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Kinetics and mechanism of Ru (III) catalysed and uncatalysed oxidation of DL-alanine by N-bromosuccinimide

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The kinetics of Ru(III) catalysed and uncatalysed oxidation of DL-alanine by N-bromosuccinimide (NBS) was studied in aqueous acetic acid and in the presence of perchloric acid and Hg (II). In both Ru(III) catalysed and uncatalysed oxidations, the kinetic orders were: first order in NBS, fractional order in substrate. The rate of the reaction decreased with the increase in perchloric acid concentration and addition of halide ions. The reactions were of fractional order with respect to Ru (III). Addition of Os(VIII) had no effect on the rate of oxidation of DL-alanine by NBS. The presence of catalysis with Ru (III) and the absence of catalysis with Os(VIII) in NBS oxidations was traced to different factors. A factor other than complexation could be a more powerful oxidant species like Ru (V) which accelerates the NBS oxidations. The effect of temperature was also investigated. By varying the solvent composition it was found that the reaction rate decreased with the decrease in dielectric constant of the solvent. All kinetic features were explained by postulating suitable mechanisms and rate laws.

Keywords: kinetics, oxidation, ruthenium(III), DL-alanine, N-bromosuccinimide

INTRODUCTION

Amino acids can undergo many types of reactions depending on whether a particular amino acid contains non-polar groups or polar substituents. The oxidation of amino acids is of interest as the oxidation products differ for different oxidants. These oxidation reactions display diverse reaction mechanisms, oxidative deamination and decarboxylation [1]. Thus, the study of amino acids becomes important because of their biological significance and selectivity towards the oxidant. Oxidation of alanine has received much attention because it is a degraded product of nucleic acids and is involved in biological processes such as stability of glucose in the system and is associated with chronic fatigue as well as Epstein–Barr virus, when alanine level becomes excessive [2]. Ruthenium complexes are mutagenic, capable of binding to nitrogen sites on DNA bases (as octahedral Ru (III) complexes are inert, they are activated *in vivo* by reduction to active Ru (II) complexes), suppress the immune response by inhibiting the proliferation of T cells by short-circuiting electron transfer pathways and serve as prodrugs by coordinating with biomolecules (for example as potential anticancer pharmaceuticals). As ruthenium mimics iron in binding to plasma proteins, transportation and sequestration of ruthenium into tumour cells may be mediated *via* protein transport and receptor mediated uptake [3].

Attention has been paid to N-halo oxidants due to their wide range of properties [4]. Oxidation of alanine was carried out by different hypohalous agents like N-bromophthalimide in presence of sodium dodecyl sulfate [5], NBS in alkaline medium [6], chloramine-T in absence of catalyst, in presence of catalyst and in presence of micellar aggregates [7]. Silver (I) catalysed oxidation of alanine by cerium (IV) in perchloric acid medium [8] and sulfuric acid medium [9] was well studied. The oxidation of DL-alanine by permanganate ions has been studied by Verma *et al.* [10] in concentrated acid solutions and Refat *et al.* [11] in dilute acid solutions. Oxidation of L-alanine by permanganate in acidic solvent was studied by Maria *et al.* [12] and Andres *et al.* [13]. In alkaline medium, the oxidation of alanine was studied using different oxidants like Os(VIII) [14], Ag(III) complex [15], hexacyanoferrate(III) [16] and diperiodatoargentate(III) [17].

The above literature survey shows that various oxidizing agents have been studied for the oxidation 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 was undertaken using N-bromosuccinimide (NBS) as an oxidant to clarify whether oxidations of DL-alanine 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 was done in acetic acid – perchloric acid mixtures to throw light on the nature of reaction orders and mechanistic sequences.

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EXPERIMENTAL

Materials

The reagents employed were DL-alanine (Loba Chemie), N-bromosuccinimide (G.R., Merck), ruthenium (III) chloride (Johnson Matthey, London), osmium tetroxide (Johnson Matthey), mercuric acetate (G.R., Merck), other reagents used were of analytical grade. All solutions were prepared with doubly distilled water. Stock solutions of N-bromosuccinimide were prepared in pure acetic acid and standardized iodometrically.

Kinetic measurements

Kinetic studies were carried out in perchloric acid medium at a temperature of 313K under pseudo first order conditions with a large excess of DL-alanine over NBS. The progress of the reaction was followed by determining N-bromosuccinimide concentrations iodometrically in aliquots withdrawn after suitable time intervals [18].

From the titer values, plots of log [NBS] *vs.* time were drawn and from their slopes the pseudo first order rate constants k_1(min^{-1}) were obtained. To evaluate k_1, generally 8–10 values at least up to 80% completion of the reaction were used. Average values of at least two independent determinations of k_1 were taken for analysis. All first order plots were linear, with a correlation coefficient of 0.995–0.998. The obtained rate constants were reproducible within the experimental error of ±4%.

The kinetics of both uncatalysed and Ru(III) catalysed oxidation of DL-alanine by N-bromosuccinimide (NBS) were studied in acetic acid-perchloric acid medium. The kinetic rate data are given in Tables 1 and 2.

Table 1. Kinetic data for the uncatalysed oxidation of DL-alanine by NBS

[NBS] = 0.001 M [DL-Alanine] = 0.01 M [HClO4] = 0.25 M
AcOH – H_2O = 20% - 80 %(v/v) [Hg $(OAc)_2$]=0.02M Temp = 40°C

Variant	Concentration of Variant	$k_1 \times 10^4$ min^{-1}
NBS	0.5×10^{-3}M	128.1
	1.0×10^{-3}M	129.3
	2.0×10^{-3}M	124.7
DL-alanine	1.25×10^{-3}M	41.3
	2.50×10^{-3}M	56.3
	5.00×10^{-3}M	97.5
	10.00×10^{-3}M	125.3
	20.00×10^{-3}M	174.7
	40.00×10^{-3}M	305.0
H^+	0.10	319.6
	0.25	125.3
	0.50	67.4
	1.00	34.6
	2.00	14.8
Acetic Acid	5 : 95	224.3
	10 : 90	199.9
	20 : 80	125.3
	40 : 60	69.1
	60 : 40	25.3
Temperature	30^0C	46.0
	40^0C	125.3
	50^0C	426.9
Os (VIII) at [$HClO_4$]=0.5M	0.0	67.4
	6.40×10^{-5}M	83.4
	12.80×10^{-5}M	73.4
	19.20×10^{-5}M	66.4
	25.60×10^{-5}M	55.2
Addition of salt at [$HClO_4$]=0.5M	No salt	67.4
	0.02 M KF	79.1
	0.02 M KCl	30.7
	0.02M KBr	No Reaction

Table 2. Arrhenius parameters for the uncatalysed reaction at 313ºK

$\Delta E^{\neq}$ $KJmol^{-1}$	$\Delta H^{\neq}$ $KJmol^{-1}$	$\log_{10} PZ$	$-\Delta S^{\neq}$ $JK^{-1}mol^{-1}$	$\Delta G^{\neq}$ $KJmol^{-1}$
92.544	89.942	11.764	28.415	98.835

Factors influencing the rate of oxidation of DL-alanine by NBS, such as effects of (i) [NBS], (ii) [DL-alanine], (iii) [H+], (iv) ionic strength, (v) dielectric constant, and (vi) temperature, both in absence and presence of Ru (III) catalyst were studied. Rate and activation parameters were evaluated.

RESULTS AND DISCUSSION

Uncatalysed reactions

Effect of [NBS]

The kinetics of oxidation of DL-alanine was investigated under pseudo first order conditions, keeping the concentrations of DL-alanine in a large excess (nearly tenfold) over that of [NBS]. When log [NBS] was plotted against 'time', very good straight line plots were obtained indicating that the reaction was of first order with respect to [NBS] (Table 1). Effect of varying [NBS] on the rate of oxidation was studied at constant [DL-alanine], [H^+], %AcOH, [mercuric acetate] and temperature. The pseudo first order rate constants k_1 were found to be independent of [NBS], confirming the first order dependence of rate on [NBS].

Effect of [DL-alanine]

At constant [NBS], [H^+], [AcOH], [mercuric acetate] and temperature the kinetic runs were carried out with various initial concentrations of DL-alanine, which yielded rate constants whose values depended on [DL-alanine]. The pseudo first order rate constants k_1 (min^{-1}) thus obtained were found to increase with [DL-alanine] (Table 1) over the range of [DL-alanine] used. The plot of log k_1 *versus* log [alanine] was a straight line with fractional slope showing that the reaction obeys a fractional order with respect to [DL-alanine]. The formation of the complex was kinetically proven by Michaelis – Menten plot, that is, a non-zero intercept of the plot of 1/rate *vs.* 1/ [S]. The complex formation between oxidant and substrate was also reported in the literature [19].

Effect of acid

A change in the kinetic rate of the reaction with the change in the concentration of perchloric acid was observed in the present investigation. The first order rate constants decreased with the increase in perchloric acid concentration. The plot of log k_1 *versus* log [H^+] is linear and yields a fractional slope.

Effect of solvent

In order to determine the effect of dielectric constant (polarity) of the medium on the rate, the oxidation of DL-alanine 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 lowers 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 [20]. 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 [21]. In this investigation a plot of logarithm k_{obs} *versus* 1/D gives 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 can be applied [22]. Laidler and Eyring derived an expression for the free energy transfer of a polar molecule with a dipole moment μ from 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.

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

Introducing a non-electrostatic term, this becomes

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

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

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

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 linear confirming the dipole - dipole nature of the reaction. The two neutral molecules 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 hours in an inert atmosphere [23]. On diluting the reaction mixture with methanol no precipitate was observed. This indicates that no free radicals intervene in the reaction.

Rate and activation parameters

The effect of temperature on the rate of the reaction was studied in the range (303 – 323 K) and the results are shown in Table 2. From the 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. A large negative value of entropy ($-\Delta S^{\neq}$) was obtained, which can be attributed to the severe restriction of solvent molecules (electrostriction) around the transition state [24]. It also indicates that the complex is more ordered than the reactants [25]. The modest activation energy and sizeable entropy of activation supports a complex transition state in the reaction.

Effect of added salt

Different potassium halides were added to the reaction mixture and the reaction rates were determined. Addition of potassium bromide (Table 1) did not increase the kinetic rate as expected but rather stopped the reaction. This finding seems to be at variance to earlier published work [26, 27], where molecular bromine formed on addition of bromide to the system was considered to be more reactive than N-halo compounds and hence acceleration was expected. The present result of stopping the reaction may be due to the following reasons:

There is no doubt that molecular bromine is formed on addition of higher concentrations of Br^- ions.

The question to be decided is whether bromine in molecular form is always a powerful oxidant whatever may be the substrate. The observed differential rate points to the fact that molecular bromine is probably not a powerful oxidant in the present reaction compared to N-halo compounds, 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 it has been observed that NBS or HOBr or H_2OBr^- or Br^- are more reactive than molecular bromine in partially aqueous systems with aromatic substrates [28, 29]. Hence, in the present investigation extending the argument to aliphatic amino acids, the formed molecular bromine is not effective compared to the other reactive species. So, it is not surprising that the addition of Br^- did not result in an increase in the rate.

It was observed that the change in the concentration of added mercuric acetate had negligible effect on the rate. The function of the added mercuric acetate is therefore only to fix up Br^- formed in the course of the reaction as $HgBr_2$ or $HgBr_4^{2-}$.

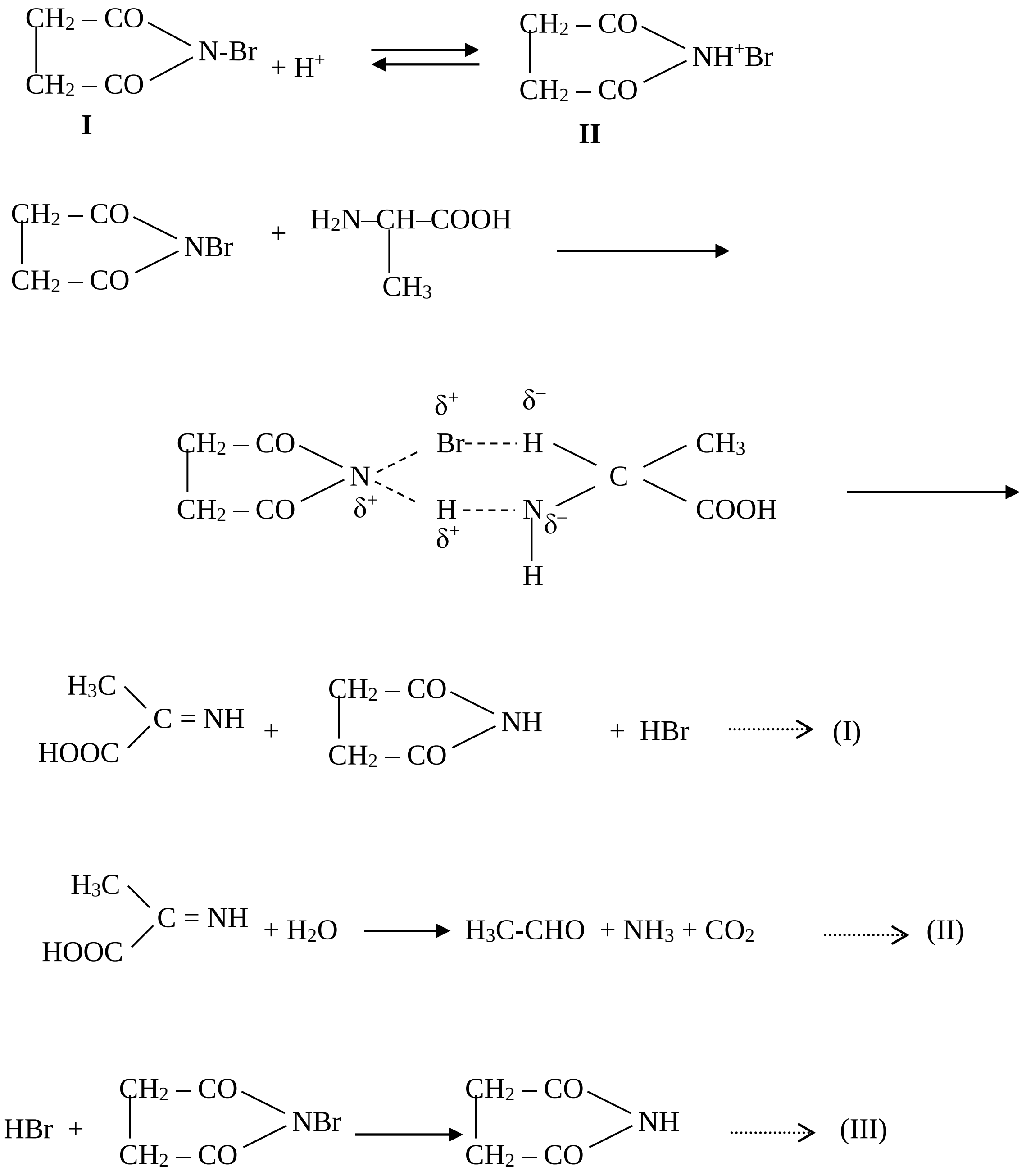
Product Analysis

The product analysis was carried out under kinetic conditions. In a typical experiment, DL-alanine (0.05M) and NBS (0.01M) were made up to 100 ml in 1:1 (V/V) acetic acid-water mixture and the reaction mixture was allowed to stay in the dark for about one day to ensure completion of the reaction. The main reaction products were succinimide, acetaldehyde, ammonia, and CO_2. Liberated ammonia was identified by Nessler’s reagent where a brownish color was observed indicating a deamination reaction [30]. Carbon dioxide was identified by freshly prepared lime water; and the solution turned milky, indicating a decarboxylation reaction [31].

The solution was then treated with an excess (200 ml) of a saturated solution of 2,4-DNP in 2M HCl and kept overnight in a refrigerator. The precipitated 2,4-DNP was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after crystallization were 94% and 89%, respectively. The DNP was found to have identical melting point and spectral data as the DNP of acetaldehyde. Further, the aldehyde group was confirmed with a qualitative test such as Tollen’s reagent [32] and spot tests [33]. Similarly, Verma *et al.* [10] and Rao *et al.* [34] indicated that ammonia and acetaldehyde are two of the reaction products from the oxidation of DL-alanine by MnO_4^- ions.

Mechanism

It is reported that the oxidation of amino acids involves the cleavage of N-H and C-H bonds in the rate determining step [35]. The rate of oxidation of DL-alanine by NBS is inhibited by the addition of H^+ ions. This may be explained by assuming the equilibrium (I=II) to be present and that the unprotonated species (I) is the reactive one.



However in presence of mercuric acetate the reaction (Eq. III) does not take place.

Rate law

$$\mathrm{NBS} + \mathrm{H}^+ \overset{K}{\rightleftarrows} \mathrm{NBSH}^+ \qquad K = \frac{\left[\mathrm{NBSH}^+\right]}{[\mathrm{NBS}][\,\mathrm{H}]^+}$$

$$\mathbf{S} + \mathrm{NBS} \overset{K_1}{\rightleftarrows} \text{Complex C}$$

Where S = alanine = CH_3 CH (NH_2) COOH

$$\begin{tikzcd} \text{Complex C} \arrow[r, "k"'] & \mathrm{CH_3C(COOH){=}{=}NH} + \mathrm{Br}^- + \text{Succinimide} \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{CH_3CHO} + \mathrm{NH_3} + \mathrm{CO_2} \end{tikzcd}$$

$$\text{Rate} = k\ [\text{Complex}]$$

$$= k\, K^1\, [S]\, [NBS] \longrightarrow (1)$$

$$[NBS]_T = [NBS] + [\text{Complex}] + \left[NBSH^+\right] = [NBS] + K^1\, [NBS]\, [S] + K\, [NBS]\, [H^+]$$

$$= [NBS]\, \{1 + K^1\, [S]\} + K\, [H^+] \longrightarrow (2)$$

from (1) and (2)

$$\text{rate} = \frac{kK^1\, [NBS]_T [S]}{1 + K^1\, [S] + \mathrm{K}[\mathrm{H}^+]} \longrightarrow (3)$$

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

Ru (III) Catalysed reactions

Ruthenium (III) chloride accelerates the oxidation of DL-alanine by NBS in acetic acid – perchloric acid medium (Table 3), whereas osmium (VIII) does not catalyze the oxidation of DL-alanine (Table 1). N-bromosuccinimide oxidation of DL-alanine catalyzed by Ru (III) was carried out in aqueous acetic acid - perchloric acid mixtures.

Effect of variation of concentration of NBS

The reaction is of first order in NBS as evidenced by the linear plots of log (a-x) *versus* time. Increase of concentration of NBS yields constant first order rate constants confirming the first order dependence on NBS (Table 3).

Effect of increase of concentration of substrate:

An increase in the concentration of DL-alanine increased the kinetic rate (Table 3). A plot of log k_1 *versus* log [S] is linear with a slope of nearly 0.5 indicating a fractional order dependence on DL-alanine.

Effect of increase in concentration of Ru (III)

The oxidation of DL-alanine by NBS is of fractional order with respect to Ru(III). The first order rate constants at different concentrations of Ru (III) are presented in Table 3. The plot of log k_1 *versus* log [Ru (III)] is linear and has a slope of 0.63 indicating that the reactions are of fractional order with respect to Ru (III).

Table 3. Kinetic data for the Ru(III) catalysed oxidation of DL-alanine by NBS

[NBS] = 0.001 M [DL-alanine] = 0.01 M Temp = 40^0C
[$HClO_4$] = 1.0 M [$Hg(OAc)_2$] = 0.02M [Ru (III)]=0.95×10^{-5}M.
AcOH – H_2O = 20% - 80% (v/v)

Variant	Concentration of Variant	$k_1 \times 10^4$ min^{-1}
NBS at [$HClO_4$] = 0.5 M	1.0×10^{-3}M	98.6
	2.0×10^{-3}M	99.6
	4.0×10^{-3}M	100.3
DL-alanine at [Ru (III)]=3.8×10^{-5}M	0.625×10^{-3}M	41.4
	1.25×10^{-3}M	49.8
	2.5×10^{-3}M	59.1
	5.0×10^{-3}M	98.3
	10.0×10^{-3}M	145.8
	20.0×10^{-3}M	192.3
	40.0×10^{-3}M	272.6
Ru(III)	0.0	34.6
	0.95×10^{5}M	66.9
	1.90×10^{5}M	111.9
	3.80×10^{5}M	145.8
	7.60×10^{5}M	243.1
	15.20×10^{5}M	271.0
H^+	0.25	239.9
	0.5	98.6
	1.0	66.9
	2.0	27.9
	4.0	No Reaction
Acetic Acid : Water at [Ru(III)] = 3.8×10^{-5} M	5 : 95	197.2
	10 : 90	164.2
	20 : 80	145.8
	40 : 60	111.6
	60 : 40	36.00
Temperature at Ru(III)] = 3.8×10^{-5} M	30^0C	28.7
	40^0C	145.8
	50^0C	387.6
	60^0C	1545.2

Effect of variation of [H^+]

The effect of acid concentration on the reaction kinetics was studied and the first order rate constants are presented in Table 3. The rate constants decrease with the increase in the concentration of perchloric acid. A linear plot with a slope of –1.045 indicates an inverse unit dependence on [H^+]. As the reaction rate decreased with the increase in H^+, free alanine molecules are probably the predominant species.

Effect of variation of solvent composition

The reactions were carried out at various solvent compositions to find the effect of change in dielectric constant and the rate constants are listed in Table 3. The reaction rate decreases with the decrease in dielectric constant as required for dipole-dipole reactions, as the major reaction is between free alanine and free NBS molecules.

Effect of variation of temperature

The reactions were carried out at four different temperatures: 30°C, 40°C, 50°C and 60°C and reaction rate constants are recorded. Plot of log k_1 *versus* 1/T is linear. Arrhenius parameters are calculated (Table 4).

Nature of Ru (III) species

The electronic spectrum of ruthenium (III) chloride shows that it probably exists as $[Ru(H_2O)_6]^{3+}$ under acid conditions [36, 26] while species like $[RuCl_5.H_2O]^{2-}$, $[RuCl(H_2O)_5]^{2+}$ $[RuCl_4(H_2O)_2]^{-}$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^{+}$, $[RuCl(H_2O)_5]^{2+}$ and $[Ru(H_2O)_6]^{3+}$ are present in aqueous solutions. The most active species is $[Ru(H_2O)_6]^{3+}$ in acid medium which is formed due to the following equilibrium:

$$[Ru\,(H_2O)_5OH]^{2+} + H^+ \rightleftarrows [Ru(H_2O)_6]^{3+}$$

Table 4. Arrhenius parameters for the catalysed reaction at 313^{0}K

$\Delta E^{\neq}$ $KJmol^{-1}$	$\Delta H^{\neq}$ $KJmol^{-1}$	$\log_{10} PZ$	$\Delta S^{\neq}$ $JK^{-1} mol^{-1}$	$\Delta G^{\neq}$ $KJmol^{-1}$
102.117	99.515	14.4	3.431	98.441

Mechanism and rate law for Ru (III) catalyzed oxidation of DL-alanine by NBS

$$S + H^+ \overset{K}{\rightleftarrows} S\,H^+$$

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

$$Ru(V) + S \overset{K_2}{\rightleftarrows} Complex\ C$$

$$Complex\ \ C \xrightarrow[\text{Slow}]{k_1} products$$

$$S_T = \ S + S\,H^+ + Complex = S + K\,[S]\,[H^+] + K_1K_2\,[S]\,[NBS]\,[Ru\,(III)]$$

$$= \quad [S]\ \ \{1 + KH^+ + K_1K_2\,[NBS]\,[Ru\,(III)]\}$$

$$[S] \quad = \frac{S_T}{1 + K[H^+] + K_1K_2[NBS][\mathrm{Ru(III)}]}$$

$$Rate \quad = \quad k_1\,C$$

$$= \quad k_1\,K_2\,[Ru(V)][S] = \ k_1K_1K_2\,[NBS]\,[Ru(III)][S]$$

$$= \quad \frac{k_1\,K_1\,K_2\,[NBS][\mathrm{Ru(III)}]\,S_T}{1 + K[H^+] + K_1K_2[NBS][\mathrm{Ru(III)}]}$$

The above rate law explains the apparent first order in N-bromosuccinimide, the fractional order in Ru (III), the fractional order in alanine and the inverse unit order in [H+].

CONCLUSIONS

In summary, the following points can be delineated in the oxidation of DL-alanine by NBS in acid medium.

a) Alanine can be classified as a substrate which is not catalysed by Os (VIII). The reason may be the absence of direct complex formation between Os (VIII) and alanine.

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

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

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КИНЕТИКА И МЕХАНИЗЪМ НА ОКИСЛЕНИЕТО НА DL-АЛАНИН С N-БРОМОСУКЦИНИМИД С И БЕЗ РУТЕНИЕВ Ru (III)-КАТАЛИЗАТОР

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(Резюме)

Изследвана е кинетиката на окислението на DL-аланин с N-бромосукцинимид (NBS) с и без рутениев Ru (III)-катализатор във водна среда и в присъствие на перхлорна киселина и Hg (II).И в двата случая (с и без катализатор) реакциите са с кинетика от първи порядък по отношение на NBSи от дробен порядък по отношение на субстрата. Скоростта на реакцията се понижава с нарастване на концентрацията на перхлорната киселина и добавянето на халогениден йон. Реакцията е от дробен порядък по отношение на Ru(III). Добавянето нйа Os(VIII) няма ефект върху скоростта на окисление. Наличието на катализа при Ru(III) и отсъствието при Os(VIII) може да се търси в други фактори. Освен комплексообразуването ускоряването на окислението на NBS може да търси в по-мощни окислители, като Ru (V). Изследван е и ефекта на температурата. Установено е, че промените в състава на разтворителя промяната на скоростта на реакцията се свързва с промяна в диелектричната константа на средата.

Всички кинетични ефекти са обяснени с приети подходящи механизми и кинетични закони.