STUDIES ON THE KINETICS AND MECHANISM OF
THE OXIDATION OF CARBOHYDRATES IN THE
ABSENCE AND PRESENCE OF SURFACTANTS

ABSTRACT
THESIS

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Carbohydrates are widely distributed in plants and animals, where they fulfill both structural and metabolic roles. They are of three types, namely, mono–, oligo–, and polysaccharides. Monosaccharides are fundamental biomolecules in that they are building blocks of polysaccharides. They are building blocks of nucleotides also and, hence, of nucleic acids and of the chemical ADP/ATP energy storage system.

Oxidation and reduction reactions of sugars play key roles in biochemistry. Oxidation of sugars provides energy for organisms to carry out their life processes. The physiological and microbiological activities of carbohydrates depend largely in their redox behavior. Oxidation of monosaccharides by different oxidizing agents are, therefore, of special importance due to their biological relevance.\(^1\text{–}^4\) Due to multihydroxy functionality of saccharides they can chelate and coordinate to many metal ions. Cerium(IV) is used as an oxidant not only in analysis, but also in synthetic organic chemistry. Kinetic and mechanistic aspects of cerium(IV) oxidation of monosaccharides has also been studied\(^1\text{,}^5\text{–}^{10}\) but no attempt has been made on such redox systems in presence of micelles.

The chemical approach to biological problems through investigations of models rests upon the ability of the chosen system to mimic some functions of the biological ensemble. Surfactants in aqueous media have been extensively used as model systems. Surfactants are amphipathic molecules which have distinct hydrophobic and hydrophilic regions. Over a narrow concentration
range, defined as the critical micelle concentration, or cmc, surfactants dynamically associate to form large molecular aggregates, called micelles.

Rates of numerous organic and inorganic reactions are affected by micelles in aqueous solutions.\textsuperscript{11} Catalysis or inhibition is the consequence of substrate solubilization in the micellar pseudophase. Rate effects can be attributed to electrostatic, hydrophobic, electrophilic and/or nucleophilic interactions with the resultant alteration of free energy of activation for the overall process. Interest in micellar chemistry has been prompted by the proposed similarities between the structures of the globular proteins and spherical micelles and between micellar and enzymatic catalyses.

Therefore, the present thesis entitled ‘\textit{Studies on the Kinetics and Mechanism of the Oxidation of Carbohydrates in the Absence and Presence of Surfactants}’ is exclusively devoted to study the role of cationic and anionic micelles on reaction of cerium(IV) and carbohydrates. The surfactants used in this study are CTAB (cationic) and SDS (anionic) and the carbohydrates are two aldopentoses (D(+)xylose and L(+)arabinose), two aldohexoses (D(+)-glucose and D(+)-mannose), and two ketohexoses (D(–)-fructose and L(–)-sorbose). There are three chapters in the thesis, namely (i) Chapter 1 – \textbf{Introduction}; (ii) Chapter 2 – \textbf{Experimental}; and (iii) Chapter 3 – \textbf{Results and Discussion}.

\textbf{Chapter 1} includes introduction about carbohydrates, their importance, properties, chelating ability and reactivity towards metal ions, especially with cerium(IV). A brief account of the kinetics and mechanism of the cerium(IV)—carbohydrate reactions studied by different workers is also given.
The classification of surfactants, their uses, behavior and the pseudophase model and its applicability to the micellar catalyzed reactions is also provided. The chapter ends with the statement of the problem which suggests the importance of this study.

All the experimental details are described in Chapter 2. The materials used, their structure and formulas, sources and purities are given along with the method for the preparation of solutions and kinetic measurements. The method of cmc determination and procedure for the characterization and identification of products and stoichiometric determinations are also detailed in this chapter. Cerium(IV) is reduced to cerium(III), which is colorless at the maximum wavelength of cerium(IV), \( i.e., \ 385\text{nm} \). Therefore, examples of the spectra of the reaction product are also given in Chapter 2.

Chapter 3 – Results and Discussion, as the name implies, covers all the results obtained with their discussion. The oxidative degradation of carbohydrates by cerium(IV) has been found to be slow in aqueous \( \text{H}_2\text{SO}_4 \) medium with the evidence of autocatalysis. The effect of varying the concentrations of cerium(IV), carbohydrate, sulfuric acid, \( \text{SO}_4^{2-} \), \( \text{HSO}_4^- \) and surfactant was seen to elaborate their role in the cerium(IV)—carbohydrate redox reactions. The values of pseudo-first-order rate constants were independent on the initial concentrations of oxidant (cerium(IV)) indicating the first-order dependence of the reaction rate on [Ce(IV)]. The plots of rate constants \textit{versus} [reductant] were linear with zero intercepts, clearly suggesting the first-order dependence of rate constants on carbohydrates. The pseudo-first-
order rate constants decreased with increase in concentrations of $\text{H}_2\text{SO}_4$ and $\text{HSO}_4^{-}$ while a rate increase was found with increase in $[\text{SO}_4^{2-}]$. Effect of temperature on the reaction rate was studied to obtain the values of thermodynamic parameters. As regards the effect of surfactants, the rate constants increased as the concentration of cationic CTAB increased whereas anionic SDS has no effect (which may be due to the electrostatic repulsion between the negative head group of SDS and the reactive species of cerium(IV)). Lower values of activation energies for the reactions in CTAB medium as compared to aqueous medium confirm the catalysis.

Existence of various forms of monosaccharides and cerium(IV) has been discussed and $\beta$-anomer of pyranoid form is envisaged to be involved in the oxidation of monosaccharides. The rate increasing effect of CTAB and constancy of rates on varying [SDS] showed the participation of negatively charged species of cerium(IV). On the basis of $[\text{H}_2\text{SO}_4]$ and $[\text{HSO}_4^{-}]$–dependencies, species Ce($\text{SO}_4$)$_3^{2-}$ and/or HCe($\text{SO}_4$)$_3^{-}$ are proposed as the reactive species.

A probable mechanism is presented and discussed. The reactions start with formation of a complex between cerium(IV) and carbohydrate which undergoes decomposition in rate determining step. The oxidation products of the reactions are Ce(III), lactones, and aldonic acids (aldoses)/formaldehyde (ketoses).
The Mechanism for Aldonic acid anion Lactone

(A) Aldoses

\[
\begin{align*}
\text{R} & \quad \text{O} & \quad \text{OH} & + \text{Ce(IV)} & \xrightarrow{K_{C_1}} & [\beta\text{-anomer} \ldots \text{Ce(IV)}] \\
\beta\text{-anomer} & \quad \text{H} & & & & C_1
\end{align*}
\]

\[
\begin{align*}
\text{C}_1 & \quad \xrightarrow{k_1} & \text{Radical} & + \text{Ce(III)} & + \text{H}^+ \\
\text{Radical} & + \text{Ce(IV)} & \xrightarrow{\text{fast}} & \text{Lactone} & + \text{Ce(III)} & + \text{H}^+
\end{align*}
\]

(R = —H (for aldopentoses) or —CH\(_2\)OH (for aldohexoses) and Ce(IV) denotes the kinetically active Ce(IV)–species)

(B) Ketoses

\[
\begin{align*}
\text{H} & \quad \text{O} & \quad \text{OH} & + \text{Ce(IV)} & \xrightarrow{K_{C_1}} & [\beta\text{-anomer} \ldots \text{Ce(IV)}] \\
\beta\text{-anomer} & \quad \text{CH}_2\text{OH} & & & & C_1
\end{align*}
\]

\[
\begin{align*}
\text{C}_1 & \quad \xrightarrow{k_1} & \text{Lactone} & + \text{Ce(III)} & + \text{CH}_2\text{OH} & + \text{H}^+ \\
\text{Radical} & + \text{Ce(IV)} & \xrightarrow{\text{fast}} & \text{Ce(III)} & + \text{HCHO} & + \text{H}^+
\end{align*}
\]
Effect of the variables [oxidant], [reductant], [H\textsubscript{2}SO\textsubscript{4}], and temperature were also studied in presence of CTAB and it was found that the dependence of rate constants on all variables was same as in case of aqueous medium. Thus, the same mechanism operative in the aqueous medium is being followed in the CTAB micellar medium too.

The CTAB micelle-catalyzed kinetic results are interpreted by the Menger–Portnoy\textsuperscript{12} model where cerium(IV) in water associates with micellized surfactant (D\textsubscript{n}) giving micellized cerium(IV) and the reaction occurring in the aqueous and micellar pseudophases with first-order rate constants (k\textsubscript{w}' and k\textsubscript{m}').

The first-order rate constant for the overall reaction (k\textsubscript{Ψ}) is given by the following equation

$$k\textsubscript{Ψ} = \frac{k\textsubscript{w}'+ k\textsubscript{m}'K_s[D_n]}{1 + K_s[D_n]}$$  

which, on rearrangement gives

$$\frac{1}{(k\textsubscript{w}' - k\textsubscript{Ψ})} = \frac{1}{(k\textsubscript{w}' - k\textsubscript{m}' )} + \frac{1}{(k\textsubscript{w}' - k\textsubscript{m}') K_s[D_n]}$$  

The values of k\textsubscript{m}' and K\textsubscript{s} were evaluated from the slopes and intercepts of the plots of 1/(k\textsubscript{w}' - k\textsubscript{Ψ}) \textit{versus} 1/[D\textsubscript{n}].

The positive catalytic effect of CTAB micelles on the Ce(IV)–carbohydrate redox reactions has been explained in the following manner. The chemically active anionic Ce(IV)–species gets associated with the cationic micelles. The second reactant, carbohydrate, has no hydrophobicity due to the
presence of hydrophilic $-\text{OH}$ groups. As the reaction proceeds through the formation of a complex (see Eq. (1)/(5)), the associated Ce(IV)–species may form complex C1 at the Stern and Gouy-Chapman layers’ junctural region. The complex may now orient in a manner suitable for continuing the reaction. A possible arrangement (although highly schematic) could be as shown in Fig. 1.

**Fig. 1:** Schematic model showing probable location of reactants for the ionic micellar catalyzed redox reaction between cerium(IV) and carbohydrates.
Added inorganic salts (Na$_2$SO$_4$, NaNO$_3$, NaCl) inhibit the CTAB-catalyzed reaction that may be due to the exclusion of reactive species of cerium(IV) from the reaction site. The inhibitory power increases in the order Cl$^-$ < NO$_3^-$ < SO$_4^{2-}$.

On the basis of the second –order rate constant values for the reactivity of carbohydrates with cerium(IV), it is inferred that presence of $\text{—OH}$, $\text{—CHO}$ and ketonic groups increase the reducing power in the order aldohexoses < aldopentoses < ketohexoses. The trend shows that the oxidation by cerium(IV) seemingly depends on the number of $\text{—OH}$ groups, stereochemistry and the chelating ability of the monosaccharides. D(−)fructose has greater tendency to reduce cerium(IV) in comparison to L-sorbose and other monosaccharides (L(−)sorbose > L(+arabinose > D(+)xylose > D(+)mannose > D(+)glucose). It is interesting to note that the oxidation rates of various monosaccharides studied are of the same order. This means that these sugars are oxidized by a common mechanism, i.e., cerium forming a complex with C-1 hydroxyl group of the sugar prior to its rate-limiting disproportionation to a free radical.
References


