

**KINETICS AND MECHANISM OF RUTHENIUM(III) CATALYSED AND UNCATALYSED OXIDATION OF ETHYLAMINE AND BENZYLAMINE BY N-BROMOSUCCINIMIDE**

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**ABSTRACT**

The kinetics of ruthenium(III) catalysed oxidation of ethylamine and benzylamine by N-bromosuccinimide in aqueous acetic acid-perchloric acid medium has been investigated. The reactions are zero order in oxidant with both substrates. Fractional order dependence on ethylamine and apparent zero order in benzylamine are observed. An inverse fractional order dependence on  $[H^+]$  and first order dependence on Ru(III) are observed in the oxidation of both the substrates. The uncatalysed reactions in acetic acid-sodium acetate medium are first order in oxidant and fractional order in both the substrates. The increase in sodium acetate concentration resulted in an increase of the rate of the reaction. Suitable mechanisms and rate laws consistent with the observed kinetic results are proposed.

**Keywords:** kinetics, oxidation, ruthenium(III), ethylamine, benzylamines, N-bromosuccinimide.

**AIMS AND BACKGROUND**

Literature survey reveals that amine oxidations by various oxidising agents have been studied<sup>1-3</sup> while catalysed oxidations using transition metals as catalysts have not been studied in detail using co-oxidants like N-halo compounds. Hence, the present investigation has been undertaken using N-bromosuccinimide as an oxidant to clarify whether amine oxidations are catalysed by transition metal catalysts like ruthenium(III) and osmium(VIII) or whether the catalysis is selective to transition metal catalyst like Ru(III). The kinetics of uncatalysed, Ru(III) and Os(VIII) catalysed oxidation of ethylamine and benzylamine by N-bromosuccinimide in acetic acid-sodium acetate and acetic acid-perchloric acid mixtures is presented in the present paper.

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## EXPERIMENTAL

The reagents employed were ethylamine (Alfa Biochem), benzylamine (Thomas Baker), N-bromosuccinimide (Merck, G.R.), ruthenium(III) chloride (Johnson - Mathey), osmium tetroxide (Johnson - Mathey), mercuric acetate (Merck, G.R.). Other reagents used were of analytical grade reagent. All the solutions were prepared in doubly distilled water. Stock solutions of N-bromosuccinimide were prepared in pure acetic acid and standardised iodometrically. The progress of the reaction was followed by determining N-bromosuccinimide concentrations iodometrically in aliquots withdrawn after suitable time intervals.

## RESULTS AND DISCUSSION

### UNCATALYSED REACTIONS

The kinetics of uncatalysed oxidation of ethylamine and benzylamine by N-bromosuccinimide (NBS) has been carried out in acetic acid-sodium acetate medium. The kinetic rate data are given in Tables 1-3 and 4. It is found that the reactions are first order in NBS (Table 1) and fractional order in ethylamine. In case of benzylamine, the reaction rate is unchanged till concentration of  $1.25 \times 10^{-2}$  mol dm<sup>-3</sup> and further it increases with the substrate concentration increase, giving a fractional order (Table 2). The reaction rates are much slower in perchloric acid-acetic acid medium as compared to acetic acid-sodium acetate medium. Addition of sodium acetate resulted in an increase in kinetic rate and rate constants decreased with an increase in perchloric acid concentration (Table 3). Evidently, this means that free amine molecules are the reactive species.

Table 1. Effect of [N-bromosuccinimide] on the rate constant in the uncatalysed oxidation of amines [Ethylamine] =  $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [AcONa] = 0.1 mol dm<sup>-3</sup>; [benzylamine] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>; solvent composition = 20% AcOH : 80% H<sub>2</sub>O (v/v); temperature 313 K

[NBS] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	k <sub>1</sub> × 10 <sup>4</sup> (min <sup>-1</sup> )	
	ethylamine	benzylamine
0.5	28.04	-
1.0	27.66	323.32
2.0	27.20	340.40
4.0	27.74	348.78

**Table 2.** Kinetic data for the uncatalysed oxidation of amines by NBS  
 [NBS] =  $1.0 \times 10^{-3}$  mol dm $^{-3}$ ; [ethylamine] =  $5.0 \times 10^{-2}$  mol dm $^{-3}$ ; [AcONa] = 0.1 mol dm $^{-3}$ ; [benzylamine]  
 =  $1.25 \times 10^{-2}$  mol dm $^{-3}$ ; solvent composition = 20% AcOH : 80% H $_2$ O (v/v); temperature 313 K

Variant	Concentration of variant (mol dm $^{-3}$ )	$k_1 \times 10^4$ (min $^{-1}$ )	
		ethylamine	benzylamine
Substrate	$0.1562 \times 10^{-2}$	—	217.36
	$0.3125 \times 10^{-2}$	—	230.28
	$0.625 \times 10^{-2}$	—	239.15
	$1.25 \times 10^{-2}$	18.56	232.05
	$2.50 \times 10^{-2}$	21.43	323.32
	$5.00 \times 10^{-2}$	27.66	423.31
	$10.00 \times 10^{-2}$	36.44	—
	$20.00 \times 10^{-2}$	66.64	—
AcONa	$2.5 \times 10^{-2}$	24.20	148.58
	$5.0 \times 10^{-2}$	29.13	195.35
	$10.0 \times 10^{-2}$	27.66	232.05
	$20.0 \times 10^{-2}$	47.27	397.52
	$40.0 \times 10^{-2}$	63.96	639.98
	$80.0 \times 10^{-2}$	107.60	—
Salt	0	27.66	232.05
	0.005 KBr	24.63	—
	0.01 KBr	22.71	—
	0.02 KBr	18.35	140.55
	0.02 KCl	25.89	176.91

**Table 3.** Effect of [H $^+$ ] on the rate constants in the uncatalysed oxidation of amines by NBS  
 [NBS] =  $1.0 \times 10^{-3}$  mol dm $^{-3}$ ; [ethylamine] =  $5.0 \times 10^{-2}$  mol dm $^{-3}$ ; [benzylamine] =  $1.25 \times 10^{-2}$  mol dm $^{-3}$ ;  
 solvent composition = 20% AcOH : 80% H $_2$ O (v/v); temperature 313 K

[H $^+$ ] $\times 10^3$ (mol dm $^{-3}$ )	$k_1 \times 10^4$ (min $^{-1}$ )	
	ethylamine	benzylamine
2.5	12.44	—
5.0	11.29	—
10.0	11.53	—
20.0	9.75	75.16
40.0	5.67	63.45
60.0	3.80	—
80.0	1.87	30.11
160.0	1.55	30.54

Addition of potassium bromide did not increase the kinetic rate as expected, but rather decreased the rate (Table 2). This finding seems to be at a variance to the earlier published work<sup>4</sup>, wherein molecular bromine formed on the addition of bro-

mide to the system was taken to be the more reactive species than N-halo compounds and, hence, acceleration was expected. The present result of decrease in rate may be due to the following reasons:

1. There is no doubt that molecular bromine is formed on the addition of bromide ion.

2. The question to be decided is whether bromine in the molecular form is always a powerful oxidant whatever may be the substrate. The observed differential rate points to the fact that in the present amine reactions molecular bromine is probably not a powerful oxidant compared to N-halo compound or  $\text{Br}^+$  or  $\text{HOBr}$ , the most likely species in this reaction.

This seems to be quite in order as seen from the work of de la Mare<sup>5</sup> where it has been observed that NBS,  $\text{HOBr}$ ,  $\text{H}_2\text{OBr}^+$  or  $\text{Br}^+$  are more reactive than molecular bromine in partially aqueous systems with aromatic substrates. Hence, in the present investigation as well extending the argument to aliphatic amines, molecular bromine, which is formed, is not effective compared to the other reactive species. So, it is not surprising that the addition of bromide did not result in an increase in rate. Similarly, no increase in the rate with the addition of chloride is observed.

The effect of addition of mercuric acetate on the rate of the reaction is studied as it is reported to complex with the bromine, if any formed to give  $\text{HgBr}_2$  or  $\text{HgBr}_4^{2-}$  and the kinetic data are presented in Table 4.

Table 4. Kinetic data for the uncatalysed oxidation of amines by NBS  
 $[\text{NBS}] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{ethylamine}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{AcONa}] = 0.1 \text{ mol dm}^{-3}$ ;  $[\text{benzylamine}] = 1.25 \times 10^{-2} \text{ mol dm}^{-3}$ ; solvent composition = 20% AcOH : 80%  $\text{H}_2\text{O}$  (v/v); temperature 313 K

Variant	Concentration of variant ( $\text{mol dm}^{-3}$ )	$k, \times 10^4 (\text{min}^{-1})$	
		ethylamine	benzylamine
Mercuric acetate	0	27.66	232.05
	$0.5 \times 10^{-2}$	26.37	211.90
	$1.0 \times 10^{-2}$	23.68	201.57
	$2.0 \times 10^{-2}$	—	193.36
Solvent composition %AcOH : % $\text{H}_2\text{O}$ (v/v)	5 : 95	49.92	339.00
	10 : 90	34.35	319.14
	20 : 80	27.66	232.05
	40 : 60	—	89.50
	50 : 50	12.11	—
	60 : 40	—	27.86
Temperature	30°C	9.53	90.47
	40°C	27.86	232.05
	50°C	79.35	618.90

In this investigation the finding is that there is minimum retardation on the addition of mercuric acetate as seen by the rate constants in the presence and absence of mercuric acetate. The ratio of N-bromosuccinimide: mercuric acetate has been kept 1:5 and 1:10 in the present investigation. This observation coupled with effect of Br<sup>-</sup> shows that the molecular bromine is not an effective oxidant in these processes. It can be stated that the more likely species are either NBS, Br<sup>+</sup>, H<sub>2</sub>OBr<sup>+</sup> or HOBr, depending upon the experimental conditions.

#### NATURE OF THE SPECIES IN THE PRESENT INVESTIGATION

It can be stated that the most likely reactive species are NBS, Br<sup>+</sup>, H<sub>2</sub>OBr<sup>+</sup> or HOBr, depending on the experimental conditions employed. It is difficult to distinguish between Br<sup>+</sup> and H<sub>2</sub>OBr<sup>+</sup> as the energy barrier between these two is much smaller. In the present study most of the experiments has been done in acetic acid-sodium acetate mixtures where the acidity is not very large due to pH being 3.5 to 4.8. This finally settles the probable likely species as NBS and not Br<sup>+</sup> or H<sub>2</sub>OBr<sup>+</sup> in this investigation.

Kinetic rate decreases with the increase in percentage of acetic acid composition in all the substrates studied (Table 4). In other words, decrease in dielectric constant of the medium decreases the rate of the reaction. It appears that these reactions are between two dipolar molecules, N-bromosuccinimide and the amine.

For the dipole-dipole type of reaction under consideration, the equation<sup>6</sup> for specific rate constant *k* will be:

$$\ln k = \ln \left[ x \frac{kT}{h} k_0 \right] - \frac{1}{kT} \left[ \frac{D-1}{2D+1} \right] \left[ \frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} + \frac{\mu_m^2}{r_m^3} \right] + \left[ \frac{\phi_A + \phi_B - \phi_M^*}{kT} \right]$$

A plot of lg *k* versus  $\frac{D-1}{2D+1}$  will be linear if non-electrostatic terms are negligibly small. In the present investigation the plots of lg *k*<sub>1</sub> versus  $\frac{D-1}{2D+1}$  are linear confirming the dipole-dipole nature of the reaction. The two dipolar molecules, which are participating in the reaction, are NBS and amine.

The reactions were carried out at three different temperatures to compute various activation parameters (Table 4). The calculated Arrhenius parameters are of right order for bimolecular reactions (Table 5).

**Table 5.** Arrhenius parameters for the uncatalysed oxidation of amines by NBS at 313 K  
[NBS] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [AcONa] = 0.1 mol dm<sup>-3</sup>; solvent composition = 20% AcOH : 80% H<sub>2</sub>O (v/v)

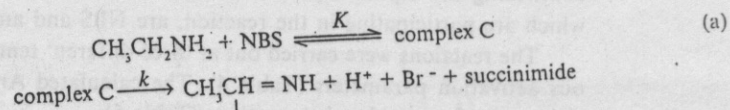
Substance	ΔE* (kJ mol <sup>-1</sup> )	ΔH* (kJ mol <sup>-1</sup> )	lg PZ	-ΔS* (J K <sup>-1</sup> mol <sup>-1</sup> )	ΔG* (kJ mol <sup>-1</sup> )
Ethylamine	86.16	83.56	10.04	61.354	102.76
Benzylamine	78.98	76.38	9.767	66.659	97.24

### COMPARISON OF RATES OF ETHYLAMINE AND BENZYLAMINE

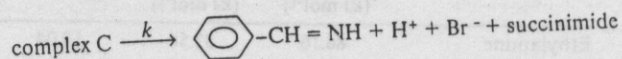
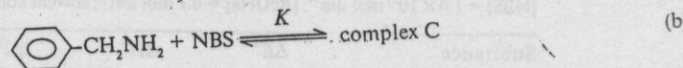
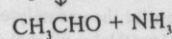
Under the experimental conditions studied benzylamine reacts faster than ethylamine as seen from the first order rate constants  $27.66 \times 10^{-4} \text{ min}^{-1}$  and  $423.313 \times 10^{-4} \text{ min}^{-1}$  for ethylamine and benzylamine, respectively at  $0.001 \text{ mol dm}^{-3}$  NBS,  $[\text{sub.}] = 5.0 \times 10^{-2} \text{ mol dm}^{-3}$ , 20% AcOH - 80%  $\text{H}_2\text{O}$ ,  $0.1 \text{ mol dm}^{-3}$  sodium acetate and  $40^\circ\text{C}$ . The reason for the higher reactivity of benzylamine is obviously the electron releasing nature of phenyl group due to its conjugate ability.

### MECHANISM OF UNCATALYSED REACTION

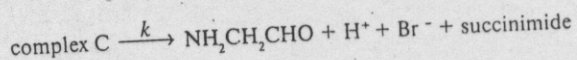
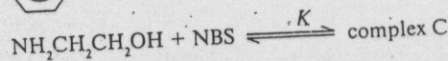
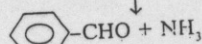
The reaction involves a prior complexation between amine and the oxidant which in a rate-determining step yields imine. The imine in a fast step hydrolyses to give the primary oxidation product aldehyde.



$\text{H}_2\text{O}$  fast



$\text{H}_2\text{O}$  fast



Rate law:

$$\text{rate} = \frac{kK[\text{NBS}]_T[\text{S}]}{1 + K[\text{S}]}$$

The above rate equation explains the first order dependence in oxidant and fractional order in substrate.

### EFFECT OF TRANSITION METAL CATALYSTS ON THE REACTION RATE

*Osmium(VIII) catalysed reactions.* The reaction rates are insensitive to the addition of  $\text{Os(VIII)}$ , indicating that  $\text{Os(VIII)}$  is not an effective catalyst in these reactions.

**Table 6.** Kinetic data for the Ru(III) catalysed oxidation of amines by NBS  
 [NBS] =  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup>; [ethylamine] =  $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>;  
 [benzylamine] =  $1.25 \times 10^{-2}$  mol dm<sup>-3</sup>; solvent composition = 20% AcOH : 80% H<sub>2</sub>O (v/v); temperature  
 313 K

Variant	Concentration of variant (mol dm <sup>-3</sup> )	$k_0 \times 10^5$ (mol min <sup>-1</sup> )	
		ethylamine*	benzylamine**
NBS	$0.5 \times 10^{-3}$	1.08	3.10
	$1.0 \times 10^{-3}$	1.10	3.19
	$2.0 \times 10^{-3}$	1.30	3.11
	$4.0 \times 10^{-3}$	1.20	-
Substrate	$0.156 \times 10^{-2}$	-	3.00
	$0.312 \times 10^{-2}$	-	2.95
	$0.625 \times 10^{-2}$	-	3.33
	$1.25 \times 10^{-2}$	0.58	3.19
	$2.50 \times 10^{-2}$	0.71	3.05
	$5.00 \times 10^{-2}$	1.10	3.38
	$10.0 \times 10^{-2}$	1.21	-
	$20.0 \times 10^{-2}$	1.37	-
Ru(III)	$40.0 \times 10^{-2}$	1.99	-
	$0.0195 \times 10^{-5}$	0.173	-
	$0.190 \times 10^{-5}$	0.317	-
	$0.475 \times 10^{-5}$	0.613	-
	$0.712 \times 10^{-5}$	0.749	-
	$0.95 \times 10^{-5}$	1.100	-
	$1.90 \times 10^{-5}$	1.742	2.46
	$3.80 \times 10^{-5}$	-	3.19
	$7.60 \times 10^{-5}$	-	5.67
	$15.2 \times 10^{-5}$	-	8.50

\*At  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup> H<sup>+</sup> and  $0.95 \times 10^{-5}$  mol dm<sup>-3</sup> Ru(III); \*\*at  $4.0 \times 10^{-2}$  mol dm<sup>-3</sup> H<sup>+</sup> and  $3.80 \times 10^{-5}$  mol dm<sup>-3</sup> Ru(III).

*Ruthenium(III) catalysed reactions.* Ru(III) catalysed oxidation of ethylamine and benzylamine has been carried out in aqueous acetic acid-perchloric acid mixture. The reactions are zero order in NBS (Table 6). Fractional order dependence on ethylamine and apparent zero order in benzylamine are observed. The oxidation reactions of both substrates are first order with respect to Ru(III), and an inverse fractional dependence on [H<sup>+</sup>] is observed in the oxidation of benzylamine. Increasing the acid concentration, the rate constants are found to be constant till 0.02 mol dm<sup>-3</sup> acid concentration in the oxidation of ethylamine and later an inverse fractional dependence on [H<sup>+</sup>] is found (Table 7). As the reaction rate decreased with increase in [H<sup>+</sup>], probably the free amine molecules are the predominant species. The reaction rate decreases with decrease in dielectric constant as required for dipole-dipole reactions. Therefore, the major reaction is between free amine and free NBS molecules. The rate of the reaction decreased with an increase in the

Variant	Concentration of variant (mol dm <sup>-3</sup> )	k <sub>1</sub> × 10 <sup>4</sup> (min <sup>-1</sup> )
H <sup>+</sup>	1.0 × 10 <sup>-2</sup>	1.10
	2.0 × 10 <sup>-2</sup>	1.10
	4.0 × 10 <sup>-2</sup>	0.65
	8.0 × 10 <sup>-2</sup>	0.45
	16.0 × 10 <sup>-2</sup>	0.31
Solvent composition % AcOH : % H <sub>2</sub> O (v/v)	5:95	1.06
	10:90	1.04
	20:80	1.10
	40:60	0.308
	60:40	0.099
	80:20	0.031
Temperature	30°C	0.38
	40°C	1.10
	50°C	1.84

composition of acetic acid (Table 7). The variation of temperature is carried out and the Arrhenius parameters are calculated (Table 8).

**Table 7.** Kinetic data for the Ru(III) catalysed oxidation of amines by NBS  
[NBS] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [ethylamine] = 5.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [benzylamine] = 1.25 × 10<sup>-2</sup> mol dm<sup>-3</sup>; solvent composition = 20% AcOH : 80% H<sub>2</sub>O (v/v); temperature 313 K

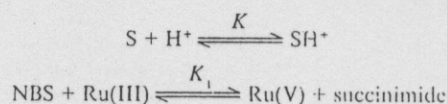
Variant	Concentration of variant (mol dm <sup>-3</sup> )	k <sub>1</sub> × 10 <sup>4</sup> (min <sup>-1</sup> )	
		ethylamine*	benzylamine**
H <sup>+</sup>	1.0 × 10 <sup>-2</sup>	1.10	3.33
	2.0 × 10 <sup>-2</sup>	1.10	3.28
	4.0 × 10 <sup>-2</sup>	0.65	3.19
	8.0 × 10 <sup>-2</sup>	0.45	3.31
	16.0 × 10 <sup>-2</sup>	0.31	3.37
	40.0 × 10 <sup>-2</sup>	—	2.55
	80.0 × 10 <sup>-2</sup>	—	2.28
Solvent composition % AcOH : % H <sub>2</sub> O (v/v)	5:95	1.06	5.60
	10:90	1.04	5.22
	20:80	1.10	3.19
	40:60	0.308	1.80
	60:40	0.099	0.86
Temperature	30°C	0.38	2.06
	40°C	1.10	3.19
	50°C	1.84	9.11

\*At 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> H<sup>+</sup> and 0.95 × 10<sup>-5</sup> mol dm<sup>-3</sup> Ru(III); \*\*at 4.0 × 10<sup>-2</sup> mol dm<sup>-3</sup> H<sup>+</sup> and 3.80 × 10<sup>-5</sup> mol dm<sup>-3</sup> Ru(III).

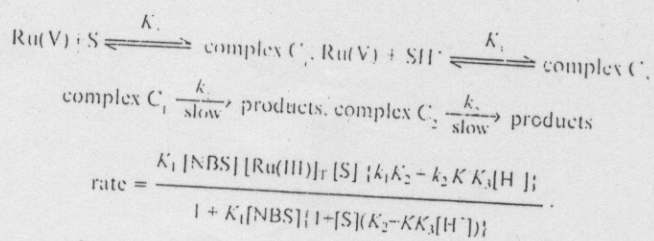
**Table 8.** Arrhenius parameters for the Ru(III) catalysed oxidation of amines by NBS at 313 K  
[NBS] = 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; [Hg(OAc)<sub>2</sub>] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>; solvent composition = 20% AcOH : 80% H<sub>2</sub>O (v/v)

Substance	ΔE* (kJ mol <sup>-1</sup> )	ΔH* (kJ mol <sup>-1</sup> )	lg PZ	-ΔS* (J K <sup>-1</sup> mol <sup>-1</sup> )	ΔG* (kJ mol <sup>-1</sup> )
Ethylamine	66.06	63.45	4.28	171.61	117.17
Benzylamine	59.36	56.75	3.63	184.17	114.90

MECHANISM AND RATE LAW FOR Ru(III) CATALYSED OXIDATION OF ETHYLAMINE AND BENZYLAMINE BY NBS







The above rate law explains the apparent zero order in N-bromosuccinimide, first order in Ru(III), fractional order in ethylamine and apparent zero order in benzylamine, inverse fractional order in  $[\text{H}^+]$  with ethylamine and benzylamine.

### CONCLUSIONS

Uncatalysed oxidation of ethylamine and benzylamine by N-bromosuccinimide reveals the following features: benzylamine reacts faster than ethylamine due to the conjugated influence of the aromatic ring. The reaction is first order in oxidant and fractional order in both the substrates.

Ru(III) catalysed oxidation of these two substrates shows that the reaction is zero order in oxidant, first order in Ru(III), inverse fractional order on  $[\text{H}^+]$  and the order on substrate varies fractional with ethylamine to zero order in benzylamine. Os(VIII) is ineffective in these reactions as a catalyst.

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