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Effect of microheterogeneous environments of CTAB, Triton X-100, and Tween 20 on the oxidative degradation of D-fructose by nanoparticles of MnO₂

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Abstract

The kinetics of the oxidative degradation of D-fructose by nanoparticles of MnO₂ has been studied in dilute sulfuric acid medium and also in the presence of surfactants of cetyl trimethyl ammonium bromide (CTAB), Triton X-100 (TX-100), and Tween 20. Amorphous nanoparticles of MnO2 in the form of spherical particulates of size 50-200 nm, as detected by a transmission electron microscope, have been found to exist, supported on two-dimensional gum acacia sheets. The reaction is first order in MnO₂ but complex order with respect to fructose and H⁺. The reaction is inhibited due to adsorption of reaction products on the surface of MnO₂ nanoparticles. The reaction takes place through an intermediate complex formation between β -D-fructopyranose and protonated MnO₂. A one-step two-electron transfer reaction ultimately leads to the formation of an aldonic acid and formic acid. The entropy of activation plays the key role for the reaction in the absence of surfactants. In the surfactant-mediated reaction, partitioning of both the reactants takes place between the aqueous and micellar pseudophases and reaction occurs following Berezin's model. Binding of fructose with the surfactants in the Stern/palisade layer takes place through the ion-dipole interaction and H-bonding while protonated MnO₂ remains at the outer side of the Stern/palisade layer within the micelle. Both the enthalpy and entropy changes associated with the fructose-water interaction, fructose-micelle interaction, and micelle-water interaction finally control the fructose-micelle binding.

KEYWORDS

Berezin model, fructose, kinetics, MnO2 nanoparticles, surfactant effects

1 | INTRODUCTION

Over the past few decades, a great deal of work has been undertaken to explore the mechanistic pathways for the oxidation of both inorganic^{1–3} and organic^{4–11} substrates by permanganate in acidic and alkaline media. However, the +4 oxidation state of manganese has received less attention until now, due to its solubility problem There are reports^{12,13} on the preparation of colloidal MnO₂ by the reduction of KMnO₄ with sodium thiosulfate under neutral conditions. Such form of colloidal manganese dioxide may show better oxidizing properties owing to its having a larger specific surface. A number of kinetic studies^{14–16} on the oxidation of a few organic compounds by colloidal solution of MnO_2 have already been reported.

Carbohydrates are the structural backbone of the DNA, RNA, and nucleic acids,¹⁷ and they serve as store and source of energy in biological systems and play important roles in different nutrition processes.¹⁸ Monosaccharides are involved in carbohydrate metabolism, and the mechanisms of their oxidative degradations are of immense importance from biological point of view.^{19–21} There are a number of reports on the