

Mechanism of Ru(III) Catalysis in Oxidation of Levulinic Acid by Acidic Solution of N-Bromobenzamide

SHANTI KUMARI PANDEY, S.P.S. YADAV,
MANJU PRASAD and JANAK PRASAD*
Department of Chemistry
Magadh Univeristy, Bodh Gaya-824 234, India.

Kinetic data observed in Ru(III) catalysed oxidation of levulinic acid (LA) by N-bromobenzamide (NBB) in perchloric acid in the presence of mercuric acetate as Br⁻ scavenger have been reported. The reaction shows first order at low [NBB] but zero order in higher concentration range of NBB. First order in Ru(III) and zero order in LA were observed. Positive effect of [H⁺] and negative effect of addition of sodium perchlorate, potassium chloride and benzamide was observed. A suitable mechanism in conformity with the observed kinetics has been proposed.

INTRODUCTION

Although N-bromobenzamide (NBB)¹ has been, earlier, reported to be an effective oxidant, but as yet no kinetic report is available on Ru(III) catalysed oxidations with NBB as oxidant. Therefore, in the present communication, an attempt has been made to investigate the kinetics and mechanism of oxidation of levulinic acid by acidic solution of NBB using ruthenium(III) chloride as catalyst, with an aim to identify the reactive species of NBB and Ru(III) chloride.

EXPERIMENTAL

Ru(III) chloride (Johnson and Matthey) solution was prepared by dissolving its sample in 0.01 M HCl and was made up to one litre by maintaining 0.01 M HCl concentration. Aqueous solution of levulinic acid, sodium perchlorate, sodium thiosulphate, mercuric acetate, potassium chloride and benzamide, all of E. Merck grade, were prepared by dissolving their samples in doubly distilled water.

All reactants except NBB were mixed and thermostated at 35°C for thermal equilibrium. A measured amount of NBB solution, also thermostated at the same temperature, was rapidly added to the reaction mixture. The progress of the reaction was monitored by estimating the amount of unconsumed [NBB] at regular time intervals iodometrically.

RESULTS AND DISCUSSION

The kinetic data obtained for the oxidation of levulinic acid by acidic solution of N-bromobenzamide in the presence of Ru(III) chloride as catalyst show first

order in NBB at its low concentrations and first order tends to zero order at its higher concentrations. The reaction shows zero order in levulinic acid but first order kinetics is observed in Ru(III) (Table-1). The first order rate constant value increases with increase in $[H^+]$ but decreases on increasing $[NaClO_4]$, $[KCl]$ and $[Benzamide]$, showing positive effect of $[H^+]$ and negative effect of ionic strength (μ), $[Cl^-]$ and $[NBH]$ on the rate constant (Table-2). Addition of mercuric acetate did not influence the reaction rate constant, which proves that it does not catalyse the reaction and its involvement as oxidant is ruled out as the reaction does not proceed with its presence and in absence of NBB under similar conditions. The data at 30, 35, 40 and 45°C reported in Table 1 led to compute activation energy which was found to be 15.20 kcal/mole.

TABLE-1
EFFECT OF [REACTANTS] ON REACTION RATE AT 35°C
UNLESS OTHERWISE STATED

$[HClO_4] = 2.00 \times 10^{-2}$ M, $[KCl] = 5.00 \times 10^{-2}$ M, $[Hg(OAc)_2] = 4.50 \times 10^{-3}$ M,
 $\mu = 8.35 \times 10^{-2}$ M

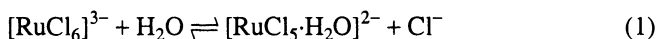
$[NBB] \times 10^3$ M	$[Levulinic\ Acid] \times 10^2$ M	$[Ru(III)] \times 10^6$ M	$\left(\frac{-dc}{dt}\right) \times 10^7$ mL ⁻¹ s ⁻¹
1.00	1.00	1.00	1.62 (1.80 ^a)
1.25	1.00	1.00	2.00 (1.82 ^a)
1.68	1.00	1.00	2.78 (1.85 ^a)
2.00	1.00	1.00	3.08 (1.71 ^a)
2.50	1.00	1.00	3.60 (1.64 ^a)
4.00	1.00	1.00	5.44 (1.55 ^a)
1.00	2.00	1.00	1.68
1.00	3.00	1.00	1.60
1.00	4.00	1.00	1.66
1.00	4.50	1.00	1.64
1.00	5.60	1.00	1.65
1.00	1.00	1.00	1.80 ^a
1.00	1.00	2.00	3.64 ^a
1.00	1.00	3.00	5.38 ^a
1.00	1.00	4.00	6.88 ^a
1.00	1.00	5.00	9.02 ^a
1.00	1.00	6.00	10.62 ^a
1.00 ^b	1.00	1.00	1.29 ^a
1.00 ^c	1.00	1.00	2.62 ^a
1.00 ^d	1.00	1.00	3.93 ^a

a $\rightarrow k_1 \times 10^4$ s⁻¹, b $\rightarrow 30^\circ\text{C}$, c $\rightarrow 40^\circ\text{C}$ and d $\rightarrow 45^\circ\text{C}$.

TABLE-2
EFFECT OF $[H^+]$, $[Cl^-]$, $[NBH]$ AND IONIC STRENGTH (μ) VARIATION ON
RATE CONSTANT AT 35°C

[Levulinic acid] = 1.00×10^{-2} , [Ru(III)] = 1.00×10^{-6} , $\mu = 8.35 \times 10^{-2}$						
$[HClO_4] \times 10^2$ M	0.50	1.00	2.00	3.00	4.00	5.00
$k_1 \times 10^4$ s ⁻¹	0.76	1.20	1.80	2.40	3.20	4.53
[NBB] = 1.00×10^{-3} M, [Hg(OAc) ₂] = 4.50×10^{-3} M, [KCl] = 1.00×10^{-2} M						
$[KCl] \times 10^2$ M	1.00	2.00	3.00	4.00	5.00	6.00
$k_1 \times 10^4$ s ⁻¹	3.86	3.40	2.98	2.20	1.80	1.31
[NBB] = 1.00×10^{-3} M, [Hg(OAc) ₂] = 4.50×10^{-3} M, [HClO ₄] = 2.00×10^{-2} M						
Ionic Strength						
$(\mu) \times 10^2$ M	7.60	8.10	9.10	10.60	11.60	12.60
$k_1 \times 10^4$ s ⁻¹	1.94	1.80	1.48	1.33	1.23	1.10
[NBB] = 2.00×10^{-3} M, [HClO ₄] = 2.00×10^{-3} M, [KCl] = 5.00×10^{-2} M and [Hg(OAc) ₂] = 2.00×10^{-3} M						
$[NBH] \times 10^3$ M	0.00	0.20	0.60	1.00	1.50	2.00
$k_1 \times 10^4$ s ⁻¹	1.94	1.61	1.24	1.00	0.71	0.45
[NBB] = 2.00×10^{-3} M, [HClO ₄] = 2.00×10^{-2} M, [KCl] = 5.00×10^{-2} M and [Hg(OAc) ₂] = 2.00×10^{-3} M						

The complexes of platinum group metals are well known. Ru(III) chloride is stable in hydrochloric acid and the following equilibrium has been reported to exist.^{2, 3}

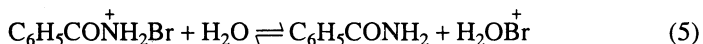


The negative effect of addition of Cl^- on the reaction rate suggests involvement of $[RuCl_5 \cdot H_2O]^{2-}$ as catalytic species in the reaction.

N-bromobenzamide may exist in the following equilibria in acidic medium like N-bromoacetamide.^{4, 5}



or

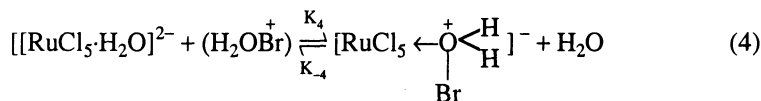
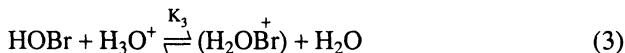
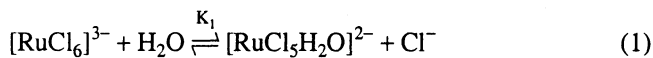


Thus in acidic medium, the reaction species of N-bromobenzamide may be either NBB itself or protonated NBB *i.e.* (NBBH) or $(H_2OBr)^+$ or HOBr may be involved in the oxidation as active species. Negative effect of benzamide neither supports involvement of NBB as such nor protonated NBB as reactive species. If HOBr is assumed as actual species then reaction should proceed even in the absence of mineral acid contrary to our observation. Hence its involvement is

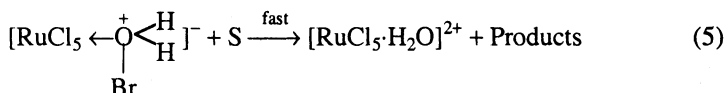
also ruled out. Hence, the only choice left is to assume (H_2OBr^+) as reactive species as it gives the rate law which explains all the observed kinetic data. Thus under the experimental conditions (H_2OBr^+) is proposed as active species of NBB in the presence of mercuric acetate as Br^- scavenger.⁶

On the basis of above discussions and kinetic data the following reaction scheme is suggested.

Reaction Scheme



Forward reaction is slowest step



where S stands for levulinic acid. Considering steps (1–4) and on applying steady state treatment to $[\text{RuCl}_5\text{H}_2\text{O}]^{2-}$, the rate of the reaction may be written in terms of loss of [NBB] as eqn. (6).

$$\frac{-d[\text{NBB}]}{dt} = \frac{k[\text{Ru(III)}][\text{NBB}][\text{H}^+]}{k_{-1}[\text{Cl}^-][\text{NBH}] + k'[\text{NBB}][\text{H}^+]} \quad (6)$$

where

$$k = k_1 k_4 k_2 k_3 \text{ and } k' = k_4 k_2 k_3$$

The rate law (6) explains all the experimental observations. Thus the mechanism seems to be valid.

REFERENCES

1. A. Poorey, L.V. Shastry, V.K. Seeriya and V.R. Shastry, *Asian J. Chem.*, **4**, 744 (1992).
2. R.C. Connik, *J. Am. Chem. Soc.*, **80**, 2646 (1958).
3. W.P. Griffith, *The Chemistry of Rare Platinum Metals*, Interscience, New York, p. 141 (1967).
4. P.S. Radhakrishnamurthi and N.C. Sahu, *Indian J. Chem.*, **20A**, 269 (1981).
5. J. Mukherjee and K.K. Banerji, *J. Org. Chem.*, **46**, 2323 (1981).
6. J.C. Bailor (Jr.), *The Chemistry of Coordination Compounds*, Reinhold, New York, p. 4 (1956).

(Received: 24 August 1998; Accepted: 3 November 1998)

AJC-1593