Ce(IV) oxidation of alcohols using cetyltrimethylammonium ceric nitrate

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Cetyltrimethylammonium ceric nitrate (CTACN) has been used to oxidize some primary aliphatic and alicyclic alcohols in acetonitrile medium and the reaction kinetics have been investigated by spectrophotometric method. The decrease in the rate with increased concentration of CTACN has been attributed to the formation of reversed micelles by the oxidant in organic medium. An asymptotic decrease in rate with increase in [CTAB] supports the reversed micellization in the reaction medium. The plots of rate constants with [substrate] reflect the partitioning of the substrate in the reversed micellar system of CTACN. The kinetic isotope effect (\(k_H/k_D\)) of 1.97 has been attributed to the dehydrogenation mechanism for the oxidation of alcohols.

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Cetyltrimethylammonium (CTA) ion is well known for its amphipathicity, i.e., having the characteristics of being solubilized in both aqueous as well as non-aqueous medium. In continuation to our search for novel oxidizing agents suitable for substrates in organic solvents, we have made an attempt to synthesize and establish cetyltrimethylammonium ceric nitrate (CTACN) as a lipopathic agent. Unlike other quaternary ammonium ions (tetrabutyl or octylammonium ions), CTA ion has a relatively small head group with more exposed charge and a well-balanced hydrophobic group to carry the ion to both water and organic medium. CTA ion with bromide as the counterion can form micelles in aqueous medium and can form reversed micelles in chloroform. Onium with its counterion forms a tight ion pair in organic solvents, while in aqueous medium it dissociates.

Cerium (IV) compounds represent some of the most notable oxidants among the lanthanide reagents in various transformations of synthetic importance. As might be expected for very powerful one-electron oxidants, the chemistry of Ce(IV) in oxidations of organic molecules is dominated by radical and radical cation chemistry. CAN-mediated intermolecular radical reactions in ionic liquids have been reported. Ce(IV) compounds have also been used to study new carbon-carbon bond forming reactions leading to the one-pot synthesis of dihydrofurans, tetrahydrofurans, and aminotetralins.

Most of the works carried out with cerium oxidation so far have been done in aqueous media in presence of acid. However, kinetics of Ce(IV) oxidations of organic compounds in non-aqueous and neutral media have not yet been reported. Herein, we present the oxidation kinetics of some primary and secondary alcohols by cetyltrimethylammonium ceric nitrate (CTACN) in organic solvent without acid. This reagent is water insoluble in cold condition, but sparingly soluble in hot condition. It is soluble in many organic solvents. In the present study acetonitrile has been used as the reaction medium.

Materials and Methods

CTACN was prepared by the treatment of aqueous solutions of cetyltrimethylammonium bromide (Sisco, Mumbai, India) and ceric ammonium nitrate (Qualigens, India) as reported earlier. Alcohols (Sisco, Mumbai, India) were distilled before use. Acetonitrile (Merck, Mumbai, India) was purified by suspending ceric ammonium nitrate for 48 hours and
then distilled at its boiling point. CD$_3$OD was of NMR grade and was used as such. The surfactants, CTAB (Siscochem, Mumbai) and SDS (SLR, Mumbai), were purified using the recrystallization method and their purity was checked from physical constants. Triton X-100 (Qualigens, India) was used without further purification.

Kinetics of oxidation was measured in a (Perkin-Elmer Lambda 25) UV-vis spectrophotometer having thermostatic cell holders. Constant temperature was maintained in the cell by circulating water using a Kuret cryostat. Oxidation of alcohols and deuterated methanol was followed by monitoring the decrease in the absorbance of CTACN at a wavelength of 273 nm. All experiments were repeated at least three times and the rates of reactions were obtained with an error of ± 8%.

The products of oxidation of alcohols are found to be the corresponding carbonyl compounds. The products were characterized from the melting point of the 2,4-dinitrophenyl hydrazone derivatives and also from IR spectral data. The oxidation product was found to contain Ce(III) as the reduced product of Ce(IV). The stoichiometry of the reaction is found to be 2:1 for Ce(IV) and substrate.

**Results and Discussion**

CTACN is soluble in most of the organic solvents, wherein it exists as a tight ion pair of CTA$^+$ and ceric nitrate anion. The ionic conductance values of CTACN in acetonitrile are found to increase with the increase in [CTACN] bilinearly, with a transition point at a concentration of 3.8-4.2 × 10$^{-5}$ M (Fig. 1).

This bilinearity of the plot may be attributed to the aggregation of CTACN in acetonitrile. Structurally, CTACN behaves as a double tailed surfactant with ceric nitrate and quaternary ammonium ions combined as the hydrophilic head group with two cetyl chains as the hydrophobic tails. In non-polar solvent CTACN may form reverse micelles, wherein, ceric nitrate with the ammonium unit of CTA constitutes the core, and two cetyl chains in each unit envelop the core forming the mesophase. The conductance values of CTACN have been compared with cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium dichromate (CTADC) at the same concentration range. From the trend of the conductance values it is seen that the tightness of the ion pair is as follows:

CTADC > CTACN > CTAB.

While studying the oxidation by cetyltrimethyl permanganate (CTAP) in organic medium, Dash and Mishra$^{16}$ have observed a self-oxidation phenomenon. CTAP oxidizes CTA ion to the corresponding aldehyde. The absorbance of CTACN in various organic solvents is also found to decrease with time, but at a slow rate. However, in acetonitrile medium no appreciable change was observed till 72 hours$^{17}$. Hence, all the kinetic runs have been carried out in acetonitrile medium.

The oxidation kinetics of some aliphatic alcohols (Table 1) were investigated in acetonitrile medium in the absence of acid and the products were found to be the corresponding carbonyl compounds. The effects

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Table 1—Rate constants ($k_{obs}$) at three different temperatures (25-35°C), log P values, and thermodynamic parameters for oxidation of the alcohols at [CTACN] = 0.5 × 10$^{-4}$ M

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$k_{obs} \times 10^4$ (s$^{-1}$) at temp. (°C)</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>log P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>6.59 (25), 10.9 (30), 12.50 (35)</td>
<td>49.02</td>
<td>18.15</td>
<td>46.54</td>
<td>95.26</td>
<td>-0.66</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.33 (25), 6.38 (30), 8.03 (35)</td>
<td>31.23</td>
<td>18.68</td>
<td>28.75</td>
<td>33.80</td>
<td>-0.16</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>3.32 (25), 7.95 (30), 9.21 (35)</td>
<td>78.34</td>
<td>19.85</td>
<td>75.86</td>
<td>187.95</td>
<td>0.34</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.62 (25), 1.38 (30), 3.65 (35)</td>
<td>135.23</td>
<td>24.01</td>
<td>132.75</td>
<td>364.89</td>
<td>0.84</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>0.54 (25), 1.07 (30), 2.73 (35)</td>
<td>123.0</td>
<td>24.34</td>
<td>120.52</td>
<td>322.78</td>
<td>1.34</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>1.96 (25), 8.64 (30), 14.18 (35)</td>
<td>151.64</td>
<td>21.15</td>
<td>149.16</td>
<td>429.55</td>
<td>2.84</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>4.64 (25), 6.07 (30), 7.07 (35)</td>
<td>32.20</td>
<td>19.02</td>
<td>29.73</td>
<td>35.93</td>
<td>1.64</td>
</tr>
</tbody>
</table>
of variation of [substrate], [oxidant] and [additive] on the rate constants were studied with a few typical substrates like methanol, isopropanol and cyclohexanol.

The dependence of rate on the concentrations of substrate and oxidant can be explained through Scheme 1.

\[
\text{ROH} + \text{CTACN} \overset{k_1}{\longrightarrow} \text{Complex} \\
\text{Complex} \overset{k_2}{\longrightarrow} \text{Product}
\]

Scheme 1

Rate = \( k_{\text{obs}} [\text{ROH}]^a[\text{CTACN}]^b \), where \( k_{\text{obs}} \) is the observed rate constant, ‘a’ and ‘b’ are the orders with respect to substrate and oxidant and are positive and negative quantities respectively.

With the increase in substrate concentration the rate constant, \( k_{\text{obs}} \), increases in methanol and cyclohexanol nonlinearly (Fig. 2). With an increase in the concentration of oxidant, \( k_{\text{obs}} \) decreases linearly in the case of methanol (Fig. 3). In the case of cyclohexanol and isopropanol, the decrease in rate constants follows bilinear plots (Fig. 3). Such an observation may be explained through the proposition of a stable reverse micellar organization of CTACN in acetonitrile medium. In a CTACN reversed micelle, the hydrophilic oxidant may constitute the polar core and the hydrophobic cetyl tails may protrude to the organic bulk. The localization of the substrates in the reversed micelle plays an important role in the reactivity. Methanol penetrates into the reversed micellar organization with its hydroxy group directed towards the polar core and undergoes ready oxidation whereas cyclohexanol participates in aggregation with the oxidant to form reversed micellar assembly and gets oxidized.

The transition in the change in rate constant of cyclohexanol with change in [CTACN] is found to be at \( 4.1 \times 10^{-5} \text{ M} \), which corresponds to the CMC of CTACN in acetonitrile. The nature of plots for methanol and cyclohexanol represents the extent of their partitioning in the CTACN reversed micellar system.

Additional confirmation for reversed micellar organization of CTACN was observed during the oxidation of isopropanol, a secondary alcohol. The variation of CTACN during the oxidation process with constant substrate concentration also shows a bilinear plot with a cut point at \( 4.1 \times 10^{-5} \text{ M} \) which may be attributed to the critical aggregation concentration of the reversed micelle.

The ratio of the slope before and after the CMC in the plots may correlate with the accessibility of the substrate to the oxidant before and after the CMC, the ratio being 1.00 for methanol, 0.32 for cyclohexanol, and 11.15 for isopropanol.

The inverse dependence of [CTACN] with rate is a general observation in oxidation kinetics with phase transferring oxidants like CTAP\(^1\) and CTADC\(^2\). Such inverse dependence may be due to reversed
micellization of the oxidant in the organic medium. With increase in [CTACN] there is an increase in the buried Ce(IV) and thus decrease in the effective concentration of Ce(IV).

It has already been established that a cationic surfactant like CTAB forms stable micelles in water medium and reversed micelle in organic medium\textsuperscript{18,19}. CTACN also forms micelles in water medium\textsuperscript{19}. Addition of CTAB to the reaction mixture in acetonitrile leads to a steady decrease in the rate of oxidation. The rate constants are found to be 8.17, 5.2, 2.3 and 1.8 × 10\textsuperscript{4} s\textsuperscript{-1} at 0.4, 1.0, 2.0 and 3.0 × 10\textsuperscript{-4}M of CTAB respectively. This observation gives supporting evidence regarding the formation of reversed micelle by CTACN in organic medium. CTAB being a cationic surfactant assists in the organization of CTACN thus stabilizing the reversed micelle to a greater extent and leading to a decrease in the rate. Anionic surfactant like SDS and non-ionic surfactant like TX-100 do not have any impact on the rate of reaction.

At 25°C, the rate constant decreases with increase in alkyl chain length from methanol to 1-pentanol. However, for 1-octanol, it increases and shows a slight decrease for cyclohexanol (Table 1). The trend in the rate may be ascribed to the partitioning of the substrate from the bulk to the reversed micellar core. The plot of log \( P \) (\( P \) being the partition coefficient of solvent distribution in the two phase water-octanol system\textsuperscript{20}) against rate constant is in agreement with the above observation wherein methanol to 1-pentanol maintain one group and 1-octanol and cyclohexanol behave as another group so far as partitioning into reversed micellar system in acetonitrile medium is concerned. The alcohols with lower chain length (methanol to 1-pentanol) possess smaller partition coefficients, which decrease with the increase in chain length, and hence rates of oxidation by CTACN decreases whereas, 1-octanol and cyclohexanol with higher partition coefficients possess higher rates of oxidation. The sharp decrease in rate constant with increase in oxidant concentration in methanol shows that the corresponding substrate remains outside the reversed micellar system of CTACN whereas, the bilinear plot in the case of cyclohexanol and isopropanol (Fig. 3) is an indication of the partitioning of the substrate into the reversed micellar system.

The thermodynamic parameters \( \Delta G^\circ, \Delta H^\circ \) and \( \Delta S^\circ \) have been obtained by using the Arrhenius and Eyring equations and are reported in Table 1. These parameters show an increasing trend with increase in alkyl chain up to 1-octanol with slight drops at ethanol and pentanol. However, a sharp decrease in the value is observed for cyclohexanol, which may be attributed to the ease of removal of \( \alpha \)-H present in secondary alcholic group when compared to primary alcohols.

The Exner’s plot of \( \Delta H^\circ \) versus \( \Delta S^\circ \) is linear with an excellent correlation \( (r^2 = 0.999) \), with an isokinetic temperature of 310.4 K. This plot indicates a good compensation effect between enthalpy and entropy changes. This linearity indicates that a similar type of mechanism must be occurring in the oxidation reaction for all the substrates.

Addition of acrylonitrile to the reaction medium does not induce any polymerization. Hence, free radical involvement in the reaction may be ruled out.

A set of reactions was carried out with deuterated methanol CD\(_3\)OD and the rate constant was compared with that of methanol oxidation. The isotope effect of 1.97 (\( k_{\text{H}}/k_{\text{D}} \)) in the present study supports the involvement of \( \alpha\)-C-H in the rate-determining step\textsuperscript{21}. However, this small kinetic isotope effect may be explained on the basis of a dehydrogenation mechanism. Rocek et al.\textsuperscript{22} and Lee and Stewart\textsuperscript{23} had investigated the kinetic isotope effect of Cr(VI) oxidation of alcohols and had proposed that both ester formation and cleavage of the C-H bond contributed to the rate determining step. They observed a kinetic isotope effect of about 2 and 1.32 for 60% aqueous acetic acid and 95.3% sulfuric acid, respectively. However in the present study, the dehydrogenation process has been carried out in a completely anhydrous neutral medium where a concerted dehydrogenation may be occurring resulting in the formation of the required product.

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**References**


17 There is a decrease of 4% in OD, which is within experimental error.


