



Mechanism and kinetics of 4-hydroxy-2-butanone formation from formaldehyde and acetone under supercritical conditions and in high-temperature liquid-phase

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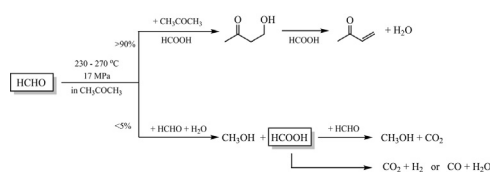
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HIGHLIGHTS

- An autocatalytic synthesis of HB with a yield of 90% is studied.
- The by-product HCOOH catalyses the aldol reaction.
- HCOOH is generated via self-disproportionation of HCHO.
- A kinetic model for the forming and dehydration of HB is proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this paper is to explore the reason for the catalyst-free phenomenon of synthesizing 4-hydroxy-2-butanone from formaldehyde and acetone under supercritical conditions and in high-temperature liquid-phase. Experiments were conducted in a tubular flow-type reactor at temperatures between 230 and 270 °C for residence times between 0.5 and 8 min. Under these conditions, a small amount of formic acid appeared via noncatalytic self-disproportionation of formaldehyde. The generated formic acid proved to play a role as catalyst in main reactions. A mechanism-based detailed chemical kinetics model for main reactions was suggested to assess the effect of temperature. This model applied well both under supercritical conditions and in high-temperature liquid-phase. The activation energies for forming and dehydration of 4-hydroxy-2-butanone were 97.5 ± 3.5 kJ/mol and 120.6 ± 5.8 kJ/mol, respectively.

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1. Introduction

The aldol reaction is widely applied for C–C bond formation in both chemical industry and laboratory. However, the typical procedure for aldol reaction mainly has two drawbacks from the

viewpoint of green chemistry (Mestres, 2004; Stevens et al., 2009). One is the poor selectivity resulted from the high reactivity of carbonyl group. The other is that the aqueous base catalyst generates large volumes of waste that needs separation and neutralization after reaction. Some attempts have been made to conduct aldol reaction in inert supercritical fluids such as supercritical carbon dioxide to obtain higher selectivity and flexibility of separation operation (Hagiwara et al., 2005; Liu et al., 2010; Stevens et al., 2009).

Recently, Huang et al. (2013) reported a synthesis method of 4-hydroxy-2-butanone (HB) from formaldehyde and supercritical acetone (critical data of acetone: $T_c=508.1$ K, $P_c=4.70$ MPa Haynes, 2010) without adding any acid/base catalysts. HB is an

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important intermediate in the industrial manufacture of methyl vinyl ketone (MVK), vitamin A, raspberry ketone and other fine chemicals. The typical synthesis procedure of HB is conducted under the catalysis of base with a yield of about 70%. However, the synthesis of HB under supercritical conditions reported by Huang does not need the addition of any catalyst, and the yield of HB by this method could reach 73.8%. Thus, the problem of alkalic waste is completely solved.

It is reported that some other reactions proceed well in supercritical acetone in absence of catalysts that are essential under ambient conditions (Kamitanaka et al., 2007, 2009; Osada et al., 2004; Royon et al., 2011). However, understanding of the mechanisms of these reactions is still limited. Some researchers (Royon et al., 2011) attributed the catalyst-free phenomenon in supercritical acetone to the enhanced acidity of the acetone's α -H. This explanation was deduced from the studies that enol concentration of acetone is several orders of magnitude higher in superheated water (Brodovitch et al., 2009; Ghandi et al., 2003). However, the relationship between acetone's acidity and the enol concentration has not been revealed yet.

Intrigued by the advantages of synthesizing HB as Huang et al. (2013) reported, we have performed a quantitative study under supercritical conditions and in high-temperature liquid-phase to explore the reason for the catalyst-free phenomenon. It occurred to us that non-catalytic self-disproportionation of formaldehyde could carry out under hydrothermal conditions (Bröll et al., 1999; Osada et al., 2004; Tsujino et al., 1999; Watanabe et al., 2003). Thus, there is a big possibility that the formic acid rather than acetone plays a role as catalyst. In this study, the formic acid-catalysed mechanism was proved through experiments and the corresponding mechanism-based detailed chemical kinetics model (DCKM) was built.

2. Materials and methods

2.1. Materials

Formaldehyde solution (36–40 wt% in water) was purchased from Xilong Chemical Co., Ltd., China. Acetone (purity of 99.5%) was supplied by Sinopharm Chemical Reagent Co., Ltd., China. 4-Hydroxy-2-butanone (purity of 95%), formic acid (purity of 99%) and 2-pentanone (purity of 99%) were supplied by Aladdin Industrial Co., China. They were all used without further purification.

2.2. Experimental apparatus and procedure

The experiments were performed in Supercritical Fluid Reaction System SFR0.1 manufactured by SEPAREX and modified by ourselves. The schematic diagram of experimental apparatus is presented in Fig. 1. The experimental apparatus mainly consisted of two HPLC pumps, a preheater, a cooler and a replaceable 316L stainless steel tube reactor with a total volume of 12 mL, 24 mL, 42 mL and 85 mL (I.D. 4.57 mm). The system pressure was controlled by a programmable back pressure valve located at the exit of the reactor. A gas/liquid separator was used to facilitate the sampling. The pressure sensor and the temperature sensors logged at several points throughout the system were corrected before the experiments, and the accuracies of the temperature and pressure were within ± 1 °C and ± 0.1 MPa, respectively.

All experiments in synthesis of HB herein were conducted at a constant pressure of 17 MPa with a fixed acetone/formaldehyde solution mass ratio of 15:1 in the feed. Preheated acetone was mixed with unheated formaldehyde solution. The temperature of the preheater was specified to make the feed mixture meet the

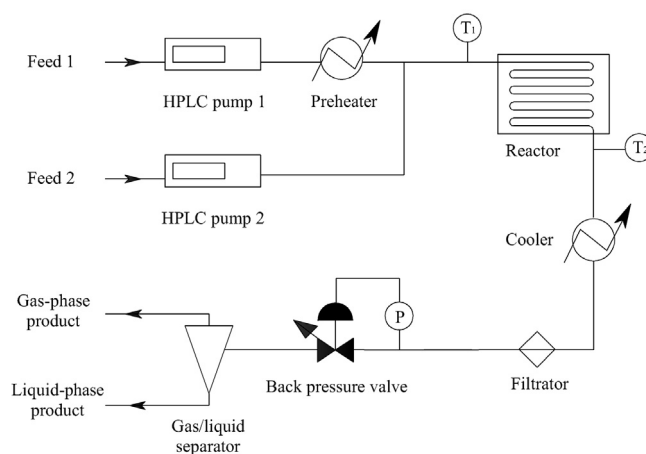


Fig. 1. Schematic diagram of experimental apparatus.

reaction temperature. The product was collected for further analysis, when the reaction temperature and pressure were stabilized and the composition of the product no longer changed.

The residence time was calculated as the volume of the reactor divided by the volumetric flow rate of the reaction mixture at the nominal reaction condition. The volumetric flow rate was calculated as the mass flow rate of the feed mixture divided by the density of the raw mixture at the nominal reaction condition. An assumption was introduced that the density of the reaction mixture could be set as a fixed value during the reaction. It is reasonable as the difference between the density of raw mixture and the one of product is very small. The densities of the feed mixture at the nominal reaction condition were calculated by Aspen Plus[®] V7.2 with Peng–Robinson equation of state with Wong–Sandler mixing rules (PRWS EOS).

2.3. Analytical methods

The gas-phase and liquid-phase products were analysed qualitatively by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890 GC system equipped with a mass spectrometry detector. The liquid-phase products were determined quantitatively using an Agilent 7820A GC system with a 30 m \times 0.25 mm \times 0.25 μ m Agilent HP-5 capillary column and a flame ionization detector. The oven temperature was isothermal at 70 °C for 4.5 min, increased from 70 °C to 200 °C at a rate of 30 °C/min, then held at 200 °C for 5 min. The temperatures of GC injector and detector were 250 °C. HCHO was determined quantitatively using a Fuli 9820 GC system with a GC packed column (length 2.5 m, GDX-403 packing, mesh size 60/80) and a flame ionization detector. The oven temperature was isothermal at 90 °C for 1 min, increased from 90 °C to 130 °C at a rate of 40 °C/min, then held at 130 °C for 3 min. The temperatures of GC injector and detector were 250 °C. The content of formic acid was determined by acid–base titration with bromothmolph blue as the indicator.

3. Results and discussion

3.1. The reaction pathways

According to GC–MS analysis, the reaction of HCHO solution and acetone in high-temperature liquid-phase and under supercritical conditions only yielded two major products: HB and MVK. Small amount of diacetone alcohol and mesityl oxide were also detected. A rather high acetone/HCHO solution mass ratio of 15:1 was fixed in all experiments to suppress the subsequent

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