Kinetic and Analytical Studies of Oxidation of Cellulose Acetate and Cotton Linters with Ammonium Hexanitratocerate (IV)

U R CHAUDHARI and B MADHAVA RAO
Department of Chemistry, Visvesvaraya Regional College of Engineering, Nagpur 440 011, India
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The kinetics of oxidation of cellulose acetate was extensively studied to evaluate the thermodynamic parameters and the formation constant \( K_r \) of the intermediate complex and to work out the optimal conditions for analytical determination of cellulose content in cellulose acetate and cotton linter varieties/hybrids through an established stoichiometry. Second order rate constants obtained in these investigations were used to correlate the effects of variation of \([CA]\), \([Ce(IV)]\), \([H^+]\), \(\cdotNO_2\) and added \([Ce(III)]\). The mechanism of oxidation of cellulose involved the formation of a transitory cyclic complex, followed by disproportionation of the complex. The disproportionation of the intermediate complex is the rate-determining step. The values for \( K_r \), \(\Delta F^* \), \(\Delta \ln A^* \), \(\Delta S^* \) and \(\log A \) were found to be \(2.81 \times 10^2 \text{ mol}^{-1}\), 16.11, 16.52, 3.45 kcal mol\(^{-1}\), -42.44 eu and 9.37 respectively. A series of analytical estimations of cellulose content in these polymeric materials were undertaken using the optimal conditions and stoichiometry of oxidation of cellulose.

Keywords: Ammonium hexanitratocerate (IV), Cellulose acetate, Cotton linters, Kinetics, Polymeric materials

1 Introduction

With a view to establishing optimal analytical conditions, the kinetics of oxidation of cellulose acetate with cerium(IV) was studied. Literature on the kinetics of oxidation of, and analytical estimations of, cellulose in cellulose acetate and cotton linters by cerium(IV) in nitric acid medium is sparse. Higgins and Mc-Kenzie\(^1\) made an infrared spectroscopic study on the oxidation of \(\alpha\)-cellulose pulp with \(\text{HIO}_4\) and by air at 250°C. Koz'mina\(^2\) carried out the oxidation of cellulose ethers and esters by oxygen at 120°C. Mayat \textit{et al.}\(^3\) investigated into the mechanism of oxidation of cellulose by atmospheric oxygen in alkaline medium in \(\text{BuOH-pyridine-water}\) and \(\text{AcOH-AcOH-water}\) systems. In the synthesis of graft copolymerization from the oxidation of cellulose derivatives by Ce(IV) salts Galbrait\textit{h et al.}\(^4\) observed the formation of macroradicals as a result of pyranose ring splittings. In the oxidation of cellulose and starch materials by \(\text{Cl}_2\) gas Whistler\(^5\) noticed the disproportionation of cellulose due to the rupture of glycosidic bond. Tun Sun \textit{et al.}\(^6\) studied the oxidation of cellulose and its related products with 0.05 \( N \text{Ce(NO}_3)_2\) and established -CHO and 5,6-glycol units as reactive sites. Kulkar\textit{n et al.}\(^7\) showed that the rate of consumption of Ce\(^{4+}\) is higher during grafting of acrylonitrile monomer than during oxidation of cellulose alone, perhaps owing to the formation of homopolymers. Tumanova \textit{et al.}\(^8-11\) studied the oxidation of unbleached cotton cellulose by \(\text{ClO}_2\) as well as the hypochlorite oxidation kinetics of cotton cellulose and concluded that the total degradation of cellulose takes place at 50°C after 4 h. Kurylinkina \textit{et al.}\(^12,13\) studied the oxidation of cellulose and hydroxyl-containing compounds by Ce(IV) and observed that the oxidation of cellulose takes place with the splitting of formic acid and \(\text{CO}_2\) and also with a decrease in the mol. wt of cellulose sample. A detailed mechanistic study of Ce(IV) oxidation of \(\alpha\)-glucose and cellulose was carried out by Pottenger and Johnson\(^14\). She\textit{nai and Narkar}\(^15\) carried out the oxidation of dyed and undyed cotton yarns by sodium metaperiodate and observed a slower rate of oxidation in the presence of reactive dyes. In the oxidation of carboxymethyl cellulose with NaOCl, Kamel\(^16\) observed an increase in the rate of oxidation from alkaline to acid through neutral media. The behaviour of cellulose molecule during oxidation reactions was reviewed by Parthasarathi\(^17\). A number of references\(^18-25\) on the mechanistic study of oxidation of cellulose and its related substrates with various oxidants, viz. \(\text{NO}_2\), \(\text{N}_2\text{O}_4\), \(\text{ClO}^-\) and \(\text{IO}_4^-\), with and without Mn(II) and Co(II) catalysts are available.

A few analytical methods, employing cerium(IV) perchlorate, periodate and lead tetraacetate, for the quantitative estimation of cellulose in...
CA and also commercial cotton linters/hybrids are reported\textsuperscript{2,26,27}. However, some of these reactions are non-stoichiometric.

Cerium(IV) species in nitric acid medium differs from those in HClO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} media and further Cerium(IV) as ammonium hexanitratocerate(IV) is available to the highest purity (i.e. Anal-R E. Merck). These oxidation reactions are faster and finally lead to an established and reproducible stoichiometry.

2 Experimental Procedure

The materials employed were of highest purity (AnalaR E. Merck, GR, etc). A 0.1 \textit{N} Ce(IV) solution was prepared in 1.0 \textit{N} nitric acid and was further standardized by standard Fe(II). A 0.01 \textit{M} CA solution was prepared by dissolving a requisite amount of CA (BDH) in 62 ml of 4.0 \textit{N} HNO\textsubscript{3} and finally diluted to 250 ml with conductivity water ([HNO\textsubscript{3}] = 1.0 \textit{N}). Further, this solution was standardized through a cerate oxidimetry method\textsuperscript{26,27}. Stoichiometry of the reaction between Ce(IV) and CA was established for the experimental conditions employed as well as for 24, 48 and 72 h of reaction. In each case, it was found that 1 mol of cellulose of CA requires 12.0 equivalents of Ce(IV) for complete oxidation to formic acid stage as shown below:

\[
\text{C}_6\text{H}_{10}\text{O}_5 + 12\text{Ce}^{4+} + 7\text{H}_2\text{O} \rightarrow 6\text{HCOOH} + 12\text{Ce}^{3+} + 12\text{H}^+ 
\]

The progress of the reaction was followed by arresting the reaction mixture in a known excess of Fe(II) and back-titrating the unreacted Fe(II) with standard Ce(IV) sulphate solution.

The reaction follows the simple second-order kinetics under the conditions [Ce(IV)] = [CA]. A plot of \(1/(a-x)\) vs time \(t\) is linear, indicating that the total order is two. At different [Ce(IV)] and [CA], the plot \(\frac{2.303}{\text{log} \ (a-x)/(a-b)}\) vs time \(t\) is also linear, indicating first order dependence each in Ce(IV) and CA. As observed in the linear plot of \(1/k_2\) vs \(1/[\text{CA}]\) (Fig.1), the rate increases with increase in [CA] under the experimental conditions: [Ce(IV)] = 2.0 \times 10\textsuperscript{-2} \textit{M}, [HNO\textsubscript{3}] = 1.0 \textit{M} at 35 \pm 0.05°C. From the intercept and slope of this plot, the stability constant of 1:1[Ce(IV)-CA] complex was evaluated at the above mentioned conditions as \(K_i = 2.81 \times 10^3\ \text{mol}^{-1}\).

3 Results and Discussion

The reaction involves the formation of a prior complex between Ce(IV) and CA which further disproportionates into Ce(III) and a macro-free radical. The free radical subsequently undergoes a fast reaction with excess of Ce(IV) to give the formic acid as shown below.

\[
\text{Ce}^4+ + \text{H}_2\text{O} \rightarrow \text{CeOH}^3+ + \text{H}^+ \quad (1)
\]

\[
\text{Glucose unit of Cellulose} + \text{Ce}^4+ \rightarrow \text{Complex} \quad (1a)
\]

\[
\text{Glucose unit of Cellulose} + \text{Ce}^4+ + \text{NO}_3^- \rightarrow \text{Complex} \quad (1b)
\]

\[
\text{Glucose unit of Cellulose} + \text{Ce}^4+ + 3\text{H}_2\text{O} \rightarrow 6\text{HCOOH} + 12\text{Ce}^{3+} + 12\text{H}^+ \quad (1c)
\]

\[
\text{CaH}_{10} \text{O}_{4} + 12\text{Ce}^4+ + 7\text{H}_2\text{O} \rightarrow 6\text{HCOOH} + 12\text{Ce}^{3+} + 12\text{H}^+ \quad (1d)
\]

\[
\text{CaH}_{10} \text{O}_{4} + 12\text{Ce}^4+ + 7\text{H}_2\text{O} \rightarrow 6\text{HCOOH} + 12\text{Ce}^{3+} + 12\text{H}^+ \quad (1e)
\]

The rate of oxidation decreases with increase in [Ce(IV)], i.e. decreases by about half of its original value \(8.66 \times 10^{-3} \text{ mol}^{-1} \text{s}^{-1}\) at 2.0 \times \text{10}^{-2} \textit{M} [Ce(IV)] to 4.34 \times 10\textsuperscript{-2} \text{ mol}^{-1} \text{s}^{-1} at 4.0 \times \text{10}^{-2} \textit{M}[Ce(IV)] at 35 \pm 0.05°C, [HNO\textsubscript{3}] = 1.0 \textit{M} and [CA] = 1.666 \times \text{10}^{-3} \textit{M}, while the initial rate proportionately increases. Such an accelerating effect in the initial rate may be due to the availability of kinetically reactive Ce(IV) species, viz. (CeOH)\textsuperscript{3+}, in the reaction mixture. The effect of [H\textsuperscript{+}] on the second order rate constant (Fig.1) shows that there is a continuous, proportional decrease in the rate constant as the concentration of dissociated [H\textsuperscript{+}] increases from 0.5 \textit{N} to 6.0 \textit{N}. This observation is in agreement with that of Duke and Forist\textsuperscript{28}. The values of dissociated [H\textsuperscript{+}] at different concentrations of nitric acid were obtained from the spectroscopic data of Rao\textsuperscript{29}.

The rate of oxidation decreases proportionately with the activity of added nitrate ion (Fig.2). The added nitrate ion may complex with the reactive (CeOH)\textsuperscript{3+} species, converting it into less reactive species, viz. [Ce(OH)(NO\textsubscript{3})\textsuperscript{2+}] and [Ce(OH)(NO\textsubscript{3})\textsubscript{3}]\textsuperscript{+}. Such observations are also made by Shorter\textsuperscript{30}. The activity data were taken from Landolt-Bornstein Tabellen, Vol. III (1936). The marginal retardation effect of added Ce(III) (Fig.2) may be due to the association of reactive (CeOH)\textsuperscript{3+} with Ce(III), which consequently de-
increases the total concentration of reactive (CeOH)³⁺ species. Such instances of association of reactive Ce(IV) species with Ce(III) were already established by Yost et al.31 and also separately by Blaustein and Gryder32. Comparatively lower values for thermodynamic parameters, viz. \( \Delta E'' = 16.11 \text{ kcal mol}^{-1}, \Delta H'' = 16.52, \Delta F'' = -3.45 \text{ kcal mol}^{-1}, \Delta S'' = -42.44 \text{ eu} \) and frequency factor \( A = 2.34 \times 10^9 \text{ s}^{-1} \) respectively obtained in these investigations necessarily show that the reaction proceeds through a prior intermediary complex followed by a C-C bond cleavage and a free radical mechanism.

![Fig. 1](image1)

**Fig. 1 — Cellulose acetate — Ce(IV) reaction in 1 M nitric acid medium: effect of variation of [CA] and [H⁺]**

**Table 1 — Determination of Cellulose Content in Cellulose Acetate and Cotton Linters/Hybrids by Ammonium Hexanitratocerate(IV) in Nitric Acid Medium (~0.5 N) at 45 ± 10°C for 30-60 min**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Cellulose acetate</th>
<th>Cotton linters/hybrids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt of cellulose</td>
<td>Wt of cellulose</td>
</tr>
<tr>
<td></td>
<td>acetate/litre</td>
<td>found/litre</td>
</tr>
<tr>
<td>1</td>
<td>0.2520</td>
<td>0.1389</td>
</tr>
<tr>
<td>2</td>
<td>0.4898</td>
<td>0.2695</td>
</tr>
<tr>
<td>3</td>
<td>0.3563</td>
<td>0.1959</td>
</tr>
<tr>
<td>4</td>
<td>0.2943</td>
<td>0.1623</td>
</tr>
<tr>
<td>5</td>
<td>0.3084</td>
<td>0.1698</td>
</tr>
<tr>
<td>6</td>
<td>0.6169</td>
<td>0.3403</td>
</tr>
<tr>
<td>7</td>
<td>0.5359</td>
<td>0.2954</td>
</tr>
</tbody>
</table>

Cellulose acetate sample was supplied by BDH Chemicals Ltd, Poole, England.

Cotton varieties/hybrids were supplied by the Central Cotton Research Institute, Nagpur.

*Average cellulose content is based on five determinations.*

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**Oxidimetric determination of cellulose in cellulose acetate and commercially available cotton linters/hybrids with ammonium hexanitratocerate(IV)**

**Recommended procedure:** Transfer an aliquot of cellulose acetate solution (5-20 mg CA) or about 5-50 mg of any variety of cotton linter/hybrid (previously dissolved in 1.0 N nitric acid) into an Erlenmeyer flask along with 10 ml of 1.0 N nitric acid. Then add 2 to 4 times known excess of cerium(IV) solution in 1.0 N nitric acid, more than the required stoichiometry for oxidation to formic acid stage and also add a requisite volume of 1.0 N nitric acid and distilled water to maintain the

**Fig. 2 — Cellulose acetate — Ce(IV) reaction in 1 M nitric acid medium: effect of variation of [NO₃⁻] and [Ce(III)]**
From the above kinetic studies, it is evident that the rate of oxidation of cellulose is greatly facilitated at lower concentrations of nitric acid (~0.5 N). The reaction mixture should be kept at 45 ± 0.5°C for about 30-60 min for oxidation to formic acid stage. In all these determinations the unused Ce(IV) was back-titrated with standard Fe(II) to a ferroin indicator endpoint as well as potentiometric endpoint. Some typical results are given in Table 1.

The results on cellulose content in cotton linters/hybrids are in good agreement with the percentage of cellulose contents in different cotton linters/hybrids available in the literature. Furthermore, the fibre characteristics of the linters/hybrids are given in Table 2.

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