©Printed in India.

KINETICS AND MECHANISM OF Ru(III)-CATALYSED OXIDATION OF BENZYL ALCOHOL AND SUBSTITUTED BENZYL ALCOHOLS BY TRICHLOROISOCYANURIC ACID (TCCA) IN ACID MEDIUM

SUBAS C PATI *and* P S C PATRO

Department of Chemistry, Berhampur University, Berhampur 760 007, Orissa, India

Kinetics and mechanism of Ru(III)–catalysed oxidation of benzyl alcohol and substituted benzyl alcohols like *o*-, *m*-, and *p*-nitro benzyl alcohol by trichloroisocyanuric acid (TCCA) have been studied in aqueous acetic acid-perchloric acid medium. The reaction is first order with respect to [TCCA] and [Ru (III)]. The reaction is insensitive towards the change in acid concentration. Change in [S] has no effect on the reaction rate. Addition of chloride ion accelerates the rate of the reaction. The rates were determined at four different temperatures and the net activation parameters were evaluated. A suitable mechanism involving the formation of [S . . . Ru (III)] complex prior to the rate determining step has been proposed.

INTRODUCTION

OXIDATION of benzyl alcohol and substituted benzyl alcohols by various oxidants like periodate,[1] phenyl iodosyl acetate,[2-3] bromate,[4] ceric ammonium nitrate[5] (in trifluoro acetic acid), NBS,[6] Tl (III),[7] PDS,[8] Nitric acid[9] and permanganate[10] etc has already been reported. In continuation to the work on TCCA with various organic substrates such as hydrocarbons[11] like toluene and substituted toluenes, benzhydrol and *p*-chloro benzhydrol,[12,13] diols and cyclanols,[14] ketones,[15] benzaldehyde and substituted benzaldehydes,[16] the authors here report their results on Ru(III)-catalysed oxidation of benzyl alcohol and substituted benzyl alcohols by TCCA in order to throw light in the mechanistic pathways involved in the system in the present communication.

EXPERIMENTAL

All reagents used were of extra pure. Trichloroisocyanuric acid (TCCA) was of Analar (Fluka) grade. $RuCl_3$ solution was standardised by the method of Horiuchi *et al.*[17] Standard iodometric procedure was adopted.[18]

Kinetic Measurements

All reactions were followed iodometrically upto 70 per cent and rate constants were calculated from the linear plots of log titre versus time. Duplicate kinetic runs showed that the rates were reproducible within ± 5 per cent error.

The product was found to be the corresponding aldehyde in all the cases.

RESULTS

Effect of Change in [TCCA] on the Reaction Rate

The plots of log titre versus time for individual runs were linear. The fair constancy in the rates in the range studied indicates a unit dependence on [TCCA].

Effect of Change in [Substrate] on the Reaction Rate

The k_1 values presented in Table I, show that the reaction is independent with respect to change in [S]. This apparent zero order nature of the substrate has to be explained. It is seen that this is a limiting tendency observed though there is complex formation between substrate and Ru(III) as the complex formed is of high stability and carrying k_2 [S] $\gg$ 1.

TABLE I

Effect of varying [substrate] on the reaction rate

[TCCA] = 0.0005 M, [HClO$_4$] = 0.01 M, Solvent = 20% HOAc (v/v),
[Ru(III)] = 1.53 $\times$ 10^{-6} M, Temp. = 35 °C.

Substrate	$10^3 \times$ [S] M	$10^4 \times k_1$ sec^{-1}
Benzyl alcohol	2.5	4.34
	5.0	4.04
	10.0	4.06
	20.0	3.99
4-NO$_2$ Benzyl alcohol	2.5	3.73
	5.0	3.92
	10.0	3.43
2-NO$_2$ Benzyl alcohol	1.25	4.04
	2.50	4.41
	5.00	4.60
	10.00	4.39

Effect of Acidity

The reaction was carried out by changing the initial [H$^+$] and the rate is unaffected by varying [H$^+$].

Effect of Change in [Ru (III)] on the Reaction Rate

Increase in [Ru(III)] increases the reaction rate (Table II). The plots of log k_1 versus log [Ru(III)] are linear with unit slopes confirming the unit dependence of [Ru(III)] on the reaction rate.

Role of Solvent

The reaction was carried out at various solvent compositions. The rate constants decrease with the increase in percentage composition of acetic acid in

TABLE II

Effect of varying [Ru(III)] on the reaction rate

[S] = 0.005 M, [TCCA] = 0.0005, [HClO$_4$] = 0.01 M, Solvent = 20% HOAc (v/v), Temp. = 35 °C.

Substrate	$10^6 \times$ [Ru(III)] M	$10^4 \times k_1$ sec^{-1}
Benzyl alcohol	0.19	0.68
	0.38	1.24
	0.765	2.31
	1.53	4.04
	3.06	8.14
4-NO$_2$ Benzyl alcohol	0.765	2.44
	1.53	3.92
	3.06	8.04
2-NO$_2$ Benzyl alcohol	0.765	2.15
	1.53	4.60
	3.06	9.21

the reaction mixture i.e., with decrease in the dielectric constant of the medium. The plots of log k_1 vs. $1/D$ and log k_1 versus $(D - 1)/(2D + 1)$ are both perfectly linear pointing to the reaction to be of dipole-dipole type.

Effect of [Cl$^-$] on the Reaction Rate

The reaction was carried out at different [Cl$^-$] and the rates show that addition of chloride ion has an accelerating effect on the reaction rate. Such an acceleration in rates may be due to the formation of molecular chlorine. The rates observed in case of benzyl alcohol are 5.8×10^{-4}, 9.12×10^{-4}, 12.53×10^{-4} and 14.39×10^{-4} s^{-1} at 0.0005M, 0.0025M, 0.005M, and 0.01M KCl respectively.

Effect of Temperature

The reaction has been carried out at various temperatures (308 °K to 323 °K) and the plots of log k_1 vs. $1/T$ are found to be linear. The computed values of different activation parameters have been recorded in Table III. The plot of log$_{10}$ A vs. $1/\sqrt{E}$ is linear. The lower log$_{10}$ A values indicate that the rate is much lower than the calculated one from collision theory. This shows that at least one of the following factors is at work :—

1. Endothermic formation of a complex prior to the reaction proper.

2. The necessity for the ionisation of either or both of the reactants.

3. Deactivation by solvent molecules.

4. Stringent conditions of orientation or of internal phase of the reacting molecules at the moment of impact, and

5. The existence of strong forces of attraction.

TABLE III

Arrhenius activation parameters

Substrate	E_a k J mol^{-1}	$\Delta H^{\neq}$ k J mol^{-1}	$-\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\log_{10}A$
Benzyl alcohol	25.0	22.5	237.0	1.25
2–NO$_2$ Benzyl alcohol	26.5	24.0	231.0	1.16
4–NO$_2$ Benzyl alcohol	41.0	38.0	185.0	3.53

A plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ is linear with the parameter C = 4.5 kcals/mole of β = 300 °C. Complex formation is also indicated by the isokinetic temperature, β = 300 °C, which is very close to the values found for complexation equilibria.[19]
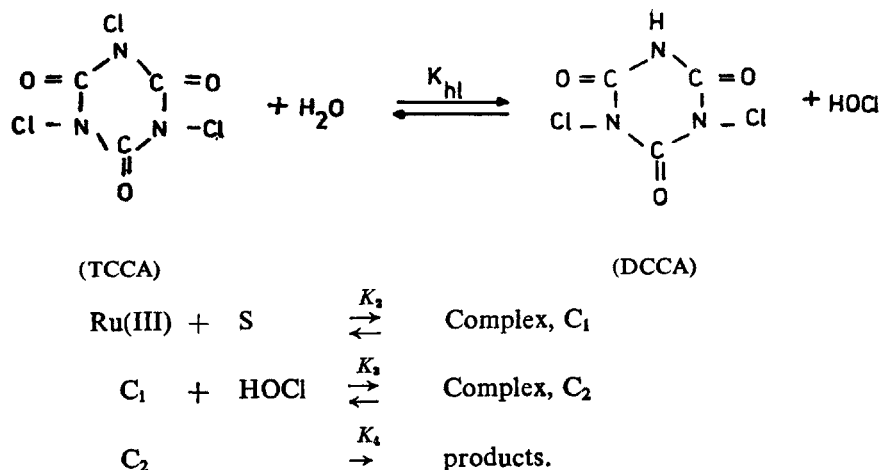
Effect of Added Salts

The dependence of the reaction on the ionic strength of the medium by a supporting electrolyte, NaClO$_4$ in the concentration range (0 to 0.01 M) has also been studied. The rates show that the reaction is insensitive towards the change in ionic strength.

DISCUSSION

The order with respect to TCCA in the Ru(III)-catalysed oxidation of benzyl alcohol and substituted benzyl alcohols is unity. The observed zero order dependence on substrates, and unit dependence on Ru(III)-catalyst establishes the formation of a rigid complex between the substrate and the catalyst. The formation of such a rigid complex is well supported by the observed high entropy values.

Based on the observed kinetic results, a most probable mechanism is given in Scheme 1.

SCHEME 1

(TCCA)   (DCCA)

$$\text{Ru(III)} + \text{S} \underset{\longleftarrow}{\overset{K_2}{\rightharpoonup}} \text{Complex, } C_1$$

$$C_1 + \text{HOCl} \underset{\longleftarrow}{\overset{K_3}{\rightharpoonup}} \text{Complex, } C_2$$

$$C_2 \overset{K_4}{\rightarrow} \text{products.}$$

$$\text{Rate} = k_4 \cdot C_2$$

$$C_2 = \frac{K_3 C_1 \, [\text{HOCl}]}{1 + K_3 C_1 \, [\text{HOCl}]}$$

$$C_1 = \frac{K_2 \, [\text{Ru(III)}] \, [\text{S}]}{1 + K_2 \, [\text{S}]}$$

$$C_2 = \frac{K_3 K_2 \, [\text{Ru(III)}] \, [\text{S}] \, [\text{HOCl}]/(1 + K_2 \, [\text{S}])}{1 + \dfrac{K_3 K_2 \, [\text{Ru(III)}] \, [\text{S}] \, [\text{HOCl}]}{1 + K_2 \, [\text{S}]}}$$

$$= \frac{K_3 K_2 \, [\text{Ru(III)}] \, [\text{S}] \, [\text{HOCl}]}{(1 + K_2 \, [\text{S}]) + K_2 K_3 \, [\text{Ru(III)}] \, [\text{S}] \, [\text{HOCl}]} \qquad \ldots(1)$$

$$\text{But } [\text{HOCl}] = \frac{K_{h1} \, [\text{TCCA}]_T}{([\text{DCCA}] + K_{h1})}$$

Substituting for [HOCl] in eqn. (1).

$$\text{Rate} = \frac{\dfrac{k_4 K_3 K_2 \, [\text{Ru(III)}] \, [\text{S}] \, K_{h1} \, [\text{TCCA}]_T}{([\text{DCCA}] + K_{h1})}}{(1 + K_2 \, [\text{S}]) + \dfrac{K_3 K_2 \, [\text{Ru(III)}] \, [\text{S}] \, K_{h1} \, [\text{TCCA}]_T}{([\text{DCCA}] + K_{h1})}}$$

$$= \frac{k_4 K_3 K_2 K_{h1} \, [\text{Ru(III)}] \, [\text{TCCA}]_T \, [\text{S}]}{([\text{DCCA}] + K_{h1})(1 + K_2 \, [\text{S}]) + K_3 K_2 K_{h1} \, [\text{Ru(III)}] \, [\text{S}] \, [\text{TCCA}]_T}$$

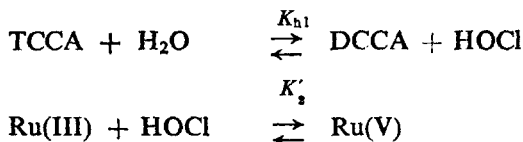Assuming DCCA term in the denominator to be negligible, the above eqn. becomes,

$$= \frac{k_4 K_3 K_2 K_{h1} \, [\text{Ru(III)}] \, [\text{TCCA}]_T \, [\text{S}]}{K_{h1}(1 + K_2 \, [\text{S}]) + K_3 K_2 K_{h1} \, [\text{Ru(III)}] \, [\text{TCCA}]_T \, [\text{S}]} \qquad \ldots(2)$$

The above rate law explains all the kinetic orders observed.

Alternatively a Scheme 2 can also account for the observed results with that of TCCA.

In Case of Scheme 2 : In case where Ru(III) gets oxidised to Ru(V)[20,21] by HOCl, which then complexes with the substrate. The complex breaks in a fast step to give the product. Hence, the Scheme can be derived as follows :—

Scheme 2

$$\text{TCCA} + H_2O \underset{}{\overset{K_{h1}}{\rightleftharpoons}} \text{DCCA} + \text{HOCl}$$

$$\text{Ru(III)} + \text{HOCl} \underset{}{\overset{K'_2}{\rightleftharpoons}} \text{Ru(V)}$$

$$\text{Ru(V)} + \text{S} \quad \underset{}{\overset{K_3'}{\rightleftharpoons}} \quad \text{Complex}$$

$$\text{Complex} \quad \overset{K_4'}{\rightarrow} \quad \text{Product}$$

$$\text{Rate} \quad = \quad k_4' \text{ Complex} \quad = \quad k_4' k_3' \text{ [Ru(V)] [S]}$$

$$= \quad k_4' k_3' k_2' \text{ [Ru(III)] [HOCl] [S]}$$

$$\text{[Ru(III)]}_T \quad = \quad \text{[Ru(III)]} + \text{Complex}$$

$$= \quad \text{[Ru(III)]} + K_3' \text{ [Ru(V)] [S]}$$

$$= \quad \text{[Ru(III)]} + K_3' K_2' \text{ [Ru(III)] [HOCl] [S]}$$

$$= \quad \text{[Ru(III)]} (1 + K_3' K_2' \text{ [HOCl] [S]})$$

$$\therefore \text{ [Ru(III)]} \quad = \quad \frac{\text{[Ru(III)]}_T}{1 + K_3' K_2' \text{ [HOCl] [S]}}$$

$$\text{Rate} \quad = \quad \frac{k_4' K_3' K_2' \text{ [Ru(III)]}_T \text{ [HOCl] [S]}}{(1 + K_3' K_2' \text{ [HOCl] [S]})} \qquad \ldots(3)$$

$$\text{But [HOCl]} \quad = \quad \frac{K_{h1} \text{ [TCCA]}_T}{(\text{[DCCA]} + K_{h1})}$$

Substituting for [HOCl] in the eqn. (3), the rate becomes,

$$= \frac{\dfrac{k_4' K_3' K_2' K_{h1} \text{[Ru(III)}_T \text{ [TCCA]}_T \text{ [S]}}{(\text{[DCCA]} + K_{h1})}}{1 + \dfrac{K_3' K_2' K_{h1} \text{ [TCCA]}_T \text{ [S]}}{(\text{[DCCA]} + K_{h1}}}$$

$$= \frac{k_4' K_3' K_2' K_{h1} \text{ [Ru(III)]}_T \text{ [S] [TCCA]}_T}{(\text{[DCCA]} + K_{h1}) + K_3' K_2' K_{h1} \text{ [TCCA]}_T \text{ [S]}} \qquad \ldots(4)$$

Assuming [DCCA] term in the denominator to be negligible, eqn.(4) become,

$$= \frac{k_4' K_3' K_2' K_{h1} \text{ [Ru(III)]}_T \text{ [TCCA]}_T \text{ [S]}}{(K_{h1} + K_3' K_2' K_{h1} \text{ [TCCA]}_T \text{ [S]}}$$

The above rate law explains all the kinetic orders observed.

Both schemes (1) and (2) explain all the kinetic orders observed, first order both in [TCCA] and [Ru(III)] and zero order in [Substrate]. The only difference between schemes (1) and (2) is that, the complexation is with Ru(III) in one case

and in another it is with Ru(V), which is transient species formed from Ru(III). But it is difficult to decide on either mechanism unequivocally.

In all the cases the final product is the corresponding aldehyde.

REFERENCES

1   Subas C Pati and Y Sriramulu   *Proc natn Acad Sci India* **51**(A) (1981) II
2   R C Mahapatro   *PhD Thesis* Berhampur Univ (1980)
3   L D Sadangi   *PhD Thesis* Berhampur Univ (1982)
4   Ch Sanjeeva Reddy and E V Sundram   *Indian J Chem* **23** A (1984) 911
5   M A Rodkin I P Beletskaya and D I Kokorikov   *Bull Acad Sci USSR D Chem Sci* **34** (1985) 2061
6   N S Srinivasan and N Venkatasubramanian   *Indian J Chem* **10** (1972) 1014
7   V S Srinivasan and N Venkatasubramanian   *Indian J Chem* **13** (1975) 526
8   S P Srivastava R G Sharma and S K Singhal   *J Indian Chem Soc* **53** (1976) 725
9   Y Ogata Y Sawaki F Matsunaga and H Tezuka   *Tetrahedron* **22** (1966) 2655
10   Kalayan K Benerjee   *J chem Soc Perkin II* (1973) 435
11   Subas C Pati and C Sarangi   *Indian J Chem* **24** A (1985) 745
12   Subas C Pati A K Sahu and Y Sriramulu   *Oxidation Commun Hungary* **8** (1985) No 3 243
13   Subas C Pati A K Sahu and Y Sriramulu   *Proc Indian natn Sci Acad* **52** A (1986) 1205
14   Subas C Pati H P Pathy and B R Dev   *Oxidation Commun* Hungary **10** (1987) Nos 1-2 19-29
15   P S Radhakrishnamurti and N K Rath   *Indian J Chem* **24** A (1985) 300
16   Subas C Pati A K Sahu and Y Sriramulu   *Indian J Chem* **26** A (1987) 693-695
17   Horiuchi Yoshizo and Ichijyo Osamu   *Chem Abstr* **72** (1970) 50624
18   A Berka J Zyka and J Vultevin   *Newer Redox Titrant* Pergamon Press New York (1965) 43
19   J E Leffler and E Grunwald   *Rates and Equilibria of Organic Reactions* Wiley New York (1963) 342
20   P S Radhakrishnamurti and H P Panda   *Gazet Chim Italiana* **109** (1979) 637
21   Yatsimirskii   *J Indian chem Soc* **51** (1974) 32