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Ruthenium(VIII) Catalyzed Oxidation of Some Cyclic Alcohols by Sodium Periodate in Alkaline Medium

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Kinetic investigations on ruthenium(VIII) catalyzed oxidation of cyclic alcohols (*viz.*, cyclopentanol, cyclohexanol and cycloheptanol) by alkaline solution of sodium periodate in the presence of mercury(II) acetate as a scavenger have been made in the temperature range of 30-45ºC. The rate of oxidation shows first order kinetics with respect to sodium periodate and Ru(VIII) while order of the reaction is zero with respect to substrate and positive with respect to hydroxyl ions. Insignificant influence of mercury(II) acetate and ionic strength of the medium was observed. A suitable mechanism in conformity with the kinetic observations has been proposed and the thermodynamic parameters computed.

Key Words: Kinetics, Ruthenium(VIII), Oxidation, Cyclic alcohols, Sodium periodate.

INTRODUCTION

Sodium periodate has been earlier used as an oxidant in oxidation of some compounds[1-4]. Less attention has been paid to the activity of sodium periodate in the presence of catalyst in acidic[5-7] as well as in alkaline media[8], but the results have not been interpreted so as to reveal a clear picture of the mode of catalyzed process. The utility of ruthenium(VIII) oxide as a non-toxic and homogeneous catalyst has been reported by several workers[9-14]. This prompted us to undertake the present investigation, which consists of Ru(VIII) catalyzed oxidation of some cyclic alcohols by alkaline iodate in presence of mercury(II) acetate as a scavenger.

EXPERIMENTAL

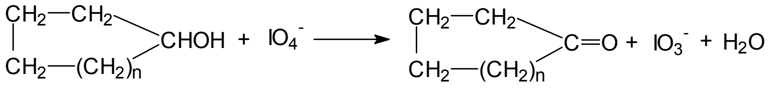
Aqueous solution of cyclic alcohols, sodium periodate (BDH, AR), sodium perchlorate and mercury(II) acetate (E. Merck) were prepared by dissolving the weighed amount of samples in triple distilled water. Sodium hydroxide was prepared by dissolving weighed amount of sample in triple distilled water and its solution was used as a source of hydroxyl ions. Ruthenium(VIII) oxide (Johnson Matthey) solution was prepared by dissolving the sample in sodium hydroxide of known strength. All other reagents were of highest quality available. Sodium perchlorate was used to maintain the ionic strength of the medium. The reaction stills were painted black from outside to prevent photochemical effects.

A thermostated water bath was used to maintain the desired temperature within ± 0.1 ºC. Requisite volumes of all reagents, including substrate, were taken in a reaction vessel and thermostated at 35 ºC for thermal equilibrium. A measured volume of sodium periodate solution, also maintained separately at the same temperature, was rapidly poured into the reaction vessel. The kinetics was followed by iodomteric estimation of unconsumed sodium periodate at regular time intervals using starch as indicator.

RESULTS AND DISCUSSION

Kinetics and oxidation of cyclic alcohols *i.e.*, cyclopentanol, cyclohexanol and cycloheptanol by sodium periodate in the presence of ruthenium(VIII) oxide as a homogeneous catalyst and mercuric acetate as a scavenger in the temperature range of 30-45 ºC are being reported in basic medium.

The stoichiometry of the reaction was ascertained by equilibrating the reaction mixture containing excess of sodium periodate over cyclic alcohols separately (in varying ratios) at 50 °C for 48 h. Estimation of residual iodate in different reactions showed that 1 mol of cyclic alcohol consumes 1 mol of iodate, according to the eqn. 1:



(1)

where n = 1, 2 and 3 in cyclopentanol, cyclohexanol and cycloheptanol, respectively. The corresponding ketone was confirmed by TLC and also through the dinitrophenyl hydrazine (DNP) derivative[15].

The reaction follows identical kinetics for the cyclic alcohols. The kinetic results were collected at several initial concentrations of the reactants (Table-1). First order rate constants k_1 *i.e.* (-dc/dt)/[IO_4*] (*indicating the concentration of $NaIO_4$ at which (-dc/dt) was determined) were calculated from the plots of unconsumed iodate *vs.* time. It was observed that the values of k_1 were constant at all initial concentrations of iodate showing thus first order dependence on [oxidant]. Variation in concentration of cyclic alcohols did not influence the value of k_1 appreciably, showing zero order kinetics in cyclic alcohols. This depicts its involvement in a fast step. Positive effect of change in [OH^-] on the rate of reaction has been observed (Table-1).

TABLE-1
EFFECT OF REACTANTS ON THE REACTION RATE AT 35 ºC

10^3 [IO_4^-] (M)	10^2 [S] (M)	10^4 [OH^-] (M)	Cypen	10^4 k_1[s^{-1}] Cyhex	Cyhep
0.80	2.00	3.33	0.82	1.36	1.86
1.00	2.00	3.33	0.84	1.28	1.78
1.25	2.00	3.33	0.78	1.30	1.80
1.67	2.00	3.33	0.86	1.34	1.88
2.50	2.00	3.33	0.80	1.36	1.84
3.33	2.00	3.33	0.82	1.34	1.88
1.00	0.50	3.33	0.80	1.26	1.76
1.00	0.67	3.33	0.84	1.28	1.80
1.00	1.00	3.33	0.76	1.26	1.82
1.00	1.33	3.33	0.78	1.34	1.80
1.00	2.50	3.33	0.82	1.30	1.86
1.00	4.00	3.33	0.86	1.32	1.74
1.00	2.00	5.00	1.08	1.56	2.06
1.00	2.00	6.60	1.32	1.78	2.40
1.00	2.00	8.00	1.54	2.08	2.76
1.00	2.00	10.00	1.86	2.36	3.02
1.00	2.00	13.20	2.10	2.70	3.44
1.00	2.00	20.00	2.48	3.02	3.86

[Ru(VIII)] = 13.20×10^{-6} M; [$NaClO_4$] = 1.40×10^{-2} M; [$Hg(OAc)_2$] = 4.00×10^{-3} M; Cypen = cyclopentanol; Cyhex = cyclohexanol; Cyhep = cycloheptanol.

First order dependence on [RuO_4] is evident from close resemblance between the slope of k_1 *vs.* [Ru(VIII)] plot (Fig. 1) {0.66×10^{-2} for cyclopentanol, 1.00×10^{-2} for cyclohexanol and 1.25×10^{-2} for cycloheptanol at 35ºC} and the average value of second order rate constant k_2 or k_1/[RuO_4] {0.64×10^{-2} for cyclopentanol, 0.96×10^{-2} for cyclohexanol and 1.34×10^{-2} for cycloheptanol at 35ºC}. Negligible effect of variation in the ionic strength of the medium and addition of mercury(II) acetate on the reaction rate was observed (Table-2). The negligible effect of mercury(II) acetate excludes the possibility of its involvement either as a catalyst or as an oxidant because it does not help the reaction proceed without iodate. Hence, the function of mercury(II) acetate is to act as a scavenger[16] for any I^- ion formed in the reaction. It helps to eliminate parallel oxidation by iodine.

Kinetic observations were also made at different temperatures (30-45 ºC) and various activation parameters were calculated for oxidation of cyclopentanol, cyclohexanol and cycloheptanol (Table-3). The reactive species of $NaIO_4$ in both acidic and alkaline medium is IO_4^-.

TABLE-2
EFFECT OF VARIATION OF RuO_4, MERCURY(II) ACETATE AND IONIC STRENGTH (μ)

10^6 [RuO_4] (M)	10^3 [$Hg(OAc)_2$] (M)	10^2 [$NaClO_4$] (M)		10^4 k_1 [s^{-1}]	
			Cypen	Cyhex	Cyhep
6.66	4.00	1.40	0.44	0.68	0.90
13.20	4.00	1.40	0.84	1.28	1.78
19.80	4.00	1.40	1.36	1.92	2.72
26.40	4.00	1.40	1.84	2.80	3.66
33.00	4.00	1.40	2.36	3.62	4.48
39.60	4.00	1.40	2.78	4.18	5.36
13.20	1.00	1.40	0.80	1.24	1.80
13.20	1.25	1.40	0.86	1.20	1.86
13.20	1.42	1.40	0.78	1.22	1.78
13.20	1.67	1.40	0.80	1.30	1.76
13.20	2.00	1.40	0.76	1.34	1.82
13.20	2.50	1.40	0.82	1.32	1.80
13.20	3.33	1.40	0.78	1.28	1.84
13.20	5.00	1.40	0.84	1.26	1.74
13.20	4.00	2.00	0.78	1.30	1.86
13.20	4.00	3.00	0.80	1.28	1.86
13.20	4.00	6.00	0.84	1.36	1.84
13.20	4.00	10.00	0.84	1.34	1.80
13.20	4.00	12.50	0.82	1.36	1.78

[$NaIO_4$] = 1.00×10^{-3} M; [S] = 2.00×10^{-2} M; [NaOH] = 3.33×10^{-4} M; Temp. 35 ºC; Cypen = cyclopentanol; Cyhex = cyclohexanol; Cyhep = cycloheptanol.

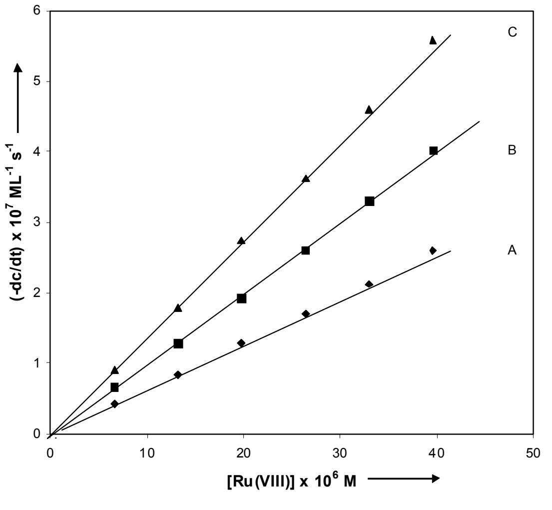


Fig. 1. Plot between (-dc/dt) and [Ru(VIII)] oxidation of cyclopentanol (A), cyclohexanol (B) and cycloheptanol (C). [$NaIO_4$] = 1.00×10^{-3} M ; [$Hg(OAc)_2$] = 4.00×10^{-3} M; [cyclopentanol] = 2.00×10^{-2} M; [cyclohexanol] = 2.00×10^{-2} M; [cycloheptanol] = 2.00×10^{-2} M; [NaOH] = 3.33×10^{-4} M; Temp. 35 ºC

TABLE-3
ACTIVATION PARAMETERS FOR ACID IODATE OXIDATION OF CYCLOPENTANOL, CYCLOHEXANOL AND CYCLOHEPTANOL AT DIFFERENT TEMPERATURE

Parameters	Temp. (ºC)	Cypen	Cyhex	Cyhep
$K_{obs} \times 10^4$ (s^{-1})	30	0.58	0.88	1.26
$K_{obs} \times 10^4$ (s^{-1})	35	0.84	1.28	1.78
$K_{obs} \times 10^4$ (s^{-1})	40	1.20	1.86	2.52
$K_{obs} \times 10^4$ (s^{-1})	45	1.72	2.66	3.58
ΔE^* (k J mol^{-1})	–	57.46	63.78	58.91
ΔH^* (k J mol^{-1})	35	47.70	64.24	54.39
ΔS^* (J K mol^{-1})	35	-6.09	-0.37	-3.48
ΔG^* (k J mol^{-1})	35	49.58	64.26	54.41
log A	–	11.66	12.92	12.24

$[NaIO_4] = 1.00 \times 10^{-3}$ M; $[Hg(OAc)_2] = 4.00 \times 10^{-3}$ M; [cyclopentanol] = 2.00×10^{-2} M; [cyclohexanol] = 2.00×10^{-2} M; [cycloheptanol] = 2.00×10^{-2} M; [NaOH] = 3.33×10^{-4} M; [Ru(VIII)] = 13.20×10^{-6} M.

In order to ascertain the reactive species of ruthenium tetroxide in alkaline medium, UV/Vis spectra were taken under different concentrations of sodium hydroxide solution (Fig. 2). It is clear from the plots of absorbance *vs.* wavelength (λ) that ruthenium tetroxide with sodium hydroxide concentrations from 5.00×10^{-4} to 6.66×10^{-3} mol dm^{-3} remains completely in the form of Ru(VIII), as shown by a single peak (Fig. 2, curves 1, 2, 3) at the wavelength 380 nm. However at a sodium hydroxide concentration of 1.00×10^{-2} mol dm^{-3}, it starts converting into Ru(VI) *via* Ru(VII) as indicated by a peak at the wavelength 465 nm (Fig. 2, curve 4). The significant feature of RuO_4 spectra, recorded in the presence of different concentrations of NaOH, is that above 1.00×10^{-2} mol dm^{-3} sodium hydroxide concentration Ru(VIII) is converted completely into Ru(VI) (Fig. 2, curves 5, 6). Therefore in NaOH concentration range 3.33×10^{-3} mol dm^{-3}, ruthenium tetroxide remains fully in the form of Ru(VIII).

In aqueous solution RuO_4 exists in the following equilibria[17].

$$RuO_4 + H_2O \rightleftharpoons H_2RuO_5 \quad \text{(i)}$$

$$H_2RuO_5 + OH^- \rightleftharpoons H_2O + HRuO_5^- \quad \text{(ii)}$$

$$RuO_4 + OH^- \rightleftharpoons HRuO_5^- \quad \text{(iii)}$$

It is clear from the above equilibria that ruthenium tetroxide may catalyze reactions either through RuO_4 as such or through $HRuO_4^-$. On assuming RuO_4 as the reactive species, the rate law requires negative effect of hydroxide ion contrary to its positive effect obtained. Hence RuO_4 as such will not be involved in the catalytic process and $HRuO_5^-$ can safely be assumed to be the reactive species of ruthenium tetroxide.

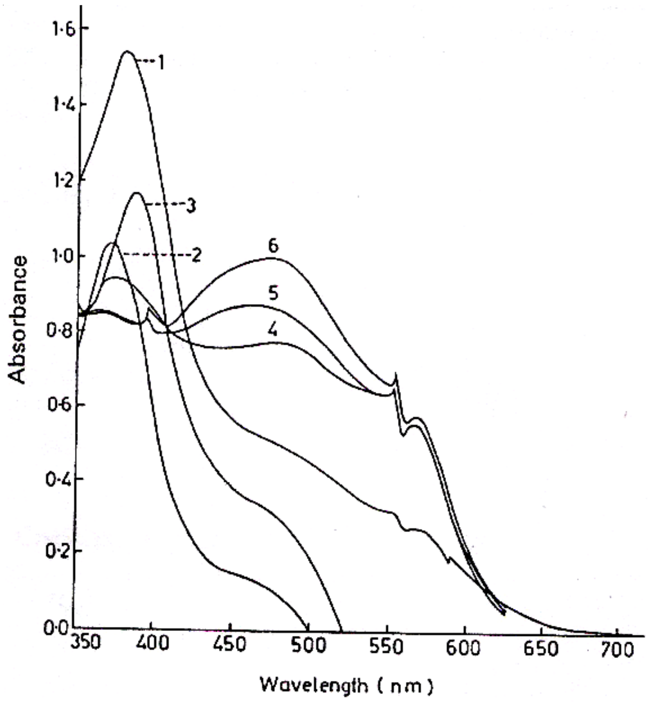
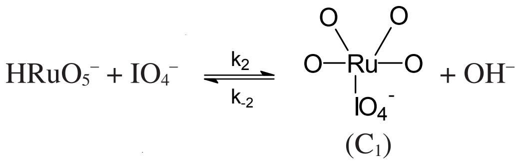


Fig. 2. UV spectra of RuO_4 at different sodium hydroxide concentrations; $[RuO_4] = 6.05 \times 10^{-4}$ mol dm^{-3} [curves 1 and 2], 3.029×10^{-5} mol dm^{-3} [curves 3, 4, 5 and 6]; $[NaOH] = 5.00 \times 10^{-4}$ mol dm^{-3} (curve 1), 7.50×10^{-4} mol dm^{-3} (curve 2), 6.66×10^{-3} mol dm^{-3} (curve 3), 1.00×10^{-2} mol dm^{-3} (curve 4), 2.00×10^{-2} mol dm^{-3} (curve 5), 1.00×10^{-1} mol dm^{-3} (curve 6)

Now on the basis of above statements and other kinetic observations, the following steps are suggested as reaction route

$$RuO_4 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRuO_5^- \qquad (4)$$



$$HRuO_5^- + IO_4^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(C_1)}{[RuO_4(IO_4)]^-} + OH^- \qquad (5)$$

$$(C_1) + H_2O \xrightarrow[\text{slow and rate determining step}]{k_2} HRuO_5^- + IO_3^- + OH^- \qquad (6)$$

$$(CH_2)_nCHOH + IO_3^- + OH^- \xrightarrow{\text{fast}} (CH_2)_nC{=}O + HIO_3 + H_2O \qquad (7)$$

where n = 4, 5 and 6 for cyclopentanol, cyclohexanol and cycloheptanol, respectively.

Application of steady state treatment with reasonable approximation yields rate law (8) in terms of disappearance of sodium periodate:

$$\frac{-d[NaIO_4]}{dt} = k_3[C_1] \tag{8}$$

or

$$\frac{-d[NaIO_4]}{dt} = \frac{K_1k_2k_3[RuO_4][OH^-][IO_4^-]}{k_{-2}[OH^-]+k_3} \tag{9}$$

Conclusion

The rate law eqn. 9 is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength which also explains the involvement of a dipole in the rate determining step. It is also concluded that $HRuO_5^-$ is the real reactive species of Ru(VIII) oxide.

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