

ORIGINAL PAPER

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

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Received 7 August 2012; Revised 29 October 2012; Accepted 4 November 2012

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 (K₂CO₃, KHCO₃, and sodium acetate) used in the reduction of pyruvic acid were also investigated. The results showed that by adding K₂CO₃ (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, K₂CO₃ 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.

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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 (K₂CO₃, KHCO₃, 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-

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tives could effectively accelerate the reduction of pyruvic acid.

Experimental

Pyruvic acid and formic acid were commercially available from Tokyo Chemical Industry Co. (Tokyo, Japan) at a purity of ≥ 99 mass % and were used as received. Pure water was redistilled after deionisation. K₂CO₃, KHCO₃, NaAc, KOH, and HCl (37 mass %) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

The reaction was conducted in a high-pressure stainless steel batch reactor (Shandong Precision and Scientific Instrument Co., Jinan, China) 4.5 mm I.D. \times 40 mm length, with internal volume of 0.5 cm³ and consisting of a body and fastening cap. Solutions were based in mole % by dissolving the additives in the double-distilled water (Chang et al., 2012). The reactor was placed in additional bath tank which was preheated to a temperature higher than the desired reaction temperature to ensure that the reaction system could reach the desired temperature rapidly. After approximately $1 \sim 5$ min, the reactor attained the desired temperature and was controlled by a temperature controller $(\pm 1^{\circ}C)$ with a thermocouple inserted into the dip nozzle in the reactor. The reactor was removed from the molten salts tank and immersed into an ice water bath to terminate the reaction on elapse of the desired reaction time, and was opened after pressure reduction (Duan et al., 2007a). Five replicate experiments were conducted to ensure precision. The individual components were analysed by a high-performance liquid chromatograph (HPCL, Waters Systems, Waters SAX 5 µm analytical column $(4.6 \text{ mm I.D.} \times 250 \text{ mm}))$ equipped with a UV detector operating at a wavelength of 210 nm, with a mobile phase of 0.005 M H₂SO₄, and methanol (4 vol. %) in water at a flow-rate of 1.0 mL min⁻¹ (Duan et al., 2007b). The result of HPLC for the K_2CO_3 (20 mole %) solution sample after 30 min is shown in the Supplementary Data, which give information on reagents and by-products of this reaction such as lactic acid, acrylic acid, acetic acid, and other products.

Results and discussion

Greatest consideration was given to the Cannizzaro reaction, because the pyruvic acid underwent redox reaction with formic acid, which is a non-enolisable aldehyde. The conversion of pyruvic acid with formic acid in near-critical water appeared to take place in several stages: the reduction of pyruvic acid and the decomposition of lactic acid and pyruvic acid (Sato et al., 2004). The reduction of pyruvic acid would afford lactic acid. Dehydration and decomposition were the key reactions of the by-products. In the following discussions, the main products of pyruvic acid were divided into three parts: lactic, acrylic, and other acids.

Effect of temperature and pressure

The effects of temperature and pressure on the reduction process in $2 \mod L^{-1}$ formic acid with different mole ratios of pyruvic acid/water mixtures (1:40,1:50, 1:60, and 1:70) were investigated. Then, the three-dimensional charts were designed with temperature and pressure as the abscissae and the lactic acid yield as the vertical axis, as depicted in Fig. 1. In the process of pyruvic acid reduction, changes in the solvent property had a significant effect on the yield of lactic acid. In this experiment, the pressure was changed in accordance with the temperature control. It is well known that each temperature corresponded to a pressure (Wang et al., 2012). Fig. 1 shows that the lactic acid yield increased gradually, ultimately achieving its maximum value with the increase in temperature and pressure. The lactic acid yield decreased followed by the appearance of large quantities of byproducts, especially at high temperature and pressure. The increase in pressure was disadvantageous for the reduction reaction, in accordance with Le Chatelier's principle (if a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counter the imposed change and a new equilibrium is established). The lactic acid could be decomposed and dehydrated under high temperature and pressure conditions, which led to the decreasing yield. Hence, this clearly demonstrated that the formation rate of lactic acid was faster than the rate of dehydration at 573.15 K and 8.59 MPa.

The optimal temperature of the pyruvic acid reduction in formic acid was approximately 573.15 K. The maximum lactic acid yields were 23.4 %, 24.6 %, 31.3 %, and 28.5 % in Figs. 1a–1d, respectively. Therefore, under the r/w mole ratio = 1 : 60 of pyruvic acid/water, at temperature of 573.15 K and pressure of 8.59 MPa, the lactic acid yield achieved a value as high as 31.3 %.

Effect of reaction time

The contents of lactic acid and the conversion of pyruvic acid are shown in Fig. 2 at varying times with (Fig. 2a) and without (Fig. 2b) K_2CO_3 (25 mole %) addition. Fig. 2a clearly demonstrates that in the conversion of pyruvic acid, the contents of lactic, acrylic, and other acids were slowly increasing throughout the time. In the case of lactic acid, the content decreased slightly between 60–90 min. This was because that the HCOOH decomposed in both sub- and supercritical water (Yagasaki et al., 2002).

Fig. 2b shows that the conversion increased significantly with the addition of 25 mole % K₂CO₃. The pyruvic acid reduced rapidly and the conversion was



Fig. 1. Lactic acid yield at different pyruvic acid/water mole ratios: 1 : 40 (a), 1 : 50 (b), 1 : 60 (c), 1 : 70 (d); varying temperature and pressure, and reaction time of 60 min.



Fig. 2. Conversion of pyruvic acid (\blacksquare) and content of lactic (\bullet), acrylic (\blacktriangle), and other (\lor) acids at varying reaction times: T = 573.15 K, pyruvic acid/water = 1 : 60, [HCOOH] = 2 mol L⁻¹ (a); T = 573.15 K, K₂CO₃ = 25 mole %, pyruvic acid/water = 1 : 60, [HCOOH] = 2 mol L⁻¹ (b).

almost 90 % after 80 min. The same trend was apparent for the content of lactic acid. However, the yield of acrylic acid exhibited a different trend, which was less than that in Fig 2a. This indicated that K_2CO_3 could catalyse the reduction of pyruvic acid to lactic acid and reduce the decomposition of lactic acid. The highest content of lactic acid (70.7 %) was obtained at 60 min, while the conversion of pyruvic acid was 78.8 %. The lactic acid content exhibited a rapid growth compared to that without K_2CO_3 . The decomposition of lactic acid, pyruvic acid, and formic acid increased with time rather than the form of lactic acid. Hence, the lactic acid content decreased over 60 min.

Fig. 3 shows a comparison between the conversion



Fig. 3. Effect of reaction time on pyruvic acid conversion (a) and content of lactic acid (b) at pyruvic acid/water mole ratio of 1:60; [HCOOH] = 2 mol L⁻¹; and T = 573.15 K (\blacksquare), T = 593.15 K (\bullet), and T = 573.15 K in the presence of K₂CO₃ (\blacktriangle).



Fig. 4. Effect of formic acid concentration on pyruvic acid conversion (■) and contents of lactic (●), acrylic (▲), and other (▼) acids. t = 60 min, T = 573.15 K, no other additives.

of pyruvic acid and the content of lactic acid with and without K_2CO_3 at different temperatures. In general, it may be concluded that the addition of K_2CO_3 effectively promoted the conversion of pyruvic acid and the content of lactic acid. The yield of lactic acid at 573.15 K with 25 mole % of K_2CO_3 even exceeded the value at 593.15 K without the catalyst. It may, therefore, be concluded that K_2CO_3 may reduce the temperature of the reduction of pyruvic acid. In comparison with the reduction in NCW without the catalyst, pyruvic acid would achieve a faster reduction at a lower temperature and lactic acid would achieve an optimum yield with K_2CO_3 .

Effect of different concentrations of HCOOH

Fig. 4 presents the content of lactic acid, acrylic acid, and other acids and the conversion of pyru-



Fig. 5. Yield of lactic acid in the presence of different additives: NaAc (■), KHCO₃ (●), K₂CO₃ (▲), t = 60 min, T = 573.15 K.

vic acid in the presence of different concentrations of formic acid (0.25 mol L^{-1} , 0.5 mol L^{-1} , 1 mol L^{-1} , 1.5 mol L^{-1} , and 2 mol L^{-1}) at 573.15 K after 60 min. The yield of lactic acid increased sharply, from 20.1 % to 31.3 %, with the concentration of HCOOH (0.25–2 mol L^{-1}). Fig. 4 shows that the content of all by-products increased slightly and that the formic acid had a significant effect on the content of lactic acid rather than the acrylic acid and other acids, due to the formic acid performing as a proton donor in the mechanism of the Cannizzaro reaction (Naskar & Bhattacharjee, 2007). All the concentrations of formic acid tested could accelerate the reduction of pyruvic acid.

Effect of additive concentration

On the basis of the conventional Cannizzaro reaction mechanism, the presence of base could favour the formations of products. In the experiments performed,



Fig. 6. Conversion of pyruvic acid (a) and content of lactic acid (b) for varying reaction times at 573.15 K, concentration of catalyst (K₂CO₃ (■), KOH (●), or HCl (▲)) was 25 mole %.

three different additives (K₂CO₃, KHCO₃, and NaAc) were introduced to study the mechanism of the reaction. Fig. 5 shows the tendency of the lactic acid content reflects the additives introduced into NCW ranging from 5 mole % to 35 mole % at 573.15 K, 60 min. The yields with additives were much higher than those without additives and the effect of additives on the yield was in the order: K_2CO_3 , NaAc, and KHCO₃, with the highest yields of 70.7 %, 61.2 %, and 55.4 %, respectively. In the reaction, the formic acid ultimately converted to CO_2 . According to the Le Chatelier's principle, the CO_2 absorbed by the base was propitious to the balance of lactic acid. Nevertheless, the yield decreased in the presence of 30 mole % and 35 mole % of the additives' solution. Fig. 5 shows that a high concentration of base additives was disadvantageous to the formation of lactic acid. A high content of additives can generate large quantities of by-products such as acrylic acid, acetic acid, and other by-products. The decomposition of lactic acid in near-critical water can produce acetaldehyde and acetic acid (Li et al., 1999), as shown in HPLC chromatogram (refer to Supplementary Data).

The effects of K_2CO_3 , KOH, and HCl on reduction of pyruvic acid were also compared. Fig. 6a shows that K_2CO_3 and KOH displayed the same trend of sharply accelerating the reduction of pyruvic acid. According to this trend, HCl had less influence on the conversion of pyruvic acid, suggesting that the reaction was a base-catalysed mechanism. As treated by NCW and alkali, the stability of the lactic acid declined. Fig. 6b shows that the lactic acid content decreased when the time exceeded 1.5 h on KOH, while the lactic acid concentration decreased slowly in the K₂CO₃ system. However, the yield of lactic acid in HCl increased very slightly. These results showed that K_2CO_3 was more effective in pyruvic acid reduction in NCW.



Fig. 7. Second-order reaction kinetics for pyruvic acid reduction at temperature: 533.15 K (■), 543.15 K (▲), 553.15 K (●), and 563.15 K (▼). Fit of experimental data by second-order reaction kinetics (lines).

Kinetics and mechanism of reduction of pyruvic acid in HTW

In order to obtain a more dynamic characterisation of the reduction of pyruvic acid, the relationship between the concentration of pyruvic acid and time was investigated. The best-fit model predictions for second-order reaction kinetics at different temperatures are shown in Fig. 7. If a plot of $1/[CH_3COCOOH]$ vs. time produced a straight line with a slope of k, the reaction followed the secondorder reaction kinetics for this reactant. Fig. 7 shows that the scattered plots were more fitted in a line. Therefore, the reduction of pyruvic acid showed a coincidence of second-order reaction kinetics in the reactant at the temperature ranges investigated, with the slopes of the line being the various rate constants.

The various rate constants at different temperatures are listed in Table 1 based on the second-order

Table 1. Second-order reaction rate constant $k/(L \text{ mol}^{-1} \text{ s}^{-1})$ for reduction of pyruvic acid in high temperature water at different temperatures

T/K	$k \cdot 10^2 / ({\rm L~mol^{-1}~s^{-1}})$	
543.15 553.15 563.15 573.15	$\begin{array}{c} 1.35\pm0.02\\ 1.41\pm0.01\\ 1.90\pm0.02\\ 2.64\pm0.04\end{array}$	

reaction kinetics. The temperature dependence of the rate constant k could be described by the Arrhenius equation (Kabyemela et al., 1997):

$$k = A \exp\left(-E_{\rm a}/RT\right) \tag{1}$$

where $k/(\text{L mol}^{-1} \text{ s}^{-1})$ is the reaction rate constant, $A/(\text{L mol}^{-1} \text{ s}^{-1})$ pre-exponential factor, $E_{\text{a}}/(\text{kJ mol}^{-1})$ activation energy, and $R/(\text{J K}^{-1} \text{ mol}^{-1})$ the universal gas constant.

The apparent activation energy of the hydrogenation reaction of pyruvic acid was calculated according to Eq. (1) using the average rate constants data from Table 1. The activation energy E_a and logarithm of pre-exponential factor $\ln A$ were evaluated as (59.5 ± 2.1) kJ mol⁻¹ and 8.7 ± 0.2 at the temperature ranges investigated. Socha et al. (1981) reported a value of 68.6 kJ mol⁻¹ for the Cannizzaro reaction of formaldehyde in Ca(OH)₂ acting as a catalyst at ambient temperature. Clearly, NCW accelerated the reaction by reducing the energy barrier for the chemical transformation.

Swain et al. (1979) proposed that the mechanism of the Cannizzaro reaction in an aqueous solution followed several pathways: a rate-determining step was the formation of an intermediate with the C-O-C bond between two aldehyde molecules, followed by the rearrangement or intermolecular hydride shift. Another reasonable structure for the transition state was an intermediate with the C—H—C bond between two aldehyde molecules, while the carbonyl oxygen atom of one or both aldehydes was polarised by solvent (water or alcohol) molecules, and the protons then underwent a hydride shift. Under the supercritical water conditions, Ikushima et al. (2001) and Bröll et al. (1999) reported on the reaction mechanism with or without the base catalyst added, respectively. Under the base catalysis conditions, Ikushima investigated whether the OH[•] radical or OH⁻ ion catalysed the Cannizzaro reaction. The experimental results showed that the correct mechanism was that based on the presence of OH^{-} ions. Geissman (1944) investigated the reaction of pyruvic acid and formic acid in subcritical ethanol at 573.15 K. Under these conditions, the lactic acid yield was 3 %, inferring that the subcritical ethanol lacked the OH⁻ ion responsible for the reduction reaction catalysis. When the volume ratio of water/ethanol was 1:20, the lactic acid yield attained 8 %, which indicated that the OH^- was necessary to activate the reaction. On the basis of the experiment and data, a possible mechanism for the hydrogen transfer reduction of pyruvic acid was proposed. Fig. 8 shows that the mechanism generally postulated for the reduction involved a pre-equilibrium addition of OH⁻ to the formic acid and a rate-determining intermolecular hydride transfer between the formic acid and pyruvic acid, followed by the production of intermediates leading to the formation of lactic acid. The OH⁻ ion was required to form the product, lactic acid, and the participation of the OH⁻ ion in the reduction using NCW was clearly demonstrated (Ashby et al., 1983, 1987; Chung, 1982). Fig. 8 indicates that formic acid (I) was attacked by OH⁻ to transfer the electron to the carbonyl. Next, H in the deprotonated formic



Fig. 8. Proposed mechanism for reduction of pyruvic acid to lactic acid in near-critical water.

acid (II) could be the initiator. Due to the pyruvic acid (III) being attacked by H and the carbonyl bonds broken, the intermediate (IV) was formed. The stable products (deprotonated lactic acid V and CO_2) were then formed directly in the rate-determining step. Finally, deprotonated lactic acid (V) combined rapidly with the proton (H⁺) from the solution to form lactic acid.

Conclusions

The experiment disclosed an effective process for reducing pyruvic acid to lactic acid. Pyruvic acid was reduced in NCW at 533.15-593.15 K to yield lactic acid. The influences of temperature, pressure, reaction time and concentration of formic acid and additives on the product yield and conversion of pyruvic acid were investigated. A series of experiments indicated that the yield of lactic acid was low (31.3 %) at 573.15 K (t = 60 min, [HCOOH] = 2 mol L⁻¹). Nevertheless, when additives were introduced, the yield markedly increased to 70.7 % in the K_2CO_3 solution under the same reaction conditions. Clearly, the reduction reaction of pyruvic acid in near-critical water was a base catalysis in near-critical water. It also showed that additives (such as K_2CO_3) not only provided sufficient amount of OH⁻, but also achieved a more rapid reduction at a lower temperature used in the experiments. Due to the second-order kinetics of this reaction, the rate constants, average apparent activation energy and frequency factors were evaluated according to the Arrhenius equation.

Acknowledgements. The authors wish to express their gratitude for the financial support received from the National Natural Science Foundation of China (Nos. 21073064, 21003049) and the Fundamental Research Funds for the Central Universities.

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