Kinetics & Mechanism of Oxidation of Amines by Ceric Ammonium Nitrate in Nitric Acid Medium

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The kinetics of oxidation of methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, dimethyl and trimethyl amines by Ce(IV) in moderately concentrated acid medium has been studied. The rate law for the oxidation of amines is:

$$\frac{-d[Ce^{IV}]}{dt} = k' [Ce^{IV}] [amine]$$

A mechanism involving the attack of the oxidant at the nitrogen atom has been suggested. Ammonia and the corresponding aldehyde or ketone are the products of oxidation of aliphatic primary amines while formaldehyde and other amines are the products when dimethyl and trimethyl amine are used as the substrates. The thermodynamic parameters for the oxidation of amines are also presented.

Although ceric salts are among the most versatile oxidants used in organic chemistry, their reaction with amines has not received much attention. In the oxidation of amines by oxidants like permanganate, lead tetraacetate, cobaltic perchlorate and chlorine dioxide, two distinct mechanisms, one involving the dehydrogenation and other an an attack at the lone pair of electrons on nitrogen in the rate-determining step, have been suggested. The state of Ce(IV) in nitric acid medium is complicated by hydrolysis, dimerisation and association with Ce(III). The title investigation has been undertaken with a view to identifying (i) the reactive Ce(IV) species, (ii) the reactive form of the aliphatic amine, and (iii) the site of attack.

Materials and Methods

All the chemicals used were of extra pure quality. Analar grade ceric ammonium nitrate (CAN) was used as the oxidant. Approximate amount of the salt was weighed so as to give 0.1M solution which was standardised by titrating against standard ferrous ammonium sulphate and diluted with HNO₃ (0.5M) to give 0.01M solution. The salts of the amines of the general formula RCH₂NH₂NO₂; were prepared by mixing one mol of amine with one mol of nitric acid. The kinetics was followed by estimating unreacted Ce(IV) at definite time intervals volumetrically. The method of evaluating the rates, orders and other kinetic parameters are the same as reported in our earlier paper.

Product analysis — Ammonia and the corresponding aldehyde or ketone were the products of oxidation of aliphatic primary amines while formaldehyde and other amines were the products when dimethyl amine and trimethyl amine were used as the substrates. Ammonia was detected with Nessler's reagent. Formaldehyde and the corresponding aldehyde or ketone were identified by their characteristic tests and further confirmed by m.p. of their 2,4-DNP derivatives.

Results and Discussion

Under the conditions [Ce(IV)] < [amine], the order in [Ce(IV)] was found to be unity as observed from the linear plot of log (a-a-x) versus time (Fig. 1A). The order in [amine] was also unity as revealed by the slope of the linear plot of log $k'$ versus log [amine] (Fig. 1B). Increase in [H+] decreased the rate of oxidation at constant ionic strength (Table I). The presence of NH₄NO₃ in increasing amounts decreased the rate and it was found that the rate varies inversely with [NO₃⁻]² (Table I).

Wylie, based on solvent extraction technique suggested the existence of H₂Ce(NO₃)₆ in moderately strong nitric acid solutions. Shorter who studied the oxidation of acetone by ceric nitrate in nitric acid assumed that Ce(OH)₅⁺ was the reactive species. Similar conclusions were drawn by Mathur and Bakor in the oxidation of s-butanol and isopropanol. However, Sethuram and Muhammad and Santappa and Sethuram concluded from the effect of [NO₃⁻] and [H⁺] on the rate of oxidation of formaldehyde and some alcohols in nitric acid medium, that the neutral Ce(NO₃)₂(H₂O)₂ to be the most likely reactive species of Ce(IV). The probable species that could exist in nitric acid solution of Ce(IV) are Ce(NO₃)₃⁺, Ce(NO₃)₂⁺, Ce(NO₃)₂ and Ce(OH)(NO₃)₂ at fairly high [nitrate ion]. The choice of the reactive species was rather difficult but the fact that the rate of oxidation of amines by Ce(IV) in nitric acid was retarded by added NH₄NO₃, coupled with the fact that the oxidation in the perchloric acid medium was inhibited by the addition of nitrate ions indicated that the reactive species might be a neutral ceric nitrate molecule Ce(NO₃)₄ or more correctly Ce(NO₃)₄
The presence of a species \([\text{Ce(OH)}_2(\text{H}_2\text{O})]^{3+}\) could not be discounted, though at high acid concentrations employed in the present work, these hydroxylated species could be neglected. The inverse dependency of rate on \([\text{NO}_3^-]\) may be explained if one assumes neutral Ce(NO_3)_4 to be the reactive species according to the following equilibria:

\[
\text{Ce(NO}_3)_4 + \text{NO}_3^- \rightleftharpoons \text{Ce(NO}_3)_5^{+} \\
\text{Ce(NO}_3)_5^{+} + \text{NO}_3^- \rightleftharpoons \text{Ce(NO}_3)_6^{6-}
\]

This is in contrast to that reported by Mehrotra et al.\(^{14}\) who assumed the hydrolysed species as the reactive species on the basis of the inhibitory effect of \([\text{H}^+]\) on the rate of oxidation of formaldehyde by Ce^{4+} in nitric acid medium.

In the present investigation it was found that an increase in \([\text{H}^+]\) decreased the reaction rate. This could be either due to the hydrolysed species acting as the reactive species

\[
\text{Ce(NO}_3)_4(\text{H}_2\text{O})_2 \rightleftharpoons [\text{Ce(NO}_3)_4(\text{OH})(\text{H}_2\text{O})]^+ + \text{H}^+
\]

or due to the presence of equilibrium of the type

\[
\text{RNH}_2 + \text{H}^+ \rightleftharpoons \text{RNH}_3^+
\]

with RNH_3 as the reactive species. To find out whether hydrolysed species is the reactive one we have studied the effect of \([\text{H}^+]\) on the oxidation of n-propanol (Table 1), where the protonation equilibrium is not likely. It was found that increase in \([\text{H}^+]\) increases the rate of oxidation of n-propanol, clearly pointing to the existence of hydrolysis equilibrium and that neutral ceric nitrate is the reactive species. Since, \([\text{Ce}^{4+}]\) and \([\text{HNO}_3]\) are same in the amines oxidation (Table 1), we believe that in this case the unhydrolysed species is the reactive one. The rate of retardation by added \([\text{H}^+]\) could, therefore, be attributed to the removal of the reactive free amine by protonation.

From spectrophotometric measurements, it is observed that there is no change in the absorption maximum of ceric nitrate solution in the presence of amine, thereby ruling out the possibility of complex formation between the oxidant and the amine prior to oxidation. Induced polymerisation of acrylamide indicated the formation of free radicals. Based on the above experimental observations, the most probable mechanism appears to be as shown in Scheme 1.

\[
\begin{align*}
\text{RCH}_2\text{NH}_2 + \text{Ce}^{4+} & \rightarrow k' \text{RCH}_2\text{NH}_3^+ + \text{Ce}^{4+} \\
\text{RCH}_2\text{NH}_3^+ & \rightarrow \text{k}\ \text{RCH}_2\text{NH}_2 + \text{H}^+ \\
\text{RCH}_2\text{NH}_2 + \text{Ce}^{4+} & \rightarrow \text{RCH}_2\text{NH}_2 + \text{Ce}^{4+} \\
\text{RCH}_2\text{NH}_2 & \rightarrow \text{H}_2\text{O} \\
\text{RCH}(_2\text{OH})\text{NH}_2 & \rightarrow \text{RCHO} + \text{NH}_3
\end{align*}
\]

(R is any alkyl group of the aliphatic amine)

\[^*\text{Ce(NO}_3)_4(\text{H}_2\text{O})_2\] is written as Ce^4+ for simplicity.

\[\text{Scheme 1}\]

The products obtained from various amines as well as the observed rate law (1) and stoichiometry of the reaction confirm the proposed mechanism.

\[\frac{\text{d}[\text{Ce}^{4+}]}{\text{dt}} = k' [\text{Ce}^{4+}] [\text{amine}] \quad (1)\]

In the mechanism shown in Scheme 1, direct attack by the oxidant at the lone pair of electrons on the nitrogen is envisaged and mechanisms involving the attack of the oxidant either at the \(\alpha\)-C-H or N-H bonds of the amine is ruled out on the basis of the following experimental observations:

(i) The oxidation of trimethyl amine proceeds at measurable rate, thus ruling out the attack at N-H bond. (ii) If the attack is at \(\alpha\)-C-H then increase in polar effect of the alkyl groups as we go from methyl to n-butyl amine should increase the strength of \(\alpha\)-C-H bond and should thereby decrease the rate of oxidation as observed by Rangaswamy and Santappa\(^{16}\) in the oxidation of alcohols by Ce^{4+} in HClO_4 medium. However, a reverse order of reactivity observed in the present study (Table 2) suggests probable attack at \(\alpha\)-C-H to be less likely. (iii)

<table>
<thead>
<tr>
<th>Amine</th>
<th>(k' \times 10^{-1}) (litre mol(^{-1}) sec(^{-1})) at 328°C</th>
<th>(E_{\text{Exp}}) (kJ mol(^{-1}))</th>
<th>(\Delta H^\ddagger) (kJ mol(^{-1}))</th>
<th>(\Delta C^\ddagger) (J deg(^{-1}) mol(^{-1}))</th>
<th>(\Delta S^\ddagger) (J deg(^{-1}) mol(^{-1}))</th>
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<tr>
<td>Methyl</td>
<td>1.40</td>
<td>88.7</td>
<td>85.9</td>
<td>105</td>
<td>58.2</td>
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<tr>
<td>Ethyl</td>
<td>2.00</td>
<td>98.0</td>
<td>95.3</td>
<td>102</td>
<td>20.4</td>
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<td>n-Propyl</td>
<td>4.60</td>
<td>79.0</td>
<td>76.3</td>
<td>101</td>
<td>75.3</td>
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<tr>
<td>Isopropyl</td>
<td>3.58</td>
<td>51.0</td>
<td>48.3</td>
<td>96.4</td>
<td>146</td>
</tr>
<tr>
<td>n-Butyl</td>
<td>7.48</td>
<td>85.0</td>
<td>82.2</td>
<td>100</td>
<td>54.3</td>
</tr>
<tr>
<td>Isobutyl</td>
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<td>99.0</td>
<td>96.3</td>
<td>101</td>
<td>14.5</td>
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<tr>
<td>t-Butyl</td>
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<td>88.6</td>
<td>86.0</td>
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<td>57.9</td>
</tr>
<tr>
<td>Dimethyl</td>
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<td>79.5</td>
<td>76.8</td>
<td>96.5</td>
<td>60.0</td>
</tr>
<tr>
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<td>13.1</td>
<td>92.0</td>
<td>89.2</td>
<td>99.0</td>
<td>29.9</td>
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</table>

Table 1 — Effect of \([\text{NO}_3^-]\) and \([\text{H}^+]\) on Rate of Oxidation of n-Propanol and \(n\)-Propyl Amine by Ce^{4+}

<table>
<thead>
<tr>
<th>[Salt] or [acid] (M^{-1})</th>
<th>(Amine)</th>
<th>(k' \times 10^{-1}) (min(^{-1}))</th>
<th>(Alcohol)</th>
<th>(k \times 10^{-2}) (min(^{-1}))</th>
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<tbody>
<tr>
<td>0.05</td>
<td>—</td>
<td>5.90</td>
<td>7.00</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>—</td>
<td>9.35</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>—</td>
<td>4.82</td>
<td>7.30</td>
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<tr>
<td>0.80</td>
<td>—</td>
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</tr>
<tr>
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<td>—</td>
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<td>1.80</td>
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<td>2.05</td>
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<tr>
<td>2.00</td>
<td>—</td>
<td>1.50</td>
<td>9.50</td>
<td></td>
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</table>
Fig. 1 — (A) Plot of log ([α]/α-α) versus time ([Ce⁴⁺] = 0.005 M, [MeNH₂] = 0.800 M; [HNO₃] = 0.500 M, temp. = 333 K, \( μ = 0.55 \)); (B) Plot of (3 + log \( k' \)) versus (1 + log [MeNH₂]) conditions same as in (A); (C) Plot of \( ΔH^\ddagger \) versus \( ΔS^\ddagger \).

From the data in Table 2, it is clear that the order of reactivity of the amines is, secondary > tertiary > primary. This could be due to the fact that a substituent on the nitrogen atom affects the electron density on nitrogen to a greater extent than it does on the bond strength of the α-C-H bond. Therefore, the relative reactivities mostly reflect the changes in the electron density at the nitrogen atom rather than the more remote electronic influences at α-C-H bond.

The reactivity of amines is in the order: dimethyl > trimethyl > n-butyl > n-propyl > ethyl > methyl (Table 2). This is attributed to the operation of polar effects. In the present work the plots of log \( k' \) versus 1/T for all the amines studied do not intersect at a common point indicating that the isokinetic phenomenon is probably not strictly applicable in the present study. However, the linear plot obtained (Fig. 1C) for \( ΔH^\ddagger \) versus \( ΔS^\ddagger \) (Table 2) could be due to the compensation of errors. This however, should not distract us from concluding that the reactions studied follow a similar type of mechanism. The isokinetic temperature (\( θ = 409 \) K) obtained from the slope of above plot is much higher than the temperature range used (313-333 K) indicating that the reactions are ethalpy-controlled.

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References