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A kinetic and mechanistic study of Rh(III) catalysed oxidation of 2-ketoglutaric acid by bromamine–T in acidic medium

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ABSTRACT

The Rh(III) catalyzed oxidation of 2-ketoglutaric acid by bromamine-T in acid medium has been studied. The reaction is first order each in bromamine - T and acid, less than unity order in both substrate and catalyst. The reaction constant is positive and increase with increase in temperature. The mechanism is influenced by participation of the neighboring group of 2- ketoglutaric, and intermolecular catalysis of Rh(III) is proposed. Insignificant effect of þ- toluenesulphonamide was observed. The processes are controlled by electron withdrawing and electron releasing substituents. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Reaction mechanism;
Rhodium;
[BAT] oxidation;
2-keto glutaric acid.

INTRODUCTION

In last few decades the most commonly transition metal ion reagents such as cerium (IV)[1] and vanadium (V)[2] have been used as catalyst in redox reactions. Some less familiar oxidizing agents likes manganese (III)[3], osmium (VIII)[4], ruthenium (III)[5], ruthenium (VIII)[6], iridium (III)[7] and palladium (II)[8] have also been used as catalyst. The transition metal ion such as rhodium used as homogeneous catalyst in many redox reactions[9] helping us to study for the role of this transition metal in biological as well as in industrial sector.

Oxidation states of rhodium complexes ranging from + 1 to + 6.The most stable oxidation was found to be +3 than other oxidation states. The Rh(III) is belongs to class of compounds d^6 species and form octahedral complex, cationic neutral and anionic in contrast to Co (III). The cationic and neutral complex of the Rh(III) is generally kinetically inert, but the anionic complex of Rh(III) is usually labile . Rhodium complex cations have been proved particularly suitable for studying trans effect in octahedral complex.

Magnetic and spectral properties of the Rh(III) complex are fairly simple. All the complex and intended all compounds of rhodium are diamagnetic. Thus the inherent tendency of the octahedral d^6 configuration to adopt the low spins $t_6$2g arrangement together with the relatively high ligand field strength prevailing in these complexes of tri positive higher transition series ions

After the initial report[10] that group VIII metals (Ni, Ru, Rh, Pt, Pd, Ir) catalyze many reactions, active debate continues about the relative intrinsic reactivity's of different metals, while Rh is generally considered to be one of the most stable group VIII metals[11–16]. Rh/Al_2O_3[12–24], Rh/ZrO_2[17,23], Rh/SiO_2[17,19,23,25,26,28], Rh/MgO[28], Rh/La_2O_3[27], Rh/TiO_2[29,30], Rh/NaY[31], and Rh/ZSM-5[32] have also been used to catalyzed so many other types of reactions.

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It is reported that Rh (III) form complex with pyridine and its derivatives which shows antitumor activity. Rhodium and its compounds used as potential agents in cancer treatment for humans[33]. Numerous platinum other platinum and non-platinum metal compounds were shown to be effective against animal model tumors as well as tumors in man. However, the introduction of novel transition metal agents in clinical treatment is exceptionally slow. Rhodium belongs to the same group as platinum and ruthenium. However, rhodium compounds, analogues to the corresponding platinum and ruthenium compounds that possess significant anti tumor properties were found to be less effective as anticancer agents mainly due to their toxic effects. Dimeric mu-Acetato dimers of Rh(II) as well as monomeric square planar Rh(I) and octahedral Rh(III) complexes have shown interesting anti tumor properties[34].

In 2-keto glutaric acid, two carbon atoms separate the carbonyl and carbonyl group and thus they behave both as oxo compounds as well as acids with out the direct influence of the other group. The above mentioned compounds are active substrate in terms of their mechanistic aspects because in acidic medium 2- keto glutaric acid can undergo enolization. However, the catalysis in the iodination of some keto acids has been studied elsewhere[35].

However, Micro determination of 2-ketoglutaric acid in plasma and cerebrospinal fluid by capillary gas chromatography mass spectrometry; application to pediatrics and 2-ketoglutarate dehydrogenase deficiency with intermittent 2-ketoglutaric acid urea have been reported elsewhere[36].

Bromamine T which is also known as sodium salts of N-bromo -þ- toluene sulphonamide, is a newer and less familiar oxidant, which has been recently employed as effective oxidant in many reactions which have been kinetically based. The use of Bromamine T is due to its easy preparation. Recently it has been used for the direct and indirect estimation of inorganic and organic substances, but very little attempts[37-42] have been made, so far the oxidation kinetics with bromanine-T. It was found that bromanine- T is very effective oxidant in the presence of Rh(III) chloride in acidic medium. Various hydrolysis products depending upon pH of the bromanine T solution have been supposed to be formed like chloramines-T products. The use of bromate oxidation leads over metal ion oxidation due to its recyclable and environmentally benign.

In present investigation, an attempt has been made to interpret the kinetic results obtained for the oxidation of 2-ketoglutaric acid by acidic solution of bromamine-T in the presence of Rh(III) as homogeneous catalyst.

MATERIAL AND METHODS

Bromamine-T solution was prepared by the following methods[43]. 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 °C 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 2- ketoglutaric acid was obtained from E. Merck Chemical Company and were prepared by dissolving weight amount of 2- ketoglutaric 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 perchlorate (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 p- 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 (± 0.1°C) as reported in literature[44]. Appropriate volume of all the reactants i.e. BAT, Rh (III), p-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 2-ketoglutaric acid solution. The bottle containing the reaction mixture was placed in an electrically operated thermostat for thermal equilibrium. Appropriate volume of solutions of 2-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

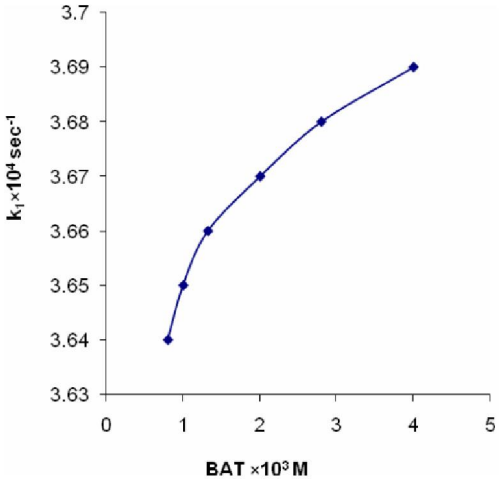
The unanalyzed oxidation of 2-ketoglutaric acid by BAT in a medium containing p-TSA is very slow and followed first order each in BAT, 2-ketoglutaric acid and $[H^+]$, under the present experimental conditions. However the reaction rate is faster (10-12 times) in the presence of less quantity of Rh(III). The rate constants for the catalyzed reaction are given here under

k catalyzed = k overall –k uncatalyzed

The oxidation kinetics was carried out at various concentrations of reactants at 308 K. The rate of reaction increases in directly proportional with increase in the initial Bromamine-T as shown in TABLE 1 and Figure 1.

TABLE 1 : Effect of variation of BAT on the rate constant at 35 °C

Non variable constituents	Variable constituent	$k_1 \times 10^4 sec^{-1}$
	[BAT] × 10^3 M	
2-ketoglutaric acid = 5.00 × 10^{-2} M	0.80	3.64
Rh(III) = 2.64 × 10^{-6} M	1.00	3.64
$HClO_4$ = 1.25 × 10^{-2} M	1.32	3.65
KCl = 5.00 × 10^{-2} M	2.00	3.66
	2.80	3.68
	4.00	3.69



Condition : 2-ketoglutaric acid = 5.00 × 10^{-2} M; Rh(III)= 2.64 × 10^{-6} M; $HClO_4$= 1.25 × 10^{-2} M; KCl= 5.00 × 10^{-2} M

Figure 1 : Plot between k_1 and [BAT*] at 35 °C for oxidation of 2-ketoglutaric acid

The effect of 2 -ketoglutaric acid on the reaction rate was studied in the concentration range 0.5 – 5.00 mol dm^{-3} at constant concentration of oxidant, acid and catalyst (TABLE 2). The plot of kc' against [substrate] ½ plots was linear with varying intercept and slope, confirming that the order in [substrate] is less than unity. Under the same experimental conditions the uncatalyzed reaction rate, through very slow, exhibited first order with respect to 2-ketoglutaric acid [Figure 2].

TABLE 2 : Effect of variation of 2-ketoglutaric acid on the rate constant at 35 °C

Non variable constituents	Variable constituent	$k_1 \times 10^4 sec^{-1}$
	2-ketoglutaricacid × 10^2 M	
[BAT] =1.00 × 10^{-3} M	0.50	0.38
Rh(III) = 2.64 × 10^{-6} M	1.00	0.72
$HClO_4$ = 1.25 × 10^{-2} M	1.50	1.23
KCl = 5.00 × 10^{-2} M	2.0	1.56
	3.30	2.71
	5.00	3.64

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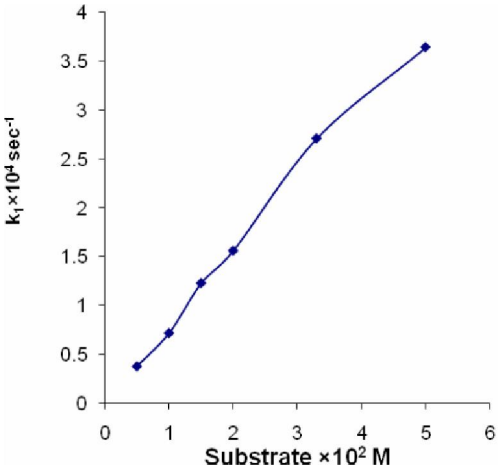


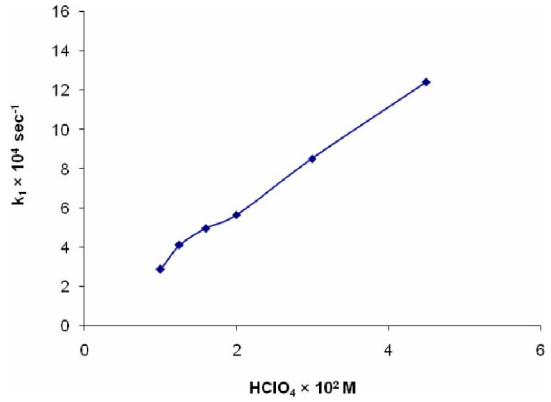
Condition: [BAT]= 1.00 × 10^{-3} M; Rh(III)= 2.64 × 10^{-6} M; $HClO_4$= 1.25 × 10^{-2} M; KCl= 5.00 × 10^{-2} M

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

The effect of [H^+] on the reaction rate was studied in order to establish the active species of reactants present in the solution. At same concentration of substrate, BAT, catalyst, and other condition remaining constant, the reaction rate increase linearly. (TABLE 3) with increase in [$HClO_4$] and the order with respect to acid was found to be unity [Figure 3].

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

Non variable constituents	Variable constituent	$k_1 \times 10^4 sec^{-1}$
	$HClO_4$ = × 10^2 M	
[BAT] = 1.00 × 10^{-3} M	1.00	2.86
Rh(III) = 2.64 × 10^{-6} M	1.25	4.11
2-ketoglutaricacid =5.00 × 10^{-2} M	1.60	4.97
KCl = 5.00 × 10^{-2} M	2.0	5.64
	3.00	8.52
	4.50	12.43



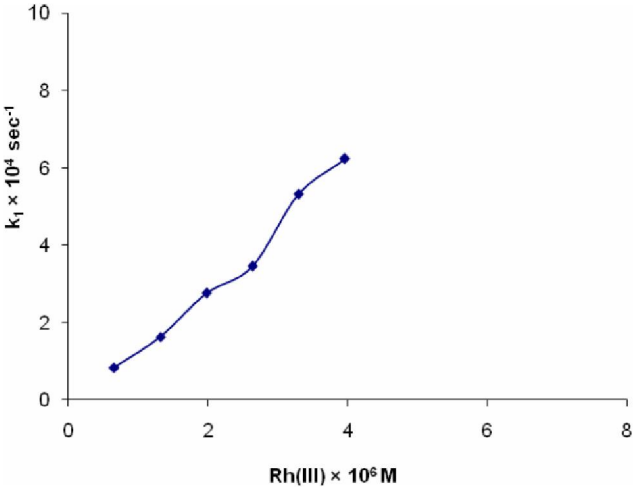
Condition:[BAT]= 1.00 × 10^{-3}M; Rh(III)= 2.64 × 10^{-6} M; 2-ketoglutaricacid = 5.00 × 10^{-2} M; KCl= 5.00 × 10^{-2} M

Figure 3 : Plot between k_1 and [$HClO_4$] at 35 ºC for oxidation of 2-ketoglutaric acid

The effect of catalyst concentration on the rate of reaction was studied between the concentrations of 0.66 × 10^{-6} and 3.96 × 10^{-6} mol dm^{-3} (TABLE 4). The catalyst order was found to be 0.50 ± 0.01 as determined the slope of log kc against log [catalyst] plots, and the slope of kc' against [catalyst] 0.5 were found to be liner relationship showing the first order [Figure 4].

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

Non variable constituents	Variable constituent	$k_1 \times 10^4 sec^{-1}$
	Rh(III) = × 10^6 M	
[BAT] = 1.00 × 10^{-3} M	0.66	0.83
$HClO_4$ = 1.25 × 10^{-2} M	1.325	1.63
2-ketoglutaricacid= 5.00 × 10^{-2} M	1.98	2.75
KCl = 5.00 × 10^{-2} M	2.64	3.45
	3.30	5.31
	3.96	6.23



Condition: [BAT]= 1.00 × 10^{-3}M; $HClO_4$= 1.25 × 10^{-2}M; 2-ketoglutaricacid = 5.00 × 10^{-2}M; KCl= 5.00 × 10^{-2} M

Figure 4 : Plot between k_1 and Rh(III) at 35 ºC for oxidation of 2-ketoglutaric acid

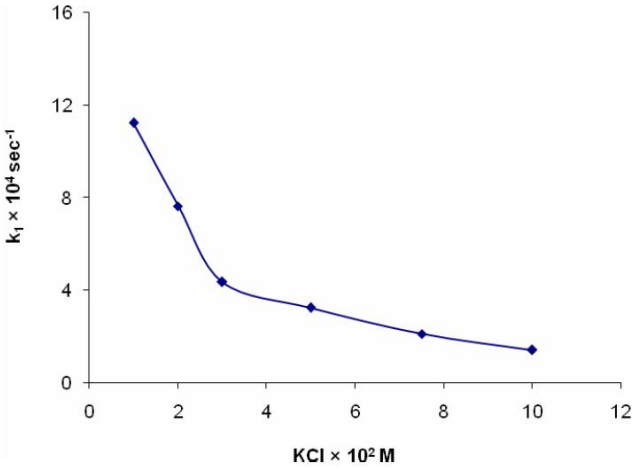
It is clear from TABLE 5 that on increasing the concentration of potassium chlorides the value of first order rate constant decreases in case of oxidation of 2-ketoglutaric acid. The above observation is also clear from the curve obtained on plotting k_1 value against [KCl] which shows a decrease in concentration of potassium chloride (Figure 5).

The effect of ionic strength of the medium of the reaction rate was studied using $NaClO_4$ with other experimental condition held constant. We do not observe any significant change of ionic strength on the re-

action rate (TABLE 6); hence the ionic strength of the medium was not fixed at any constant value. Blank experiments were also run to monitor the oxidation of acetic acid by [BAT]. It was found that acetic acid was not oxidized by [BAT] under the same set of conditions.

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

Non variable constituents	Variable constituent	$k_1 \times 10^4 sec^{-1}$
	KCl = × 10^{-2} M	
[BAT] = 1.00 × 10^{-3} M	1.00	11.23
$HClO_4$ = 1.25 × 10^{-2} M	2.00	7.64
2-ketoglutaricacid = 5.00 × 10^{-2} M	3.00	4.37
Rh(III) = 2.64 ×10^{-3} M	5.00	3.25
	7.50	2.11
	10.00	1.42



Condition: [BAT]= 1.00 × 10^{-3} M; $HClO_4$ = 1.25 × 10^{-2} M; 2-ketoglutaricacid = 5.00 × 10^{-2} M; Rh(III) = 2.64 × 10^{-3} M

Figure 5 : Plot between k_1 and [KCl] at 35 °C for oxidation of 2-ketoglutaric acid

TABLE 6 : Effect of variation of ionic strength on the rate constant at 35 °C

Non variable constituents	Variable constituent	Ionic strength	$k_1 \times 10^4 sec^{-1}$
	$NaClO_4$ = × 10^{-2} M	μ × 10^{-2} M	
[BAT] = 1.00 × 10^{-3} M	0.00	6.25	3.46
$HClO_4$ = 1.25 × 10^{-2} M	0.75	7.00	3.51
2-ketoglutaricacid =5.00 × 10^{-2} M	1.75	8.00	3.43
Rh(III) = 2.64 × 10^{-3} M	3.75	10.00	3.41
	6.25	12.50	3.67
	12.50	18.75	3.72
	18.75	25.0	3.74

In this study an attempt has been made to monitor the effect of variation of addition of p-toluenesulphonamide on the reaction rate. Various experiments with different amount of þ-toluenesulphonamide but at fixed concentration of other reactant have been calculated and the results are summarized in TABLE 7. A close examination of date of TABLE 7 indicates that addition of þ-toluenesulphonamide one of the reaction product] does not bring about any change in the reaction velocity of oxidation of 2- ketoglutaric acid by acidified bromamine-T in the presence of Rh(III).

TABLE 7 : Effect of variation of p-toluenesulphonamide on the rate constant at 35 °C

[þ-TSA ×10^3M]	$k_1 \times 10^4 sec^{-1}$
0.00	3.69
0.50	3.69
1.00	3.70
1.50	3.72
2.00	3.65
3.00	3.62
4.00	3.74

The oxidation reactions rates were studied in the temperature range of 303 to 318 K, keeping all the constituents of the solution constant (TABLE 8). Activation energy of the reactions was calculated from the least square slope of linear Arrhenius plots of log kc' versus 1/T (Figure 6). In this case, a straight line with slope equal to $-\Delta E/2.303$ R is obtained and thus from the slope the value of ΔE i.e. energy of activation is calculated. The value of ΔE comes out to be 15.64 for 2- ketoglutaric acid.

TABLE 8 : Effect of variation of temperature on the rate constant at 35 °C

Temperature °C	$k_1 \times 10^4 sec^{-1}$
30	2.34
35	3.85
40	6.38
45	7.46

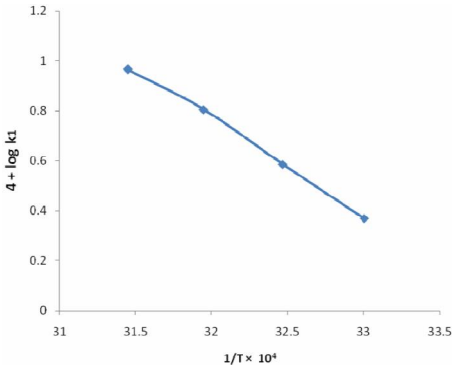


Figure 6 : Plot between log k_1 and (1/T) at 35 °C for oxidation of 2-ketoglutaric acid

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NATURE OF REACTIVE SPECIES OF RHODIUM (III) CHLORIDE IN ACIDIC MEDIUM

Before the kinetic data are used to elucidate the reaction paths for various reactions, it is essential here first to discuss the reactive species of bromamine-T and Rh (III) in acidic media. In the following section the summary of kinetic observations are given.

The nature of reactive species of rhodium (III) chloride in acidic medium will depend upon the effect of variation of chloride ions concentration on the reaction rate. In hydrochloric acid, Rh (III) chloride has been reported to form $[RhCl_6]^{3-}$ which is in equilibrium with $[RhCl_5.H_2O]^{2-}$ as given below.

$$[RhCl_6]^{3-} + H_2O \rightarrow [RhCl_5.H_2O]^{2-} + Cl^- \quad (1)$$

Our kinetic results indicate negative effect of chloride ions which favors equilibrium (1) to the right side. Thus it can be safely assumed that $[RhCl_5.H_2O]^{2-}$ is the real reactive species of rhodium (III) chloride in acidic media.

NATURE OF REACTIVE SPECIES OF BROMAMINE -T IN ACIDIC MEDIA

In acidic media, bromamine-T exists in many forms. Hence before mechanisms of various redox processes are put forward, it is essential to discuss the exact reactive species of bromamine-T involved here on the basis of experimentel observations.

Bromamine-T being a strong electrolyte[37-42] dissociates as given below.

$$\underset{(BAT)}{CH_3C_6H_4SO_2NNaBr} \rightarrow \underset{(BAT)^-}{CH_3C_6H_4SO_2NBr^-} + Na^+ \quad (1)$$

In acidic medium BAT^- would take up the proton to form þ-toluenesulphobromamide as given below.

$$(BAT)^- + H^+ \rightarrow \underset{(BAT)}{CH_3C_6H_4SO_2NHBr} \quad (2)$$

In addition to the formation of BAT a part of BAT^- is also expected to be converted into DBT (dibromo p-toluenesulphonamide) and free sulphonamide (PTS) as given below.

$$2\ BAT^- + 2H^+ \rightarrow \underset{(DBT)}{CH_3C_6H_4SO_2NBr_2} + \underset{(PTS)}{CH_3C_6H_4SO_2NH_2} \quad (3)$$

It is now quite obvious from the above discussion that any of the three species, BAT^-. [BAT] and DBT is responsible for oxidizing property of bromamine-T in the acidic medium. In the present case if either BAT^- or DBT as reactive species of bromamine-T is assumed, the rate law derived on this basis does not conform to the experimentally observed kinetic results. Hence either of these two species discussed above can not be taken as real reactive species involved in the reactions and thus in view of above the only choice left is BAT which may be assumed to be actively involved in the redox processes. Also when the rate law is derived on the basis of [BAT] as reactive species, it was found to be in agreement with the kinetic results. Hence [BAT] may be taken to be the reactive species in the present case.

MECHANISM OF Rh(III) CATALYSED OXIDATION OF 2-KETOGLUTARIC ACID BY ACIDIC BROMAMINE-T SOLUTION

The reaction mechanism for the title reactions may now be elucidated with the help of reactive species of bromamine-T and rhodium (III) chloride in acidic media where S stands for 2-ketoglutaric acid.

$$\underset{(C_1)}{[RhCl_6]^{3-}} + H_2O \xrightarrow{K_1} \underset{(C_2)}{[RhCl_5(H_2O)]^{2-}} + Cl^- \quad (I)$$

$$C_2 + S \xrightarrow{K_2} \underset{(C_3)}{[RhCl_5S]^{2-}} + H_2O \quad (II)$$

$$\underset{(BAT^-)}{CH_3C_6H_4SO_2NBr^-} + H+ \underset{K_{ii}}{\overset{K_i}{\rightleftharpoons}} \underset{(BAT)}{CH_3C_6H_4SO_2NBr} \quad (III)$$

$$C3 + BAT \xrightarrow{k2} [RhCl5H]^{3-} + Y + H+ \quad (IV)$$

Slow and rate determining step

where Y is an intermediate.

$$[RhCl_5H]^{3-} + BAT + H_2O \xrightarrow{K_3} \underset{+Br^- + [RhCl_5(H_2O)]^{2-}}{CH_3C_6H_4SO_2NH_2} \quad (V)$$

$$Y + BAT \xrightarrow{k4} \text{Final products} \quad (VI)$$

On the basis of above proposed reaction steps, the rate law may be derived as given below.

The total [Rh (III)] may be written as eqn (1).

$$[Rh\ (III)]_T = [C_1] + [C_2] + [C_3] \quad (1)$$

From equilibrium (I) we have

$$k_1 = \frac{[C_2]\ [Cl^-]}{[C_1]} \text{ or}$$

$$[C_1] = \frac{[C_2]\ [Cl^-]}{K_1} \quad (2)$$

Similarly from equilibrium (II) we have

$$[C_2] = [C_3]/K_2\,[S] \quad (3)$$

on comparing eqns (2) and (3) we have eqn (4)

$$[C_1] = \frac{[C_3]\ [Cl^-]}{K_1K_2\ [S]} \quad (4)$$

on substituting the values of $[C_1]$ from eqn (4) and $[C_2]$ from eqn (3) in eqn (1) we obtain finally eqn (5) on simplification.

$$[Rh(III)]_T = \frac{[C_3]\ [Cl^-]}{K_1K_2\ [S]} + \frac{[C_3]}{K_2\ [S]} + [C_3]$$

$$\text{or} \quad [Rh(III)]_T = [C_3]\left(\frac{[Cl^-]}{K_1K_2\ [S]} + \frac{1}{K_2\ [S]} + 1\right)$$

$$\text{or} \quad [Rh(III)]_T = [C_3]\ \frac{[Cl^-]+K_1+K_1K_2[S]}{K_1K_2\ [S]} \quad (5)$$

$$[C_3] = \frac{K_1K_2[S]\ [Rh(III)]}{[Cl^-] + K_1 + K_1K_2\ [S]}$$

Now the rate of the reaction may be written in terms of consumption of bromamine-T as given by eqn (6)

$$-\frac{d[BAT]}{dt} = nk_2[C_3]\ [BAT] \quad (6)$$

where n is the number of moles of BAT required to oxidise one mole of substrate.

Considering equation (5) and (6) we have the following resulting equation (7)

$$-\frac{d[BAT]}{dt} = \frac{nk_2\,K_1K_2[S]\ [Rh(III)]\ [BAT]}{[Cl^-] + K_1 + K_1K_2\ [S]} \quad (7)$$

On applying steady state treatment to [BAT] and considering eqn (7) we obtain equation (8)

$$-\frac{d[BAT]}{dt} = \frac{nk_2\,K_1K_2\,K_3\,[BAT]\ [S]\ [H^+]\ [Rh(III)]}{K_1K_2\ [S] + K_1 + [Cl^-]} \quad (8)$$

where $K_3 = K_1/K_1$

Again on assuming $K_1K_2\ [S] << (k_1 + [Cl^-])$ we have eqn (9)

$$-\frac{d[BAT]}{dt} = \frac{nk_2\,K_1K_2\,K_3\,[BAT]\ [S]\ [H^+]\ [Rh(III)]_T}{K_1 + [Cl^-]} \quad (9)$$

The rate law (9) fully satisfies and is in agreement with all the observed kinetic results. It clearly explains all kinetic orders with respect to all the reactants. It shows negative effect of chloride ions. It also shows negligible effect of þ-toluenesulphonamide and ionic strength of the medium. Thus the proposed mechanism is valid.

CONCLUSION

Oxidation of Rh(III) compound by bromamine–T show that, the reaction is in first order in bromamine –T was exhibited and first order dependence on each ketoglutaric acid was observed. Perchloric acid variation shows first order in H^+ ions. First order in Rh(III) was observed in this case. Insignificant effect of ionic strength was observed. Addition of þ-toluene sulphonamide did not influence the reaction. Addition of chlorine ions decreases the reaction rate. Rise in temperature increased the reaction rate markedly.

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