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Oxidation of Cycloheptanol by Chloramine-T in Acidic Medium Catalysed by Ru(III)

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Abstract

This type of reaction involves the conversion of cycloheptanol into corresponding ketone or aldehyde. Due to its seven membered ring structure. This is 1st order reaction which catalysed by Ru(III). The kinetics of Ru(III) catalysed oxidation of cycloheptanol by chloramine-T has been investigated in acidic medium. The reaction shows first order kinetics with respect to cycloheptanol, chloramine-T, H^+, and Ru(III). There is insignificant effect of ionic strength, PTS and KCl on the reaction rate. The dielectric constant of the medium has positive effect. Elevation of temperature increases the rate of reaction in oxidation of cycloheptanol. A mechanism consistent with the above kinetic results has been suggested.

Keywords: Kinetics, Ru(III), Oxidation, Cycloheptanol, Chloramine-T.

Introduction:

Catalysts chloramin-T in acidic medium behave as an oxidizing agent in which alkali medium, it shows variety of pH and reaction medium.[1] The use of transition metal like such as Ruthenium single or binary mixture catalysed this type of conversion. Less widely used but potent oxidant chloramine-T with high redox potential (E_{red} = 1.138 V at pH 0.65) has been used in kinetic studies involving it as an oxidant both in acidic as well as in alkaline media.[2-3] Catalysed oxidation of cycloalcohols are reported in few papers[4,5] but Ru(III) catalysed oxidation of cycloheptanol by chloramine-T is not reported to today. Thus the use of catalytic amount of ruthenium(III) chloride[6,7] prompted us to investigate the kinetics and mechanism of ruthenium(III) catalyzed oxidation of cycloheptanol by chloramine-T.

Experimental:

All chemicals were of A.R. grade and doubly distilled water was used throughout. The stock solution of chloramine-T (CAT) (E. Merk) was prepared by dissolving its weighed amount in doubly distilled water and its strength was checked by estimating it iodometrically using starch as indicator. Ruthenium(III)chloride (Johnson Matthey) solution was prepared by dissolving the sample in hydrochloric acid of known strength[8-10].

All the kinetic measurements were carried out at constant temperature (± 0.1°C). The reaction was initiated by rapid addition of chloramine-T (CAT) to the reaction mixture,[11-13] containing appropriate quantities of cycloheptanol, perchloric acid, Ru(III) chloride and water by mixing them by vigorous shaking. The progress of the reaction[14-16] was monitored by estimating the amount of unconsumed CAT at regular time intervals iodometrically.

Result and Discussion:

The kinetics of cycloheptanol was investigated at several initial concentrations of the reactants (Table-1). First order dependence in CAT was followed at all initial concentrations of CAT.[17-18] The order in substrate (cycloheptanol) computed from the slop of log k_1 vs. log [Substrate] Fig-1 was found to be approximately one.[19-21] This established that the reaction follows first order kinetics with respect to cycloheptanol. The rate of reaction was found to be highly influenced by [Ru(III)].[22-23] It was observed that with increasing [Ru(III)] the first order rate constant increased linearly (Table-1) which proves first order dependence on [Ru(III)].[24-26] From the plot of –dc/dt vs. $[H^+]$ it is clear that the reaction is also first order with respect to $[H^+]$.

TABLE-1

Effect of Variation of $[H^+]$, [CAT], Cycloheptanol and Catalyst on Reaction Rate Constant, At

T = 35°C, KCl = 5.00×10^{-2} mol dm^{-3}

[Cycloheptanol] $\times 10^{-2}$ mol dm^{-3}	[CAT] $\times 10^{-3}$ mol dm^{-3}	[HClO4] $\times 10^{-3}$ mol dm^{-3}	[Ru(III)] $\times 10^{-5}$ mol dm^{-3}	[−dc/dt] $\times 10^{-7}$ mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
1.00	1.00	2.00	2.00	1.62	1.80
1.00	1.25	2.00	2.00	1.84	1.84
1.00	1.67	2.00	2.00	2.68	1.78
1.00	2.00	2.00	2.00	3.26	1.81
1.00	2.50	2.00	2.00	4.32	1.80
1.00	4.00	2.00	2.00	6.58	1.82
0.50	2.00	2.00	2.00	1.62	0.90
0.65	2.00	2.00	2.00	2.07	1.15
0.85	2.00	2.00	2.00	2.77	1.54
1.00	2.00	2.00	2.00	3.25	1.81
1.25	2.00	2.00	2.00	4.05	2.25
2.50	2.00	2.00	2.00	8.18	4.58
1.00	2.00	1.00	2.00	1.63	0.91
1.00	2.00	1.00	2.00	3.29	1.84
1.00	2.00	1.00	2.00	5.00	2.78
1.00	2.00	1.00	3.00	6.76	3.76

1.00	2.00	1.00	4.00	8.56	4.76
1.00	2.00	1.00	5.00	9.75	5.42
1.00	1.00	1.00	1.00	1.84	0.91
1.00	1.00	1.25	1.00	2.05	1.14
1.00	1.00	1.60	1.00	2.57	1.93
1.00	1.00	2.00	1.00	3.24	1.80
1.00	1.00	2.50	1.00	3.85	2.13
1.00	1.00	4.80	1.00	7.74	4.30

Figure - 1

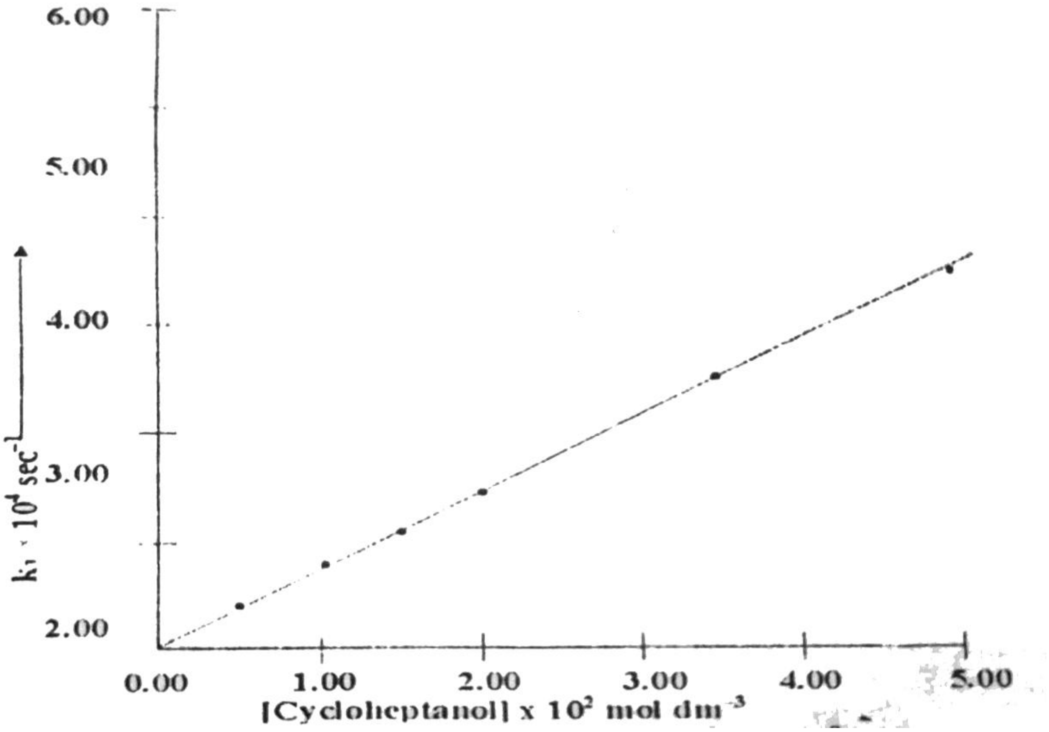


Figure 1: Plot of k1 Vs [Cycloheptanol] at 35°C]

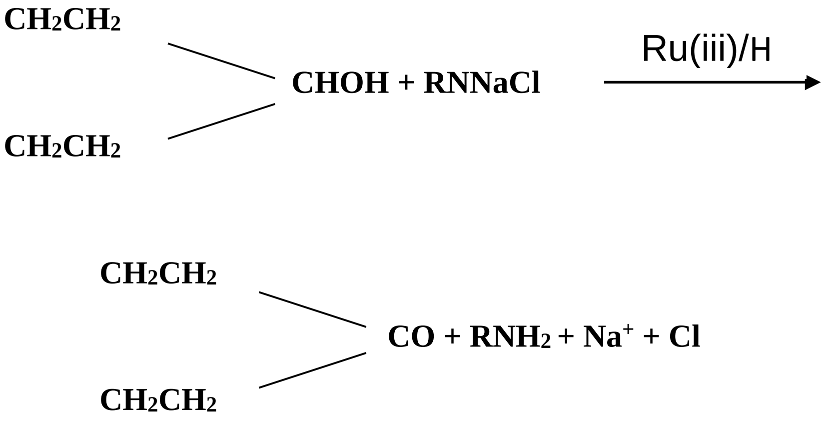
[HClO4] = 1.25×10^{-2} mol dm^{-3} [CAT] = 1.00×10^{-3} mol dm^{-3}

[Ru(III)] = 2.84×10^{-5} mol dm^{-3} [KCl] = 5.00×10^{-2} mol dm^{-3}

It is also seen that on variation of ionic strength, *p*-toluene sulphonamide (PTS) and KCl the rate of reaction does not change[27-28] (Table-2), showing negligible effect of these.

STOICHIOMETRY AND PRODUCT ANALYSIS:

The reaction mixture containing a known excess of [chloramine-T] over [Cyclohexanol] was kept in the presence of $HClO_4$ and ruthenium (III) at 35°C for 72 hours. Estimation of the unreacted chloramine-T showed that one mole of cyclohexanol consumes one mole of chloramine-T.[29-30] The presence of corresponding cycloketones was confirmed by spot tests and also through dinitrophenylhydrazine (DNP) derivatives.[31-32]



R is p – $CH_3C_6H_4SO_2$ – group.

Mechanism:

The reactive species of chloramine-T in acidic medium is given by considering the dissociation of chloramine-T as [33]

$$RNCINa \rightleftharpoons RNCl^- + Na^+$$

(CAT) (CAT$^-$)

Where R = $CH_3C_6H_4SO_2$

Table -2

EFFECT OF IONIC STRENGTH, CHLORIDE ION, PTS AND TEMPERATURE

$[CAT] = 2.50 \times 10^{-3}$ mol dm^{-3} $[Cyclohexanol] = 1.00 \times 10^{-2}$ mol dm^{-3}

$[HClO_4] = 2.00 \times 10^{-1}$ mol dm^{-3} $[Ru(III)] = 1.00 \times 10^{-6}$ mol dm^{-3}

Temp. ^{0}C	Ionic strength (μ) × 10^5 mol dm^{-3}	[KCl] × 10^3 mol dm^{-3}	[PTS] × 10^3 mol dm^{-3}	$k_1 \times 10^7$ sec^{-1}
35°C	7.00	0.00	0.00	1.80
	10.00	0.00	0.00	1.84
	14.00	0.00	0.00	1.79
	17.00	0.00	0.00	1.85
	21.00	0.00	0.00	1.82
	24.00	0.00	0.00	1.87
35°C	6.25	0.00	1.00	1.45
	6.25	0.00	2.00	1.40
	6.25	0.00	3.00	1.39
	6.25	0.00	4.00	1.47
	6.25	0.00	5.00	1.44
35°C	6.25	1.00	0.00	1.84
	6.25	2.00	0.00	1.81
	6.25	3.00	0.00	1.86
	6.25	4.00	0.00	1.82
	6.25	6.00	0.00	1.79
30°C	6.25	0.00	0.00	1.22
40°C	6.25	0.00	0.00	2.33
45°C	6.25	0.00	0.00	3.96

Table 3: Thermodynamic parameters

Ea kJ mol^{-1}	log A	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
66.29	7.49	63.73	25.12	71.47

In acidic medium CAT$^-$ would take up the proton to form RNHCl as given below

$$RNCl^- + H^+ \rightleftharpoons RNHCl$$

(CAT$^-$)   (CAT)

In addition to above i.e. CAT a part of CAT$^-$ is also expected to form DCS (dichloro sulphonamide) and free paratoluene sulphonamide (PTS) as

$$2CAT^- + 2H^+ \rightleftharpoons RNCl_2 + RNH_2$$

(DCS) (PTS)

Following equilibrium may also exit in acidic media.

$$2\,RNHCl \rightleftharpoons RNCl_2 + RNH_2$$

(CAT)   (DCS) (PTS)

$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl$$

$$RNCl_2 + H_2O \rightleftharpoons RNH_2 + HOCl$$

Thus in the acidified solution of chloramine-T, the possible oxidizing species are RNHCl, RNCl2, HOCl and CAT as such.[34-35] If $RNCl_2$ were to be reactive species, the rate law would require second order dependence on CAT, which is contrary to the experimental observation. If HOCl were to be the reactive species, a first order retardation of the rate[36] by added PTS would be expected which is again contrary to the observed zero effect.[37] Further if RNHCl were to be reactive species then fractional order with respect to (PTS) would be required which is also contrary to observed zero effect of (PTS).[38-39] Hence in view of above description CAT itself may be taken as real reactive species of chloramine-T. Sometimes CAT− is also taken as reactive species with CAT.[40]

The following steps are suggested for the oxidation of cycloheptanol under the experimental conditions. Here S stands for cycloheptanol and (CAT^-) has been used for CAT as CAT exists in solution as (CAT^-).

$$S + H+ \rightleftharpoons SH^+$$

$$[RuCl_6]^{3-} + SH+ \underset{k-1}{\overset{k1}{\rightleftharpoons}} C1\ (ii)$$

k_2

Complex

k_{-2}

$$(CAT) + C_1 \xrightarrow[\text{slow and rate determining step}]{} [RuCl_6H]^{4-} + \text{Product (iii)}$$

$$[RuCl_6H]^{4-} + (CAT) \xrightarrow{\text{Fast}} [RuCl_6]^{3-} + PTS + HOBr\ (IV)$$

Where (CAT^-) represents $CH_3C_6H_4SO_2NCl^-$. The rate of the reaction may be determined in term of rate of loss of [CAT] as given below.

$$-\frac{d[CAT]}{dt} = k_d[CAT^-][C1] \text{ ---(1)}$$

On applying steady state approximation to $[C_1]$ we have from step (ii) and (iii) as

$$-\frac{d[C1]}{dt} = 0 = k_2\,[RuCl_6]^{3-}\,[SH^+]$$

$$- k_{-2}[C_1] - k_d[CAT^-]\,[C_1]$$

Or $[C_1] = k_{-2} + k_d\,[CAT^-]$

$$= k_2[RuCl_6]^{3-}\,[SH^+]$$

$$[C_1] = \frac{k_2[RuCl_6]^{3-}[SH^+]}{k_{-2} + k_d[CAT]} \text{ ---(2)}$$

On comparing equations (1) and (2), we have

$$-\frac{d[CAT]}{dt} = \frac{k_2k_d[RuCl_6]^{3-}[SH^+][CAT}{k_{-2}+k_d[CAT]} \quad ---(3)$$

Again applying steady state approximation to $[SH^+]$ we have from steps (i) and (ii) as given below

$$\frac{d[SH+]}{dt} = 0 = k_1[S][H^+] - k_{-1}[SH^+]$$

$$- k_2[SH^+][RuCl_6]^{3-}$$

Or $[SH^+] = \frac{k1[S][H+]}{k-1 + k2[RuCl6]3-}$ ---(4)

On comparing equations (1) and (2), we have

$$-\frac{d[CAT]}{dt} = \frac{k_2k_d[RuCl_6]^{3-}[SH^+][CAT}{k_{-2}+k_d[CAT]} \quad ---(3)$$

Again applying steady state approximation to $[SH^-]$ we have from steps (i) and (ii) as given below

$$-\frac{d[SH^+]}{dt} = 0 = k_1 [S] [H^+] - k_{-1} [SH^-] - k_2 [SH^-] [RuCl_6]^{3-}$$

Or $$[SH^-] = \frac{k_1[S]\left[H^+\right]}{k_{-1} + k_2\left[RuCl_6\right]^{3-}} \quad ---------- (4)$$

By comparing eqn. (3) and (4) we have

$$\frac{d[CAT]}{dt} = \frac{k_1k_2k_d[S]\left[CAT^-\right]\left[RuCl^6\right]^3\left[H^+\right]}{\left(k_{-1} + k_2\left[RuCl_6\right]^{3-}\right)\left(k_2 + k_d\left[CAT^-\right]\right)} \quad ----------- (5)$$

On assuming $k_{-2} >> k_d [CAT^-]$ and $k_{-1} >> k_2 [RuCl_6]^{3-}$ we have

$$-\frac{d[CAT]}{dt} = \frac{k_1k_2k_d[S]\left[CAT^-\right][S]\left[H^+\right]\left[RuCl_6\right]^{3-}}{(k_{-1})(k_2)} \quad ----------- (6)$$

Since $[CAT^-] = [CAT]$

$$\frac{d[CAT]}{dt} = K_1 K_2 k_d [CAT][S][H^+][RuCl_6]^{3-}$$

Where $K_1 = \frac{k_1}{k_{-1}}$ and $K_2 = \frac{k_1}{k_{-2}}$

The rate law (7) explains first order dependence on chiromine-T, Cycloheptanol, medium (H^+) and Ru(III). From the above rate law it is also clear that there is no effect of para toluene sulphonamide (PTS) and KCl.

CONCLUSION:

Cyclo heptonol oxidation reaction catalyses by Ru(III) is common for considering rate of reaction in acidic medium kinetic of oxidation by chloramines-T in the presence of HCl and Ru(III) chloride was studied at 303 K . These reactions are identical in transition metals in acidic medium. The activation parameters have been evaluated from the observation graph.

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