December 2008 *Volume 3 Issue 2-3*

Physical CHEMISTRY
An Indian Journal

Trade Science Inc.

Full Paper

PCAIJ, 3(2-3), 2008 [121-125]

Kinetics of rhodium(III)-catalysed oxidation of some cyclic alcohols by diperiodatocuprate (III) in aqueous alkaline medium

Ravi Chandar Maroju*, T.Ravi Prasad, K.Nagi Reddy

Department of Metallurgy and Materials Technology, Mahatma Gandhi Institute of Technology,
Gandipet, Hyderbad-75, (INDIA)
E-mail: rcmaroju@gmail.com

Received: 20th September, 2008 ; Accepted: 25th September, 2008

ABSTRACT

Rh(III) Chloride catalysed oxidation of some cyclic alcohols by diperiodatocuprate (III) (DPC) in aqueous alkaline medium has been studied spectrophotometrically at 414 nm. The order in [DPC] is zero and one each in [Rh(III)] and [alcohol]. The rate of oxidation was unaffected by variation in [OH^-] and [salt]. Stoichiometric studies revealed that one mole of alcohol consumed two moles of DPC giving the corresponding carbonyl compound as the reaction product. It has been proposed that Rh(III) catalysis in the oxidation of cyclic alcohol is a direct reaction between Rh(III) and alcohol to give products via a complex formation and hydride ion abstraction by Rh(III).

KEYWORDS

Rh(III) chloride;
Cyclic alcohols;
Diperiodatocuprate(III);
Carbonyl compounds;
Hydride ion abstraction.

INTRODUCTION

Transition metal ions like Iridium(III), Ruthenium (III), Os(VIII) and Rh(III) have been found to be good homogenous catalysts in a number of redox reactions. Os(VIII) catalysed oxidation of various organic compounds like alcohols[1], aldehydes[2], Ketones[3] by the oxidants like hexacyanoferrate, chloramine -T, periodate and by Diperoidatocuprate-III (DPC)[4] has been reported. In the Os(VIII) and Ru(III) catalysed oxidation of alcohols, aldehydes and ketones by DPC, a zero order dependence in [oxidant] and unit order in both [substrate] and [catalyst] were reported involving a mechanism in which complexes formation between substrate and OsO_4 which decomposes to give products in rate determining step .A similar mechanism was also proposed in Os(VIII) catalysed oxidation of some aliphatic alcohols by hexacyanoferrate(III)[5]. In the case of alcohols, Os(VIII)[4] and Ru(III)[6] and Rh(III)[7] were shown to react via hydride ion abstraction from α- carbon atom of the substrate.

Oxidation of alcohols by Ce(IV)[8], and Mn(III)[9] proceeds through 1:1 complex between oxidant and alcohol, while with ceric(IV)[10-11] and Co(III)[12] proceed by a bimolecular reaction, but no complex formation was observed in the oxidation by Cu(III)[13] and an outer sphere mechanism between alcohol and Cu(III) has been suggested. In Os(VIII) catalyzed and ucatalyzed oxidation of some cyclonols[14] by Cu(III), the order in [cyclonol] is fractional and in Cu(III), it is unity.

Oxidation of alcohols proceeds either by rupture of –O-H bond or α -CH bond, former is observed in case of allylalcohol by cericnitrate in acidic medium^{15}. α-CH bond breakage was found in the of oxidation of α-deutero hexanol and cyclohexanols by Mn(III)[12] and V(V)[16], in the oxidation of benzylalcohol and allyl alcohol by Co(III)[17] in sulphuric acid medium and in the oxidation of alcohol by Cu(III). Ir(III) catalysed oxidation of some aliphatic alcohols by DPC (III) has been reported[18] and a complex formation was proposed between substrate and catalyst and the reactivity was increased with chain length.

Rh(III) catalysed oxidation of aliphatic alcohols by periodate[19], Os (VIII) catalyzed oxidation of cyclic alcohol by DTC in alkaline medium[14], effect of ring size on kinetics of oxidation of cyclonols by ditelluratoargentate[20] were reported. Many laboratory applications in organo-metallic chemistry and catalysis involve organo-Rhodium chemistry and a wealth of Rh-coordination complex is known[21]. Catalytic activities of three transition metals such as Ir(III),Rh(III),Pd(III) were compared in the oxidation of cyclohexanol and benzylalcohol by 50% H_2O_2[22].

Literature shows no report on the use of Rh(III) as homogenous catalyst in the oxidation of cyclic alcohols by diperiodatocuprate(III) in aqueous alkaline medium and hence the title investigation.

Instruments, chemicals and reagents

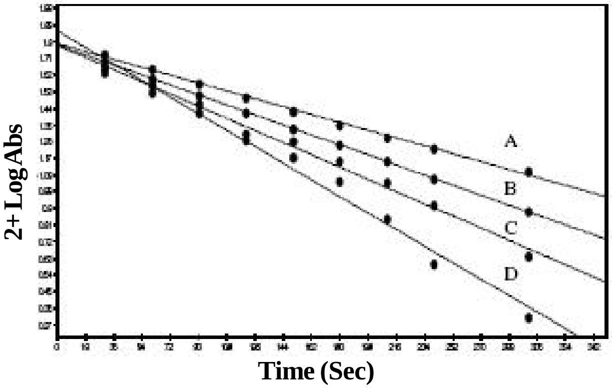
1. Elico make, U.V – visible spectrophotometer
2. Thermostat
3. Copper sulphate, potassium periodate, potassim persulphate.
4. $RhCl_3$
5. Cyclopentanol, cyclohexanol, cycloheptanol ad cycloocatanol

EXPERIMENTAL

All the chemicals used were of AR grade and wherever necessary were purified by standard methods. The DPC was prepared and standardized by literature method[23]. The kinetics was followed in the temperature range of 293 to 308 by studying the disappearance of diperiodatocuprate (III) (DPC) at regular time intervals spectrophotometrically at 414nm using Elico make spectrophotometer. In all kinetic runs, blank reactions were also carried out and necessary corrections were made for any self-decomposition of DPC. Stoichiometric studies revealed that one mole of alcohol consumed two moles of DPC. Corresponding carbonyl compounds were identified as products of oxidation and confirmed by preparing their 2,4-dinitrophenylhydrazone derivatives.

TABLE 1: Effect of [Cyclic alcohol] and [Rh(III)] on rate constant (k/) in DPC- Cyclo hexanol reaction catalysed by Rh(III)([KOH] = 5 × 10^{-3} mol dm^{-3}; Temperature = 298 K)

[Rh(III)]×10^6 mol dm^{-3}	[Alcohol] ×10^3mol dm^{-3}	k'×$10^3$$s^{-1}$
1.85	1.5	3.00
3.70	1.5	6.90
5.55	1.5	10.02
7.40	1.5	12.50
3.7	0.5	2.40
3.7	1.0	4.60
3.7	1.5	6.90
3.7	2.0	9.00
3.7	3.0	14.30



Alcohol		k′ (Graphically)
Cyclopentanol (A)	:	**5.5×10^{-3} s^{-1}**
Cyclohexanol (B)	:	**6.9×10^{-3} s^{-1}**
Cycloheptanol (C)	:	**8.5×10^{-3} s^{-1}**
Cycloactonol (D)	:	**11.6×10^{-3} s^{-1}**

Figure 1 : Determination of pseudo first order rate constant (k′)

RESULTS AND DISCUSSIONS

In the present study, under the experimental conditions [alcohol] >> [DPC], the rate of oxidation was independent of initial [DPC] and the plot of absorbance versus time was linear (Figure 1) and from the slopes of which the pseudo first order rate constant k′ values have been evaluated.

The determined pseudo first order rate constant is due to the complex formation with the reaction between substrate and catalyst, since zero order dependence was shown in DPC. The rate constant (k′) increased with increase in [Rh(III)] and [alcohol] indicating the order in each of them was one (TABLE 1). The rate of

TABLE 2: Catalytic co-efficient

Alcohol	S_0[Alcohol] $\times 10^3$ mol dm^{-3}	$k_0 \times 10^3 s^{-1}$	$1/S_0$	$1/k_0$	Slope	Intercept	K_m=Slope/ Intercept
	0.5	1.90	2000.00	526.31			
	1.0	3.86	1000.00	259.06			
Cyclopentanol	1.5	5.60	666.66	178.57	0.2614	1.8367	0.1423
	2.0	7.80	500.00	128.20			
	3.0	10.70	333.33	93.45			
	0.5	2.40	2000.00	416.66			
	1.0	4.60	1000.00	217.39			
Cyclohexanol	1.5	690	666.66	140.84	0.2068	5.0245	0.0411
	2.0	9.00	500.00	111.11			
	3.0	14.30	333.33	69.93			
	0.5	3.00	2000.00	333.33			
	1.0	5.80	1000.00	172.41			
Cycloheptanol	1.5	8.50	666.66	117.64	0.1630	8.1540	0.0199
	2.0	11.10	500.00	90.09			
	3.0	16.50	333.33	60.60			
	0.5	4.30	2000.00	232.55			
	1.0	8.70	1000.00	114.94			
Cyclooctanol	1.5	11.60	666.66	86.20	0.1115	8.3117	0.0134
	2.0	15.40	500.00	64.93			
	3.0	22.30	333.33	44.84			

reaction was found to be unaffected by varying [OH$^-$] and [salt].

$RhCl_3$ in alkaline solutions exists as $Rh(OH)_3$ and $Rh(OH)_6$[24-26]. In the present investigation the rate was independent of [OH$^-$] indicating that the equilibria of any type involving Rh(III) species and OH$^-$ ion may not be operative. No polymerization of acrylamide was observed, when added to reaction mixture in N_2 atmosphere which rules out the possibility of a free radical mechanism. No reactions were observed with t-butanol. A clean first order dependence both in [alcohol] and [Rh(III)] and non-dependence in [OH$^-$] indicated a direct reaction of the substrate either with $Rh(OH)_3$ or $Rh(OH)_6$. Based on the above information a probable mechanism involving hydride ion abstraction from α-carbon of alcohol by Rh(III) to give the product and Rh(III) hydride has been proposed.

Based on above results the following scheme has been proposed.

$$RCH_2OH + Rh\,(OH)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCH_2O - Rh\,(OH)_2 + H_2O$$

$$RCH_2O - Rh\,(OH)_2 \xrightarrow[\text{slow}]{k_2} RCHO + Rh\,(H)\,(OH)_2$$

$$Rh\,(H)\,(OH)_2 + 2\,Cu\,(III) \xrightarrow[H_2O]{\text{fast}} Rh\,(OH)_3 + 2\,Cu(II) + 2H^+$$

As the rate of formation of Rh(III)hydride is equal to half the rate of disappearance of [oxidant] which in turn is equal to rate of disproportionation of the complex, the rate law can therefore be written as,

$$[\text{Complex}] = \frac{k_1[S][C]}{k_{-1} + k_2}$$

$$-\frac{1}{2}\frac{d[Cu(III)]}{d_t} = k_2\,[\text{Complex}]$$

$$-\frac{1}{2}\frac{d[Cu(III)]}{d_t} = k_0 = \frac{k_2 k_1 [S][C]}{k_{-1} + k_2} \quad \text{where } K_m = \frac{k_{-1} + k_2}{k_1}$$

$$-\frac{1}{2}\frac{d[Cu(III)]}{d_t} = k_0 = \frac{k_2[S][C]}{K_m}$$

In terms of initial concentrations the rate expression is given as,

$$\frac{-d[\text{oxidant}]}{d_t} = \frac{k_2[S]_0[C]_0}{[S]_0 + [C]_0 + K_m}$$

Two limiting cases of above equation are important which can be used for testing the applicability of the above rate law. In case, [C_0] << [S], then [C_0] can be dropped from the denominator and rate equation is written as,

$$k_0 = \frac{k_2[S]_0[C]_0}{[S]_0 + K_m}$$

According to the above rate law, the initial rate is proportional to the catalyst concentration. Same observation was found in the reaction. The reciprocal of the above equation at constant [C_0],

$$\frac{1}{k_0}=\frac{1}{k_2[C]_0}+\left(\frac{K_m}{k_2[C]_0}\right)\frac{1}{[S]_0}$$

and this predicts plot of $1/k_0$ Vs $1/[S]_0$ linear, which in fact was obtained in the present case. This enables to calculate $k_2[C_0]$ and K_m from the intercept and slope (TABLE 2).

The dependence of the initial rate on $[S_0]$ is interesting. Since $[S_0] << K_m$ then $[S_0] + K_m = K_m$, then the rate is written as

$$k_0=\frac{k_2[S]_0[C]_0}{K_m}=k_{cat}\,[S0]$$

When $k_{cat}=\frac{k_2[C]_0}{K_m}$

This shows that the first order dependence on [S] which is consistent with the experimental observations, confirming the proposed mechanism that the Rh (III) catalysed oxidation of alcohols by Cu (III) in basic medium proceeds through the formation of complex between Rh (III) and substrate which in turn disproportionates in a slow step to form product and Rh(III)hydride. Rh(III)hydride further gets oxidized in a fast step by oxidant regenerating $Rh(OH)_3$ and Cu(II).In this mechanism the catalyst preferentially oxidizes the substrate first, probably via 1:1 complex. This happens due to the oxidations potential of $C^{n+}/C^{(n+x)+}$ is higher than that of $OX^{m+}/OX^{(m+x)+}$.

The reactivities of cyclonols followed the order, cyclopentanol<cyclohexanol<cycloheptanol< cyclooctanol. Activation energies determined for all these alcohols conforms to the above order. Activation parameters, $\Delta H^{\#}$ indicates that the formation of transition state is endothermic, high $\Delta G^{\#}$ value due to positive $\Delta H^{\#}$ and negative $\Delta S^{\#}$ suggest that the stability of transition state is according to the order of reactivity of alcohols (TABLE 3).

The order of reactivity in the present case is in accordance with the order of ring size and in conformity with Bayer Strain theory. The higher reactivity of cyclohexanol compared to cyclopentanol could be explained by assuming the flexible boat form to be active and not the chair form. In the boat form, though there is no angle strain, there is bond opposition strain involving 4 pairs of hydrogens at the side of the boat and also the Strain due to the pair of hydrogens at the top of the boat known as the bowsprit flag pole interaction. As a result of these interactions the boat form appears to be less stable than the chair form.

TABLE 3: Activation parameter for DPC- cyclic alcohol reaction catalysed by Rh (III)

Alcohol	E_a kJ mole^{-1}	$\Delta H^{\#}$ kJ mole^{-1}	$\Delta G^{\#}$ kJ mole^{-1}	$\Delta S^{\#}$ J.mole^{-1} degree^{-1}
Cyclopentanol	70.022	67.520	69.879	-7.917
Cyclohexanol	63.637	61.234	61.614	-26.941
Cycloheptanol	61.726	59.216	68.566	-31.376
Cyclooctanol	59.727	57.182	67.828	-35.726

[Alcohol] = 1×10^{-3} mol dm^{-3}; [DPC] = 8.4×10^{-5} mol dm^{-3} ; [KOH] = 5×10^{-3} mol dm^{-3}; [Rh (III)] = 3.7×10^{-6} mol dm^{-3}. Temp = 298 K

The assumption of hydride ion abstraction by Rh (III) from α-carbon atom of alcohol receives support from the previous studies made by Charman and Sing et al.[27,28].

Positive value of catalytic co-efficient (K_m) shows the effect of catalyst and it proves the proposed mechanism involving the formation of a complex with the reaction of substrate and catalyst initially. Almost similar values of K_m for all the substrates indicate that the rate of reaction is influenced by the nature of the substrate since the effect of catalyst seems to be same in all the reactions irrespective of the substrate.

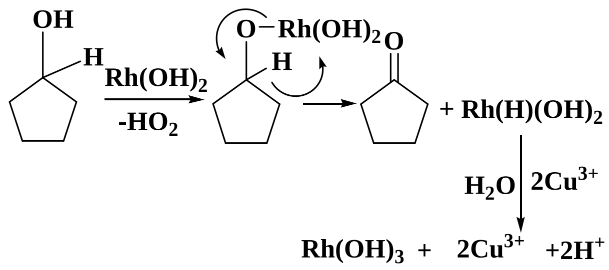


TABLE 4: Comparison of rate of oxidation of Rh(III)-Catalysed and uncatalysed oxidation of cyclic alcohols by DPC

[Alcohol] = 1.5×10^{-3} mol dm^{-3}	Catalysed [Rh(III)]=3.7×10^{-6} mol dm^{-3} $k' \times 10^{3}$ s^{-}	$k' \times10^{3}$ s^{-1} Uncatalysed
Cyclopentanol	5.6	2.5
Cyclohexanol	6.9	3.6
Cycloheptanol	8.5	4.2
Cyclooctanol	11.6	6.1

[DPC] = 8.4×10^{-5} mol dm^{-3}; [OH$^-$] = 5×10^{-3} mol dm^{-3} ; temp = 298 K

ACKNOWLEDGMENTS

I am very much thankful to Dr. Prasada Rao, Professor of Chemistry, P.G. Centre, Osmania University, Hyderabad for his valuable suggestions. I express my gratitude to Head- Department of chemistry, Dean-sciences, Chairman - BOS (Chemistry) of K.U., and also The Director and Management of MGIT for allowing me to carry out my research work.

REFERENCES

[1] H.S.Singh, S.P.Singh, A.K.Singh, S.M.Arya, A.K. Sisodia; J.Phy.Chem., **79**, 1920 **(1975)**.

[2] S.P.Mushran, M.C.Agarwal, Sanahi Rindian; J. Chem., **12**, 311 **(1974)**.

[3] V.N.Singh, H.S.Singh, B.B.L.Saxena; J.Am.Chem. Sci., **91**, 2643 **(1969)**.

[4] A.VRamanacharya; Ph.D. Thesis, Kakatiya University, **(1989)**.

[5] H.S.Singh, S.P.Singh, S.M.Arya, A.K.Singh, A.K. Sisodia; J.Phys.Chem., **79**, 1920 **(1975)**.

[6] K.Bal Reddy; Ph.D. Thesis, Kakatiya University, **(1981)**.

[7] K.Bal Reddy, B.Setharam, T.Navaneetha Rao; Indian J.Chem., **27A**, 730-731 **(1988)**.

[8] S.S.Muhammad, K.V.C.Rao; Bull.Chem.Soc., Japan, **36**, 943 **(1963)**.

[9] C.F.Wells, C.Barnes; J.Chem.Soc., **A**, 1626 **(1968)**.

[10] B.Sethuram, S.S.Muhammad; Acta Chim.Hung, **46**, 112 **(1965)**.

[11] N.Santappa, B.Sethuram; Proc.Indian Acad.Sci., **67A**, 78 **(1968)**.

[12] D.G.Hoare, W.A.Waters; J.Chem.Sco., 2552,2560 **(1964)**.

[13] C.P.Murthy, B.Sethuram, T.Navaneeth Rao; Z.Phy. Chem., Leipzig, **262**, 366 **(1981)**.

[14] K.Bal Reddy, C.P.Murthy, B.Sethuram; Indian J.Chem., **20A**, 272-275 **(1981)**.

[15] B.Sethuram; Curr.Sci., **35**, 254 **(1956)**.

[16] W.A.Waters, J.S.Littler; J.Chem.Soc., 4046 **(1959)**.

[17] A.Meenakshi, M.Santappa; Curr.Sci., **37**,**43**, 313 **(1968)**.

[18] P.Shekar Rao; Ph.D. Thesis, Kakatiya Unvi., **(1992)**.

[19] K.Bal Reddy, B.Sethuram, T.Navaneeth Rao; Indian Journal of Chem., **27**A, 730-731 **(1988)**.

[20] T.Ravi Prasad, B.Sethuram, T.Navaneeth Rao; Indian Journal of Chem., **21A**, 170-171 **(1982)**.

[21] Jan Meine Erusting, Sender Garmesh Cornelis; J.Magnetic Resonance in Chemistry, **42**, 721-736 **(2004)**.

[22] Praveen K.Tandon, Gayatri, Sumita Sahgal, Manish Srivastava, Santosh B.Singh; Applied Organometallic Chemistry, **21(3)**, 135-138 **(2006)**.

[23] P.K.Jaiswal, K.L.Yadava; Indian J.Chem., 837 **(1973)**.

[24] W.P.Griffiteh; The Chemistry of Race Platinum metals, Inter Science, New York, 332 **(1967)**.

[25] B.F.G.Johnsom; A specialist periodic report: Inrganic chemistry of the transition elements, Chemical Society, London, 385 **(1973)**.

[26] B.N.vanon, B.N.Emin, L.D.Borzoval, A.M.Egron, S.G.Malyuguia; Aust J.Chem., **16**, 1474 **(1974)**.

[27] H.B.Charman; J.Chem.Soc., **B**, 629 **(1967)**.

[28] H.S.Singh, K.K.Singh, S.M.Singh, P.Singh, D.Thakur; Indian J.Chem., **21A**, 816 **(1982)**.