

Mechanistic Study of Ruthenium(III) Catalyzed Oxidation of Cyclohexanone by Acidic Bromate

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Abstract

In this work, kinetics and mechanism of Ru(III) catalyzed oxidation of cyclohexanone by acidified solution of potassium bromate has been studied. Present study employ mercuric acetate $Hg(OAc)_2$ as a scavenger for Br^- ion to prevent parallel oxidation by bromine. The kinetics and mechanism have also been studied in the temperature range of $30^\circ C - 45^\circ C$. The reaction exhibits first order kinetics with respect to Ru (III), while zero order kinetics with respect to $KBrO_3$ and $HClO_4$. The influence of $Hg(OAc)_2$ and ionic strength on the rate of reaction was found to be insignificant. Positive effect in the reaction mixture was also observed upon addition of chloride ion; while as the negative effect was revealed with acetic acid. A suitable mechanism in conformity with the kinetic observations has been proposed and the rate law is derived on the basis of obtained data. The various activation parameters such as energy of activation (ΔE^*), Arrhenius factor (A), entropy of activation (ΔS^*) were calculated from the rate measurements at $30^\circ C$, $35^\circ C - 40^\circ C$ and $45^\circ C$.

Keywords

Kinetics, Ru (III), Oxidation, Ketone, Bromate, Acidic, Order

1. Introduction

Catalysis by transition metals plays a significant role in understanding the mechanism of redox reactions. Ruthenium(III) acts as an efficient catalyst in many redox reactions. Besides this, a number of oxidants like N-bromoacetimide (NBA) [1] [2], N-bromosuccinimide (NBS) [3] [4], Sodium periodate ($NaIO_4$) [5] [6] have been used incorporation with transition metal ions like Osmium(VIII), Iridium(III), Ruthenium(VIII), etc. [7] [8] [9] for oxidation of var-

ious compounds. The kinetics of redox reactions involving such catalysts and oxidants has been extensively investigated. However, a scant attention has been paid towards use of KBrO_3 as an oxidant in various metal catalyzed reactions [10] [11]. The utility of ruthenium(III) chloride as a homogeneous catalyst has been reported by several workers [12] [13], but scant attention has been paid to explore catalytic role of ruthenium(III) chloride with potassium bromate as an oxidant. This fact prompted us to undertake the present investigation which consists of Ru(III) catalyzed oxidation of cyclohexanone by bromate in acidic medium.

2. Materials and Methods

2.1. Solutions and Reagents

- The solution of oxidant KBrO_3 (CDH), Cyclohexanone (CDH), KCl (CDH) and perchloric acid (CDH) were prepared by dissolving its weighed sample in distilled water.
- The solution of Ruthenium trichloride (Loba) was prepared in HCl of known strength.
- $\text{Hg}(\text{OAc})_2$ (CDH) solution was prepared by dissolving it in 10 % CH_3COOH solution in distilled water.
- 4% solution of KI (CDH) was prepared by dissolving its sample in distilled water.
- 5.1% starch (CDH) solution was prepared a fresh each day.

2.2. Methodology

A thermo stated water bath was used to achieve and maintain the desired temperature within $\pm 0.1^\circ\text{C}$. Requisite volume of all reagents including substrate, were taken in a reaction vessel and temperature was maintained around $35^\circ\text{C} \pm 0.1^\circ\text{C}$ for thermal equilibrium. Here measured volume of KBrO_3 solution was poured rapidly into the reaction vessel which was also maintained separately at similar temperature. The kinetics was followed by examining desired portions of reaction mixture for KBrO_3 iodometrically using starch as indicator after suitable time intervals. In all our titration experiments, micro burettes were used.

2.3. Stoichiometry

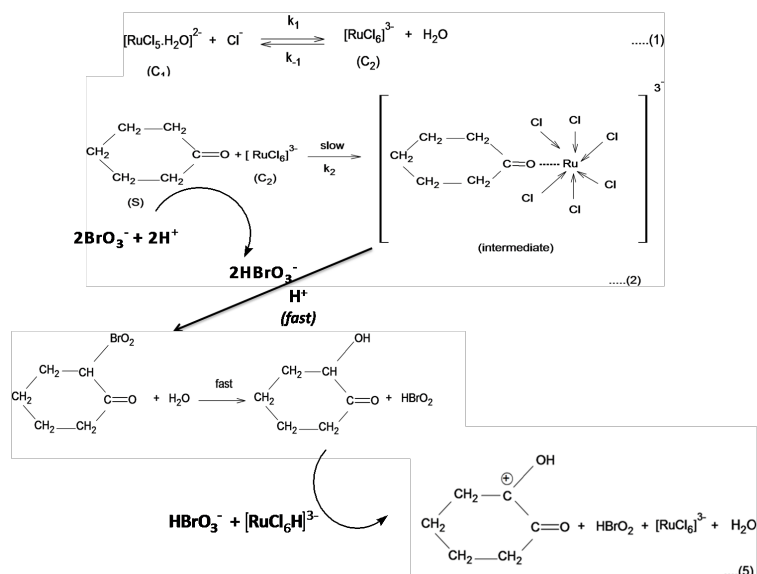
The stoichiometry of the reaction was determined by equilibrating varying ratios of $[\text{KBrO}_3]$ to cyclohexanone at 35°C for 48 hrs. Estimation of unconsumed KBrO_3 revealed that one mole of the substrate consumes two moles of the oxidant. The product analysis by conventional method [12] shows the formation of diketone after the reaction. The stoichiometric determination indicated the overall reaction (**Scheme 1**).

3. Results and Discussions

In order to propose a probable reaction mechanism for Ru(III) catalyzed

mentioned conditions indicate that addition of chloride ion has a probable effect on the reaction velocity.

The above observations lead us to suggest the following reaction mechanism in the title reaction.



Now on the basis of above proposed reaction steps, and further applying steady state approximation, it yields rate law in terms of loss of concentration of potassium bromated:

$$\frac{-d[\text{BrO}_3^-]}{dt} = k_2 [\text{C}_2][\text{S}] \quad \dots(7)$$

$$\frac{-d[\text{BrO}_3^-]}{dt} = \frac{k_2 k_1 [\text{Ru(III)}]_T [\text{C}^-] [\text{S}]}{k_{-1} + k_1 [\text{C}^-]} \quad \dots(8)$$

$$\text{Where } [\text{Ru(III)}]_T = [\text{C}_1] + [\text{C}_2]$$

The rate law is in agreement with all observed kinetics. The proposed mechanism is in consistent with the activation parameters given in **Table A1** (Supplementary Information). The high positive values of change in free energy of activation (ΔG^\ddagger) indicates highly solvated transition state, while fairly high negative values of change in entropy of activation (ΔS^\ddagger) suggest the formation of an activated complex with reduction in the degree of freedom of molecules.

4. Conclusion

The experimental results obtained in this work revealed that the reaction rate

doubles upon doubling the concentration of the catalyst [Ru(III)]. The rate law is in conformity with all kinetic observations and the proposed mechanistic steps are supported by the negligible effect of ionic strength. Negative effect of acetic acid addition signifies a positive dielectric effect. From these investigations, it is concluded that HBrO_3 [13] and $[\text{RuCl}_6]^{-3}$ are the reactive species of KBrO_3 and Ru(III) chloride respectively in acidic medium.

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Supplementary Information

Table A1. Effect of variation of reactants on the reaction rate.

[Substrate] × 10 ² mol·dm ⁻³	[KBrO ₃] × 10 ³ mol·dm ⁻³	Ru(III) × 10 ⁻⁶ mol·dm ⁻³	[HClO ₄] × 10 ³ mol·dm ⁻³	(-dc/dt) × 10 ⁷ mol·dm ⁻³ ·s ⁻¹	k ₁ × 10 ⁴ s ⁻¹
0.33	1	96	1	1.2	1.29
0.4	1	96	1	1.38	1.5
0.5	1	96	1	1.75	1.94
0.66	1	96	1	2.28	2.62
1	1	96	1	3.4	4.14
2	1	96	1	6.66	10.24
1	0.83	96	1	3.5	5.14
1	1	96	1	3.4	4.14
1	1.25	96	1	3.5	3.39
1	1.66	96	1	3.43	2.48
1	2.5	96	1	3.33	1.58
1	3.33	96	1	3.34	1.19
1	1	9.6	1	0.4	0.41
1	1	24	1	0.92	0.99
1	1	48	1	1.75	1.92
1	1	72	1	2.6	2.98
1	1	96	1	3.4	4.14
1	1	120	1	4.3	5.73
1	1	96	0.83	3.5	4.26
1	1	96	1	3.4	4.14
1	1	96	1.25	3.42	4.17
1	1	96	1.66	3.45	4.2
1	1	96	2.5	3.55	4.32
1	1	96	5	3.33	4.06

[Ru(III)] = 96.00 × 10⁻⁶ M, [KCl] = 1.00 × 10⁻³ M [Hg(OAc)₂] = 1.25 × 10⁻³ M.

Table A2. Effect of variation of chloride ion, mercury (II) acetate and sodium perchlorate at 35°C.

[KCl] × 10 ⁻³ mol·dm ⁻³	[Hg(OAc) ₂] × 10 ³ mol·dm ⁻³	[NaClO ₄] × 10 ³ mol·dm ⁻³	(-dc/dt) × 10 ⁷ mol·dm ⁻³ ·s ⁻¹	k ₁ × 10 ⁴ s ⁻¹
0.83	1.25	-	3.25	3.91
1	1.25	-	3.4	4.14
1.25	1.25	-	3.5	4.26
1.66	1.25	-	3.63	4.48

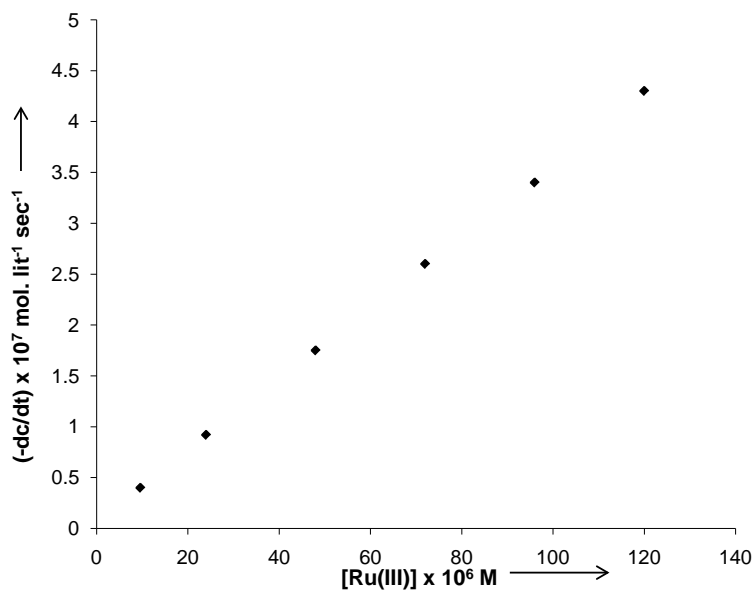
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2.5	1.25	-	3.8	4.75
5	1.25	-	4	5.06
1	0.83	-	3.5	4.26
1	1	-	3.33	4.01
1	1.25	-	3.4	4.14
1	1.66	-	3.6	4.33
1	2.5	-	3.4	4.09
1	5	-	3.5	4.21
1	1.25	1	3.5	-
1	1.25	2	3.43	-
1	1.25	2.5	3.33	-
1	1.25	5	3.5	-
1	1.25	10	3.42	-
1	1.25	12.5	3.52	-

[Ru(III)] = 96.00×10^{-6} M, [cyclohexanone] = 2.00×10^{-2} M [HClO₄] = 1.00×10^{-3} M, [KBrO₃] = 1.00×10^{-3} M.

Table A3. Activation parameters for Ru(III) catalyzed oxidation of cyclohexanone by acidic bromated.

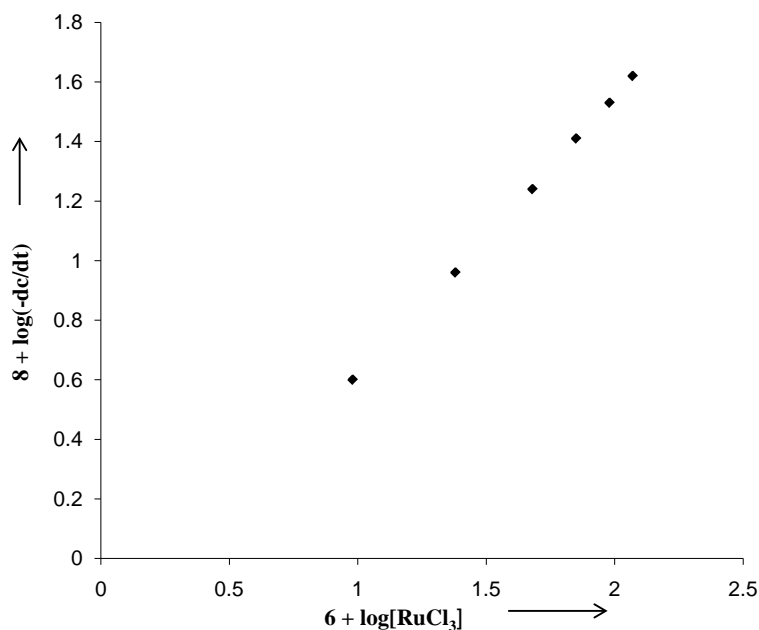
Activation parameters	Temp/°C	Cyclohexanone
$k_r \times 10^4 \text{ s}^{-1}$	30	2.81
$k_r \times 10^4 \text{ s}^{-1}$	35	4.14
$k_r \times 10^4 \text{ s}^{-1}$	40	6.59
$k_r \times 10^4 \text{ s}^{-1}$	45	9.88
log A	---	8.8
$\Delta E^*(\text{kJ}\cdot\text{mol}^{-1})$	---	54.77
$\Delta G^*(\text{kJ}\cdot\text{mol}^{-1})$	35	79.62
$\Delta H^*(\text{kJ}\cdot\text{mol}^{-1})$	35	73.7
$\Delta S^*(\text{JK}^{-1}\cdot\text{mol}^{-1})$	35	-19.21



Plot between $(-dc/dt)$ and $[Ru(III)]$ at $35^{\circ}C$.

$[cyclohexanone] = 1.00 \times 10^{-2} M$ $[KCl] = 1.00 \times 10^{-3} M$
 $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$ $[KBrO_3] = 1.00 \times 10^{-3} M$
 $[HClO_4] = 1.00 \times 10^{-3} M$

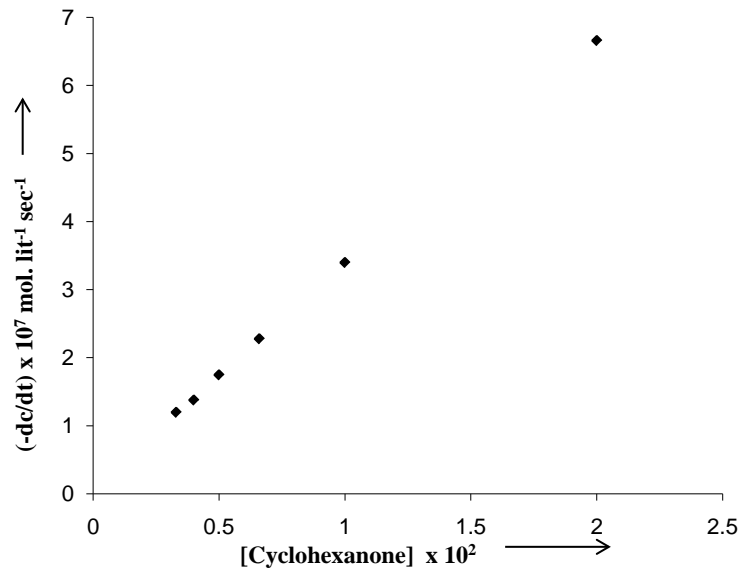
Figure A1. Plot between $(-dc/dt) \times 10^{-7} ML^{-1}.s^{-1}$ and $[Ru(III)] \times 10^{-6} M$ for oxidation of cyclohexanone at $35^{\circ}C$.



Plot between $\log(-dc/dt)$ and $\log[Ru(III)]$ at $35^{\circ}C$.

$[cyclohexanone] = 1.00 \times 10^{-2} M$ $[KCl] = 1.00 \times 10^{-3} M$
 $[Hg(OAc)_2] = 1.25 \times 10^{-3} M$ $[KBrO_3] = 1.00 \times 10^{-3} M$
 $[HClO_4] = 1.00 \times 10^{-3} M$

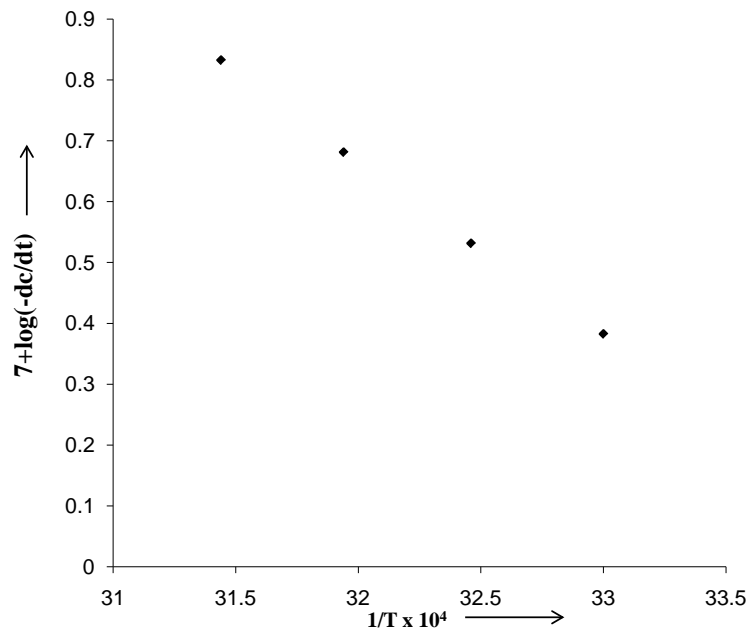
Figure A2. Plot between $8 + \log(-dc/dt)$ and $6 + \log[Ru(III)]$ for oxidation of cyclohexanone at $35^{\circ}C$.



Plot between $(-dc/dt)$ and $[Cyclohexanone]$ at $35^{\circ}C$.

[KCl] = 1.00×10^{-3} M [KBrO₃] = 1.00×10^{-3} M
 [Hg(OAc)₂] = 1.25×10^{-3} M [Ru(III)] = 96.00×10^{-6} M

Figure A3. Plot between $(-dc/dt) \times 10^{-7} \text{ ML}^{-1} \cdot \text{s}^{-1}$ and $[Cyclohexanone] 10^{-2}$ M for oxidation of cyclohexanone at $35^{\circ}C$.



Plot of $\log(-dc/dt)$ Vs. $1/T$

[cyclohexanone] = 1.00×10^{-2} M [KCl] = 1.00×10^{-3} M
 [Hg(OAc)₂] = 1.25×10^{-3} M [Ru(III)] = 96.00×10^{-6} M
 [HClO₄] = 1.00×10^{-3} M [KBrO₃] = 1.00×10^{-3} M

Figure A4. Plot between $7 + \log(-dc/dt)$ and $1/T$ for oxidation of cyclohexanone at $35^{\circ}C$.