



Effect of CHAPS and CPC micelles on Ir(III) catalyzed Ce(IV) oxidation of aliphatic alcohols at room temperature and pressure



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ABSTRACT

Kinetics of cerium(IV) oxidation of aliphatic alcohols: ethanol, propanol, propan-2-ol, 1-butanol and 2-butanol were studied at 30 °C in the presence and absence of surfactants in acidic medium. The reaction was studied under pseudo-first-order conditions, $[\text{alcohol}]_r \gg [\text{Ce(IV)}]_r$. Ir(III)-salt used as catalyst had a significant effect on reaction rate. Cationic surfactant CPC (*N*-cetylpyridinium chloride) inhibits the reaction rate but zwitterionic surfactant CHAPS (3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate) catalyzes the oxidation reaction significantly. CMC value of CHAPS was determined by a spectrofluorometer. The reaction rate increased with increase in the acid concentration of the medium. NMR and FTIR spectra confirmed the oxidized products. The aggregation of surfactants in the reaction condition was studied through Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM). Dynamic light scattering (DLS) was used to characterize the shape changes of the aggregates. The variations of the reaction rates for the different alcohols in the presence of surfactants and metal ion catalyst are discussed qualitatively in terms of Berezin's model, nature of surfactants, and charge of surfactants. Ir(III) in association with CHAPS micellar catalyst exhibited ~500–2000 fold rate enhancements compared to the uncatalyzed reaction path.

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1. Introduction

Selective oxidation of alcohols to carbonyl compounds is one of the most important transformations in industrial chemistry. Aldehydes and ketones are precursors for many drugs, vitamins, fragrances and it opens up the possibility of using renewable biomass-derived feed stocks. The synthesis of carbonyl compounds is generally carried out in environmentally harmful organic solvents at high temperature and pressure by using stoichiometric oxygen donors (such as chromate and permanganate) producing large amount of wastes [1,2]. The oxidation of alcohols to aldehydes or ketones [3–6] has been traditionally based on the use of stoichiometric amounts of higher valent toxic transition metal oxidants, which renders the catalytic reaction expensive and unattractive from an environmental point of view [7–10] in both the laboratories and industries.

Cerium chemistry is a very broad area of considerable attention through the recent years, resulting in substantial advance both in the synthetic and mechanistic categories. Cerium(IV) is a well known oxidant [11] in acidic media having reduction potential 1.44 V of the couple Ce(IV)/Ce(III) in H₂SO₄ medium and is stable only in a high acid concentration [12]. Most of the cerium(IV) oxidation reactions are catalyzed by

transition metals such as Cr(III), Ag(I), Ir(III), Pd(III), Ru(III), Os(VIII), and Mn(II) [13–15]. It is previously reported that a variety of transition-metal-catalyzed transformations can be carried out within micellar media [16]. The potential of iridium(III) chloride as a homogeneous catalyst was best recognized when it was used in an acidic medium for oxidation of a range of alcohols to aldehydes, ketones or carboxylic acids proceeds in good yield. The Iridium(III) catalyzed oxidation of aliphatic and substituted alcohols, diols and aromatic compounds by cerium(IV) in an acidic medium has been investigated early [17,18]. To discover the effect of iridium(III) chloride in catalyzing the oxidation of aliphatic alcohols, we have studied the oxidation of ethanol, propanol, propan-2-ol, butanol and 2-butanol in the presence of iridium(III) chloride by cerium(IV) in an aqueous sulfuric acid medium. However, so far it was not investigated the influence of the metal catalyst on the reaction rates of oxidation reaction in micellar solutions.

Most of the organic substrates are often poorly soluble in water. Micellar systems are often used to overcome the solubility problems of the organic reactants [19,20]. Recently, great attention has been paid to the development of organic reactions in water [21]. Compared with other organic solvents, water is the most abundant “greenest” solvent among all solvents, it is ubiquitous on the earth as well as being a clean, and easy-to-handle [1]. The advantage of using micellar solution as catalyst, avoiding large amounts of organic solvents and the micellar catalyst can be recycled by simple techniques [22]. In addition to the avoidance of organic solvents and the recycling of the aqueous medium,

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the valuable micellar catalyst offers an additional benefit of facile reaction monitoring of room temperature reactions [23]. Nowadays the effect of micellar catalysis on reaction kinetics is growing popularly [6, 24–29]. Micellar catalysis [30] represents a viable solution to solubilization problems; in fact, surfactant aggregation driven by the hydrophobic effect ensures the formation of apolar nano-environments where both substrates as well as catalysts can be efficiently dissolved and interact with higher local concentrations [31,32]. It is to mention here that the most suitable surfactants are still selected for capable of solubilizing all species of proteins is 3-[(3-cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS). It has many applications in various fields of biological, medical, and pharmaceutical sciences [33]. CHAPS is a zwitterionic derivative of cholic acid having combined properties of both sulfobetaine type detergents and bile salts. It is frequently used in membrane protein isolation, surface modifier for specific protein adsorption, protein solubilization, purification, and denaturation [34]. But no such experiment was performed about the catalytic efficiency of CHAPS in kinetics. We have thus taken a more precise and detail experimental effort on the catalyzing properties of non-toxic [35] surfactant CHAPS over the *N*-cetylpyridinium chloride (CPC) in oxidation kinetics.

The important aim of this study was to determine the effects of structural variations of alcohols and effect of various surfactants on the rate of oxidation by Ce(IV). Besides that the other objectives were to find out the main kinetically reactive species (Scheme 1), main oxidation product, deduce the rate law and probable reaction site in the presence of catalyst.

2. Experimental

2.1. Materials and methods

2.1.1. Chemicals

Ethanol (SRL, AR, Mumbai, India), propanol (SRL, AR, Mumbai, India), propan-2-ol (SRL, AR, Mumbai, India), 1-butanol (SRL, AR, Mumbai, India), 2-butanol (SRL, AR, Mumbai, India), *N*-cetylpyridinium chloride (CPC) (SRL, AR, Mumbai, India), CHAPS (SRL, AR, Mumbai, India), H₂SO₄ (E. Merck, AR), Na₂SO₄ (E. Merck, AR), HCl (E. Merck, AR), pyrene (SRL, AR, Mumbai, India), iridium(III) chloride (SRL, AR, Mumbai, India), cerium(IV) ammonium sulfate (E. Merck, AR) and all other chemicals

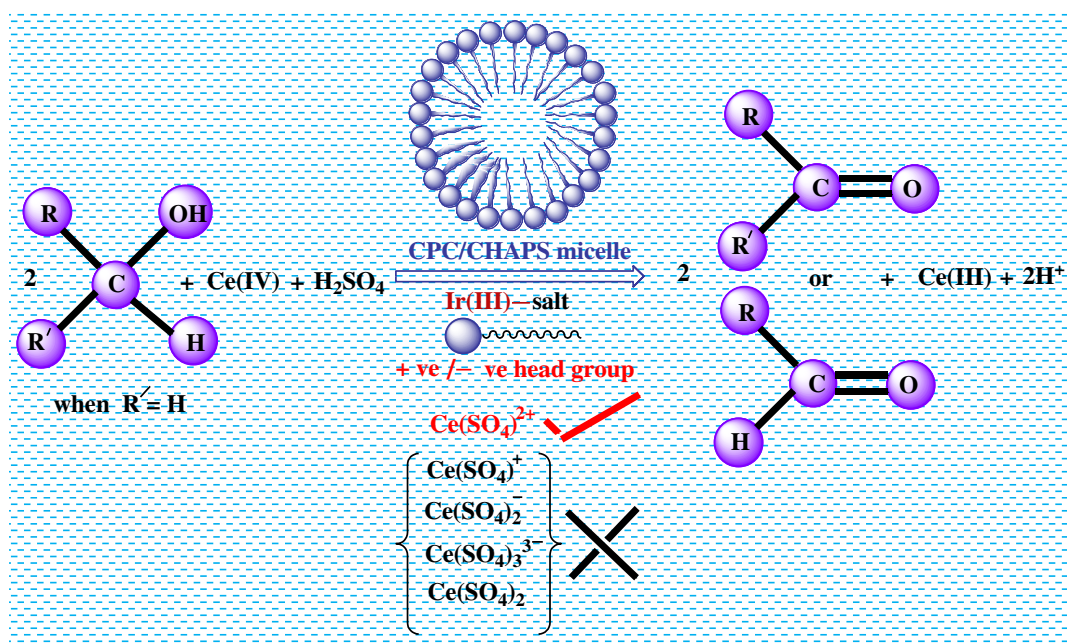
used were of the highest purity available commercially. The stock solution of Ce(IV) was obtained by dissolving cerium(IV) ammonium sulfate in 1 mol dm⁻³ sulfuric acid and was standardized with iron (II) ammonium sulfate solution using ferroin as an external indicator [18,36]. Cerium(IV) solution was always made up and stored in a black coated flask to prevent photochemical reaction. A solution of iridium(III) chloride was prepared by dissolving the sample in a minimum amount of concentrated hydrochloric acid. Conductivity water was used throughout the study.

2.2. Instrumentation

The weighing balance (Sartorius BSA224S-CW), sonicator (Digital Ultrasonic Cleaner CD 4820), centrifuge (Z206A, Hermle Labortechnik GmbH), UV-vis NIR spectrophotometer (UV-VIS-NIR-3600, SHIMADZU), stopped flow spectrophotometer (SX20 Stopped-Flow Spectrometer), DLS instrument (Malvern Zetasizer Nano ZS-90 instrument), optical microscope (LEICA DM 1000), SEM (S530 HITACHI SEM) instrument using IB 2 ion coater, HR-TEM microscope (JEOL JEM 2100), FTIR spectrophotometer (RX1, Perkin-Elmer), ¹H NMR (400 MHz, Bruker Ascend) and spectrofluorometer (LS 55, Perkin-Elmer) were used for various purpose of experiments.

2.3. Kinetic measurements

Reaction mixtures containing the known quantities of the substrate (i.e., ethanol, propanol, propan-2-ol, 1-butanol and 2-butanol), and acid under the kinetic conditions, [alcohol]_T ≫ 10[Ce(IV)]_T were thermostated at 30 °C (±0.1 °C). The reaction was initiated by mixing the requisite amounts of the oxidant and catalyst [surfactant or Ir(III) in particular case] with the reaction mixture. All kinetic measurements were made at an ionic strength of 2.0 mol dm⁻³ at 30.0 ± 0.1 °C. The progress of the reaction was followed by monitoring the decrease in absorbance of cerium(IV) at 320 nm [37] by the use of a UV-vis spectrophotometer equipped with 1 cm quartz cells in a thermostated cell holder and a Temperature Control System. The surfactant CHAPS was used above the critical micelle concentrations (6.3 mM at 303 K) [35] in all experiments to make sure of the existence of micellar aggregates in solution. The pseudo-first-order rate constants (*k*_{obs}, s⁻¹) were



Scheme 1. A probable scheme for the main reactive species involved in the oxidation in micellar media.

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