



Kinetic investigation of oxidation of alkanolamine by Cerium(IV) in acidic medium: catalytic effect of Mn(II)

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Abstract. The decomposition kinetics of ethanolamine in acid medium using Ce(IV) as oxidant and Mn(II) as a catalyst has been reported. Michaelis–Menten type of kinetic pattern is suggested based on the nature of rate dependence on substrate concentration. First-order dependence of rate on oxidant was observed up to more than three half-lives. The rate constant decreased with an increase in acid concentration and the negative slope of Zuckerman–Hammett plot demonstrates inverse dependence of rate on the acid concentration. Ce(OH)³⁺ is considered as the most active species of Cerium in the reaction medium based on the kinetic observations. The rate increased with the catalyst concentration although the order is fractional. The products formed have not shown any effect on the progress of the reaction. From the temperature dependence studies, activation parameters for the oxidation reaction are evaluated and the entropy of activation was found to be negative. Based on all kinetic findings and presuming a complex species formation between the substrate, catalyst and the oxidant suitable mechanism has been proposed. The micro-rate constants involved in the proposed reaction mechanism has also been determined.

Keywords. Ethanolamine; Michaelis–Menten; absorbance; activation parameter; entropy.

1. Introduction

Industrial as well as biological reactions for energy production and synthesis of fine chemicals involving electron transfer are significant processes for the sustenance of life. To fine-tune these processes and improve the overall efficiency knowledge of the mechanistic aspects is an advantage. Absorption or sequestration of industrial gases like CO₂, H₂S, etc., from the industrial exhausts efficiently is of prime importance from climate change and environment protection point of view as well as to satisfy the mandatory requirements of policies levied upon the industries. In this connection, bi-functional species amino alcohols are quite useful and known to be good scrubbers or absorbers of industrial exhaust gases.^{1,2} These hydrophilic amino alcohols (basic in nature) are also used in the pharmaceutical industry, beauty products and as corrosion inhibitors. Because of the excessive use of these reagents, industrial waste and effluents contain them and so pose threats for the survival of many living species and hence are to be

degraded chemically before being released into the atmosphere. Knowledge of proper and efficient reagents like oxidants, catalysts, acidity requirements, the effect of temperature and the mechanism of these degradation processes are quite crucial and bear significance. In continuation of our work on electron transfer processes,^{3–6} the present study focuses on the mechanistic aspects of conversion processes of an amino alcohol, monoethanolamine (MEA) by Ce(IV).

Although articles are available^{7–10} on the oxidation of amino alcohols with various oxidants, the approach of different reaction models (kinetic expressions, complex formation and rate-determining steps) and reports of varied product formation has prompted us to execute the present work. Here we present the outcome of our investigation on Mn(II) catalyzed oxidation of MEA by Ce(IV) in perchloric acid medium. The selection of Ce(IV), a versatile reagent as an oxidant is because of its strong oxidizing ability in an acidic environment with a reduction potential in the range of 1.3–1.8 volts for (Ce⁴⁺, Ce³⁺) couple.^{11–17} In presence of sulphuric acid, Ce(IV) can exist in a number of sulphate or protonated sulphate complex

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species, which may be neutral, [e.g., $\text{Ce}(\text{SO}_4)_2$] or bear either positive [e.g., $\text{Ce}(\text{SO}_4)_2^{2+}$, $\text{Ce}(\text{HSO}_4)_3^+$] or negative [e.g., $\text{Ce}(\text{SO}_4)_3^{2-}$] charges.^{18–20} In perchloric acid medium Ce(IV) can exist^{21–23} (although at high acid concentration) as Ce^{4+} , $[\text{Ce}(\text{OH})]^{3+}$, $[\text{Ce}(\text{OH})_2]^{2+}$, $[\text{Ce}-\text{O}-\text{Ce}]^{6+}$, and $[\text{HO}-\text{Ce}-\text{O}-\text{CeOH}]^{4+}$. An attempt has been made to ascertain the most reactive species of the oxidant under the reaction conditions. The choice of Mn(II) as a catalyst is because of its efficiency to catalyze^{24–26} the electron transfer reactions that are sluggish maybe by forming a complex with the substrates.

2. Experimental

AR grade samples of amino alcohol (Qualigen), ceric ammonium sulphate (Qualigen), manganese sulphate tetrahydrate (SD Fine) and sulphuric acid (E. Merck) were used. Literature method²⁷ of standardization of acidic solution of ceric ammonium sulphate was adopted. The constant ionic strength (μ) is maintained by the addition of a requisite amount of sodium perchlorate (anhydrous) to perchloric acid as and when required. All solutions were prepared in doubly distilled conductivity water. Since the chemicals in their purest form were procured, they were used as received. Nitrogen gas was bubbled for at least 10 min into the solutions just before they are equilibrated to thermostatic conditions.

All kinetic measurements were performed spectrophotometrically maintaining pseudo-first-order conditions using a Shimadzu UV 1700A spectrophotometer and 1cm quartz cell. Remi Cryostat Model 396 LAG is used to maintain the temperature at the desired value. The reactions in an aqueous medium were initiated by mixing pre-equilibrated (thermostated) solutions in the order acid, amino alcohol, Mn(II) and finally Ce(IV). The progress of the reaction was monitored by following the decrease in absorbance of Ce(IV) at 380 nm as a function of time. Figure 1 shows the spectral changes of Ce(IV) during the reaction progression. Interference from other reagents was negligibly small at this wavelength. Beer's law was obeyed with $\epsilon = 533 \pm 20 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in the concentration range of Ce(IV) studied. The product analysis has been carried out after about four hours of the reaction using the characteristic tests.²⁸ The error analysis has been done by the method of linear regression.

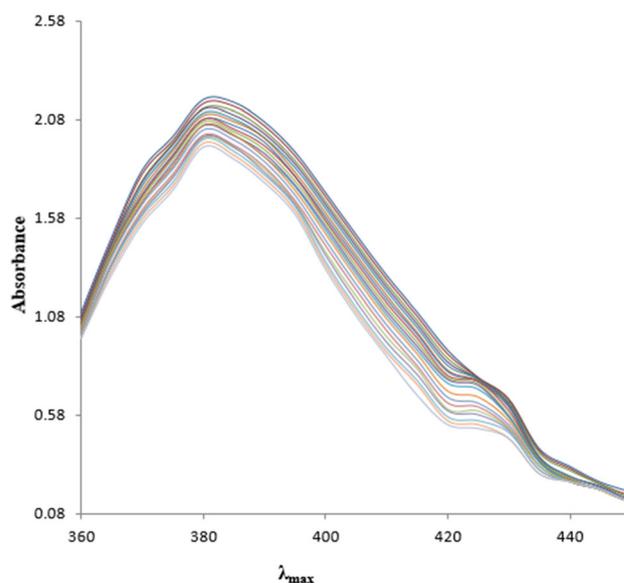


Figure 1. Spectral changes of Ce(IV) during the reaction progression at 30 °C. $[\text{MEA}] = 3 \times 10^{-2}$, $[\text{Mn}(\text{II})] = 3 \times 10^{-4}$, $[\text{Ce}(\text{IV})] = 3 \times 10^{-3}$ and $[\text{H}^+] = 4.0 \text{ mol dm}^{-3}$.

3. Results and Discussion

Reference to the experimental section, the kinetics of Mn(II) catalyzed oxidation of MEA has been monitored spectrophotometrically under pseudo-first-order conditions by measuring the absorbance at 380 nm as a function of time. The oxidant, ceric ammonium sulphate (CAS) has the λ_{max} value at 390 nm (Curve-b, Figure 2). However, when the reactants are added in the sequence, water, acid, MEA (substrate), Mn(II) (catalyst) and Ce(IV) (oxidant), there is an instantaneous shift in λ_{max} position to 380 nm (Curve-a, Figure 2). Hence this wavelength is chosen for kinetic study and the disappearance kinetics is monitored by measuring absorbance at 380 nm. The reactions have been carried out in an acidic medium (4N) using perchloric acid. Any attempt to lower the acid concentration below 1N resulted in almost instantaneous precipitation having brown coloration. Preliminary investigation revealed that at 4N acid concentration, the orange-yellow coloration of the reaction mixture at the beginning faded slowly with time to a colorless solution which on standing overnight formed a brown precipitate. When the acid concentration is lowered below 4N, the appearance of brown precipitate becomes proportionally faster. Exclusion of any one of the components like the oxidant, substrate or catalyst in the reaction mixture resulted in some interesting

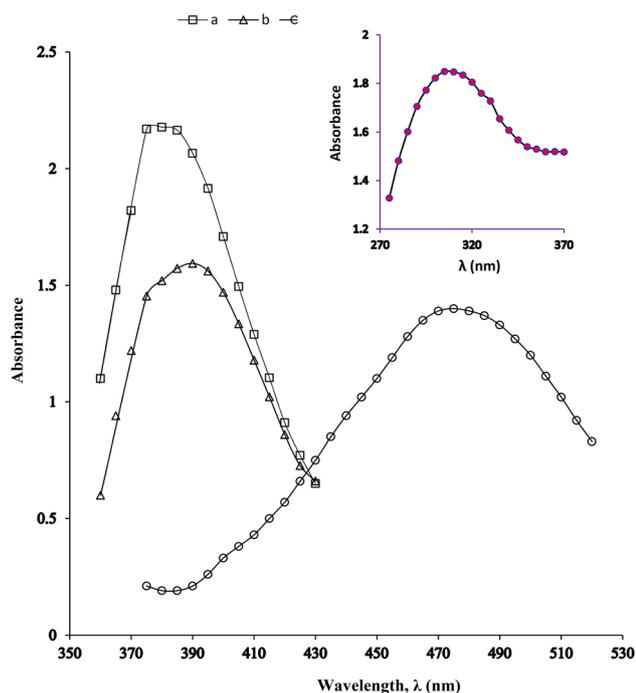


Figure 2. Visible spectra for different combination of reactants: a = MEA ($3 \times 10^{-2} \text{ mol dm}^{-3}$), Mn(II) ($3 \times 10^{-4} \text{ mol dm}^{-3}$) and Ce(IV) ($3 \times 10^{-3} \text{ mol dm}^{-3}$) taken together, b = only Ce(IV) ($3 \times 10^{-3} \text{ mol dm}^{-3}$), c = mixture of Ce(IV) ($3 \times 10^{-3} \text{ mol dm}^{-3}$) and Mn(II) ($1 \times 10^{-1} \text{ mol dm}^{-3}$). Inset shows the spectrum of Mn(II) ($1 \times 10^{-1} \text{ mol dm}^{-3}$) only. All experiments are done under conditions of $[\text{H}^+] = 4.0 \text{ mol dm}^{-3}$.

observations. Selected observations are presented in Figure 2 and the findings are summarized as follows:

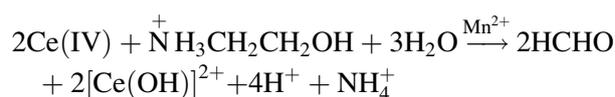
- (i) There is no reaction between substrate and catalyst in the absence of oxidant. This is inferred from the constancy in the absorbance value at 305 nm, the wavelength for maximum absorption of Mn(II), even after 30 min of mixing.
- (ii) When only the oxidant and the catalyst are taken with $[\text{catalyst}] \gg [\text{oxidant}]$ there is an almost instantaneous fall in the absorbance value of the oxidant and the λ_{max} value shifts from 390 to 475 nm (Curve-c, Figure 2). It may be noted that the concentration of the catalyst is kept here 33.3 times more than that used in the usual kinetic study.
- (iii) When the oxidation reaction is carried out in the absence of the catalyst, there is a sluggish fall in the absorbance value and the rate of decrease of absorbance is many folds slower compared to the catalyzed reaction.

- (iv) The pre-equilibrated thermostated solutions of $1 \times 10^{-3} \text{ M}$ Ce(IV) and $1 \times 10^{-4} \text{ M}$ Mn(II) were mixed and the absorbance was noted at the λ_{max} of Ce(IV). The observation is, even after monitoring for about 1 h, hardly any change in the absorbance value was noticed.

The above observations clearly indicate that the oxidant is almost spontaneously reduced by the catalyst Mn(II) when the latter is present in large excess. This is to be expected from the standard reduction potentials of $(\text{Ce}^{4+}, \text{Ce}^{3+})$ and $(\text{Mn}^{3+}, \text{Mn}^{2+})$ couples. The potential of $(\text{Ce}^{4+}, \text{Ce}^{3+})$ couple ranges from 1.3 to 1.8 V in strong acid condition and depends on the electrolyte as well as on the anionic groups complexed to the cerium ion.²⁹⁻³¹ On the other hand, the $(\text{Mn}^{3+}, \text{Mn}^{2+})$ couple has a potential of 1.51 V.³² Although the difference in reduction potential is marginal, but when present in large excess Mn(II) could reduce Ce(IV) instantaneously.³³

3.1 Stoichiometry and product analysis

The stoichiometry of the oxidation reaction has been determined taking tenfold excess of Ce(IV) compared to [MEA]. After 1 h of mixing, the reaction mixture is titrated with a standard As_2O_3 solution containing few drops of osmic acid using N-phenylanthranilic acid as an indicator. From the sharp color change from light yellow to purple the amount of Ce(IV) required to oxidize the known amount of MEA is noted from which the stoichiometry is obtained as



Under kinetic conditions of reactant concentrations *viz.*, $[\text{Ce(IV)}] = 3 \times 10^{-3}$, $[\text{MEA}] = 3 \times 10^{-2}$, $[\text{Mn(II)}] = 3 \times 10^{-4}$ and $[\text{H}^+] = 4.0 \text{ mol dm}^{-3}$, the product analysis has been carried out at the end of oxidation reaction, i.e. after four hours for the reaction at 30 °C. The final products have been identified as formaldehyde and ammonia by characteristic tests.²⁸ To find the active form or the microspecies of the substrate under the condition of the acid, ChemAxon software tool was used. The composition of different microspecies under varying pH, the structures of the possible microspecies are predicted and it is observed that the active species of the substrate is the one mentioned in the stoichiometry equation.

3.2 Rate dependence on oxidant and substrate

In an acidic medium, the concentration of Ce(IV) is varied from 1×10^{-3} to 5×10^{-3} mol dm⁻³, at a constant concentration of Mn(II) (3×10^{-4} mol dm⁻³) and the substrate MEA (3×10^{-2} mol dm⁻³). The ionic strength of the medium is as such kept constant by the high concentration (4N HClO₄) of acid used and so no secondary electrolyte is taken in the present study. The rate of disappearance of Ce(IV) has been obtained by absorbance measurement at 380 nm. A first-order dependence of rate on [oxidant] is clear. Figure 3 shows that the plot of log (absorbance) vs time is linear up to more than three half-lives ($r^2 = 0.987$). The observed pseudo-first-order rate constants (k_{obs}) remain almost unchanged (S.D. = 1.023×10^{-6}) over the concentration range of study. In other words, k_{obs} is independent of the initial concentration of Ce(IV), thereby indicating the first-order dependence of rate on Ce(IV). Accordingly, the rate law for the Ce(IV) dependence can be written as in Equation 1 and the rate constant values are contained in Table 1.

$$-\frac{d(\text{Ce(IV)})}{dt} = k_{\text{obs}}[\text{Ce(IV)}] \quad (1)$$

The concentration of monoethanolamine is varied from 2×10^{-2} to 5×10^{-2} mol dm⁻³ at constant concentration of oxidant (3×10^{-3} mol dm⁻³), catalyst (3×10^{-4} mol dm⁻³), H⁺ ion (4.0 mol dm⁻³)

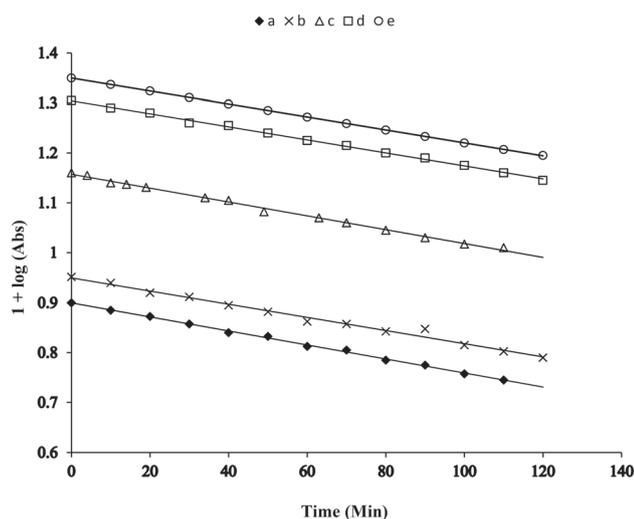


Figure 3. Pseudo first order plots for Mn(II) catalyzed oxidation of MEA at different concentration of Ce(IV) at 30 °C. [MEA] = 3×10^{-2} , [Mn(II)] = 3×10^{-4} and [H⁺] = 4.0 mol dm⁻³. a = 1×10^{-3} , b = 2×10^{-3} , c = 3×10^{-3} , d = 4×10^{-3} and e = 5×10^{-3} mol dm⁻³ of Ce(IV).

and temperature 30 °C. At lower concentration of substrate, the pseudo-first-order rate constant values increase almost linearly with an increase in concentration, but at higher concentration, these values show a tendency to level off thereby indicating Michaelis–Menten type of dependence of rate on substrate concentration. Again, the double reciprocal plot of $1/k_{\text{obs}}$ versus $1/[\text{MEA}]$ is a straight line (Figure 4) with a positive slope. Accordingly, the dependence of rate constant on substrate concentration can be written as

$$k_{\text{obs}} = \frac{a[\text{MEA}]}{b + c[\text{MEA}]} \quad (2)$$

where a, b and c are constants. The rate constant values are contained in Table 1.

3.3 Effect of catalyst variation

The catalyst concentration is varied from 1×10^{-4} to 5×10^{-4} mol dm⁻³ to study the role of the catalyst in the oxidation of amino alcohol by Ce(IV). The k_{obs} values systematically increase with an increase in [Mn(II)]. However, the rate of increase in k_{obs} values gradually fall off especially for higher concentrations of Mn(II). Graphical presentation of the result is exhibited in Figure 5. The k_{obs} values as a function of [Mn(II)] are listed in Table 1. Thus the order of the reaction with respect to [Mn(II)] is fractional. This observation is similar to the dependence of rate on substrate concentration.

3.4 Influence of acid strength

Rates of oxidation have been measured in presence of a wide range of HClO₄ acid concentrations [1.5N–4N]. Under high acid concentration conditions of HClO₄, Ce(IV) is found^{21,22} to exist as Ce⁴⁺, [Ce(OH)]³⁺, [Ce(OH)₂]²⁺ along with dimeric or polymeric forms, [Ce–O–Ce]⁶⁺, and [HO–Ce–O–CeOH]⁴⁺. It is observed that the rate constant decreases with an increase in [H⁺] and the Zucker-Hammett plot (Figure 6) are linear with a negative slope demonstrating inverse dependence of rate on the acid concentration. It is worthy to mention again that the orange-yellow coloration of the reaction mixture primarily due to Ce(IV) at the beginning of the reaction fades away slowly in the 4N acid conditions in comparison to other acid strength. When the acid concentration is lowered below 4N, the disappearance of yellow coloration becomes proportionally faster. The reaction becomes too fast to be observed kinetically below 1N

Table 1. Rate constants for Mn(II) catalyzed oxidation of monoethanolamine by Ce(IV) in acidic media at 30 °C.

$10^3 \times [\text{Ce(IV)}]$ (mol dm ⁻³)	$10^2 \times [\text{MEA}]$ (mol dm ⁻³)	$[\text{H}^+]$ (mol dm ⁻³)	$10^4 \times [\text{Mn(II)}]$ (mol dm ⁻³)	$10^5 \times k_{\text{obs}}$ (s ⁻¹)
1.0	3.0	4.0	3.0	5.56
2.0				5.37
3.0				5.41
4.0				5.10
5.0				4.90
3.0	2.0	4.0	3.0	4.80
	2.5			4.08
	3.0			5.41
	3.5			7.83
	4.0			8.50
	4.5			9.98
	5.0			10.50
	6.0			13.26
3.0	3.0	1.5	3.0	13.64
		2.0		10.47
		2.5		8.53
		3.0		7.17
		3.5		5.75
		4.0		5.41
3.0	3.0	4.0	1.0	1.98
			1.5	2.94
			2.0	3.83
			3.0	5.41
			4.0	6.89
			5.0	8.90

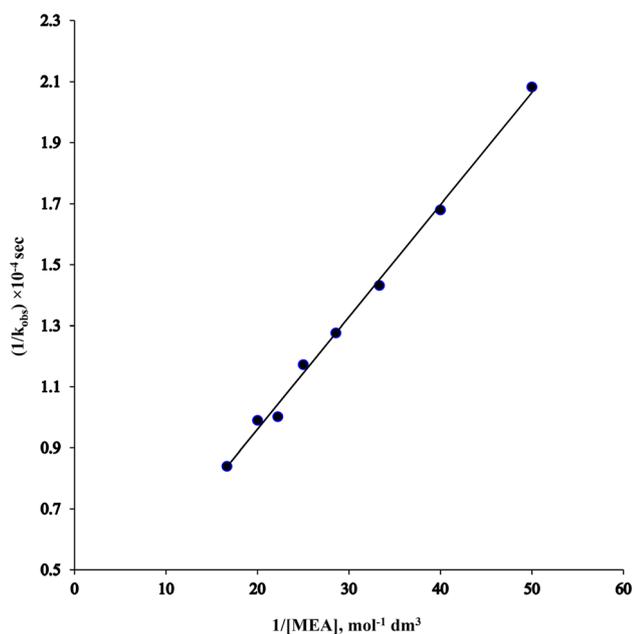


Figure 4. Double reciprocal plot showing the effect of variation of MEA concentration on the oxidation reaction at 30 °C. $[\text{Ce(IV)}] = 3 \times 10^{-3}$, $[\text{Mn(II)}] = 3 \times 10^{-4}$ and $[\text{H}^+] = 4.0 \text{ mol dm}^{-3}$.

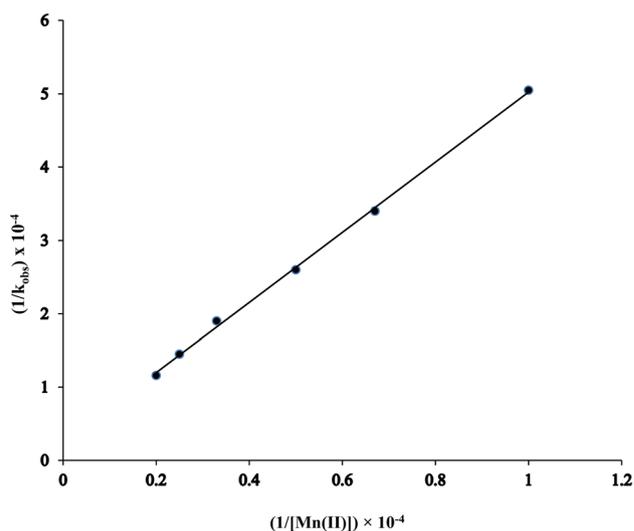


Figure 5. Plot of $1/k_{\text{obs}}$ versus $1/[\text{Mn(II)}]$ for the oxidation of monoethanolamine by Ce(IV) at 30 °C. $[\text{Ce(IV)}] = 3 \times 10^{-3}$, $[\text{MEA}] = 3 \times 10^{-4}$ and $[\text{H}^+] = 4.0 \text{ mol dm}^{-3}$.

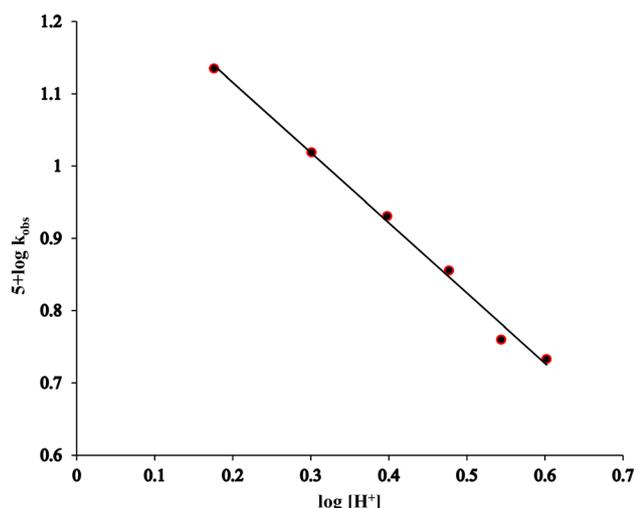
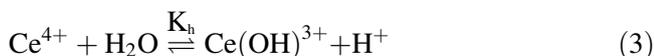


Figure 6. Zucker–Hammett plot showing the effect of $[H^+]$ on the Mn(II) catalyzed oxidation of MEA by Ce(IV) at 30 °C. $[MEA] = 3 \times 10^{-2}$, $[Ce(IV)] = 3 \times 10^{-3}$ and $[Mn(II)] = 3 \times 10^{-4} \text{ mol dm}^{-3}$.

acid strength and is the reason for instantaneous loss of the colour of Ce(IV).

Similar observations have been reported^{11,20,34} for oxidation of ketones, substituted ketones and nitrogen-containing compounds in a sulphuric acid medium using Ce(IV) as oxidant. The retardation by $[H^+]$ is explained by the hydrolysis of Ce(IV) species to $Ce(OH)^{3+}$ as given by equation 3.^{35,36}



In fact, the influence of higher cationic charge and smaller ionic size make ceric salts much more susceptible to hydrolysis in an aqueous medium. In consequence, ceric salt solutions are strongly acidic.³⁷ Hence in the present study $[Ce(OH)^{3+}]$ is considered as the active species in the oxidation of amino alcohol, MEA. A second hydrolysis reaction of Ce(IV) represented by the following equation can also occur in the acid strength conditions maintained here.



Furthermore, the predominant species that participate in the oxidation reaction can be regarded as $[Ce(OH)^{3+}]$ owing to the relatively small value of K_{h2} ³⁸ under the acidity condition of kinetic analysis. Inverse dependence of rate on $[H^+]$ has also been reported by several Mn(II) catalyzed reaction³⁹ although no specific explanation is assigned. It may be noted that for experiments where $[H^+]$ is varied, the constant ionic strength is maintained by the addition of

a requisite amount of sodium perchlorate as and when required.

3.5 Temperature dependence

The temperature effect on oxidation reaction has been studied at six different temperatures in the range 30–50 °C. For all these experiments the concentration of various reacting species are kept constant as $[Ce(IV)] = 3 \times 10^{-3}$, $[MEA] = 3 \times 10^{-2}$, $[Mn(II)] = 3 \times 10^{-4} \text{ mol dm}^{-3}$ and $[H^+] = 4.0 \text{ mol dm}^{-3}$. It has been found that the first-order rate constant values increase with an increase in temperature (Table 2). The Arrhenius plot of $\log k_{obs}$ versus $1/T$ (Figure 7) is linear with a negative slope. The activation energy is calculated from the slope of the line as $2.303 R \times \text{slope}$ and is found to be $61.74 \text{ kJ mol}^{-1}$. Other thermodynamic parameters including the entropy of activation have been calculated and are presented in Table 3.

3.6 Effect of solvent composition and added salt

The effect of change in solvent composition on the reaction rate has been studied by taking different mixed solvents of acetonitrile and water. The dielectric constant D is thus varied in the range 76.75–60.74. It has been found that increasing the proportion of acetonitrile decreases the reaction rate (Table 4). The plot of $\log k_{obs}$ versus $1/D$ is linear (Figure 8) with a negative slope and this indicates intermediate complex formation preferably involving ions of similar charge.⁴⁰ In the present study the formal ionic strength is outside the range for which the activity coefficient corrections can be calculated.⁴¹ However, the effect of an added electrolyte like $NaClO_4$ has been studied by taking a different concentration of $NaClO_4$ at the constant condition of other reaction parameters. It is found that the effect of added electrolyte on the Mn(II) catalyzed oxidation reaction is marginal. The pseudo-first-order rate constant values are almost constant (Table 4).

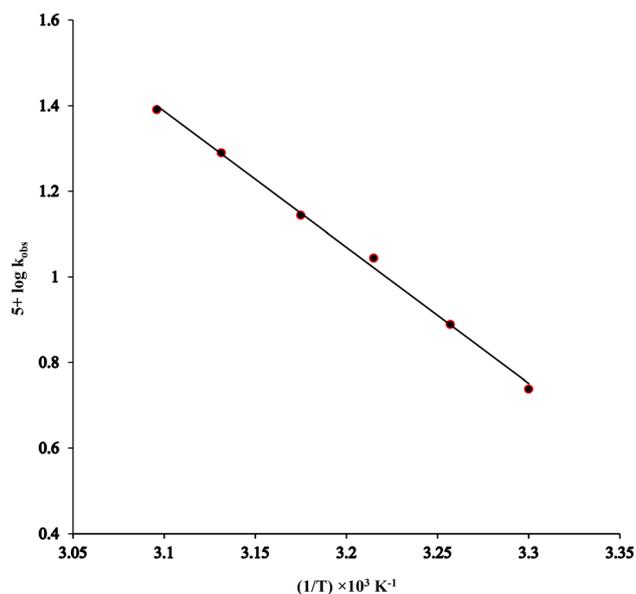
3.7 Test for free radicals

Polymerization of certain molecules can be initiated by free radicals generated as transient intermediate, in the course of redox reaction. In order to test for free

Table 2. Variation of rate constant with temperature for Mn(II) catalyzed oxidation of monoethanolamine by Ce(IV) in acidic medium.

Temperature (T) (K)	$10^4 \times k_{\text{obs}}$ (s ⁻¹)	$10^3 \times (1/T)$ (K ⁻¹)	$5 + \log k_{\text{obs}}$
303	0.541	3.300	0.738
307	0.776	3.257	0.889
311	1.109	3.215	1.044
315	1.396	3.175	1.144
319	1.952	3.134	1.290
323	2.466	3.096	1.391

[MEA] = 3×10^{-2} , [Ce(IV)] = 3×10^{-3} , [Mn(II)] = 3×10^{-4} and [H⁺] = 4.0 mol dm⁻³.

**Figure 7.** Arrhenius plot for the Mn(II) catalyzed oxidation of MEA by Ce(IV). [MEA] = 3×10^{-2} , [Ce(IV)] = 3×10^{-3} , [Mn(II)] = 3×10^{-4} and [H⁺] = 4.0 mol dm⁻³.**Table 3.** Activation parameters for the Mn(II) catalyzed oxidation of monoethanolamine by Ce(IV) (Ref: Figure 7).

$10^5 \times k_{\text{obs}}$ (s ⁻¹)	E (K J mol ⁻¹)	ΔH (K J mol ⁻¹)
5.41	61.74	59.22
ΔG (K J mol ⁻¹)	ΔS (J K ⁻¹ mol ⁻¹)	A (mol ⁻² dm ⁶ s ⁻¹)
99.01	- 131.32	2.372×10^6

radicals in the reaction, acrylamide solution is added to the reaction mixture containing the reacting species in the nitrogen atmosphere. A silky white precipitate is observed on standing, due to the polymerization of acrylamide. This indicates the generation of free

radicals during the oxidation reaction. However, there is no evidence that acrylamide is oxidized by Ce(IV) in presence of the amino alcohol. The electron transfer step from the reducing agent to the oxidant is accompanied by the scission of an intermediate to produce active free radical species. The ceric ion, Ce(IV) with a suitable reducing agent is known to initiate redox polymerization.⁴²

3.8 Reaction scheme

On the basis of kinetic information and spectrophotometric evidence, a plausible reaction scheme is proposed for the Mn(II) catalyzed oxidation of amino alcohol by Ce(IV). The kinetic information is summarized as follows:

1. The reaction is first order with respect to [Ce(IV)].
2. The dependence of rate on substrate concentration suggests Michaelis-Menten type kinetic pattern.
3. The rate increases with an increase in Mn(II) concentration, but the order of dependence is fractional.
4. There is a slow but steady decrease in rate with an increase in H⁺ ion concentration.
5. The plot of log k_{obs} versus 1/D has a negative slope.
6. The entropy of activation is negative.

The last two mentioned observations suggest intermediate complex formation preferably involving ions of similar charges. Complex formation is also envisaged from the dependence of rate on both [substrate] and [Mn(II)]. Thus, the oxidation of MEA proceeds via intermediate complex formation between any two of the three reacting species, viz., the oxidant, substrate and the catalyst. Alternatively, complex formation involving all the three reacting species cannot be ruled out. Further, the dependence of rate on H⁺ ion concentration indicates that the reactive species in the oxidation reaction may be a hydrolyzed Ce(IV)

Table 4. Value of rate constant in presence of additive and at various compositions of acetonitrile–water mixture at 30 °C.

% of acetonitrile (V/V)	1/D	[K ₂ SO ₄] (mol dm ⁻³)	10 ⁵ × k _{obs} (s ⁻¹)	5 + log k _{obs}
0.0	0.0130	0.0	5.41	0.733
		0.1	5.44	0.735
		0.2	5.36	0.729
		0.4	5.32	0.725
		0.5	5.51	0.741
10	0.0137	0.0	5.23	0.719
20	0.0146		4.87	0.687
30	0.0155		4.23	0.636
38	0.0164		3.91	0.592

[Ce(IV)] = 3 × 10⁻³, [Mn(II)] = 3 × 10⁻⁴, [MEA] = 3 × 10⁻² and [H⁺] = 4.0 mol dm⁻³.

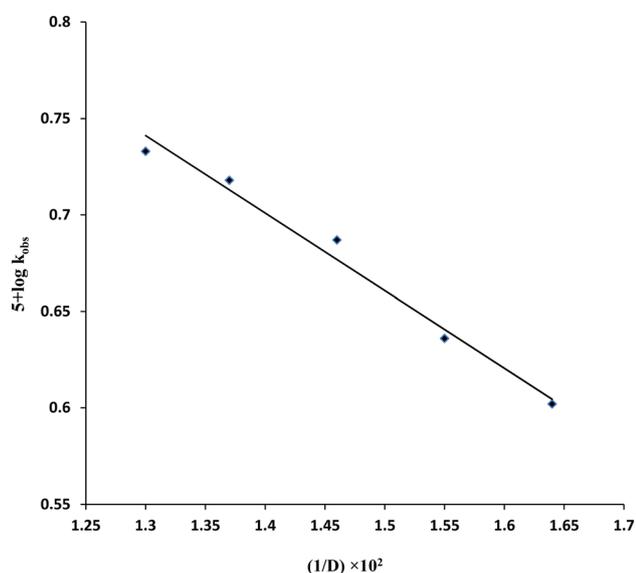


Figure 8. Plot of log k_{obs} versus 1/D for the oxidation of monoethanolamine at 30 °C. [MEA] = 3 × 10⁻², [Ce(IV)] = 3 × 10⁻³, [Mn(II)] = 3 × 10⁻⁴ and [H⁺] = 4.0 mol dm⁻³.

species formed according to equation 3. The oxidant Ce(IV) is known to exist in conjugate acid-base form.⁴³

Reference to Figure 2, when a comparison is made between the spectrum recorded for the solution of Ce(IV) and H⁺ (Curve b) with that containing MEA and Mn(II) in addition (Curve a), there is an increase in absorbance from 1.6 to 2.17 with a shift of λ_{max} towards shorter wavelength of about 10 nm. Moreover, the absorbance value increases with an increase in MEA concentration. This increase in absorbance with substrate concentration with accompanying shift in λ_{max} probably indicates the formation of complex

species of the type [Mn(II)–S–Ce(IV)], where S is the substrate MEA. Complex formation of the substrate with only the oxidant Ce(IV) or the catalyst Mn(II) is ruled out as in either case there is virtually no change in absorbance value of either Ce(IV) or Mn(II) even after an hour. Accordingly, the following mechanism for the oxidation reaction is proposed (Scheme 1).

From the reaction scheme described, the rate law can be expressed as

$$\text{Rate} = k_2[\text{C}] \quad (4)$$

Applying steady state condition on complex C,

$$k_1[\text{Ce}(\text{OH})^{3+}][\text{Mn}(\text{II})][\text{MEA}] = k_{-1}[\text{C}] + k_2[\text{C}] \quad (5)$$

$$\Rightarrow [\text{C}] = \frac{k_1[\text{Ce}(\text{OH})^{3+}][\text{Mn}(\text{II})][\text{MEA}]}{k_{-1} + k_2} \quad (6)$$

Now,

$$\begin{aligned} [\text{Ce}(\text{IV})]_{\text{T}} &= [\text{Ce}(\text{IV})] + [\text{Ce}(\text{OH})^{3+}] + [\text{C}] \\ &= \frac{[\text{Ce}(\text{OH})^{3+}][\text{H}^+]}{K_h} \\ &\quad + [\text{Ce}(\text{OH})^{3+}] + \frac{k_1[\text{Ce}(\text{OH})^{3+}][\text{Mn}(\text{II})][\text{MEA}]}{k_{-1} + k_2} \quad (7) \\ \Rightarrow [\text{Ce}(\text{OH})^{3+}] &= \frac{[\text{Ce}(\text{IV})]_{\text{T}}}{\left\{ 1 + \frac{[\text{H}^+]}{K_h} + \frac{k_1[\text{Mn}(\text{II})][\text{MEA}]}{k_{-1} + k_2} \right\}} \quad (8) \end{aligned}$$

Substituting the value of [Ce(OH)³⁺] from equation 8 in equation 6,

Equation 12), K_h is calculated as $12.89 \text{ mol dm}^{-3}$. The K_h value is close to the literature value⁴¹ of $pK_h = -1.15$. The micro rate constant values are then used in equation 11 at different concentration of Mn(II) and these are presented in Table 5. The agreement between the observed and calculated rate constant values is noteworthy and this justifies the rate law.

4. Conclusions

Spectroscopic investigation of the oxidation kinetics of ethanolamine Ce(IV) was monitored. The sluggish reaction in the acid medium has been effectively catalyzed by Mn(II). The active species of Ce(IV) was found to be $[\text{Ce}(\text{OH})]^{3+}$ based on the observations made. The hydrolysis quotient for the hydrolysis reaction of Ce(IV) was obtained. All the thermodynamic parameters are computed for the reaction carried out in the temperature range of 30–50 °C and the activation entropy was found to be negative. A suitable kinetic model has been proposed in parity with all the computations.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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