) catalysis (see above) (Table 3). The rate increased with increasing $[\text{OH}^-]$ (Table 4). The products are acetate and IO_3^- and stoichiometry is 1:1 as in the Os(VIII)-catalysed reaction. No product effect was observed.

The spectrum of Ru(III) in alkaline medium (Fig. 2) is different to those in aqueous neutral and acidic media.¹⁵ It is also observed that the absorbance of Ru(III) increases with increase in $[\text{OH}^-]$ and finally remains constant. This indicates the predominance of one species of Ru(III), presumably $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$. For this reason and the fact that the rate increases with increase in $[\text{OH}^-]$, with less than unity order in $[\text{OH}^-]$, the main Ru(III) species is likely to be $[\text{Ru}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ and its formation in the following equilibrium is of importance in the reaction:

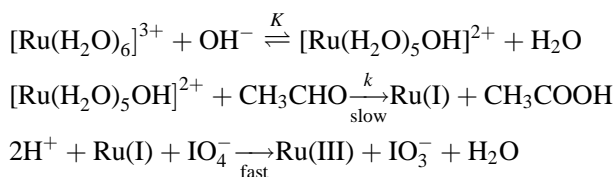


Also, as seen from the spectra of Ru(III), the existence of one or more isobestic points in a system is a good indication of an equilibrium between the two species. This conclusion is in agreement with earlier work¹⁶⁻¹⁸ and the value of the equilibrium constant obtained for such an equilibrium for this reaction also agrees with earlier work.¹⁸

Electronic spectra of Ru(III)

The weak band observed around 530 nm is assigned to the spin-forbidden ${}^4T_{1g} \leftarrow {}^2T_{2g}$ transition. The band around 390 nm is attributed to spin-allowed ${}^2A_{2g} \leftarrow {}^2T_{2g}$ and ${}^2T_{1g} \leftarrow {}^2T_{2g}$ transitions, which have similar energies. The bands observed near 225 and 280 nm are charge-transfer bands.

All the experimental results are in agreement with Scheme 2.



Scheme 2.

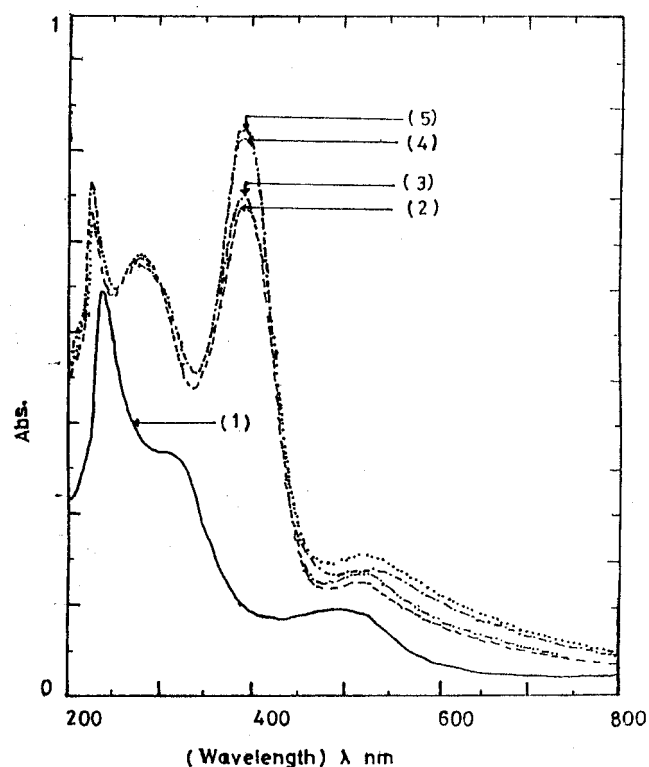


Figure 2. Spectra of Ru(III) at various $[\text{OH}^-]$. Ruthenium(III) catalysis of oxidation of acetaldehyde by periodate in aqueous alkaline medium at 25°C, (1) in aqueous medium, (2) at $[\text{OH}^-] = 5.0 \times 10^{-3}$, (3) at $[\text{OH}^-] = 1.0 \times 10^{-2}$, (4) at $[\text{OH}^-] = 5.0 \times 10^{-2}$ and (5) at $[\text{OH}^-] = 10.0 \times 10^{-2} \text{ mol dm}^{-3}$.

Ruthenium(III) is known to form complexes with hydroxide in basic media, such as $\text{Ru}(\text{OH})^{2+}$, $\text{Ru}(\text{OH})_2^+$ and $\text{Ru}(\text{OH})_3$. However, for the reasons already given, the main active species of Ru(III) is understood to be $\text{Ru}(\text{OH})^{2+}$ at the hydroxide concentrations studied in this work. The slow step (k step) involves interaction of hydroxylated species with acetaldehyde resulting in the formation of Ru(I) and acetic acid product. However, in view of the very low concentration of Ru(III) used, no kinetic evidence could be obtained for the formation of Ru(I). The formation of Ru(I) is in accordance with earlier work.⁵ The thus formed Ru(I) is oxidized by IO_4^- in the fast step to regenerate Ru(III) and to form IO_3^- .

The above mechanism leads to the rate law

$$\text{rate} = \frac{-d[\text{IO}_4^-]}{dt} = \frac{kK[\text{CH}_3\text{CHO}][\text{Ru(III)}][\text{OH}^-]}{1 + K[\text{OH}^-]} \quad (6)$$

Rearrangement of equation (6) gives

$$\frac{[\text{CH}_3\text{CHO}][\text{Ru(III)}]}{\text{rate}} = \frac{1}{kK[\text{OH}^-]} + \frac{1}{k} \quad (7)$$

According to equation (7), the plots of $[\text{CH}_3\text{CHO}][\text{Ru(III)}]/\text{rate}$ versus $1/[\text{OH}^-]$ should be linear, and they were found to be so (Fig. 1). From the slope and intercept, the values of K and k were derived as $31 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$

and $2.8 \times 10^2 \pm 10 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively. Using these values, the calculated rate constants (k_0) are in reasonable agreement with the experimental values (Tables 3 and 4). The value of K obtained kinetically is in the neighbourhood of an earlier reported¹⁸ value and a value obtained conductometrically.¹⁹

The negligible effect of ionic strength might be due to the presence of neutral molecules in the reaction. However, the effect of the dielectric constant is not easy to interpret. The positive value of the entropy of activation suggests that the transition state is less rigid than the reactants and no complex is involved in the mechanism (Scheme 2).

The enthalpy and free energy of activation indicate that Os(VIII) is more efficient than Ru(III) as a catalyst for the oxidation of acetaldehyde by IO_4^- . The Ru(III)-catalyzed reaction is slower probably owing to the inability of Ru(III) to act across a double bond. The Os(VIII)-catalysed reaction, however, is reasonably fast in view of the readiness of Os(VIII) to act across a double bond.

Acknowledgment

The authors thank Dr V. K. Revankar, Reader, Department of Chemistry, Karnatak University, Dharwad, for valuable discussions.

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