

Ru(III) catalysed oxidation of 2- buten -1-ol by trichloroisocyanuric acid in acid medium A kinetic and mechanistic study

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ABSTRACT

The kinetics of oxidation of alcohols by trichloroisocyanuric acid (TCICA) with Ru(III) catalysis have been investigated in aqueous HOAC-HClO₄ medium. The reaction is of zero order in [TCICA], first order in [alcohol] and first order in Ru(III). The reaction is insensitive towards [H⁺] and is not affected by increase in [Cl]. Effect of temperature has been studied and thermodynamic parameters are calculated and a suitable mechanism has been suggested.

Key words: Trichloroisocyanuric acid, alcohols(A.R.), oxidation, formation constant.

INTRODUCTION

N- halogenocompounds, which are good sources of positive halogen in polar solvents have been extensively employed as halogenating and oxidising agents for organic substrates¹. Amongst the N-chloro compound trichloroisocyanuric acid or 1,3,5-trichloro-2,4,6-tri oxohexahydro - s- triazine2 has wide synthetic utility as it has the most polar N-X bond among the series TCIAN, N-chlorobarbitol, N - chlorophthalimide, NCS and NBS³. TCICA has been used in synthetic organic chemistry as an oxidising and halogenating reagent⁴⁻⁷.

The slow reaction between TCICA and alcohols was found to be enhanced several times in the presence of trace amounts of Ru(III). Hence a systematic kinetic study of Ru(III) catalysed oxidation of alcohol, like 2-Buten-1-Ol by TCICA has been undertaken to have a better insight Solutions of the alcohols and TCICA of appropriate concentration were prepared in aqueous acetic acid, thermostated for two hours. Unreacted TCICA was estimated colorimetrically (Erma Japan) at 525 nm using potassium permanganate as a co-oxidant⁸.

A stock solution of Ru(III) was prepared by dissolving RuCl₃ in 0.2 moldm⁻³ HCl⁹ and its concentration was determined 1.0 x 10⁻⁴ mol dm⁻³. All reactions were generally carried out in duplicate and the rate constants were reproducible within 5%.

MATERIAL AND METHODS

All the substrates were of Alfa Aesar (Lankestar) grade. The oxidant trichlorisocyanuric acid was of AR grade. The catalyst RuCl₃ was from Research Fine Lab Industries, Mumbai and its concentration was estimated iodometrically. The solution of the oxidant was always prepared afresh; All inorganic chemicals used were of A.R. grade.

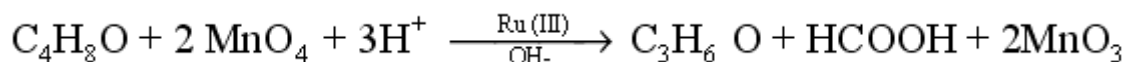
Kinetic measurements

Kinetic runs were initiated by mixing the previously thermostated reactant solutions of alcohols and Ru(III), TCICA. The rate of the reaction was monitored by estimating the disappearance of [TCICA] at different time intervals. The reaction was measured up to 70% completion.

Stoichiometry and product analysis

Different sets of reactions containing excess [TCICA] over [alcohols] with constant

concentrations of Ru(III) and [H⁺] over kept for 24h and then estimated. The results showed 1:2 stoichiometry according to the equation.



Corresponding ketones were identified by the 2,4 DNP test.

RESULTS

The kinetics of oxidation of 2-Buten-1-ol was investigated at several initial concentrations of the reactions. The reactions were carried out by varying the concentration of oxidant, keeping all other conditions constant. (Table 1 and 2)

Under the conditions [alcohol] >>> [TCICA] the reaction is zero order in [TCICA] revealed by the linear plots of [TCICA] V/s time. The zero order rate constants (k₀) were calculated from the slopes of such plots. (Table1). The rate increased with an increase in [alcohol] and the order with respect to [alcohol] was found to be one, as evidenced by the

slope (0.82353) in oxidation of 2- buten-1-ol (Table 1). The Michaelis Menten type of plot of 1/k₀ Vs 1/[alcohol] was linear with an intercept indicating the formation of a stable complex involving the substrate. The rate increased in the presence of trace amount of Ru(III) and the order with respect to [Ru(III)] was found to be unity which is obvious from the slope. into the nature of mechanism of catalysis.

The rate constants [H⁺] indicate that [H⁺] has no significant effect on the rate of the reaction. Under the conditions of [TCICA] = 1 x 10⁻² moldm⁻³, [alcohol] = 0.1 moldm⁻³, [Ru(III)] = 1 x 10⁻³ moldm⁻³, [HOAC] = 20 Vol% at 308K, the rate constants (K₀ x 10⁴ mol dm⁻³ s⁻¹) were found to be 1.81, 2.05, 2.137, 2.0, 2.23 for the [H⁺] of 0.501, 0.676, 0.845, 1.005 mol dm⁻³ respectively.

Table - 1: Rate constants for Ru(III) catalysed oxidation of alcohols by TCICA, [GCKI₄] = 0.2 mol dm⁻³, [HOAC] = 20% T = 308.15 K

S. No.	[TCICA]x10 ⁴ mol dm ⁻³	[alcohol] x 10 ³ mol dm ⁻³	Ru(III)x10 mol dm ⁻³	k ₀ x10 ⁴ mold m ⁻³ Sec ⁻¹
1	3.558	4.7	2.56	2.94
2	4.036	4.7	2.56	2.12
3	4.484	4.7	2.56	1.477
4	5.33	4.7	2.56	0.712
5	4.484	4.23	2.56	5.034
6	4.484	4.7	2.56	6.397
7	4.484	4.96	2.56	6.908
8	4.484	5.14	2.56	8.632
9	4.484	4.7	0.2242	0.486
10	4.484	4.7	2.24	0.8775
11	4.484	4.7	4.49	1.19
12	4.484	4.7	5.17	1.406

The rate increased with an increase in [alcohol] and the order with respect to [alcohol] was found to be unity (as revealed from the slope 0.8235

of oxidation of alcohols by TCICA (Table 1) . The Michaelis Menten type of plot of 1/k₀ Vs 1/[alcohol] was linear with an intercept indicating the formation

of a stable complex involving the substrate. The rate increased, in the presence of trace amounts of Ru(III) and the order with respect to Ru(III) was found to be unity (0.8572 as revealed from the slope $\log k_0$ Vs \log Ru (III), of alcohols by TCICA.

The reactions were carried out at different solvent compositions and the rate constants decreased with increasing percentage of acetic acid in the reaction mixture. The plot of $\log k_0$ Vs. $1/D$ was linear with a negative slope indicating the involvement of a dipole and a negative ion in the rate determining step. No polymerisation was observed when acrylonitrile was added to the reaction system indicating the absence of free radicals. The rate of the reaction is not affected by the addition of $[Cl^-]$ ion to the system.

DISCUSSION

The observed zero order in [TCICA] shows

that it is not involved in the rate determining step. The first order in substrate indicates that it is involved in complex formation with the catalyst. Transition metal ions are well known to form complexes with the organic substrates¹⁰. The kinetics evidence for such a complex is obtained by the $1/k_0$ Vs. $1/[alcohol]$ plot i.e. there is possibility of formation, of complex between Ru(III) and alcohol; before it decomposes to products in the rate determining step.

In aqueous acid medium TCICA produces various types of species such as dichloroisocyanuric acid (DCICA), monochloroisocyanuric acid (MCICA) isocyanuric acid (ICA), HOCl, H_2OCl^+ ¹¹. As there is involvement of TCICA in a fast step, its application will not affect the rate of the reaction.

During hydrolysis of TCICA the predominant species was found to be HOCl which may enter into protonation equilibria giving H_2OCl^+ , thus the reactive species may be HOCl and H_2OCl^+ .

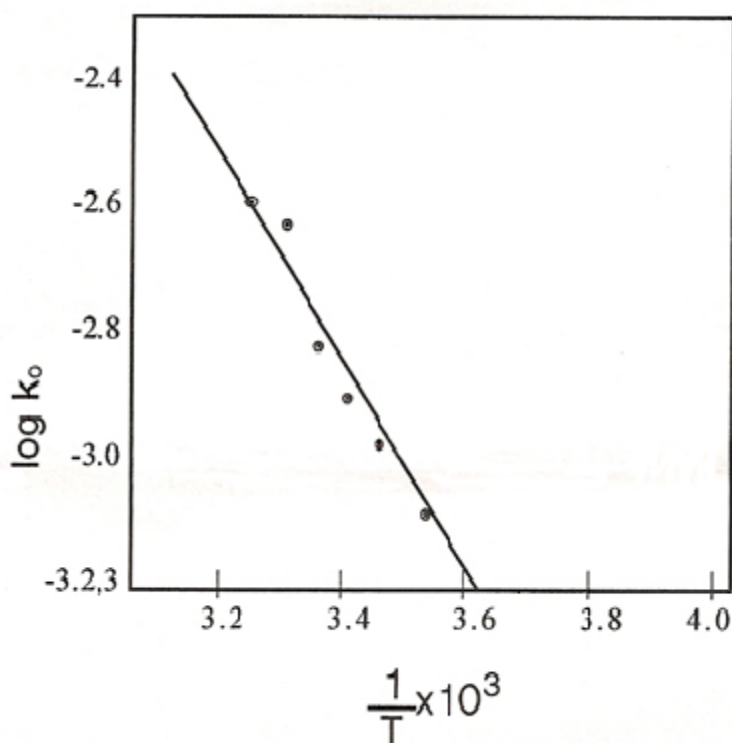


Fig. 1: plot of $\log k_0$ Vs $1/T$, [TCICA] = 01 mol dm⁻³ [Ru(III)] = 1×10⁻⁶ mol dm⁻³ [substrate] = 0.1 mol dm⁻³, [HClO₄] = 0.6 mol dm⁻³, [HOAC] = 20 vol%.

Effect of Variation of temperature

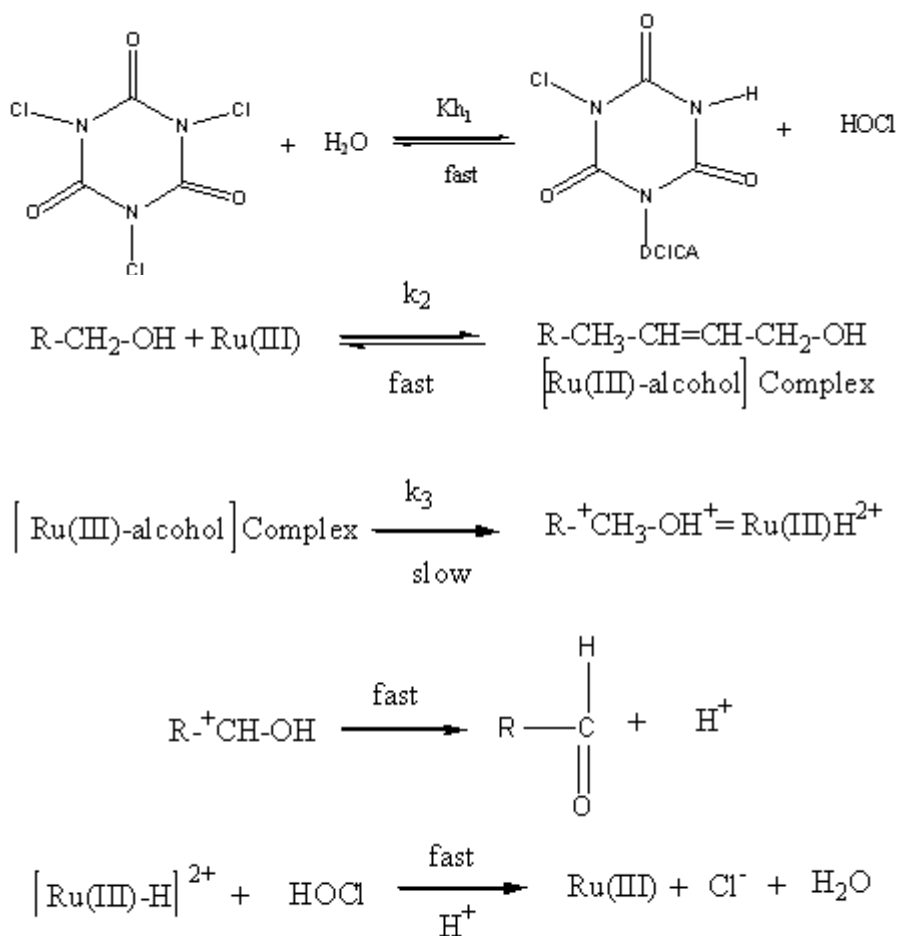
The rate of reaction increased with increasing temperature, as studied between the range of 10°C to 40°C. The activation parameters are presented in Table 2. The negative values mS^\ddagger indicate that the activated complex is more rigid compared to the reactants.

Based on the above experimental observations the following mechanism is proposed.

Table. 2 : Activation parameters for $RuCl_3$ catalysed oxidation of 2- buten-1-01 by TCICA

$[HClO_4] = 0.2 \text{ mol dm}^{-3}$, $[HOAC] = 20 \text{ vol } \%$, $T = 308.15$

No.	T	Ea Kcal mol ⁻¹	ΔH^\ddagger	ΔS^\ddagger
1	288	3.84	3.276	-61.46
2	293	3.84	3.266	-61.45
3	298	3.84	3.256	-61.22
4	303	3.84	3.246	-60.966
5	308	3.84	3.236	-58.344
6	313	3.84	3.226	-58.326



From the above mechanism the following rate law can be determined

$$\frac{d[\text{TCICA}]}{dt} = \frac{k_2 k_3 [\text{alcohol}][\text{Ru(III)}]}{1 + k_2 [\text{alcohol}] + k_3 [\text{Ru(III)}]} = k_0 \dots (1)$$

Since $[RuCl_3]$ is very small ($10^{-6} \text{ mol dm}^{-3}$) compared to $[\text{alcohol}]$ ($10^{-1} \text{ mol dm}^{-3}$) it could be neglected in the denominator-

$$\frac{d[\text{TCICA}]}{dt} = \frac{k_2 k_3 [\text{alcohol}][\text{Ru(III)}]}{1 + k_2 [\text{alcohol}]} = k_0 \dots (2)$$

$$\frac{1}{k_0} = \frac{1}{k_2 k_3 [\text{alcohol}] [\text{Ru(III)}]} + \frac{1}{k_3 [\text{Ru(II)}]} \dots (3)$$

from eq (3) a straight is obtained upon plotting $1 / k_0$ Vs. $1 / [\text{alcohol}]$ at constant $[\text{Ru(III)}]$, from the slope and the intercept of such plots the

disproportionation rate constant (k_3) and the formation constant (k_2) of the complex were calculated. For 2 - Buten- 1 -01 k_3 and K_2 were found to be 7.368.

$\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$ and $200 \text{ dm}^3 \text{mol}^{-1}$ respectively.

REFERENCES

1. Filler R. *Chem Rev* **60**: 21 (1965).
2. Fieser L & fieser M. Reagents for organic synthesis, 11 (Jhon Wiley, NY) 426 (1969).
3. Ot Siji Y. Kurida T. & Imoto N, *Bull Chem. Soc Perkin II*, 949 (1963).
4. K.S. Vasudevan, N. Venkat Subramanian, *Indian J.Chem.* **24A**: 304 (1985).
5. P.S. Radhakrishnamurti, N.K. Rath, *Indian J. Chem.* **27A**: 1028 (1988).
6. Subas C. Pati, P.S.C. Patro, - *Proc. Indian Nat. Sci. Acad.* **54**: 152 (1988).
7. H.P.Panda, K.K.Sahoo, *Indian J. Chem.* **31A**: 978 (1992).
8. T. Hara and E.B.Sande II, *Anal - Chem.* **3**: 176 (1959).
9. Ashok Kumar Singh and et.al, *catalysis Letters* **95**(3 -4) (2004).
10. D.G. Lee, M.Vanden Eugh, *oxidation in organic chemistry*, Ed.S waker trahanovsky, cpater iv, 183 (1973).
11. Subas C. Pati, Chintamani, Sarangi, *Indian J. Chem.* **27A**: 593 (1988).