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Amidation of Benzyl alcohol in supercritical water without catalyst

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Abstract

The amidation of benzyl alcohol was carried out in supercritical water at 400 ºC and at pressure 22 MPa for 1 hour. The replacement of the hydroxyl group with the amino group was found to proceed in benzyl alcohol using ammonium acetate in supercritical water without the addition of any catalyst. The final product N-benzalacetamide was identified by GC-MS spectroscopy.

Keywords: Supercritical water, Amination, Benzyl alcohol, Batch reactor, GC-MS spectroscopy.

1. Introduction

The formation of amide is a fundamental reaction in the route of chemical synthesis [1]. For enormous importance of amides in chemistry and biology, it has been studied extensively over the decades [2-4]. On the way to long journey, several synthesis methods have been recognized for the amides. But, the waste free preparation of amides under neutral conditions still remained as a challenge [1,5]. Usually, this reaction does not happen in water under catalyst free conditions, which suggests the conversion of hydroxyl groups in primary alcohols to amide groups in supercritical water without catalyst. And, the water is the best promising environment friendly solvent.

Water near or above its critical point (T= 374 °C, P= 22.1 MPa) is receiving increasing interest as a medium in organic chemistry. Instead of organic solvents, near critical or supercritical water offers much more environmental advantages in chemical reaction. As a consequence, intensive research has been carried out in this field for the applications in the various purposes such as geochemistry, materials synthesis, synthetic

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fuels preparation, biomass processing, and waste treatment. Especially, numerous articles have recently been reported about organic synthesis such as Friedel-Crafts alkylation [6], dehydration, the Diels-Alder reaction [7], aldol condensation [8], Claisen rearrangement [9], Rupe rearrangement [10] or Heck coupling [11]. Ito et al reported that ε-caprolactone was converted into ε-caprolactam in 79.2% yield using ammonia in supercritical water at 380°C and a water density of 0.5 g/cm^3 for 60 minutes [12]. They assumed that the amide bond in ε-caprolactam was formed by the intramolecular dehydration between the hydroxyl group and the amide group in 6-hydroxyhexanamide. The amidation reaction of 1-n- hexanol as a primary alcohol with ammonia did not proceed in supercritical water at 400 °C for 60 min.

In this paper, we have reported results of the reaction between benzyl alcohol and ammonium acetate in supercritical water for determining the optimum conditions where amidation can occur in a selective manner in the absence of catalyst.

2. Experimental

Ammonium acetate, Benzyl alcohol and N-Benzalacetamide were purchased from Wako Pure Chemical Ind., Ltd with the purity of 97%. All chemicals were used in reaction without further purification. Additionally, distilled ultrapure water was obtained from the ultrapure water production equipment. The entire amination experiments of benzyl alcohol were conducted in batch type reactors with an 8.8 cm^3 volume shown in fig. 1. The reactor was designed for elevated temperature and pressure ranges to a maximum of 500 °C and 50 MPa respectively. It was tested by AKICO, Tokyo, Japan. For SCW reactions, about 4.0 ml (1.66 M) of ammonium acetate and 2.0 ml (0.33 M) of benzyl alcohol were sealed within the batch reactor. The amount of water was defined on the basis of operating pressure and reactor volume, and was calculated by the software Water I, v.v.3, produced by Summit Research Corporation (1996). Afterward, an electric furnace was heated to the desired reaction temperature and the loaded reactor was inserted into the furnace for one hour. During each run, the reactor was shaken by a mechanical device in a back-and-forth motion at approximately 70cpm. After the well-defined reaction time, the furnace was stopped and the reactor was recovered and quenched in a water bath for 1 hour. The reactor was then opened and water-soluble components were collected by distilled water. Products were identified by GC-MS and by comparing their retention times with those of standards.

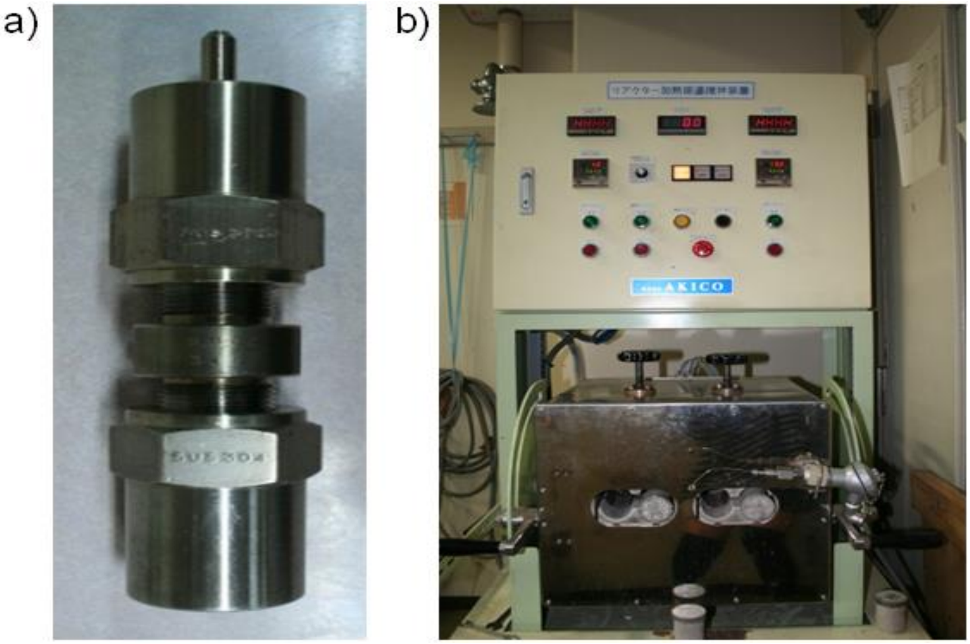

Figure 1: Partial view of a small-scale batch type reactor (a) and an electric furnace (b) for supercritical water.

2.1. Gas Chromatography mass spectroscopy (GC-MS).

Analysis of the fractions were identified by GC-MS (HP model 6890 series GC system and 5973 mass selective detector) with a HP-5 MS capillary column (J&W Scientific, length 15m, i.d. 0.25 mm, film 0.25µm). The temperature program was 1.0 min at 318 K, 5 K/min at 543K, and 10 min at 543 K. Helium carrier gas was used at a flow rate of 1.5 mL/min.

3. Results and discussion

We investigated the reaction of benzyl alcohol with ammonium acetate in supercritical water. Figure 2. shows the yields of the main products derived from benzyl alcohol as function of the reaction time at 400 ºC for 1 hour.

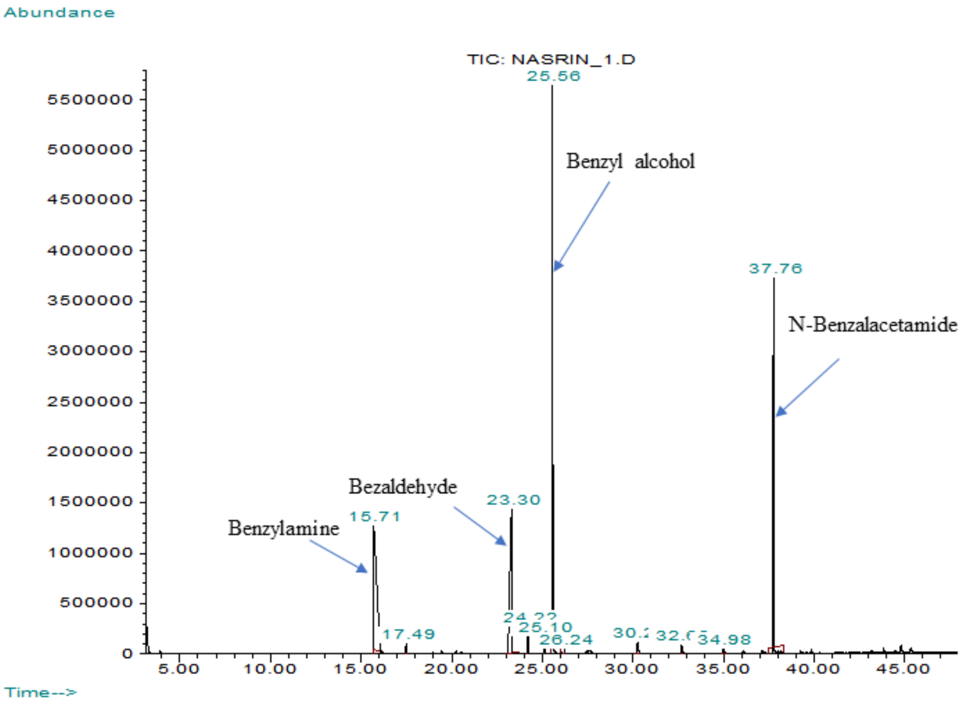

Figure 2: GC-MS Spectra after supercritical water treatment between benzyl alcohol and ammonium acetate.

Figure 3. indicates the standared subtance GC-MS spectra for N-benzalacetamide. The main products were benzylalcohol,benzylamine, benzyldehyde, benzylacetate, N-benzalacetamide. We also conducted this reaction at the same temperature for 30, 80 , 100 and 120 minutes. The recovered benzyl alcohol decreased with time. The yield of the target products N-benzalacetamide increased with reaction time. But after two hours the amidation process were decreased significanty. The authors think that when the time increased more degradation products were found.

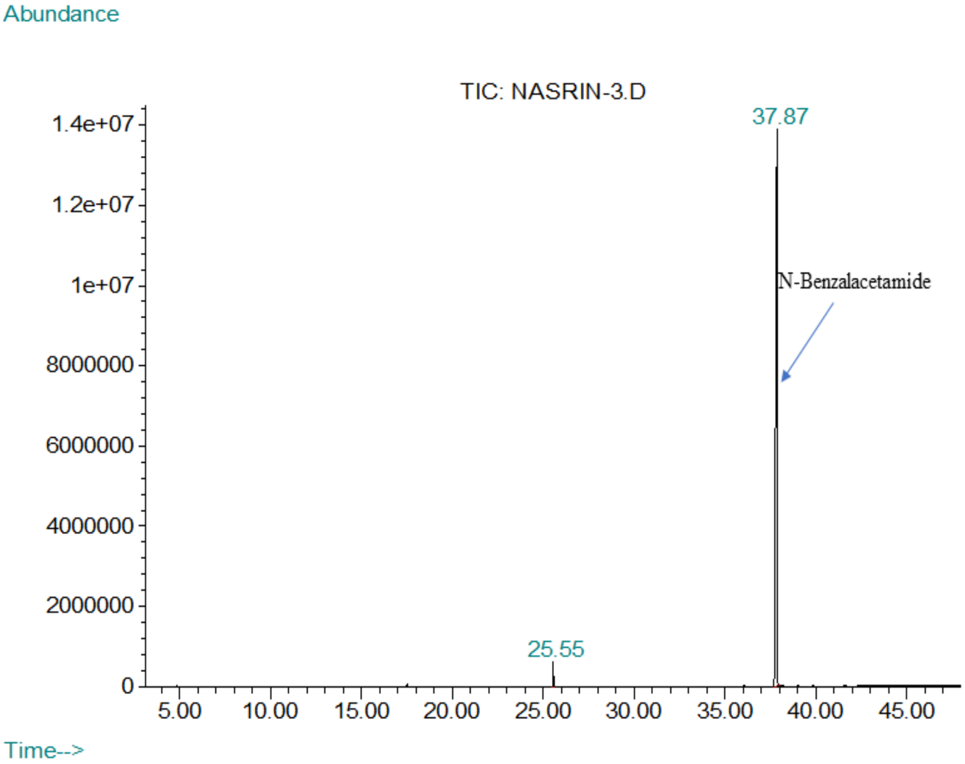

Figure 3: GC-MS Spectra for standard substance N-benzalacetamide.

From these above results, we propose the reaction pathways of bezylalcohol (**5**) and ammonium acetate (**1**) in supercritical water system as shown in figure 3. The main reaction pathway from benzyl alcohol **(5)** to N-benzalacetamide (**10**) involves the following steps, first ammonium acetate (**1**) dissociates into acetic acid (**2**) and ammonia (**3**) in supercritical water. Then acetic acid and ammonia are equilibrated with acetamide (**4**). N-benzylacetate (**8**) is formed by intermolecular dehydration between acetic acid (**2**) and benzylalcohol (**5**).

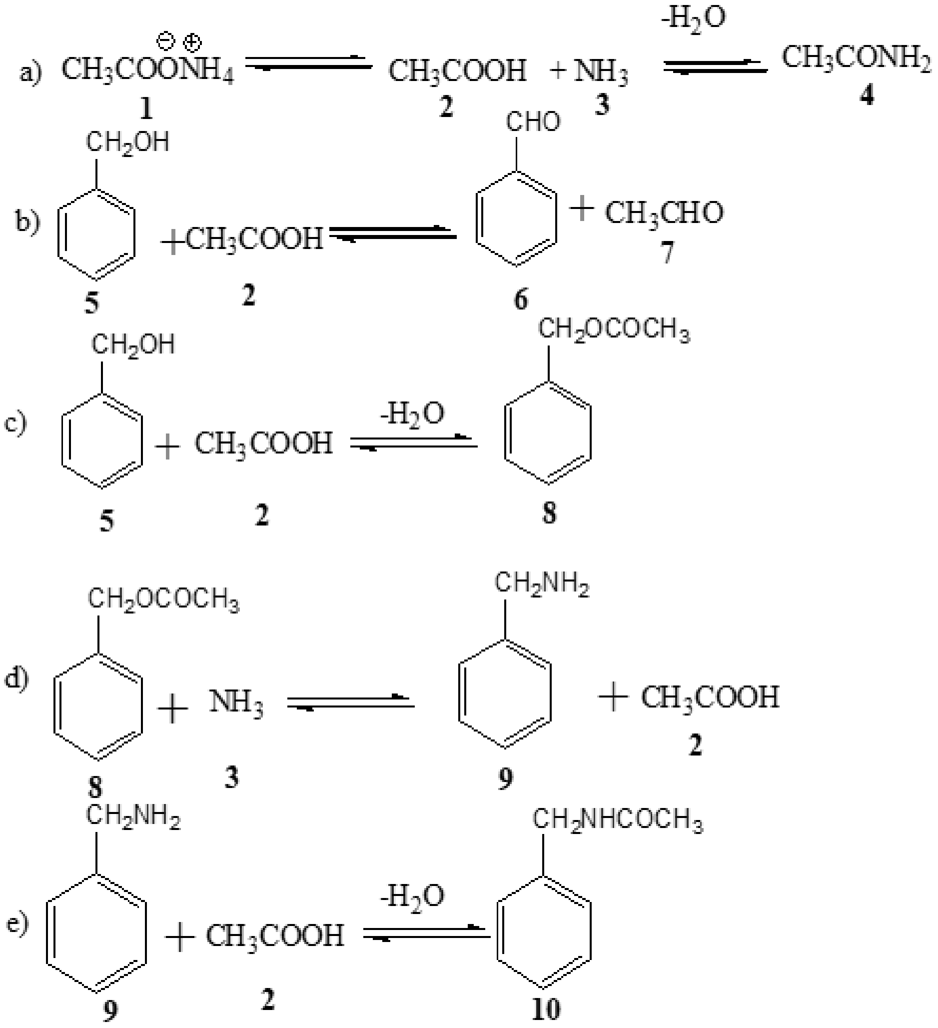

Figure 4: Main reaction pathway between benzyl alcohol and ammonium acetate in subcritical and supercritical water.

In common organic reactions under ordinary conditions, acetic acid (**2**) and benzylalcohol (**5**) are formed by the reaction between ammonia (**3**) and benzylacetate (**8**). Since the ammonia attacks the carbonyl carbon of N-benzylacetate (**8**). However, in supercritical water it was found that the unshared pair of electrons of ammonia molecule nucleophilically attacks the α-carbon atom of N-benzylacetate (**8**) to produce N-benzylamine (**9**) and acetic acid [13]. The final product N-benzalacetamide (**10**) is obtained by the acetylation of benzylamine (**9**) by acetic acid (**2**). The side reactions pathway from benzyl alcohol involves the following steps. Benzaldehyde (**6**) and acetamide (**7**) are assumed to be produced by reverse Cannizzaro reaction [14] in acetic acid and benzyl alcohol. It has already been reported that the Cannizzaro reaction takes place in supercritical water under catalyst free conditions [12]. However, the recovery of carbon from liquid products was very low because gaseous products form by the thermal degradation of benzyl alcohol. Based on these above experimental results, it was confirmed that the amidation of benzylalcohol in supercritical water was the best method for amidation without catalyst.

4. Conclusion

In summary, we have demonstrated the conversion of the hydroxyl group of benzyl alcohol to an amide group in supercritical water without catalyst. In the way to long investigations, several methods have been developed for synthesis of amides. But, the preparation of amides under neutral conditions without the generation of waste still remains a big challenge. Usually, this reaction does not take place in water under catalyst free conditions. These experimental findings lead to the development of a method for efficient production of amide compounds from aromatic alcohol. Future efforts would be directed to elucidate the reaction mechanism further and to explore optimum conditions for rapid and selective amidation in supercritical water.

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