Ru (III) CATALYSED OXIDATION OF DIACETONE ALCOHOL BY ACID BROMATE : A KINETIC STUDY

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ABSTRACT

The kinetics of Ru (III) catalysed oxidation of diacetone alcohol (DAA) by acid bromate has been studied in aqueous H_2SO_4 medium and the reaction was found to be first order each in $[BrO_3^-]$ and [Ru (III)] and fractional order in [DAA]. The order in $[H^+]$ was found to be unity. From the effect of $[H^+]$, [KCl], $[ClO_4^-]$ and [HOAc] on rate, $HBrO_3$ is established as the reactive species. The products of the oxidation were identified as acetone, acetic acid and formic acid. A mechanism involving a complex formation between DAA and Ru (III) in a fast equilibrium step followed by the oxidation of this complex by Br (V) in a slow step has been proposed.

Key words: Kinetics, Ru (III) Catalyzed oxidation, Acid bromate, Reactive species, Diacetone alcohol, Mechanism.

INTRODUCTION

Potassium bromate is a powerful two electron oxidant with a redox potential of 1.44 V capable of oxidizing a variety of organic as well as inorganic substrates[1,2]. Diacetone alcohol (DAA), a bifunctional organic substrate having -C=O and –OH groups, was oxidized by different oxidants like Ce (IV)[3,4] and Mn (III)[5]. The slow reaction between DAA and bromate is enhanced several times in the presence of trace amounts of Ru (III) ($\approx 10^{-6}$ mol dm^{-3}). Recently, a number of oxidants like Fe (III)[6], I (VII)[7], Br (V)[8], Tl (III)[9], phenyliodo acetate[10] etc., have been employed in combination with Ru (III) to oxidize relatively inert substrates. The kinetics of Ru (III) catalyzed oxidation of pyruvic acid with iodate[11], dimethyl sulfoxide with N-chlorosuccinimide[12] in aqueous medium, 2-phenylethylamine with sodium N-chlorobenezenesulfonamide[13] and ethane diol and propane -1,2-diol with chloramine B[14] have been studied. Ru (III) has also been employed

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as catalyst in the oxidation of 2-methylcyclohexanol[15] with acid bromate and oxidation of diethanolamine and triethanolamine with Br (V) in perchloric acid[16]. Recently, aquachlororuthenium (III) complex catalysis in the oxidation of malonic acid and methyl malonic acid by bromate in perchloric acid medium has been studied and evaluated[17] individual kinetic parameters[9]. In all these oxidations, the mechanism (inner sphere or outer sphere) depends on the nature of the oxidant, substrate and acid strength used. In some hydride ions abstraction reactions, the valency of Ru (III) remains unchanged. In the present study, the Ru (III) catalysed oxidation of DAA by acid bromate has been undertaken in order to understand and establish the catalytic role of Ru (III).

EXPERIMENTAL

The potassium bromate (BDH, Analar) was weighed accurately and the aqueous solution was prepared. DAA was Analar grade (BDH) and was used as such. Ru (III) solution was prepared by dissolving ruthenium (III) chloride (Johnson – Mathey) in dilute hydrochloric acid (0.10 mol dm^{-3}) and the solution was standardized by the method of Horiuchi et al[18]. H_2SO_4 (AR, BDH) was standardized with standard alkali. E. Merck sample of mercuric acetate was used to fix the bromide ions in the system. All the experiments were conducted under pseudo-first order conditions using ten fold excess of [substrate] over $[BrO_3^-]$. The progress of the reaction was followed iodometrically. The reaction mixture from actual kinetic run was analyzed and the products were identified as CH_3COOH, $HCOOH$ and acetone. Experiments for the determination of stoichiometry were carried out in the presence of excess [bromate] over [substrate], which revealed that the stoichiometry was 1 : 1.

RESULTS AND DISCUSSION

Mercuric acetate is added to trap Br as soon as it is formed. Change in the concentration of $Hg(OAc)_2$ does not affect the rate of reaction. The catalyzed reaction was studied under the conditions, where the rate of uncatlyzed reaction is negligible.

Under the conditions of [DAA] >> $[BrO_3^-]$ the order in $[BrO_3^-]$ was found to be unity as seen from the linerar plot of log $[BrO_3^-]$ vs time. The pseudo - first order rate constants (k_{obs}) were calculated from the slopes of such plots (Table 1and Fig.1). The rate increased with increase in [DAA] (2.00 – 13.0 x 10^{-2} mol dm^{-3}) and the order in [DAA] was found to be fractional (0.35) (Table 1). The reaction is acid catalyzed and the order with respect to $[H^+]$ was found to be one (Table 2 and Fig. 1). The rate increased with increase in the % of HOAc in HOAc-H_2O medium and a linear plot was obtained between

log k_{obs} and D-1/2D+1 indicating that the reaction is dipole-dipole type (Fig. 2). The order with respect to Ru (III) was found to be unity (Fig. 2) and the addition of salts like KCl and NaClO₄ had no effect on the rate of reaction (Table 2). Polymerization tests with acrylonitrile indicated that free radicals are not formed in the reaction system.

Table 1. Effect of varying [reactants] on the Ru (III) catalyzed oxidation of DAA by Br (V)

[H₂SO₄] = 1.00 (mol dm⁻³)	[Hg(OAc)₂] = 1.00 x 10⁻² (mol dm⁻³)		Temp. = 318 K
$[BrO_3^-]$ x 10^3 (mol dm⁻³)	[DAA] x 10^2 (mol dm⁻³)	[Ru (III) x 10^5 (mol dm⁻³)	k_{obs} x 10^4 (s⁻¹)
2	5	1.5	1.51
5	5	1.5	1.62
7	5	1.5	1.60
9	5	1.5	1.57
5	2	1.5	1.23
5	5	1.5	1.62
5	7	1.5	1.90
5	9	1.5	2.07
5	5	3.0	3.25
5	5	4.5	5.14
5	5	6.0	6.46
5	5	7.5	8.75

In acidic solutions, Br (V) mostly exists as protonated (HBrO₃, H₂Br⁺O₃) and unprotonated BrO_3^- forms[19].

$$H^+ + BrO_3^- \xrightleftharpoons{K_1} HBrO_3 \qquad \ldots(1)$$

$$H^+ + HBrO_3 \xrightleftharpoons{K_2} H_2Br^+O_3 \qquad \ldots(2)$$
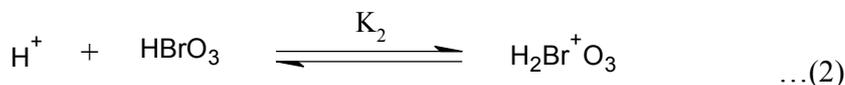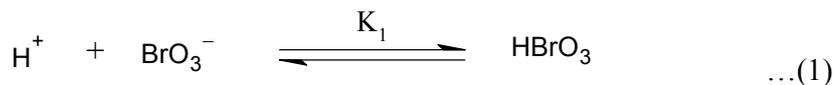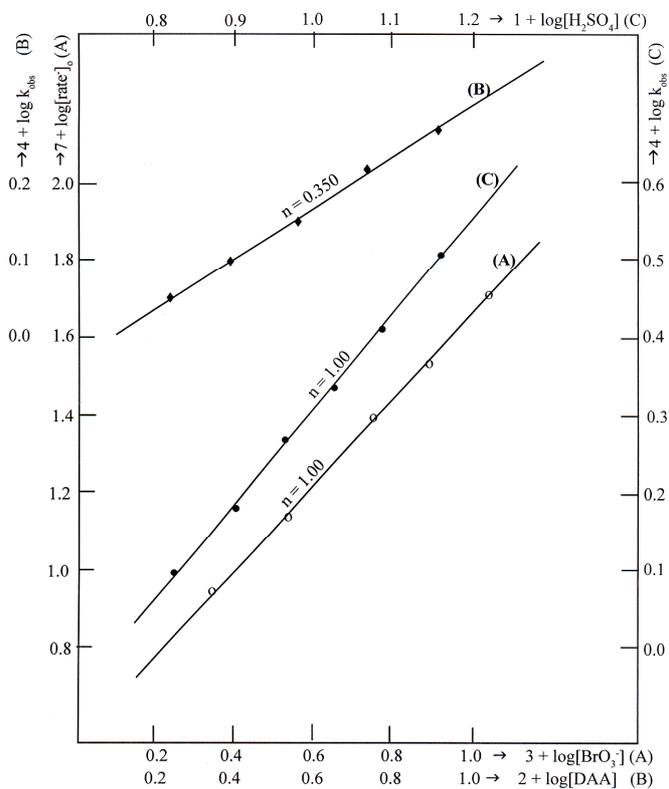
Fig. 1

(a)   Order in $[BrO_3^-]$ in BrO_3^- - DAA reaction catalyzed by Ru (III);
Plot of $7 + \log [rate]_0$ vs $3 + \log [BrO_3]$
$[DAA] = 5.00 \times 10^{-2}$ mol dm^{-3}; $[Ru (III)] = 1.50 \times 10^{-5}$ mol dm^{-3}
$[H_2SO_4] = 1.00$ mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3}; Temp. = 315 K

(b)   Order in [DAA] in BrO_3^- -DAA reaction catalyzed by Ru (III)
Plot of $4 + \log k_{obs}$ vs $2 + \log [DAA]$
$[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3}; $[Ru (III)] = 1.50 \times 10^{-5}$ mol dm^{-3}
$[H_2SO_4] = 1.00$ mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3}; Temp. = 315 K

(c)   Order in $[H^+]$ in BrO_3 - DAA reaction catalyzed by Ru (III);
Plot of $4 + \log k_{obs}$ vs $1 + \log [H_2SO_4]$
$[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3}; $[DAA] = 5.00 \times 10^{-2}$ mol dm^{-3};
$[Ru(III)] = 1.50 \times 10^{-5}$ mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3} ;
Temp. = 315 K
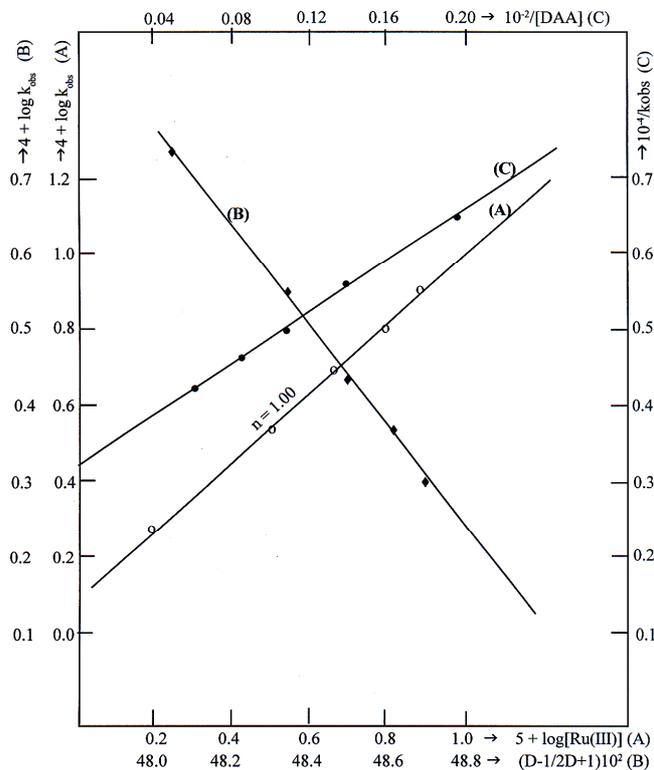
Fig. 2

(a) Order in [Ru (III)] in BrO_3^- - DAA reaction catalyzed by Ru (III);
Plot of $4 + \log k_{obs}$ vs $5 + \log$ [Ru (III)];
$[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3}; $[DAA] = 5.00 \times 10^{-2}$ mol dm^{-3}; $[H_2SO_4] = 1.00$
mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3}; Temp. = 315 K

(b) Effect of dielectric constant on k_{obs} in BrO_3^- -DAA reaction catalyzed by
Ru (III);Plot of $4 + \log k_{obs}$ vs $(D-1/2D+1)$ 10^2; $[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3};
$[DAA] = 5.00 \times 10^{-2}$ mol dm^{-3}; $[Ru (III)] = 1.50 \times 10^{-5}$ mol dm^{-3};
$[H_2SO_4] = 1.00$ mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3}; Temp. = 315 K

(c) Search for complex formation in BrO_3^- -DAA reaction catalyzed by Ru (III);
Plot of $10^{-4}/k_{obs}$ vs $10^{-2}/$ [DAA];
$[BrO_3^-] = 5.00 \times 10^{-3}$ mol dm^{-3}; ; $[Ru (III)] = 1.50 \times 10^{-5}$ mol dm^{-3};
$[H_2SO_4] = 1.00$ mol dm^{-3}; $[Hg(OAc)_2] = 1.00 \times 10^{-2}$ mol dm^{-3}; Temp. = 315 K

Table 2. Effect of $[H^+]$, [KCl] and $[NaClO_4]$ on k_{obs} in BrO_3^- - DAA reaction catalyzed by Ru (III)

$[BrO_3^-]$ = 5.00 x 10^{-3} [DAA] = 5.00 x 10^{-2} [Ru (III)] = 1.50 x 10^{-5}
       mol dm^{-3} mol dm^{-3} mol dm^{-3}

$[Hg(OAc)_2]$ = 1.00 x
       10^{-2} mol dm^{-3} Temp. = 318 K

$[H_2SO_4]$ (mol dm^{-3})	[KCl] x 10^3 (mol dm^{-3})	$[NaClO_4]$ (mol dm^{-3})	kobs x 10^4 (s^{-1})
0.75	-	-	1.23
1.00	-	-	1.62
1.25	-	-	2.04
1.50	-	-	2.40
1.00	4.00	-	1.63
1.00	6.00	-	1.58
1.00	8.00	-	1.64
1.00	10.00	-	1.67
1.00	-	0.02	1.65
1.00	-	0.04	1.59
1.00	-	0.06	1.58
1.00	-	0.08	1.56

The change in the order of [DAA] from unity to fraction in the presence of Ru (III) indicates that DAA is probably involved in the complex formation with the catalyst. Ru (III) is well known to form complexes with organic compounds[20]. Even though, there is no direct evidence for the formation of DAA-Ru (III) complex, the kinetic evidence for such complex is obtained from $1/k_{obs}$ vs 1/[DAA] plot (Fig. 2). The spectral evidence for such complex comes from the fact that λ_{max} (290 nm) of Ru (III) solution is shifted to longer wavelength (320 nm) in the presence of DAA.

It is appropriate at this stage to consider that the actual species of

aquochlororuthenium (III) is taking part in the catalysis. Ion exchange studies confirmed that RuCl$_3$ forms RuCl$_6^{3-}$ in hydrochloric acid and aquation of this species to [RuCl$_5$(H$_2$O)]$^{2-}$ takes only a few seconds[21,22]. This was assumed to be the reactive species in the Ce (IV) oxidation of ketones in sulphuric acid medium[23]. The same reactive species is assumed in the present investigation.

It is well known that the oxidation potential of an ion decreases, when it forms a complex with a substrate. Hence, the oxidation of Ru (III) in the form of a complex is much easier compared to oxidation of free ion by acid bromate. Since no radicals are detected during the course of the reaction, Ru (V) which is highly reactive, was assumed to be the reactive intermediate. This type of intermediate was also assumed by earlier workers during the oxidation of amines by Tl (III)[9].

Therefore, the proposed mechanism assumes the formation of a reversible complex between DAA and Ru (III) and oxidation of this complex by Br (V) in a slow step to Ru (V)-complex and in turn, decompostion to products in a fast step. The mechanism shown in **Scheme 1** is suggested for catalyzed reaction.
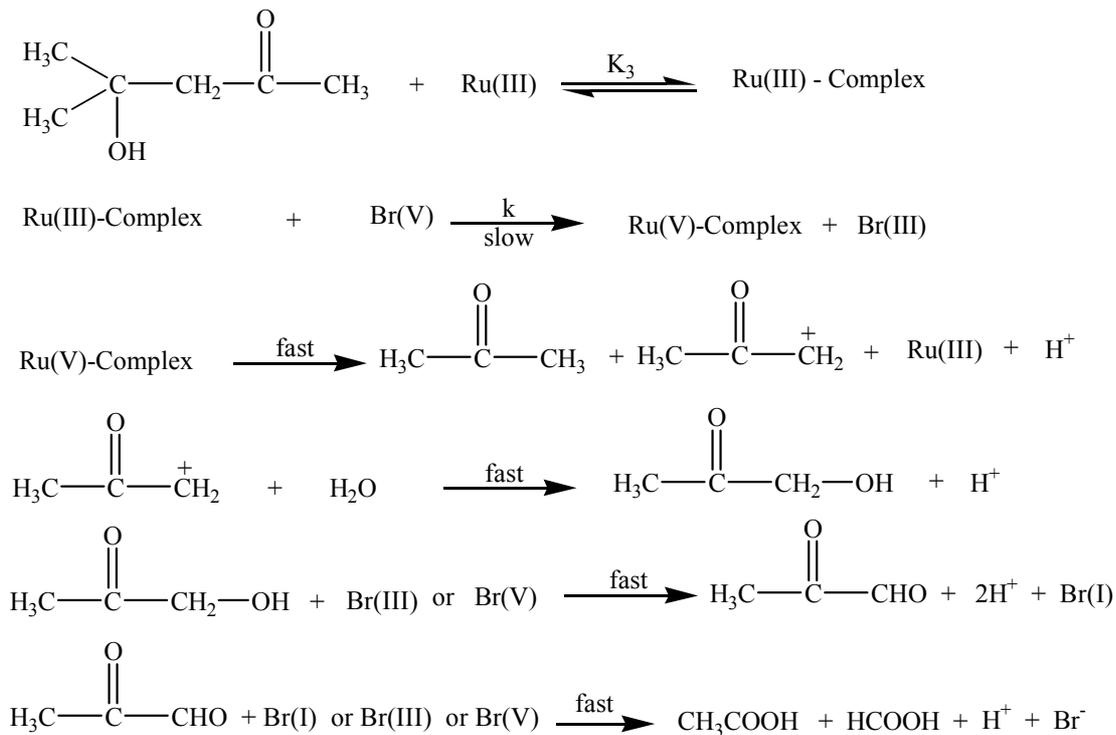
Scheme 1

The overall rate of the reaction can be written as

$$- \frac{d\,[Br(V)]}{dt} = k\,[Ru\,(III) - complex]\,[Br\,(V)] \qquad \ldots(3)$$

Since $HBrO_3$ is the reactive species of bromate, it could be substituted for Br (V) in equation (3). Substituting the values of [Ru (III)-Complex} and [Br (V)] in equation (3), we get

$$- \frac{d\,[Br\,(V)]}{dt} = \frac{k\,K_1\,K_3\,[Ru\,(III)]\,[DAA]\,[BrO_3^-]}{1 + K_3\,[DAA] + K_3\,[Ru\,(III)]} \qquad \ldots(4)$$

Since [Ru (III)] is very small (10^{-6} mol dm^{-3}, $1 >> K_3$ [Ru (III)] and hence, it can be neglected in the denominator, thus –

$$- \frac{d\,[Br\,(V)]}{dt} = \frac{k\,K_1\,K_3\,[Ru\,(III)]\,[DAA]\,[BrO_3^-]\,[H^+]}{1 + K_3\,[DAA]} \qquad \ldots(5)$$

or,

$$- \frac{2.303d\,\log\,[Br\,(V)]}{dt} = k_{obs} = \frac{k\,K_1\,K_3\,[Ru\,(III)]\,[DAA]\,[H^+]}{1 + K_3\,[DAA]} \qquad \ldots(6)$$

which explains well the experimental results obtained. k_{obs} is observed first order rate constant, k is the rate constant for the slow step and K_3 is the formation constant of the complex. Equation (6) accounts for the first order dependence of rate on $[BrO_3^-]$, [Ru (III)] and $[H^+]$ and fractional order dependence on [DAA].

Taking the reciprocal of the equation (6)

$$\frac{1}{k_{obs}} = \frac{1}{[DAA]} = [\,\frac{1}{k\,K_1\,K_3\,[Ru\,(III)]\,[H^+]}\,] + [\,\frac{1}{k\,K_1\,[Ru\,(III)]\,[H^+]}\,] \qquad \ldots(7)$$

From equation (7), it is clear that $1/k_{obs}$ vs 1/[DAA] should be linear at constant [Ru (III)] and $[H^+]$ with an intercept on Y-axis. Such plots have been in fact observed in the present study (Fig. 2). The slope of such plot is equal to $1/k\,K_1\,K_3$ [Ru (III)] $[H^+]$ and the intercept to $1/\,k\,K_1$ [Ru (III)] $[H^+]$. Taking the literature[19] value of 0.521 for the protonation constant (K_1) of BrO_3^-, the bimolecular rate constant (k) for the slow step and the formation constant of the complex (K_3) were calculated from the slope and intercept

values and are presented in the Table 3.

Table 3. Effect of temperature on rate in BrO_3^- – DAA reaction catalyzed by Ru (III)

	315 K	318 K	323 K	328 K
k x 10 $(dm^3 mol^{-1} s^{-1})$	4.07	4.67	5.75	6.92
K_3 $(dm^3 mol^{-1})$	21.7	18.9	16.1	12.7

Table 4. Activation parameters (323 K)

Reaction	E_{exp} $(k J mol^{-1})$	ΔH^* $(k J mol^{-1})$	ΔG^* $(k J mol^{-1})$	ΔS^* $(J deg^{-1} mol^{-3})$
Uncatalyzed	57.4	54.7	95.3	-125
Catalysed	38.3	35.6	83.8	-149

The activation parameters for both uncatalyzed and Ru (III) catalyzed reactions are determined and are given in Table 4. From the data, it is clear that the activation energy values are lower in the case of catalyzed reactions; thus, than in uncatalyzed reactions indicating that the reactions are enthalpy controlled. The entropy of activation (ΔS^*) is more negative in the case of catalyzed reaction showing that a rigid activated complex is formed between catalyst and substrate. The difference in ΔG^* values in uncatalyzed and catalyzed reactions indicates the operation of different mechanisms in these reactions.

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