CHEMICAL KINETICS
AND CATALYSIS

Kinetics of Ruthenium(III) Catalyzed and Uncatalyzed Oxidation of Monoethanolamine by *N*-Bromosuccinimide[1]

R. Venkata Nadh[a],*, B. Syama Sundar[b], and P. S. Radhakrishnamurti[c]

[a]GITAM University—Bengaluru Campus, Karnataka 561203, India
[b]Yogi Vemana University, Kadapa 516216, India
[c] Department of Chemistry, TJPS (PG) College, Guntur-522006, India
*e-mail: doctornadh@yahoo.co.in

Abstract—Kinetics of uncatalyzed and ruthenium(III) catalyzed oxidation of monoethanolamine by *N*-bromosuccinimide (NBS) has been studied in an aqueous acetic acid medium in the presence of sodium acetate and perchloric acid, respectively. In the uncatalyzed oxidation the kinetic orders are: the first order in NBS, a fractional order in the substrate. The rate of the reaction increased with an increase in the sodium acetate concentration and decreased with an increase in the perchloric acid concentration. This indicates that free amine molecules are the reactive species. Addition of halide ions results in a decrease in the kinetic rate, which is noteworthy. Both in absence and presence of a catalyst, a decrease in the dielectric constant of the medium decreases the kinetic rate pointing out that these are dipole—dipole reactions. A relatively higher oxidation state of ruthenium i.e., Ru(V) was found to be the active species in Ru(III) catalyzed reactions. A suitable mechanism consistent with the observations has been proposed and a rate law has been derived to explain the kinetic orders.

INTRODUCTION

Plants, animals, and vegetation emit volatile amines. Naturally aminoalcohols are produced by biodegradation amino acids [1]. Monoethanolamine (MEA) finds extensive applications in the synthesis of surfactants, pharmaceuticals, and as addition agents in the metal finishing industry [2]. Compared to other amines, MEA is cheap, has a high absorption capacity and reacts quickly with gaseous CO_2 [3, 4]. Hence, MEA is the benchmark solvent in carbon capture and storage (CCS), a technology aimed at reducing CO_2 emissions in large combustion industries [5]. To accurately assess the environmental impact of CCS, a better knowledge on the reactions of MEA is necessary. Considerable attention has been centered on the chemistry of *N*-halomines, because of their versatility in behaving as mild oxidants, halogenating agents, and *N*-anions, which act as both bases and nucleophiles. As a result these reagents react with a wide range of functional groups [6—9].

Literature collection shows that kinetics of oxidation of amino alcohols was studied using different oxidants like vanadium(V) as an oxidant in aqueous perchloric acid medium [10], potassium diperiodato-cupate(III) in alkaline medium [11], *N*-bromosuccinimide in alkaline medium in absence and in presence of non-ionic micellar aggregates [12]. Similarly, kinetics of oxidation of aminoalcohols by chloramine-T was studied in perchloric acid medium in presence of palladous chloride as catalyst [13] and in alkaline medium [14, 15].

The above literature survey shows that various oxidizing agents have studied oxidations of amino acids but catalyzed oxidations using transition metals, as catalysts have not been studied in detail by using co-oxidants like *N*-halo compounds. The present investigation has been under taken using *N*-bromosuccinimide (NBS) as an oxidant to clarify whether oxidations of monoethanolamine are catalyzed by transition metal catalysts like Ru(III) and Os(VIII) or whether the catalysis is selective to transition metal catalysts like Ru(III). Hence a systematic investigation has been done in acetic acid—perchloric acid mixtures to throw light on the nature of reaction orders and mechanistic sequences.

EXPERIMENTAL

The reagents employed were monoethanolamine (Loba sample), *N*-bromo succinimide (GR, S.Merck Grade), ruthenium(III) chloride (Johnson Mathey,

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Table 1. Rate constants for uncatalyzed oxidation of monoethanolamine by *N*-bromosuccinimide in acetic acid—sodium acetate medium. Common conditions: [NBS] = 1.0×10^{-3} M [Monoethanolamine] = 1.0×10^{-2} M, [AcONa] = 0.1 M, Temp. = 40°C, solvent = 20% AcOH : 80% H_2O (vol/vol)

Variant	Conc. of oxidant, M	$k_1 \times 10^4$, min^{-1}
Oxidant	0.5×10^{-3}	17.36
	1.0×10^{-3}	17.65
	2.0×10^{-3}	16.74
	4.0×10^{-3}	16.48
Monoethanol-amine	0.125×10^{-2}	9.79
	0.25×10^{-2}	10.79
	0.50×10^{-2}	12.27
	1.00×10^{-2}	17.65
	2.00×10^{-2}	26.59
Sodium acetate	2.5×10^{-2}	6.69
	5.0×10^{-2}	9.73
	10.0×10^{-2}	17.65
	20.0×10^{-2}	28.55
	40.0×10^{-2}	62.58
	80.0×10^{-2}	106.10
Added halide	0	17.65
	0.02 M KBr	6.29
	0.02 M KCl	11.67
Acetic acid composition	5 : 95	25.27
	10 : 90	20.74
	20 : 80	17.65
	40 : 60	8.77
	60 : 40	6.60
Os(VIII)	0.0	17.65
	6.40×10^{-5}M	17.89
	12.80×10^{-5}M	17.78
	19.20×10^{-5}M	17.91
	25.60×10^{-5}M	17.98
Temperature	40	17.65
	50	43.85
	60	120.39

London), osmium tetroxide (Johnson and Mathey Co., London), mercuric acetate (E.Merck G.R.), other reagents used were of analytical grade reagents. All the solutions were prepared by doubly distilled water. Stock solutions of *N*-bromosuccinimide were prepared in pure acetic acid and standardized iodometrically.

Kinetic studies were carried out in a perchloric acid medium under pseudo first order conditions with a large excess of monoethanolamine over NBS. The progress of reaction was followed by determining *N*-bromosuccinimide concentrations iodometrically in aliquots withdrawn after suitable time intervals [16]. Compared to the rates of present reaction, self decomposition rates of NBS were negligibly smaller under the conditions employed. The rate constants remained practically unaltered in air or in a de-aerated atmosphere. Only a representative set of the average values of kinetic data in aqueous acetic acid medium was presented here. First order rate constants were evaluated from the linear plots ($r^2 > 0.993$) of log [unreacted DCICA] against time. Rate constants and other determined values were reproducible to ±2%.

RESULTS AND DISCUSSION

Uncatalyzed Oxidations

Effect of reactants on the rate. Linear plots of $\log(a - x)$ versus time and constancy of k_1 values at different *N*-bromosuccinimide concentrations are confirming unit dependence with respect to *N*-bromosuccinimide (Table 1). Plots of log k_1 versus log [S] are linear with a slope of nearly 0.5 indicates a fractional order dependence on substrate concentration. Addition of sodium acetate results in increase in kinetic rate. Evidently this means that free amine molecules are the reactive species. A decrease of rate of reaction was observed with an addition of the reaction product (succinimide) indicating that succinimide is involved in a fast pre-equilibrium to the rate-determining step.

Effect of added salt. Potassium halides are added to the reaction mixture and the reaction rates are determined (Table 1). Addition of potassium bromide did not increase the kinetic rate as expected but rather decreased the rate. By an addition of halide ions in oxidation of aminoalcohols with chloramines-T, a decrease in rate of reaction was observed in perchloric acid medium [13], whereas, no effect of added halide ions was observed in alkaline buffer medium [15, 17]. Finding in the present case seems to be at variance to the earlier published work [18, 19], where in molecular bromine formed on the addition of bromide to the system was taken to be the more reactive species than

N-halo compounds and hence acceleration was expected. The present result of stopping the rate may be due to the following reasons:

1. There is no doubt that molecular bromine is formed on the addition of higher concentration of Br$^-$ 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 reactions molecular bromine is probably not a powerful oxidant compared to *N*-halo compound or Br$^+$ or HOBr the likely species in this reaction.

This seems to be quite in order as seen from the work of de la Mare and our earlier work where in it has been observed that NBS or HOBr or H$_2$OBr$^+$ or Br$^+$ are more reactive than molecular bromine in partially aqueous systems with different substrates [20–22]. Hence in the present investigation as well extending the argument to aliphatic amino acid, molecular bromine, which is formed, is not effective compared to the other reactive species. So, it is not surprising that the addition of Br$^-$ did not result in increase in rate. It was observed that change in the concentration of added mercuric acetate had negligible effect on the rate. The function of added mercuric acetate is therefore only to fix up Br$^-$ formed in the course of the reaction as HgBr$_2$ or HgBr$_4^{2-}$.

Nature of the species in the present investigation. It can be stated that the likely species are NBS or Br$^+$ or H$_2$OBr$^+$ or HOBr depending upon the experimental conditions employed. It is difficult to distinguish between Br$^+$ and H$_2$OBr$^+$ as the energy barrier between these two is much smaller. It is evident that Br$^+$ formation requires that Br$^+$ should be in triplet state. The conversion of singlet to triplet in 4*p* electron shell of bromine is much easier compared to 3*p* electron shell of chlorine [19]. The possibility of the species Br$^+$ or H$_2$OBr$^+$ is generally in acidic conditions. But in the present study most of the experimentation has been done in acetic acid - sodium acetate mixtures where in 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$^+$ or H$_2$OBr$^+$ in this investigation.

Effect of variation of solvent composition. In order to determine the effect of dielectric constant (polarity) of the medium on rate, the oxidation of monoethanolamine by NBS was studied in aqueous acetic acid mixtures of various compositions (Table 1). The rate of the reaction decreased with increase in the percentage of acetic acid in the mixture. In other words, decrease in the dielectric constant of the medium decreases the rate of reaction. This indicates that there is a charge development in the transition state involving a more polar activated complex than the reactants [23, 24].

Amis showed that in a straight line plot of logarithm k_{obs} versus $1/D$, a positive slope indicates a positive ion–dipole reaction, while a negative slope indicates the involvement of two dipoles or a negative ion-dipole reaction [25]. In this investigation a plot of logarithm k_{obs} versus $1/D$, give straight lines with negative slopes; these results clearly support the involvement of two dipoles in the rate determining step.

For the dipole-dipole type of reaction, Laidler and Eyring treatment [26] can be applied. Laidler and Eyring derived an expression for the free energy transfer of a polar molecule with a dipole moment μ from a vacuum to a medium of dielectric constant *D*. This equation is in the following form for a molecule of radius *r* which has symmetrical charge distribution.

$$F = \underline{k}T \ln \beta = -\frac{\mu}{r^3}\left[\frac{D-1}{2D+1}\right].$$

Introducing a non electrostatic term, this becomes

$$F = \underline{k}T \ln \beta = -\frac{\mu}{r^3}\left[\frac{D-1}{2D+1}\right] + \phi.$$

For the reaction under consideration, the equation for specific velocity constant *k* will be

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

A plot of $\log k$ versus $\frac{D-1}{2D+1}$ will be linear if non-electrostatic terms are negligibly small. In the present investigation the plots of $\log k_1$ versus $\frac{D-1}{2D+1}$ are also linear confirming dipole—dipole nature of reaction. The two neutral molecules, which are participating in the reaction, are NBS and amine.

Test for free radicals. To test for free radicals, the reaction mixture containing stabilizer free acrylonitrile was kept for 24 h in an inert atmosphere [27]. On diluting the reaction mixture by methanol and no precipitate was observed. It is indicating that there is no intervention of free radicals in the reaction.

Differential protonation in ethylamine, benzylamine, and monoethanolamine in acid medium. It is well known that the primary amines get protonated in acidic media, hence protonation is the factor of utmost importance in amine derivatives. The free amine molecules are the reactive species as there is fractional dependence of acidity in the oxidation of ethylamine and benzylamine by *N*-bromosuccinimide in aqueous acetic acid—perchloric acid medium [22]. For monoethanolamine the presence of hydroxyl group makes the protonation difficult at the amine end due to the electron with drawing nature of hydroxy group. Hence it appears that the acidity dependence has to be traced to the protonation of NBS predomi-

Table 2. Arrhenius parameters at 313 K for uncatalyzed oxidation of monoethanolamine by *N*-bromosuccinimide in acetic acid—sodium acetate medium

Substrate	$\Delta E^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\log_{10} PZ$	$-\Delta S^{\neq}$, J K^{-1} mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
Monoethanolamine	81.4	78.8	9.1	79.9	103.8

nantly. In summary what is postulated is, in simple amines protonation of the amine takes place to large extent in preference to protonation of the NBS. In monoethanolamine electron availability is reduced at the nitrogen in amino group due to the presence of hydroxyl group, so the protonation probably takes place at the NBS in preference to the monoethanolamine. This is utilized in postulating a different mechanistic pathway for oxidation of monoethanolamine compared to ethylamine and benzylamine by *N*-bromosuccinimide though oxidation of all these substrates were carried out in the same set of experimental conditions.

Comparison of rates of ethylamine and monoethanolamine. The kinetic rates are higher for oxidation of monoethanolamine compared to earlier work of ethylamine oxidation under similar conditions [22]. Strictly speaking a discussion of structural reactivity is not very ideal as the sites of oxidation in these compounds are different. In the former it is the alcoholic group that is attacked where as amine group is oxidized in the latter. But a broad comparison is relevant as alcohol oxidations are faster than amine oxidations in aliphatic series.
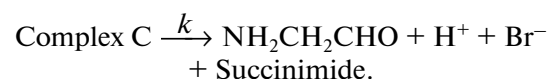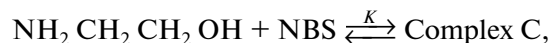
Effect of osmium(VIII). Osmium(VIII) catalyst has no effect on the rate of oxidation of monoethanolamine by *N*-bromosuccinimide in aqueous acetic acid—sodium acetate buffer medium (Table 1).

Rate and activation parameters. The effect of temperature on the rate of the reaction was studied in the range (313–333 K) and the results were shown in Table 2. From Arrhenius plot, the value of energy of activation ($\Delta E^{\neq}$), enthalpy ($\Delta H^{\neq}$), entropy ($-\Delta S^{\neq}$), and free energy ($\Delta G^{\neq}$) were computed. Large negative value of entropy ($-\Delta S^{\neq}$) are observed, which can be attributed to the severe restriction of solvent molecules (electrostriction) around the transition state [28]. It also indicates that the complex is more ordered than the reactants [29]. The observed modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

Product analysis. In alkaline buffer medium, formaldehyde, formic acid and ammonia were the reported products in the oxidation of monoethanolamines by sodium *N*-bromobenzenesulfonamide [17], sodium *N*-chloro-*p*-toluenesulphonamide [15]. In the present case, non-formation of formic acid and ammonia was confirmed from negative tests for chromotropic acid procedure [30] and Nessler's reagent test [31], respec-

tively. Formation of 2-aminoethanol as product was confirmed from the pmr peaks at δ 1.5, 3.7, and 9.7, respectively corresponding to protons of amine, methylene and aldehyde groups.

Mechanism of uncatalyzed reaction:

$$NH_2\,CH_2\,CH_2\,OH + NBS \underset{K}{\rightleftharpoons} \text{Complex C},$$

$$\text{Complex C} \xrightarrow{k} NH_2CH_2CHO + H^+ + Br^- + \text{Succinimide.}$$

Rate law:

$$\text{Rate} = k[\text{Complex}]$$
$$= kK[\text{Substrate}]\,[\text{NBS}] \rightarrow (1),$$
$$[\text{NBS}]_T = [\text{NBS}] + [\text{Complex}]$$
$$= [\text{NBS}] + K[\text{NBS}]\,[S] = [\text{NBS}]\,\{1 + K[S]\} \rightarrow (2)$$
$$\text{from (1) and (2),}$$
$$\text{rate} = \frac{kK\,[\text{NBS}]_T\,[S]}{1 + K\,[S]} \rightarrow (3).$$

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

Ru(III) Catalyzed Reactions

Ruthenium(III) chloride accelerates the oxidation of monoethanolamine by NBS in aqueous acetic acid—perchloric acid medium and the kinetic features are as follows. Plots of $\log(a - x)$ versus time for the disappearance of NBS are linear indicating first order in NBS and increase in concentration of NBS yields fairly constant first order rate constants confirming the first order dependence on NBS (Table 3). Increase in concentration of ethanolamine increased the kinetic rate and plot of $\log k_1$ versus $\log [S]$ are linear with a slope nearly 0.33 indicating fractional order on substrate concentration. Increase of concentration of Ru(III) has no effect on the reaction kinetics in the range of [Ru(III)] studied indicating apparent zero order on the catalyst Ru(III). The effect of acid concentration on the reaction kinetics has been studied and the first order rate constants are recorded in Table 3. The rate constants decrease with increase in concentration of perchloric acid. A linear plot with a slope -1.09 indicates the inverse unit dependence on [H$^+$]. As the reaction rate decreased with increase in H$^+$, probably the free substrate molecules are the predominant species. The reactions have been carried out at various solvent compositions to find the effect of

Table 3. Rate constants for Ru(III) catalyzed oxidation of monoethanolamine by *N*-bromosuccinimide in acetic acid—perchloric acid medium. Common conditions: [NBS] = 1.0×10^{-3} M [monoethanolamine] = 10.0×10^{-3} M, [Hg(OAc)$_2$] = 2.0×10^{-2} M, [H$^+$] = 1.0 M, solvent = 20% AcOH : 80% H$_2$O (vol/vol) [Ru(III)] = 3.8×10^{-5} M, Temp. = 40°C

Variant	[Variant], M	$k_1 \times 10^4$, min^{-1}
[NBS]	0.5×10^{-3}	290.93
	1.0×10^{-3}	324.95
	2.0×10^{-3}	307.84
	4.0×10^{-3}	307.91
[Monoethanolamine]	0.625×10^{-3}	113.87
	1.25×10^{-3}	166.97
	2.5×10^{-3}	211.60
	5.0×10^{-3}	273.62
	10.0×10^{-3}	324.95
	20.0×10^{-3}	450.82
	40.0×10^{-3}	555.85
[Ru(III)]	1.9×10^{-5}	353.01
	3.8×10^{-5}	324.95
	7.6×10^{-5}	331.90
	15.2×10^{-5}	348.68
[H$^+$]	0.25	390.40
	0.5	344.79
	1.0	324.95
	2.0	134.30
	4.0	78.57
Solvent composition AcOH : H$_2$O (vol %/vol %)	5 : 95 (vol/vol)	522.20
	10 : 90 (vol/vol)	408.73
	20 : 80 (vol/vol)	324.95
	40 : 60 (vol/vol)	238.98
	60 : 40 (vol/vol)	80.76
Temperature	40°C	324.35
	50°C	619.36
	60°C	1253.87

change in dielectric constant. Increase in acetic acid percentage decreases the rate, showing that decrease in dielectric constant decreases the reaction rate indicating that dipole-dipole reactions as the major reaction in between free substrate and free NBS molecules.

Table 4. Arrhenius parameters at 313 K for Ru(III) catalyzed oxidation of monoethanolamine by *N*-bromosuccinimide in acetic acid—perchloric acid medium
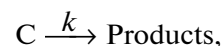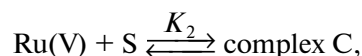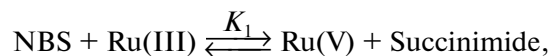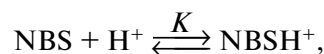
$\Delta E^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\log_{10} PZ$	$-\Delta S^{\neq}$, J K^{-1} mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
57.4	54.8	7.3	114.1	91.7

The reactions are carried out at four different temperatures 40, 50, and 60°C and reaction rate constants are recorded in. Plot of $\log k_1$ versus $1/T$ is linear. Arrhenius parameters are calculated (Table 4).

Nature of Ru(III) species. Electronic spectrum of Ru(III) chloride shows that probably it exists as [Ru(H$_2$O)$_6$]$^{3+}$ under acid conditions [18, 32, 33] while the species like [RuCl$_5$.H$_2$O]$^{2-}$, [RuCl(H$_2$O)$_5$]$^{2+}$ [RuCl$_4$(H$_2$O)$_2$]$^{1-}$, [RuCl$_3$(H$_2$O)$_3$], [RuCl$_2$(H$_2$O)$_4$]$^{+1}$, [RuCl(H$_2$O)$_5$]$^{2+}$, and [Ru(H$_2$O)$_6$]$^{3+}$ are present in aqueous solutions. The most active species is [Ru(H$_2$O)$_6$]$^{3+}$, in acid medium which is formed due to the following equilibrium:

$$[\text{Ru (H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}^+ \rightleftharpoons [\text{Ru(H}_2\text{O)}_6]^{3+}.$$

Mechanism and rate law for the Ru(III) catalyzed oxidation of monoethanolamine by *N*-bromosuccinimide. The sequence of reactions is given below:

$$\text{NBS} + \text{H}^+ \overset{K}{\rightleftharpoons} \text{NBSH}^+,$$

$$\text{NBS} + \text{Ru(III)} \overset{K_1}{\rightleftharpoons} \text{Ru(V)} + \text{Succinimide},$$

$$\text{Ru(V)} + \text{S} \overset{K_2}{\rightleftharpoons} \text{complex C},$$

$$\text{C} \overset{k}{\longrightarrow} \text{Products},$$

$$\text{Rate} = k\text{C} = kK_2 \,[\text{Ru(V)}][\text{S}]$$
$$= kK_1K_2 \,[\text{NBS}] \,[\text{Ru(III)}] \,[\text{S}],$$

$$[\text{NBS}]_\text{T} = [\text{NBS}] + [\text{NBSH}^+] + [\text{Ru(V)}] + [\text{C}]$$
$$= [\text{NBS}] + K[\text{H}^+] \,[\text{NBS}] + K_1[\text{NBS}] \,[\text{Ru(III)}]$$
$$+ K_1K_2[\text{S}][\text{NBS}][\text{Ru(III)}]$$
$$= [\text{NBS}] \{1 + K[\text{H}^+] + K_1[\text{Ru(III)}] \,(1 + K_2[\text{S}])\},$$

$$\text{Rate} = \frac{kK_1K_2 \,[\text{NBS}]_\text{T} \,[\text{Ru(III)}][\text{S}]}{1 + K\,[\text{H}^+] + K_1\,[\text{Ru(III)}](1 + K_2\,[\text{S}])}.$$

The above rate law explains the first order dependence on NBS, fractional order in substrate, inverse unit order in [H$^+$] and apparent zero order in Ru(III).

CONCLUSIONS

In summary, in the oxidation of monoethanolamine by NBS in aqueous acetic acid medium the following points can be delineated.

(a) Monoethanolaine can be classified as substrates which do not show any catalysis with Os(VIII). The reason obviously is the absence of complex formation directly between Os(VIII) with alanine.

(b) The presence of catalysis with Ru(III) and absence of catalysis with Os(VIII) in NBS oxidations has to be traced to different factors. The factor other than complexation obviously has to be a more powerful oxidant species like Ru(V) which accelerates the NBS oxidations.

Hence, Ru(V) participation is responsible for the catalysis observed in the compound like monoethanolamine in NBS oxidations.

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