

## KINETICS AND MECHANISM OF Rh(III) CATALYSED OXIDATION OF ALCOHOLS BY PERIODATE

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The kinetics of oxidation of alcohols viz., methanol ethanol, *n*-propanol, *n*-butanol, isopropanol and benzyl alcohols by periodate in the presence of rhodium(III) chloride has been studied in basic medium. The order with respect to [periodate], [alcohol] and [Rh(III)] were found to be zero, fractional and one respectively. The rate decreased with increase in [OH<sup>-</sup>] and the order in [OH<sup>-</sup>] was found to change from -0.5 to -1.0 in the hydroxide concentration range 0.0025 to 0.025M. The rate was found to be retarded in the presence of neutral salts like KCl, KNO<sub>3</sub> and NaClO<sub>4</sub>. Formation of a complex between Rh(III) and alcohol followed by its disproportionation in the rate determining step has been suggested. The effect of structure of alcohols on reactivity has also been discussed.

**Key Words :** Rhodium (III); Periodate; Catalysis; Oxidation; Alcohols; Kinetics

### INTRODUCTION

TRANSITION metal ions viz., Ru<sup>3+</sup>, Os<sup>8+</sup>, Ir<sup>3+</sup> and Rh<sup>3+</sup> have been extensively used as homogeneous catalysts in recent years. There are only sporadic references on use of Rh(III) as a catalyst in redox reactions. Radhakrishna Murti and Misra<sup>1</sup> studied the kinetics of oxidation of unsaturated hydrocarbons by periodate catalysed by Rh(III) in acid medium. Rh(III) has also been used as a catalyst in the oxidation of alcohols by ferricyanide in basic medium.<sup>2</sup> Monohydric alcohols do not undergo oxidation by periodate which is a specific oxidant for 1, 2-glycols.<sup>3</sup> But the oxidation occurs smoothly in the presence of rhodium (III) chloride. It was therefore thought worthwhile to study the kinetics of oxidation of primary alcohols by periodate in the presence of rhodium(III) chloride to establish the mechanism.

### MATERIALS AND METHOD

All the chemicals used were of BDH or AnalaR grade and purified wherever necessary by standard methods. Stock solution of rhodium(III) chloride (Johnson Mathey & Co. Ltd) was prepared in dil. HCl (~ 0.2M). To the flask containing potassium periodate, KOH, Rh(III) chloride solutions, a known quantity of alcohol was added after thermostating the solutions for one half hour. An electrically operated thermostat (Toshniwal make) with an accuracy of ±0.1 °C was used to maintain the temperature constant. The rate was followed by estimating the unreacted periodate from time to time iodometrically.<sup>4</sup>

The products of oxidation were found to be the corresponding aldehydes as confirmed from spot tests<sup>5</sup> and by checking the melting point of their corres-

ponding 2 : 4-DNP derivatives.<sup>6</sup> A stoichiometry of 1 : 1 between the oxidant and the substrate was obtained under the conditions of [periodate]  $\gg$  [substrate].

### RESULTS AND DISCUSSION

Under the conditions of [substrate]  $\gg$  [periodate] the concentration of periodate vs time plots were linear indicating zero order dependence on [oxidant]. The zero order rate constants ( $k_0$ ) were independent of periodate concentration (Table I). Results from Tables I and II indicate first order dependence on [Rh(III)] and fractional order in [alcohol]. The rate of oxidation decreased with increase in [OH<sup>-</sup>] and the order varied from -0.5 to -1.0 in the concentration range 0.0025 to 0.025M (Table III). The rates of oxidation decreased markedly with increase in the concentration of NaClO<sub>4</sub>, KCl and KNO<sub>3</sub> (Table IV). NaClO<sub>4</sub> was used to maintain the ionic strength constant.

TABLE I  
*Effect of varying [Periodate], [Rh(III)] on the rate*

[Methanol] = 0.1 mol dm <sup>-3</sup> ; [OH <sup>-</sup> ] = 2.00 × 10 <sup>-2</sup> mol dm <sup>-3</sup> ; Temp = 303 K		
[Periodate] × 10 <sup>3</sup> mol dm <sup>-3</sup>	[Rh(III)] × 10 <sup>4</sup> mol dm <sup>-3</sup>	$k_0$ × 10 <sup>5</sup> mol dm <sup>-3</sup> min <sup>-1</sup>
0.50	3.84	2.05
1.00	3.84	2.11
2.00	3.84	2.21
3.00	3.84	2.15
4.00	3.84	2.13
2.00	1.92	0.987
2.00	7.68	4.22
2.00	11.5	6.68
2.00	15.4	8.32

TABLE II  
*Effect of varying [alcohol] on the rate*

[Periodate] = 2.00 × 10 <sup>-3</sup> mol dm <sup>-3</sup> ; [Rh(III)] = 3.84 × 10 <sup>-4</sup> mol dm <sup>-3</sup> [KOH] = 2.00 × 10 <sup>-2</sup> mol dm <sup>-3</sup> ; Temp. = 303 K $k_0$ × 10 <sup>5</sup> /mol dm <sup>-3</sup> min <sup>-1</sup>					
[Alcohol] mol dm <sup>-3</sup>	Methanol	Ethanol	<i>n</i> -propanol	isopropanol	<i>n</i> -butanol
0.05	1.17	0.975	0.944	—	0.813
0.10	2.11	1.60	1.40	0.355	1.12
0.20	3.14	2.26	2.09	0.569	1.45
0.40	4.62	3.12	2.72	0.822	2.19
0.60	6.65	3.82	3.51	1.15	2.40
0.80	—	—	—	1.31	—

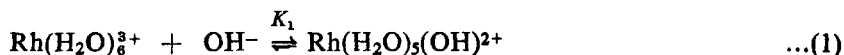
TABLE III  
Effect of  $[\text{OH}^-]$  on the rate ( $k_0$ ) in methanol oxidation by periodate

$[\text{OH}^-] \times 10^3$ mol dm <sup>-3</sup>	$k_0 \times 10^5$ mol dm <sup>-3</sup> min <sup>-1</sup>
0.250	3.88
0.500	2.82
0.750	2.40
1.00	2.07
1.50	1.41
2.00	1.11
2.50	0.847

TABLE IV  
Effect of neutral salts on the rate ( $k_0$ ) in the oxidation of methanol by periodate

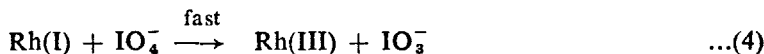
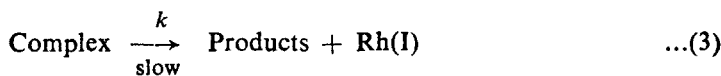
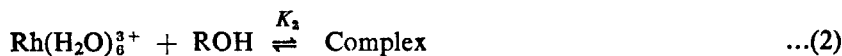
$[\text{Neutral salt}] \times 10^3$ mol dm <sup>-3</sup>	$k_0 \times 10^6/\text{mol dm}^{-3} \text{ min}^{-1}$		
	NaClO <sub>4</sub>	KCl	KNO <sub>3</sub>
0.250	13.5	—	—
0.500	10.3	13.4	12.2
1.00	9.41	12.0	11.1
2.00	7.53	11.1	9.8
3.00	6.35	9.82	8.5
5.00	—	6.82	5.90

Rh(III) is the only cation of the second transition metal series which has been shown to form a definite, well defined and reasonably stable aquo ion  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ . Rhodium(III) chloride is known to exist as  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$  or  $\text{Rh}(\text{H}_2\text{O})_{6-x}(\text{OH})_x^{3-x}$  (where  $x$  is always less than six) depending on the  $p\text{H}$  of the solution.<sup>7-9</sup> The following equilibrium might be expected to exist under the present conditions.



Under alkaline conditions employed in the present work ( $[\text{OH}^-] = 2 \times 10^{-2}\text{M}$ ), alcohol predominantly exists in its neutral form rather than in its anionic form {as  $K_a \approx 10^{-16}$ }.<sup>10</sup> Since the rate decreased markedly with increase of  $[\text{OH}^-]$ , most probably the above equilibrium exists and it also suggests that the reactive species of Rh(III) is  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ . Since the alcohols order is fractional it is believed that the mechanism involves formation of a complex between  $\text{Rh}(\text{H}_2\text{O})_6^{3+}$  and neutral

alcohol in the preequilibrium step before disproportionating to give products and Rh(I) in a rate determining step. Since the order in  $[\text{IO}_4^-]$  is zero it is believed that  $\text{IO}_4^-$  oxidises Rh(I) in a fast step.



As the rate of formation of Rh(I) is equal to rate of disappearance of  $[\text{IO}_4^-]$  which in turn is equal to rate of disproportionation of the complex. The rate law can therefore be written as

$$\frac{-d[\text{IO}_4^-]}{dt} = k_0 = \frac{k K_2 [\text{ROH}] [\text{Rh}(\text{III})]_t}{\{1 + K_2 [\text{ROH}]\} \{1 + K_1 [\text{OH}^-]\}} \quad \dots(5)$$

which is consistent with the results obtained. The applicability of eq (5) can be tested by (i) varying  $[\text{OH}^-]$  (ii) varying [alcohol].

(i) At constant [alcohol] &  $[\text{Rh}(\text{III})]$  eq (5) reduces to

$$k_0 = \frac{k_x}{1 + K_1 [\text{OH}^-]} \quad \text{where } k_x = \frac{k K_2 [\text{ROH}] [\text{Rh}(\text{III})]_t}{1 + K_2 [\text{ROH}]} \quad \dots(6)$$

by taking reciprocals of eq (6) becomes

$$\frac{1}{k_0} = \frac{1}{k_x} + \frac{k_1}{k_x} [\text{OH}^-] \quad \dots(7)$$

Eq (7) predicts a linear plot between  $1/k_0$  and  $[\text{OH}^-]$  which in fact was obtained in the present case (Fig. 1). Eq (6) also accounts for the variation of order in  $[\text{OH}^-]$  from  $-0.5$  to  $-1.0$  as the concentration of hydroxide ion was increased.

(ii) At constant  $[\text{OH}^-]$  and  $[\text{Rh}(\text{III})]$  eq (5)

$$\text{reduces to } k_0 = \frac{k_y [\text{ROH}]}{1 + K_2 [\text{ROH}]} \quad \text{where } k_y = \frac{k K_2 [\text{Rh}(\text{III})]_t}{1 + K_1 [\text{OH}^-]} \quad \dots(8)$$

$$\text{Reciprocal of eq. (8) gives } \frac{1}{k_0} = \frac{1}{k_y [\text{ROH}]} + \frac{K_2}{k_y} \quad \dots(9)$$

Eq. (9) predicts a linear plot between  $1/k_0$  and  $1/[\text{ROH}]$  with an intercept. Such plot has been obtained in the present study (Fig. 1) in case of methanol, which is taken as a typical example, confirming the proposed mechanism.

The marked retardation of rate of oxidation with increase in salt concentration might be expected as Rh(III) is known to form kinetically inactive complexes.<sup>11</sup> The order of reactivity of the alcohols was found to be benzyl alcohol > methanol > ethanol > *n*-propanol > *n*-butanol > isopropanol. Increase in chain length and branching at  $\alpha$ -carbon decreased the rate probably due to increase in

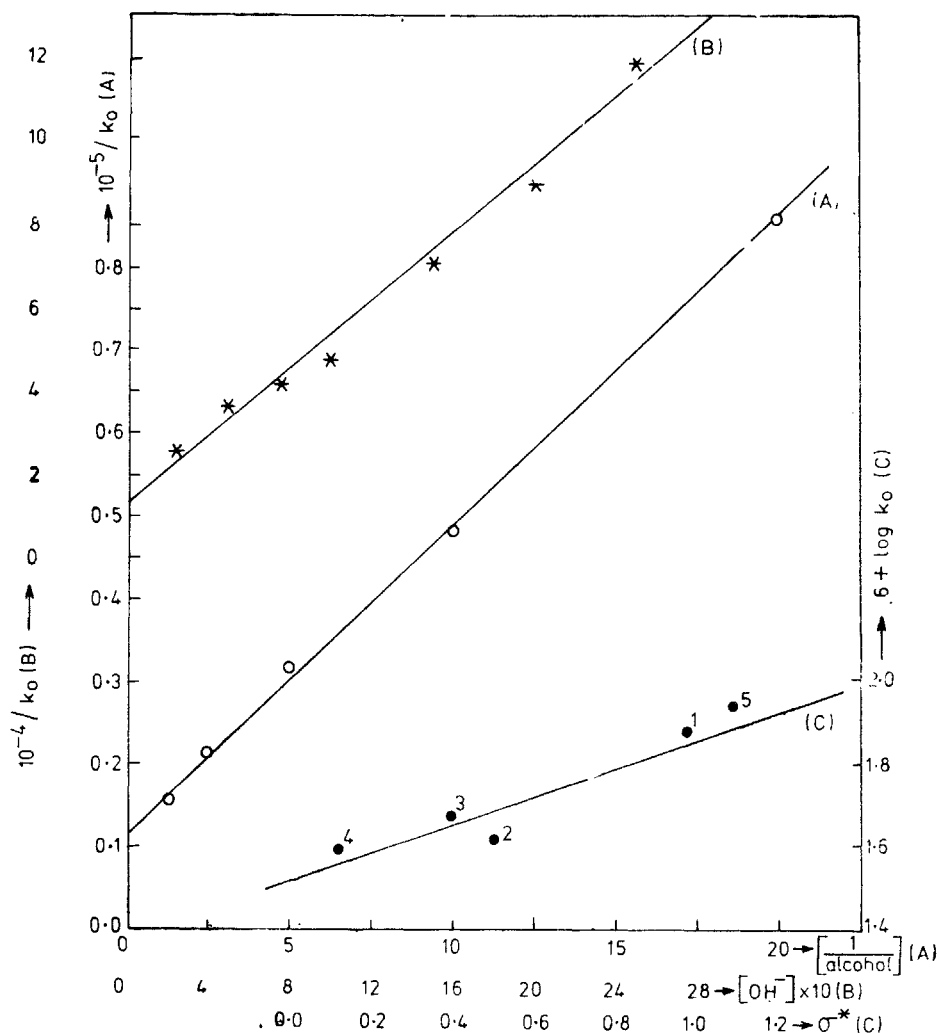


FIG 1 (A) Plot of  $1/k_0$  vs  $1/[\text{alcohol}]$   
 [Periodate] =  $2.00 \times 10^{-3}$  M;  
 [Rh(III)] =  $3.84 \times 10^{-4}$  M;  
 [KOH] =  $2.00 \times 10^{-2}$  M; Temp = 303 K.

(B) Plot of  $1/k_0$  vs  $[\text{OH}^-]$   
 [Periodate] =  $2.00 \times 10^{-3}$  M;  
 [Rh(III)] =  $3.84 \times 10^{-4}$  M;  
 [Methanol] = 0.100 M; Temp = 303 K.

(C) Plot of  $6 + \log k_0$  vs  $\sigma^*$   
 1. Methanol      2. ethanol      3. *n*-propanol      4. *n*-butanol  
 5. benzylalcohol., Temp = 313.

the electron density at this carbon, which renders it difficult to part with the hydrogen suggesting the cleavage of  $\alpha$ -CH proton in the transition state analogous

to cleavage of  $\alpha$ -CH proton from an acid.<sup>12</sup> This receives further support from a positive  $\rho^*$  value ( $\sim 0.4$ ) obtained from the Taft's plot (Fig 1) indicating the formation of an electron rich transition state.

The higher rate of oxidation in case of benzyl alcohol might be due to the electron withdrawing capacity of the phenyl group which facilitates removal of proton from  $\alpha$ -carbon of the alcohol. The lower rate of oxidation in the case of isopropanol can be attributed to steric factors overwhelming inductive effects.

The activation energy values for various alcohols viz., methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and benzyl alcohol were found to be 101, 93.6, 101, 126, 95.7 and 84.2 kJ mol<sup>-1</sup> respectively. The substrates having lower activation energy were found to undergo higher rate of oxidation indicating the reactions to be enthalpy controlled. The  $\Delta G^\ddagger$  values ( $\sim 92$  kJ mol<sup>-1</sup>) for all substrates were found to be nearly same indicating a similar mechanism to be operative.

#### CONCLUSION

The Rh(III) catalyzed oxidation of alcohols by periodate in basic medium proceeds through the formation of complex between Rh(III) and alcohol which in turn disproportionates in a slow step to form Rh(I) and the corresponding aldehyde. Rh(I) further gets oxidised in a fast step by  $\text{IO}_4^-$  giving back Rh(III) and  $\text{IO}_3^-$ .

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