

Micelle Catalyzed Oxidation of D-Mannose by Cerium (IV) in Sulfuric Acid

Kabir-ud-Din^{1,*}, Mohd. Sajid Ali¹, Zaheer Khan²

¹Chemistry Department, Aligarh Muslim University, Aligarh 202002, UP, India;

²Chemistry Department, Jamia Millia Islamia, Jamia Nagar, New Delhi 110025, India

Abstract: Kinetics of D-mannose oxidation by cerium (IV) was studied in a sulfuric acid medium at 40 °C both in absence and presence of ionic micelles. In both cases, the rate of the reaction was first-order in D-mannose and cerium (IV), which decreased with increasing [H₂SO₄]. This suggested that the redox reaction followed the same mechanism. The reaction proceeded through formation of an intermediate complex, which was proved by kinetic method. The complex underwent slow unimolecular decomposition to a free radical that reacted with cerium (IV) to afford the product. The catalytic role of cationic cetyltrimethylammonium bromide (CTAB) micelles was best explained by the Menger-Portnoy model. The study of the effect of CTAB also indicated that a negatively charged species was the reactive form of cerium (IV). From the kinetic data, micelle-cerium (IV) binding and rate constants in micellar medium were evaluated. The anionic micelle of sodium dodecyl sulfate plays no catalytic role. The oxidation has the rate expression:

$$-d[\text{Ce(IV)}]=k_1K_{c1}[\text{D-mannose}][\text{Ce(IV)}]dt$$

Different activation parameters for micelle catalyzed and uncatalyzed paths were also calculated and discussed.

Key Words: Kinetics; D-Mannose; Cerium (IV); Cationic micelles; Anionic micelles

In the carbohydrate field, many researchers have investigated the oxidative degradation of monosaccharides (aldoses and ketoses) and their derivatives. This was done by different oxidants such as chromium (VI), vanadium (V), cerium (IV), cobalt (III), and iron (III) in aqueous sulfuric, perchloric acids and alkaline medium^[1–13]. However, despite the extensive study made on the kinetics of the oxidation of monosaccharides by these oxidants, the use of surfactants in similar studies is not so common^[14–18].

In a homogenous surfactant solution (above the critical micelle concentration), the reactive site might exist in one or more of the following environments: the micelle interior (hydrophobic region), the hydrophilic region (Stern layer), the micelle water-interface, and the bulk solvent^[19–23]. Preliminary observations indicated that the addition of cationic surfactant, CTAB, enhanced the reaction rate. It was thought important to investigate the kinetics and mechanism of D-mannose oxi-

dation by cerium (IV) in the presence of surfactants. For comparison, the reaction was also studied in the absence of surfactants.

1 Experimental

1.1 Materials and reagents

D-mannose (≥99%, s.d. fine, India), ceric ammonium nitrate (99%, Qualigens, India), sulfuric acid (98%, Merck, India), CTAB (99%, BDH, England), sodium dodecyl sulfate (SDS) (99%, Sigma, USA), sodium sulfate (98%, Merck, India), sodium nitrate (99%, Merck, India), sodium chloride (99.9%, BDH, India), and acrylonitrile (99%, s.d. fine, India) were used as received. All the solutions were prepared in doubly distilled water (specific conductivity: $1.5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$).

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*Corresponding author. Email: kabir7@rediffmail.com.

1.2 Kinetic measurements

Known amounts of cerium (IV) (oxidant) in H_2SO_4 and D-mannose (reductant) solutions were heated separately to the desired temperature (± 0.1 °C) before mixing. The course of the reaction was followed (under excess D-mannose) using the disappearance of cerium (IV) at 385 nm with a Bausch & Lomb Spectronic-20 spectrophotometer. The pseudo first-order rate constants were estimated from the linear parts of the plots of $\lg A$ versus time (A : absorbance) by carrying out reactions upto ca 80% completion. Other details of the kinetic procedure were similar to that described previously^[14–18,24].

1.3 Free radical test

The generation of free radicals during the course of the oxidation was confirmed by using acrylonitrile monomer^[25]. To a reaction mixture (containing $[\text{Ce(IV)}]=1.0 \times 10^{-3}$ mol·dm⁻³, $[\text{D-mannose}]=4.0 \times 10^{-2}$ mol·dm⁻³, and $[\text{H}_2\text{SO}_4]=1.83$ mol·dm⁻³), a known amount of acrylonitrile (20 cm³) was added. Formation of a polymer (white precipitate) appeared slowly. The positive response indicated *in situ* generation of free radicals^[25].

1.4 Product identification

Qualitative analysis of the oxidized reaction mixture with the excess [D-mannose] over [Ce(IV)] (the kinetic condition) in presence of H_2SO_4 was performed. After the kinetic experiment was completed, a part of the oxidized reaction mixture was treated with alkaline hydroxylamine solution, and the presence of lactone in the reaction mixture was tested by FeCl_3 -HCl blue test^[26].

To the other part of the reaction mixture, barium carbonate was added to make the solution neutral^[4]. FeCl_3 solution that had been colored violet with phenol when added to this reaction mixture gave a bright-yellow coloration^[27], indicating the presence of aldonic acid. It is concluded that lactone, formed in the rate determining step, is hydrolyzed to aldonic acid in neutral medium in a fast step. At higher pH, the [lactone] is reduced because of the formation of aldonic acid anion that shifts the equilibrium away from lactone^[28].

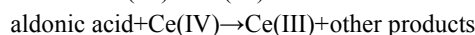
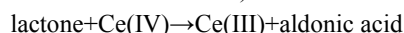
1.5 Critical micelle concentration measurement

The critical micelle concentration (cmc) values of the CTAB in the presence and absence of reactants were obtained from surface tensiometry by the ring detachment method using a S.D. Hardson tensiometer. Experiments were made under different conditions, i.e., solvent being water, water + cerium (IV) (1.0×10^{-3} mol·dm⁻³), and water + D-mannose (4.0×10^{-2} mol·dm⁻³); and the respective cmc values were 9.9×10^{-4} , 2.0×10^{-4} , and 8.3×10^{-4} mol·dm⁻³ at 40 °C. However, under the experimental conditions ($[\text{Ce(IV)}]=1.0 \times 10^{-3}$ mol·dm⁻³, $[\text{D-mannose}]=4.0 \times 10^{-2}$ mol·dm⁻³, and $[\text{H}_2\text{SO}_4]=1.83$ mol·dm⁻³), the obtained value was 1.26×10^{-5} mol·dm⁻³.

2 Results and discussion

2.1 Reaction-time curve and stoichiometry

Fig.1 shows the plots of $\lg A$ versus time for the oxidation of D-mannose by cerium (IV) at different reductant concentrations. As the plots deviate from linearity, it is clear that the oxidation kinetics proceed in two stages, i.e., initial slow stage and a relatively faster step. However, the faster step oxidation (autocatalytic reaction path) is not a true reaction path for the oxidation of D-mannose by cerium (IV). It might be the mixture of rates of oxidation of D-mannose and its products (lactone and aldonic acid).



The time, at which the deviation commenced, was found to decrease with the increase in [D-mannose] (Fig.1) and temperature. This might be because the oxidation rate of one of the oxidation products (lactone, whose concentration is small at lower [D-mannose]) becomes reasonable and shows up at higher [reductant]. Sala and coworkers^[29,30] studied the oxidation of lactones and found that the rates of their oxidation are at least 10-fold higher in comparison to the corresponding monosaccharides. Therefore, the pseudo first-order rate constants in absence (k_{obs1} , s⁻¹) and presence of surfactant (k_{sp1} , s⁻¹) were calculated from the slopes of the initial parts of the linear plots.

Several reaction mixtures with $[\text{Ce(IV)}] > [\text{D-mannose}]$, ($[\text{Ce(IV)}]=5.0 \times 10^{-4}$ mol·dm⁻³, $[\text{D-mannose}]=(0.5-4.5) \times 10^{-4}$ mol·dm⁻³ at constant $[\text{H}^+]=1.83$ mol·dm⁻³) were prepared. After completion of the reaction, unreacted cerium (IV) was estimated spectrophotometrically. The observed results suggest that two cerium (IV) ions are required for the oxidation of one molecule of D-mannose. However, due to the autoaccelerative nature of the reaction, the exact stoichiometry equation is difficult to predict.

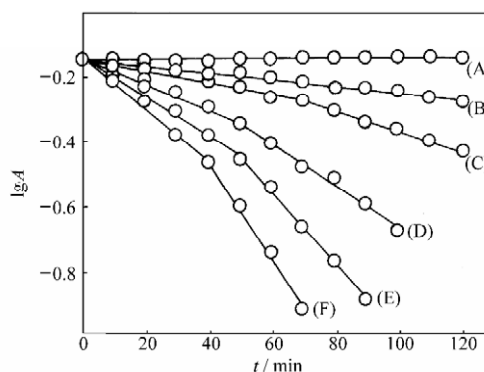


Fig.1 Plots of $\lg A$ versus time for the oxidation of D-mannose by cerium (IV)

reaction conditions: $[\text{Ce(IV)}]=1.0 \times 10^{-3}$ mol·dm⁻³, $[\text{H}_2\text{SO}_4]=1.83$ mol·dm⁻³, $[\text{D-mannose}]/(\text{mol} \cdot \text{dm}^{-3})$: 0.00 (A), 0.01 (B), 0.02 (C), 0.04 (D), 0.06 (E), 0.08 (F); $T=40$ °C

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