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Rh(III) Catalyzed Oxidation of Cyclic Alcohols by Sodium Periodate in Acidic Medium

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Kinetics investigation on Rh(III) catalyzed oxidation of cyclopentanol and cyclohexanol by acidic solution of sodium periodate ($NaIO_4$) in the presence of mercury(II) acetate as a scavenger has been carried out in the temperature range of 30-45 ºC.The reaction exhibits first order kinetics with respect to substrate and catalyst whereas zero order with respect to oxidant *i.e.* $NaIO_4$.The rate shows no effect with increasing concentration of [H^+]. The influence of [$Hg(OAc)_2$], ionic strength and [Cl^-] on the rate was found to be insignificant. The effect of varing percentage of AcOH on reaction rate was also examined. Various activation parameters have been calculated from rate measurements and the rate law derived on the basis of obtained data.

Key Words: Kinetics, Rh(III), Oxidation, Cyclic alcohols, Acidic sodium periodate.

INTRODUCTION

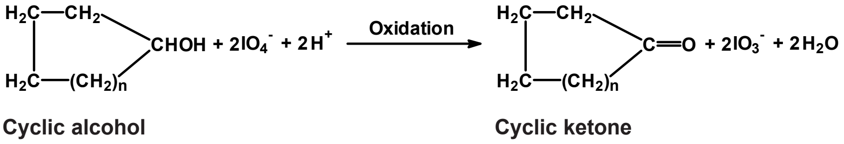
[$KBrO_3$][1-7] and [$NaIO_4$][8] have been used as oxidants for various compounds in acidic medium. N-bromoacetamide[9-12], N-bromosuccinimide[13,14] have been earlier used in oxidation of various compounds in the presence of catalyst. A little attention has been paid to sodium periodate[15-18] as an oxidant in various catalyzed reactions.The use of Rh(III) as a catalyst has been reported by several workers. Kinetics and mechanism of Rh(III) catalyzed oxidation of 1,2-glycols[19] and polyhydric alcohols by acidic $KBrO_3$[20] are also reported. No work has been reported in literature on Rh(III) catalyzed oxidation of cyclic alcohols in acidic medium. This prompted us to undertake the present investigation on Rh(III) catalyzed oxidation of cyclopentanol and cyclohexanol by periodate in acidic medium.

EXPERIMENTAL

An aqueous solution of cyclopentanol and cyclohexanol (E. Merck), sodium periodate (SD Fine Chemicals AR) $NaClO_4$ and $Hg(OAc)_2$ (E. Merck), were prepared by dissolving the weighed amount of samples in triple distilled water. Perchloric acid (60 %) of E. Merck grade was used as a source of hydrogen ions. $RhCl_3$ (Sigma Chemical Company) solution was prepared in HCl of known strength (0.018 N). All other reagents were of analytical grade. Reaction vessels were painted black to prevent photochemical decomposition.

Kinetics: The requisite volume of all reagents, including substrate, were thermostated at 35 ± 0.1 ºC to attain equilibrium. A measured volume of $NaIO_4$ solution maintained separately at the same temperature was rapidly poured into the reaction vessel. Progress of the reaction was followed by assaying aliquots of the reaction mixture for $NaIO_4$, iodometrically using starch as an indicator after suitable time intervals.

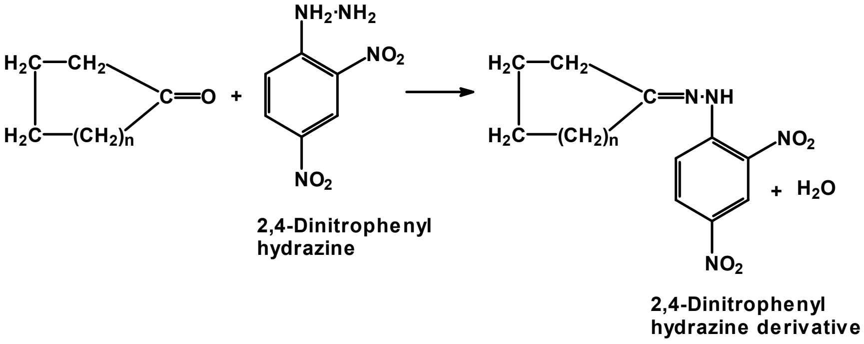
Stoichiometry and product analysis: The stoichiometry of the reaction was determined by equilibrating varying ratios of $[NaIO_4]$ to cyclopentanol and cyclohexanol separately at 35 ºC for 48 h under kinetic conditions. Estimation of unconsumed $NaIO_4$ revealed that, one mole of cyclopentanol or cyclohexanol consumes two moles of periodate



where, n = 1 and 2 for cyclopentanol and cyclohexanol respectively.

Identification of the end product formed in the above reactions *i.e.*, cyclopentanone and cyclohexanone for cyclopentanol and cyclohexanol respectively, was carried out as follows:

Took 1 mL of reaction mixture in dil. HCl, was added to 3 mL of the 2,4-dinitrophenyl hydrazine solution and shaken well. A yellowish precipitate was formed which was the corresponding hydrazone according to the following equation.



The derivatives were dried and their melting point were determined. The melting point of 2,4-dinitrophenyl hydrazine derivatives of cyclopentanone and cyclohexanone recorded 145 and 160 ºC (actual melting point being 146 and 162 ºC), respectively[21]. The corresponding ketones were also identified by TLC[22].

RESULTS AND DISCUSSION

In order to propose a probable reaction mechanism for Rh(III) catalyzed oxidation of cyclic alcohols by acidic sodium periodate it is necessary to study the effect of variation in concentration of different reactants on the rate of reaction. The kinetics of oxidation of cyclic alcohols was investigated at several initial reactant concentrations (Table-1). First order kinetics was observed with respect to the catalyst and substrate in both cases. These have also been confirmed by least square method (Fig. 2).

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

$[S] \times 10^3$ (M)	$[Rh(III)] \times 10^6$ (M)	$[IO_4^-] \times 10^3$ (M)	$(-dc/dt) \times 10^7$ mol $L^{-1} s^{-1}$	
			Cyclopent	Cyclohex
0.33	11.25	1.00	0.34	0.22
0.40	11.25	1.00	0.42	0.27
0.50	11.25	1.00	0.54	0.34
0.66	11.25	1.00	0.78	0.48
1.00	11.25	1.00	1.16	0.65
2.00	5.25	1.00	1.32	1.33
2.00	7.25	1.00	0.62	0.95
2.00	9.75	1.00	0.85	1.33
2.00	11.25	1.00	1.24	1.75
2.00	13.25	1.00	1.35	2.01
2.00	15.00	1.00	1.67	2.40
2.00	11.25	1.00	1.82	2.68
2.00	11.25	0.83	1.42	1.75
2.00	11.25	1.00	1.32	1.33
2.00	11.25	1.25	1.54	2.00
2.00	11.25	1.67	1.66	2.40
2.00	11.25	2.50	1.48	2.57
2.00	11.25	5.00	1.56	6.00

$[KCl] = 1.00 \times 10^{-3}$ (M), $[HClO_4] = 1.00 \times 10^{-3}$ (M),
$[Hg(OAc)_2] = 1.25 \times 10^{-3}$ (M)

A plot of (-dc/dt) *vs.* [Rh(III)] (Fig. 1) gives a slope = 1.26×10^{-2} s^{-1} for cyclopentanol and 1.60×10^{-2} s^{-1} for cyclohexanol which is close to the average value of first order rate constants *i.e.*, $k_1 = 1.35 \times 10^{-2}$ s^{-1} for cyclopentanol at 35 ºC and $k_1 = 1.71 \times 10^{-2}$ s^{-1} for cyclohexanol at 35 ºC. In

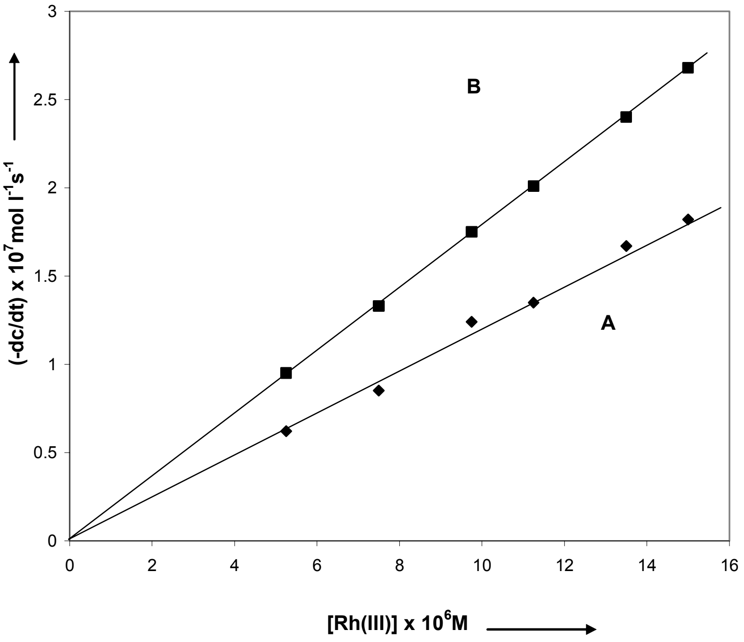


Fig. 1. Plot between [Rh(III)] × 10^{-6} M *vs.* (-dc/dt) × 10^{-7} M L^{-1} s^{-1} for oxidation of cyclopentanol (A) and cyclohexanol (B) at 35 ºC

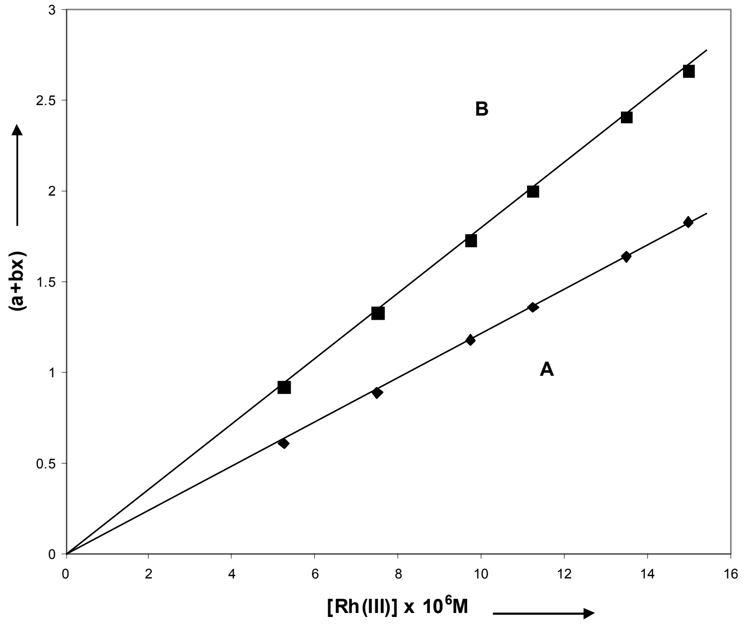
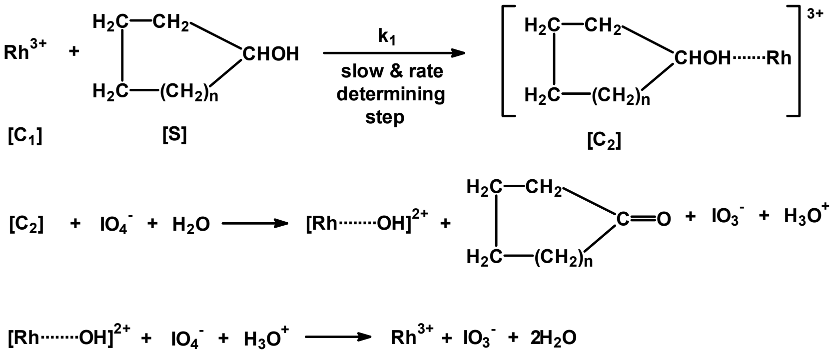


Fig. 2. Plot between [Rh(III)] × 10^{-6} M *vs.* (a + bx) for oxidation of cyclopentanol (A) and cyclohexanol (B) at 35 ºC

both cyclopentanol and cyclohexanol a fair degree of closeness in the first order rate constants obtained graphically and obtained values of (-dc/dt)/[Rh(III)] = k_1 clearly confirms the first order dependence on [Rh(III)]. Zero order kinetics with respect to oxidant ($NaIO_4$) is visualized. An insignificant effect of [Cl^-], [H^+] and [$Hg(OAc)_2$] variation were also observed.

On the basis of above effects, we have determined the order of reactions and proposed a mechanism which confirms to the observed kinetics.

Reaction mechanism and rate law derivation: The result of oxidation of cypentanol and cyhexanol shows that the reaction follows identical kinetics and thus appear to have a common mechanism. The following reaction steps are suggested on the basis of the above discussion for oxidation of cyclic alcohols by sodium periodate in the presence of rhodium(III) chloride as catalyst.



$$\text{Rate} = k_1\,[C_1]\,[S]$$

$$\boxed{\text{Rate} = k_1\,[Rh^{3+}]\,[S]}$$

where [S] is substrate.

where n =1 and 2 for cyclopentanone and cyclohexanone, respectively.

Considering the above steps and applying steady state approximation to the complex formed in step (i), the rate of reaction in terms of loss of IO_4^- may be written as:

$$\frac{-d[IO_4^-]}{dt} = K_1[Rh(III)][S]$$

From the present investigation, it is concluded that, Rh^{3+} as such is the reactive species of the catalyst in acidic medium. Table-2 depicts that variation in ionic strength of the medium *i.e.*, variation in perchlorate and mercuric acetate show negligible effect on the reaction rate. The negligible effect of mercuric 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.

TABLE-2
EFFECT OF VARIATION OF MERCURIC ACETATE, PERCHLORIC ACID AND KCl ON THE REACTION RATE AT 35 ºC

$[HClO_4] \times 10^3$ (M)	$[KCl] \times 10^3$ (M)	$[Hg(OAc)_2] \times 10^3$ (M)	$[NaClO_4] \times 10^3$ (M)	$(-dc/dt) \times 10^7$ mol L^{-1} s^{-1}	
				Cyclopent	Cyclohex
0.83	1.00	1.25	–	1.46	1.84
1.00	1.00	1.25	–	1.32	1.33
1.25	1.00	1.25	–	1.34	2.00
1.67	1.00	1.25	–	1.28	1.40
2.25	1.00	1.25	–	1.42	2.00
5.00	1.00	1.25	–	1.30	1.34
1.00	0.83	1.25	–	1.52	1.81
1.00	1.00	1.25	–	1.32	1.33
1.00	1.25	1.25	–	1.53	1.71
1.00	1.67	1.25	–	1.14	1.66
1.00	2.50	1.25	–	1.16	1.66
1.00	5.00	1.25	–	1.66	1.66
1.00	1.00	0.83	–	1.42	1.77
1.00	1.00	1.00	–	1.42	1.66
1.00	1.00	1.25	–	1.32	1.33
1.00	1.00	1.67	–	1.16	1.14
1.00	1.00	2.50	–	1.28	1.55
1.00	1.00	5.00	–	1.54	1.75
1.00	1.00	1.25	0.83	1.74	1.71
1.00	1.00	1.25	1.00	1.62	2.00
1.00	1.00	1.25	1.25	1.65	1.60
1.00	1.00	1.25	1.67	1.25	1.60
1.00	1.00	1.25	2.50	1.41	1.25
1.00	1.00	1.25	5.00	1.57	1.60

$[Rh(III)] = 11.25 \times 10^{-6}$ (M), $[S] = 2.00 \times 10^{-3}$ (M), $[IO_4^-] = 1.00 \times 10^{-3}$ (M)

TABLE-3
ACTIVATION PARAMETERS FOR ACIDIC IODATE OXIDATION OF CYCLOPENT AND CYCLOHEX

Activation parameters	Temp. (ºC)	Cyclopent	Cyclohex
$K_r \times 10^4$ s^{-1}	30	1.00	1.01
$K_r \times 10^4$ s^{-1}	35	1.32	1.33
$K_r \times 10^4$ s^{-1}	40	2.00	2.00
$K_r \times 10^4$ s^{-1}	45	2.70	2.70
log A	–	9.32	10.32
ΔE^* (kJ mol^{-1})	–	47.88	53.59
ΔG^* (kJ mol^{-1})	35	69.55	69.38
ΔH^* (kJ mol^{-1})	35	74.71	73.14
ΔS^* (J K^{-1} mol^{-1})	35	-16.77	-12.22

The kinetic results were collected at several initial concentrations of reactants. Graphs were plotted between concentration and time to calculate (dc/dt) values. The rate measurement were taken in the temperature range 30-45 ºC and the specific rate constants were used to draw a plot of log k *vs.* I/T (Fig. 3) which was linear.

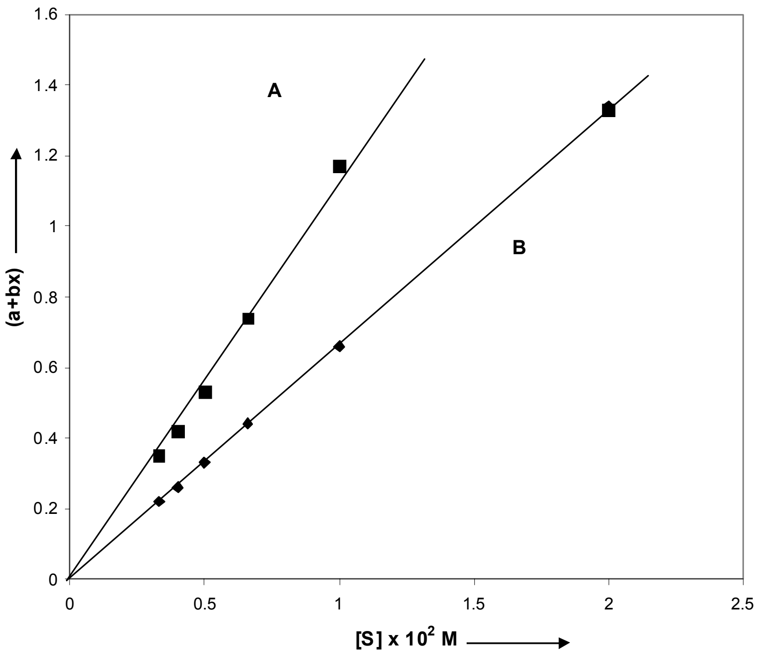


Fig. 3. Plot between [S] × 10^{-2} M *vs.* (a + bx) for oxidation of cyclopentanol (A) and cyclohexanol (B) at 35 ºC

Conclusion

The experimental results as shown reveal that the reaction rate doubles when the concentration of catalyst is doubled. The rate law equation is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength. The high +ve value of free energy of activation (ΔG*) indicates highly solvated transition state, while -ve value of entropy of activation (ΔS*) suggest the formation of an activated complex with reduction in the degree of freedom of molecule. From the present investigation, it is concluded that IO_4^- is the reactive species of periodate in acidic medium.

REFERENCES

1. Ashish, S. Singh, A. Singh and B. Singh, *Transition Met. Chem.*, **30**, 610 (2005).
2. K. Recz, M. Gurger and ZS. Nagy Ungvarai, *Int. J. Chem. Kinet.*, **38**, 503 (2006).
3. I. Ahmed, C. Muhammad and D. Ashraf, *Int. J. Chem. Kinet.*, **11**, 813 (2004).
4. S. Srivastava and S. Singh, *J. Indian Chem. Soc.*, **18**, 295 (2004).
5. S. Srivastava and S. Singh, *Oxid. Commun.*, **27**, 463 (2004).
6. S. Srivastava, R.K. Sharma and S. Singh, *J. Indian Chem. Soc.*, **83**, 282 (2006).
7. S. Srivastava, A. Kumar and P. Srivastava, *J. Indian Chem. Soc.*, **83**, 347 (2006).
8. S. Srivastava, K. Singh, M. Shukla and N. Pandey, *Oxid. Commun.*, **24**, 558 (2001).
9. S. Srivastava, V. Srivastava and A. Awasthi, *Oxid. Commun.*, **26**, 426 (2003).
10. S. Srivastava, A. Awasthi and K. Singh, *Int. J. Chem. Kinet.*, **37**, 275 (2005).
11. S. Srivastava and S. Singh, *Oxid. Commun.*, **29**, 708 (2006).
12. B. Singh, D. Singh and A.K. Singh, *Int. J. Chem.*, **20**, 501 (2004).
13. K.S. Mavalang, Nirmal, N.-Halligudi and T.-Sharanappa Nanbewoor, *React. Kinet. Catal. Lett.*, **72**, 391 (2001).
14. A.K. Singh, D. Chopra, S. Rahmani and B. Singh, *Carbohydr. Res.*, **314**, 157 (1998).
15. R.D. Kaushik, A.K. Chaubey and P. Garg, *Asian J. Chem.*, **15**, 1655 (2003).
16. R.D. Kaushik, A. Dubey and R.P. Singh, *Asian J. Chem.*, **16**, 831 (2004).
17. R.D. Kaushik, A. Shash and S. Devi, *Asian J. Chem.*, **16**, 818 (2004).
18. H.-X. Kong, L.-J. Li, H.G. Wei and L.J. Yan, *Juan Guangpy Shi Yanshi*, **20**, 70 (2003) (Chinese).
19. S. Sandu, B. Sethuram and T.N. Rao, *Transition Met. Chem.*, **15**, 78 (1990).
20. S. Srivastava, *Transition Met. Chem.*, **24**, 683 (1999).
21. R.C. Weast, Hand Book of Tables for Organic Compound Identification, CRC Press Cleveland, edn. 3 (1967).
22. F. Feigl, Spot Tests in Organic Analysis, Elsevier, New York (1966).

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