

Kinetics of Rh(III)-Catalysed Oxidation of Some Alcohols by Diperiodatocuprate(III) in Aqueous Alkaline Medium

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Rh(III) chloride catalysed oxidation of some 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 is unaffected by variation in [OH⁻]. The effect of added salts on the rate of oxidation is negligible. The stoichiometric studies reveal that one mole of alcohol consumes two moles of DPC, giving the corresponding carbonyl compounds as the reaction products. As in earlier investigation on Ru(III) catalysis in the oxidation of alcohols a direct reaction between Rh(III) and alcohol to give products via hydride ion abstraction by Rh(III) is proposed.

In our previous studies on Os(VIII) and Ru(III) catalysed oxidation of some organic compounds, viz. alcohols and ketones by Cu(III)^{1,2} in alkaline medium, a direct reaction between substrate and catalyst in the slow step was postulated. In the case of alcohols, Os(VIII)/Ru(III) were shown to react via hydride ion abstraction from α -carbon atom of the substrate and that Ru(III) was a better hydride ion abstractor than Os(VIII)². Rhodium(III) chloride also reacts with alcohols via hydride ion transfer process³. Only sporadic references are available on Rh(III) catalysis in redox reactions^{4,5}. No report seems to be available on the use of Rh(III) as a homogeneous catalyst in the oxidation of organic compounds by diperiodatocuprate(III)(DPC) in aqueous alkaline medium, and hence the title investigation.

All the chemicals used were of AR grade and wherever necessary were purified by standard methods. The kinetics was followed in the temperature range of 308 to 325 K by studying the disappearance of diperiodatocuprate(III)(DPC) at regular time intervals spectrophotometrically at 414 nm using Carl-Zeiss spectrocolorimeter. 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 mol of alcohol consumed two mol

of DPC. Corresponding carbonyl compounds were identified as products of oxidation and confirmed by preparing their 2,4-dinitrophenylhydrazone derivatives.

Under the conditions [alcohol] \gg [DPC] the rate of oxidation was independent of initial [DPC] and the plot of absorbance versus time was linear ($r=0.989$) indicating zero order dependence in [DPC]. The zero order rate constant (k_0) increased with increase in [Rh(III)] and the order in [Rh(III)] was one (Table 1). The k_0 also increased with increase in [alcohol] and the order in [alcohol] was unity (Table 1). The rate of reaction was found to be unaffected by varying [OH⁻].

It is known⁶⁻⁸ that RhCl₃ in alkaline solutions exists as Rh(OH)₃ and Rh(OH)₆. 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 in the present study. The effect of added salts on the rate of oxidation was negligible. No polymerisation of acrylamide was observed, when added to reaction mixture in N₂ atmosphere, ruling out the possibility of a free radical mechanism. No reaction was 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 is proposed,

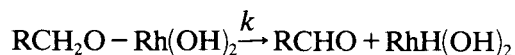


Table 1—Effect of [methanol] and [Rh(III)] on Rate in DPC-methanol Reaction catalysed by Rh(III)

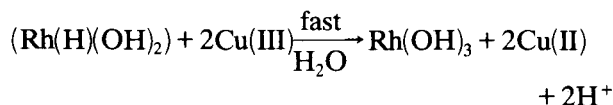
[DPC] = 6.60×10^{-3} mol dm⁻³; [OH⁻] = 0.01 mol dm⁻³;
temp = 308 K

[Methanol] $\times 10^2$ (mol dm ⁻³)	[Rh(III)] $\times 10^4$ (mol dm ⁻³)	$k_0 \times 10^7$ (mol dm ⁻³ s ⁻¹)
1.00	1.85	2.95
2.00	1.85	5.66
3.00	1.85	8.40
4.00	1.85	11.6
5.00	1.85	14.2
2.00	0.750	2.40
2.00	2.50	7.87
2.00	3.00	9.60
2.00	4.00	12.6

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Rh(III) hydride thus formed is reoxidized to Rh(III) by Cu(III) in a fast step.



The rate law in consonance with the proposed mechanism is given by Eq. (1),

$$-d[\text{DPC}]/dt = Kk[\text{Rh}(\text{III})][\text{alcohol}] \quad \dots (1)$$

which explains the kinetic data obtained.

The assumption of hydride ion abstraction by Rh(III) from α -carbon atom of alcohol receives support from the previous studies made by Charman³ and Singh *et al.*⁴

The rate data for the catalysed and uncatalysed reactions, of different alcohols are recorded in Table 2. The rates of oxidation of various alcohols are in the order: methanol < isopropanol < ethanol < *n*-propanol < *n*-butanol < *n*-pentanol < benzyl alcohol. The observed order of reactivity reveals that the rate increases with increase in +I character of alkyl group at α -carbon. This coupled with the fact that there is no reaction with *t*-butanol supports the hydride ion transfer mechanism. But the lower rate of oxidation of isopropanol as compared to that of *n*-propanol may be due to steric effect of alkyl groups overweighing the inductive effect. The higher rate of oxidation of benzyl alcohol may be due to the delocalisation of +ve charge produced at α -carbon during hydride ion abstraction.

The Taft's reaction constant (ρ^*) was found to be -0.70 ($r=0.8276$; $s=0.1769$). The negative ρ^* value indicates that the reaction is facilitated by high electron density at reaction site. This is in conformity with the observed substituent effect at

Table 2—Comparison of Rates of Oxidation of Rh(III)-catalysed and Uncatalysed Oxidations of Alcohols by DPC

[DPC] = 6.60×10^{-5} mol dm⁻³; [OH⁻] = 0.010 mol dm⁻³; temp = 308 K

Alcohol	$k \times 10^6$ (s ⁻¹)*	
	Uncatalysed	Catalysed (Rh(III) = 1.85×10^{-4}) mol dm ⁻³
Methanol	18.0	28.3
Ethanol	28.0	39.0
<i>n</i> -Propanol	30.0	45.8
Isopropanol	16.6	29.1
<i>n</i> -Butanol	43.3	70.8
<i>n</i> -Pentanol	45.2	74.2
Benzylalcohol	55.3	228

* k = Initial rate/[substrate]

the α -carbon. The negative ρ^* value also supports hydride ion abstraction in the slow step. A ρ^* -value with such magnitude is not uncommon in the literature⁹ for reactions involving hydride ion transfer.

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