Kinetics of MnO₄⁻ Oxidation of Succinic Acid in Aqueous Solution of Cetyltrimethylammonium Bromide

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ABSTRACT: The rate of electron transfer from succinic acid to permanganate increases with an increase in the concentration of cationic surfactant, cetyltrimethylammonium bromide (CTAB). The micellar catalysis is attributed to the formation of an ion pair between CTAB subaggregates and reactants as well as an increase in the concentration (solubilization) of both reactants and/or intermediate in the micellar pseudophase. The effects of inorganic salts (MnCl₂, NaF, NaBr, and NaNO₃) have also been studied and discussed. The observed results are discussed in terms of the pseudophase model of the micelles proposed by Menger and Portony. Mechanisms consistent with the observed kinetic data have been proposed. © 2010 Wiley Periodicals, Inc. Int J Chem Kinet 42: 704–712, 2010

INTRODUCTION

Aqueous solutions of surfactants have been known to exhibit unusual properties. At low concentrations, the surfactant molecules behave just like ordinary electrolytes, but after attaining a certain concentration surfactant chains tend to self-associate, resulting in the formation of various aggregates (micelles, microemulsions, and vesicles) [1–4]. The utilization of surfactants as reaction media affects reaction rates, yield of products, mechanism, regioselectivity, and stereochemistry [5]. The micellar catalysis or inhibition factor is highly sensitive to the concentration of added counterions. Changes in the nature and concentration of electrolytes that would lead to detectable differences in the reaction rate in purely aqueous systems frequently cause appreciable differences for the same reactions in micellar media. Kinetic and mechanistic studies of a variety of redox reactions in the presence of surfactants have been carried out to understand the role of micelles as well as to speed up the removal of contaminant [6–11]. Recently, we reported the cetyltrimethylammonium bromide (CTAB)-assisted oxidation of tryptophan by permanganate [12]: CTAB solubilizes the tryptophan in the palisade layer (a few carbon atoms deep toward core) and thus accelerates the rate of electron transfer.

The net 5e-reduction of Mn(VII) to Mn(II), reaction pathways, and the final products of the redox reaction depend on the nature of the reductants and reaction conditions [13–18]. The details of permanganate ion oxidation of succinic acid in the presence and/or the absence of surfactants are not yet known. In this paper,

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