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ORIGINAL PAPER

Base-catalysed reduction of pyruvic acid in near-critical water

Li Gang Luo, Zhi Qiang Hou, Yuan Yuan Wang*, Li Yi Dai*

Department of Chemistry, East China Normal University, 200241 Shanghai, China

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The reduction of pyruvic acid in near-critical water has successfully been conducted under conditions of various temperatures, pressures, reaction time and the presence of formic acid as the reducing agent. In this work, additives (K_2CO_3, $KHCO_3$, and sodium acetate) used in the reduction of pyruvic acid were also investigated. The results showed that by adding K_2CO_3 (25 mole %) a markedly higher lactic acid yield (70.7 %) was obtained than without additives (31.3 %) at 573.15 K, pressure of 8.59 MPa, 60 min, and in the presence of 2 mol L^{-1} formic acid. As a base catalyst, K_2CO_3 definitely accelerated the reduction of pyruvic acid. The reaction rate constants, average apparent activation energy and pre-exponential factor were evaluated in accordance with the Arrhenius equation. The reaction mechanism of the reduction was proposed on the basis of the experimental results.

Keywords: near-critical water, additives, pyruvic acid, reduction, lactic acid

Introduction

Worldwide demand for lactic acid has increased greatly owing to its versatile applications in the chemical industries (Panwara et al., 2012; Lasprilla et al., 2012) and as monomers in the production of biodegradable polymers (PLA) (Inkinen et al., 2011; Joo et al., 2012; Wee et al., 2006). Almost 90 % of lactic acid is synthesised through bacterial fermentation (Adsul et al., 2007). Pyruvic acid is not only an acid but also a ketone, which has been reduced to lactic acid using a number of reducing reagents, which might be the cause of environmental problems. Furthermore, ketones can be reduced to the corresponding alcohols by formic acid with Ru(II) complexes as catalysts (Matharu et al., 2006; Fujii et al., 1996), but the reaction may last several days. Therefore, formic acid could be employed as a hydrogen donor for pyruvic acid reduction.

Near-critical water (NCW, T = 423.15–647.15 K, P = 0.4–21.83 MPa), with properties such as its functioning as a high ion product, low dielectric constant, and its ability to dissolve various materials, has attracted attention as a reaction medium or reactant for many reactions of organic compounds (Watanabe et al., 2004; Siskin & Katritzky, 2001; Nolen et al., 2003). These unique properties could also be readily tuned by altering temperature and pressure. One of these properties, the ion product, was, at around 533.15 K, up to three orders of magnitude higher than its value at ambient temperature, indicating that it was possible for water to be an acid or base catalyst precursor to catalyse organic reactions such as dehydration, hydrolysis, and the Cannizzaro reaction (Kruse & Dinjus, 2007; Ikushima et al., 2001; Savage, 1999).

In this paper, a study was carried out on the reduction of pyruvic acid by formic acid in NCW in order to obtain the kinetic parameters, which has not previously been reported. The study focused on the effects of temperature ranging from 533.15–593.15 K, different reaction times, and the concentration of formic acid on the reduction product. It investigated which of the additives (K_2CO_3, $KHCO_3$, and sodium acetate (NaAc)) used to catalyse the reaction afforded the greatest yield. The purpose of this paper was to employ an environmentally friendly method to reduce pyruvic acid, to confirm that the mechanism of the reaction was a base-catalysed reaction and that addi-

*Corresponding author, e-mail: dai_liyi@163.com, yywang@chem.ecnu.edu.cn