# A Kinetic and Mechanistic Study of Rh (III) Catalysed Oxidation of 3- Ketoglutaric Acid by Bromamine -T in Acidic Medium.

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**Research Article**

### ABSTRACT

Kinetic study on rhodium(III) catalyzed oxidation of 3–ketoglutaric acid by acid medium of bromamine–T in the presence of þ– toluenesulphonamide has been carried out. The reaction follows first order with respect to 3– ketoglutaric acid. The first order kinetic was found with respect to Rh(III) chloride. Hydrogen ion shows positive effect on reaction rate. A negative effect of [Cl⁻] and insignificant effect of ionic strength of the medium were observed on the reaction velocity. A plausible mechanism of the reaction has also been proposed.

### INTRODUCTION

In chemical reactions platinum group metals are used as homogeneous catalyst [1]. The metal ions viz. ruthenium [2], palladium [3], irradium [4] has been investigated as catalyst in past. Apart from other metals, rhodium shows antibacterial and antitumor properties in the Rh (III) complex form [5]. The rhodium catalyst may react with oxo acid, keto acid and other type of reactant to generate new product [6], which have significant role in industrial and biological sector. Rh [III] is used in homogeneous as well as hydro formulation reactions also [7]. The rhodium reacts with platinum alloy which can be used for electrical contract. By knowing the nature of catalyst this may help in improvement in our chemical process to produce better product value.

BAT is used as oxidant in much chemical reaction due to its easy preparation [8]. [BAT] is primarily responsible for oxidation for the chemical reaction in acidic medium [9]. BAT appears to play a vital role in oxidation of various compounds [10]. [BAT] is effective and feasible oxidant to synthesize easily in laboratory. The physiochemical activity of this oxidant is so broad but still need to be explored widely [11]. The [BAT] based reaction of great significance and the interest because of its vast implication and understanding the nature of chemical process involves [12].

3– ketoglutaric acid also known as 3– oxo glutaric aid which can be prepared by decorboxylation and oxidation of citric acid used as building block of synthetic organic chemistry [13,14].

In view of the fact that Rh (III) complex , 3– keto glutaric acid and bromamine–T , an investigation has been made to find out the mechanism and kinetic of Rh (III) catalyzed  oxidation of 3–keto glutaric acid by bromamine–T in acidic medium.

### MATERIAL AND METHODS

Bromamine–T solution was prepared by the following methods [15]. Recrystallised chloramine –T (10 gram) was dissolved in 200 ml water and to it was added liquid bromine (2 ml) drop wise from the burette with constant stirring of the solution. The golden yellow precipitate of dibromamine–T thus obtained was thoroughly washed with water, filtered under suction pump and dried in vacuum desiccators for about 24 hours. The dried sample was found to melt at 92–93 ℃ with decomposition.

About 35 gram of dibromamine–T prepared above was dissolved in small lots at a time and with stirring in aqueous solution of about 8 gram of sodium hydroxide in 50ml of water and the solution was cooled in ice. Pale yellow crystal of bromamine –T separated out. The crystals were washed again with minimum quantity of water and dried over phosphorous pentoxide. About 0.05 M

stock solution of bromamine-T was prepared by dissolving its 16 gram in a liter of water and kept in amber colored bottle. The solution was then standardized iodometrically for its active bromine. Aqueous solutions of 3- ketoglutaric acid was obtained from E. Merck Chemical Company and were prepared by dissolving weight amount of 3- keto glutaric acid in double distilled water.

Purity of the substrate was checked by their melting points. Rhodium (III) chloride standard solution was prepared by dissolving its 1 gram in 0.05 N HCl (about 50 ml) and the solution was then made up to 1000 ml. Standard solution of perchloric acid (E. Merck) and sodium per chlorate (E. Merck) were prepared in double distilled water. Standard solution of oxalic acid and sodium hydroxide were prepared by their Merck samples. A pure sample of þ- tolune sulphonamide was dissolved in distilled water. An aqueous solution of sodium thiosulphate (BDH) was standardized against standard solution of copper sulphate (E. Merck). 4% solution of potassium iodide (E. Merck) was prepared for the titration and 1 % solution of starch (BDH) was used as indicator.

### Kinetic measurement

In order to investigate the reactions under study in the present analysis, the following procedure were adopted.

The kinetic measurement was carried out at constant temperature 35 °C ($\pm$ 0.1°C) as reported in literature [16]. Appropriate volume of all the reactants i.e. BAT, Rh(III), þ-TSA ,KCl and $NaClO_4$ were taken in a reaction bottle .The requisite volume of doubly distilled water was added to the reaction mixture so that total volume of the reaction mixture was 100 ml after addition of 3-ketoglutaric acid solution. The bottle containing the reaction mixture was placed in an electrically operated thermostat for thermal equilibrium. Appropriate volume of solutions of 3-ketoglutaric acid, also equilibrate at 35 °C, was rapidly poured into reaction mixture to initiate the reaction. The progress of reaction was followed by estimating the amount of unconsumed [BAT] iodometrically in aliquots (5ml) withdrawing from the reaction mixture at regular interval of time for about 75 % of the reaction.

The rate of reaction (-dc/dt) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of bromamine-T which is written as [BAT]*. The order of reaction with respect to each reactant was determined by the reaction between initial rate, i.e. (-dc/dt) and initial [reactant].

### RESULTS AND DISCUSSION

In the present investigation study a set of experiments were carried out with different concentration of BAT but at fixed concentration of above reagents as shown in Table-1. It has been found reactions follows first order kinetics in BAT [Figure-1]. It is clear from Table-1 and figure-1 that the value of $K_1$ remains constant, which clearly confirm the first order dependant on BAT.

It is clear from Table-2 that the value of $k_1$ are almost constant with varying concentration of reducing material showing the first order with respect to 3-ketoglutaric acid at fixed concentration of other reactants [figure-2].

An significant effect of variation [$H^+$] was observed as shown in Table- 3. Perchloric acid has been used as a source of hydrogen ions. Several experiments with varying [$HClO_4$] and at fixed concentration of all other reagents. It is evident from Table-3 that there is linear relationship between $k_1$ value and concentration of $HClO_4$, showing first order with respect to perchloric acid [figure-3].

However the effect of variation of concentration of Rh(III) on the reaction rate was observed. Table-4 gives a clear picture that there is linear relationship between $k_1$ value and concentration of Rh(III) in oxidation of substrate proving the first order dependence of the reaction on Rh(III) [figure-4].

For measuring the dependence of the reaction on $Cl^-$ ion concentration in [BAT] oxidation of 3-ketoglutaric acid, varying concentration of potassium chloride were used at fixed concentration of all other reactants [Table-5]. Data clearly a show that there is negative effect of variation in $Cl^-$ was found [figure-5].

Further to this variation in ionic strength of the medium shows insignificant effect on the reaction rate as shown in Table-6.

In this study an attempt has been made to monitor the effect of variation of addition of þ-toluenesulphonamide on the reaction rate and results are summarized in table-7. Results shows that addition of þ-toluenesulphonamide does not bring about any change in the reaction velocity of oxidation of 3-ketoglutaric acid by acidified bromamine-T in the presence of Rh(III).

In the present study, dependence of reactions on variation of temperature was observed. The different experiments were performed at 30 °C - 45 °C for the reaction [Table-8 and figure-6]. The value of activation energy is calculated from figure-6. The value of $\Delta$ E comes out to be 16.23 for 3-ketoglutaric acid.

Table 1: Effect of variation of BAT on the rate constant at 35 ℃

| Non variable constituents | Variable constituent [BAT] $\times 10^3$ M | $k_1 \times 10^4 sec^{-1}$ |
|---|---|---|
| 3-ketoglutaric acid = 5.00 $\times 10^{-2}$ M | 0.80 | 3.04 |
| Rh(III) = 4.00 $\times 10^{-6}$ M | 1.60 | 3.09 |
| HClO$_4$ = 1.00 $\times 10^{-2}$ M | 2.00 | 3.11 |
| KCl = 5.00 $\times 10^{-2}$ M | 2.60 | 2.98 |
| | 3.20 | 2.98 |
| | 4.00 | 3.07 |
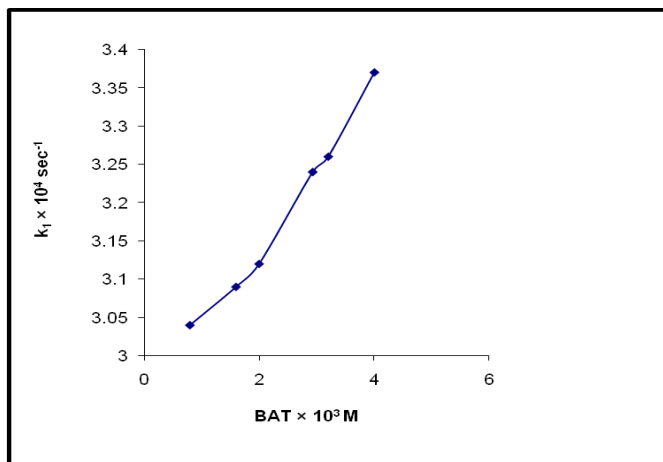


Figure 1: Plot between $k_1$ and [BAT*] at 35 ℃ for oxidation of 3-ketoglutaric acid

Condition:

| | |
|---|---|
| 3-ketoglutaricacid | = 5.00 $\times 10^{-2}$ M |
| Rh(III) | = 4.00 $\times 10^{-6}$ M |
| HClO$_4$ | = 1.00 $\times 10^{-2}$ M |
| KCl | = 5.00 $\times 10^{-2}$ M |

Table 2: Effect of variation of 3-ketoglutaric acid on the rate constant 35 ℃

| Non variable constituents | Variable constituents 3-ketoglutaricacid $\times 10^2$ M | $k_1 \times 10^4 sec^{-1}$ |
|---|---|---|
| [BAT] = 2.00 $\times 10^{-3}$ M | 1.25 | 0.67 |
| Rh(III) = 4.00 $\times 10^{-6}$ M | 2.50 | 1.42 |
| HClO$_4$ = 1.00 $\times 10^{-2}$ M | 3.75 | 2.14 |
| KCl = 5.00 $\times 10^{-2}$ M | 6.25 | 2.83 |
| | 7.50 | 3.56 |
| | 8.74 | 4.16 |
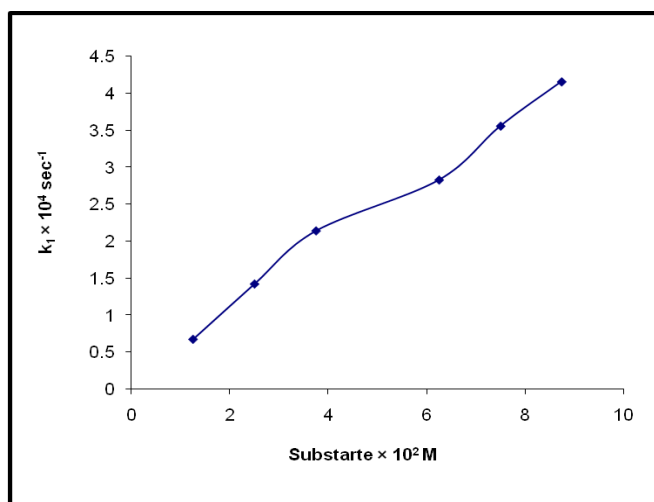


Figure 2: Plot between $k_1$ and [Substrate] at 35 ℃

**Condition:**

| | |
|---|---|
| [BAT] | $= 2.00 \times 10^{-3}$ M |
| Rh(III) | $= 4.00 \times 10^{-6}$ M |
| HClO$_4$ | $= 1.00 \times 10^{-2}$ M |
| KCl | $= 5.00 \times 10^{-2}$ M |

**Table 3: Effect of variation of H$^+$ on the rate constant at 35 °C**

| Non variable constituents | Variable constituents HClO$_4$ = $\times 10^2$ M | $k_1 \times 10^4 sec^{-1}$ |
|---|---|---|
| 3-ketoglutaricacid = $5.00 \times 10^{-2}$ M | 0.50 | 1.36 |
| Rh(III) = $4.00 \times 10^{-6}$ M | 1.00 | 3.02 |
| [BAT] = $2.00 \times 10^{-3}$ M | 1.50 | 4.32 |
| KCl = $5.00 \times 10^{-2}$ M | 2.00 | 5.98 |
| | 2.50 | 7.46 |
| | 3.00 | 9.02 |
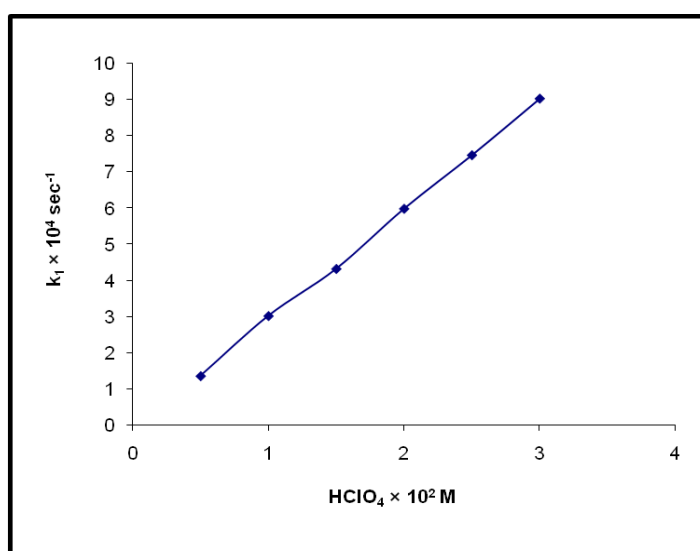


**Figure 3: Plot between $k_1$ and [HClO$_4$] at 35 °C for oxidation of 3-ketoglutaric acid**

**Condition:**

| | |
|---|---|
| [BAT] | $= 2.00 \times 10^{-3}$ M |
| Rh(III) | $= 4.00 \times 10^{-6}$ M |
| 3-ketoglutaricacid | $= 5.00 \times 10^{-2}$ M |
| KCl | $= 5.00 \times 10^{-2}$ M |

**Table 4: Effect of variation of Rh(III) on the rate constant at 35 °C**

| Non variable constituents | Variable constituents Rh(III) = $\times 10^6$ M | $k_1 \times 10^{\square} sec^{-1}$ |
|---|---|---|
| 3-ketoglutaricacid = $5.00 \times 10^{-2}$ M | 1 | 0.68 |
| [BAT] = $2.00 \times 10^{-3}$ M | 2 | 1.54 |
| HClO$_4$ = $1.00 \times 10^{-2}$ M | 3 | 2.12 |
| KCl = $5.00 \times 10^{-2}$ M | 4 | 3.02 |
| | 5 | 4.06 |
| | 6 | 4.82 |
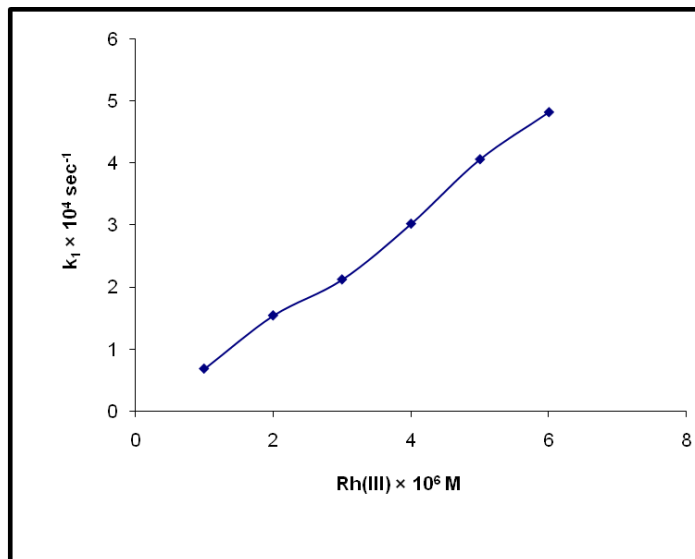
**Figure 4: Plot between $k_1$ and Rh(III) at 35 °C for oxidation of 3-ketoglutaric acid**

Condition:

| | |
|---|---|
| [BAT] | $= 2.00 \times 10^{-3}$ M |
| $HClO_4$ | $= 1.00 \times 10^{-2}$ M |
| 3-ketoglutaricacid | $= 5.00 \times 10^{-2}$ M |
| KCl | $= 5.00 \times 10^{-2}$ M |

**Table 5: Effect of variation of [Cl⁻] on the rate constant at 35 °C**

| Non variable constituents | Variable constituents KCl = × $10^2$ M | $k_1 \times 10^4$ sec⁻¹ |
|---|---|---|
| 3-ketoglutaricacid = $5.00 \times 10^{-2}$ M | 1 | 12.31 |
| Rh(III) = $4.00 \times 10^{-6}$ M | 2 | 8.60 |
| $HClO_4 = 1.00 \times 10^{-2}$ M | 3 | 4.82 |
| [BAT] = $2.00 \times 10^{-3}$ M | 5 | 3.02 |
| | 7 | 2.54 |
| | 10 | 1.67 |
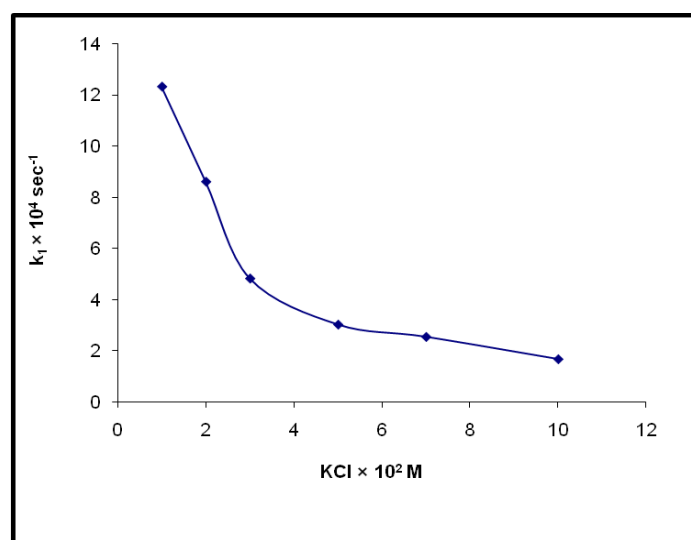


**Figure 5**
**Plot between $k_1$ and [KCl] at 35 °C for oxidation of 3-ketoglutaric acid**

| | |
|---|---|
| [BAT] | $= 2.00 \times 10^{-3}$ M |
| $HClO_4$ | $= 1.00 \times 10^{-2}$ M |
| 3-ketoglutaricacid | $= 5.00 \times 10^{-2}$ M |
| Rh(III) | $= 4.00 \times 10^{-6}$ M |

Table 6: Effect of variation of ionic strength on the rate constant at 35 ℃

| Non variable constituents | Variable constituents $NaClO_4 = \times 10^2$ M | Ionic strength | $k_1 \times 10^4 sec^{-1}$ |
|---|---|---|---|
| 3-ketoglutaricacid = $5.00 \times 10^{-2}$ M | 0.00 | 6.00 | 3.04 |
| Rh(III) = $4.00 \times 10^{-6}$ M | 3.00 | 9.00 | 3.16 |
| $HClO_4 = 1.00 \times 10^{-2}$ M | 6.00 | 12.00 | 3.05 |
| KCl = $5.00 \times 10^{-2}$ M | 9.00 | 15.00 | 3.03 |
| | 12.00 | 18.00 | 3.06 |
| | 15.00 | 21.00 | 3.10 |
| | 18.00 | 24.00 | 3.08 |

Table 7: Effect of variation of p–toluenesulphonamide on the rate constant at 35 ℃

| [p–TSA $\times 10^3$ M] | $k_1 \times 10^4 sec^{-1}$ |
|---|---|
| 0.00 | 3.06 |
| 0.50 | 3.06 |
| 1.00 | 3.08 |
| 1.50 | 3.10 |
| 2.00 | 3.04 |
| 3.50 | 3.06 |
| 3.00 | 3.08 |

Table 8: Effect of variation of temperature on the rate constant at 35 ℃

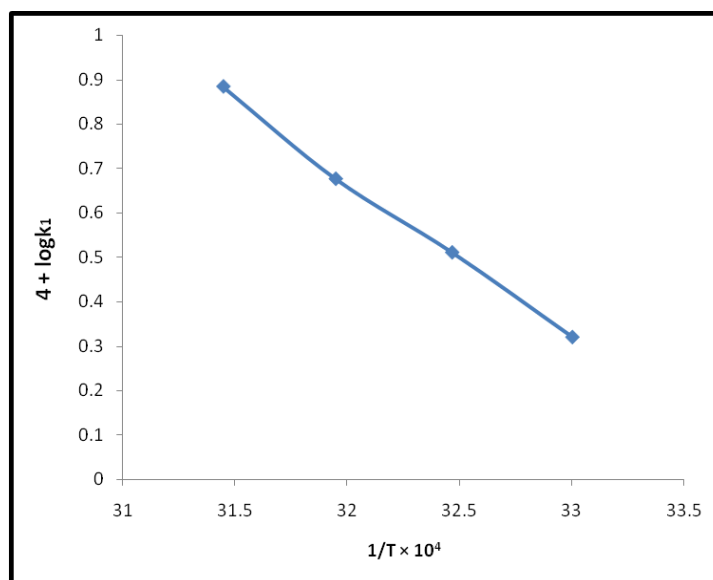| Temperature ℃ | $k_1 \times 10^4 sec^{-1}$ |
|---|---|
| 30 | 1.83 |
| 35 | 3.24 |
| 40 | 4.53 |
| 45 | 7.65 |



Figure 6: Plot between log $k_1$ and (1/T) at 35 ℃ for oxidation of 3–ketoglutaric acid

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