

ALKYLATION AND DEALKYLATION OF ALKYLPHENOLS IN SUPERCRITICAL WATER

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The reaction of phenol with 2-propanol was examined in supercritical water. At first, dehydration of 2-propanol yielded propene, which followed that alkylation of phenol gave 2-isopropylphenol as main product. The alkylation occurred almost only at ortho position of phenol. The dealkylation of 2-isopropylphenol was also examined in supercritical water at 613-713 K. This reaction proceeded through dealkylation to phenol and propene and rearrangement to 2-propylphenol. These results show that the reversible reaction of alkylation and dealkylation proceeded without catalyst in supercritical water. Further, both alkylation and dealkylation rate increased with increasing water density and alkylation rate was larger than dealkylation one in high water density and low temperature region. These results indicate that the reversible reactions could be controlled with temperature and water density in supercritical water.

INTRODUCTION

Phenolic chemicals such as phenol and alkylphenols are important intermediates for the phenol resins, pharmaceuticals, dyes and antioxidants in chemical industry and are produced at over 5 million tons per year. Both alkylation of phenol and dealkylation of alkylphenols are the major reactions related to these compounds. Alkylation of phenol is usually performed through Friedel-Crafts reaction. The Friedel-Crafts reaction essentially requires strong acids such as Lewis acids ($AlCl_3$, BF_3) and mineral acids (HF , H_2SO_4). Further, in the

alkylation of phenol, the hydroxy group of phenol strongly activates the reactivity of the ring

substituents, which leads to ortho and para orientation. On the other hand, the phenolic compounds such as alkylphenols are usually converted by the hydrogenation using hydrogen-donor solvents or catalysts. The use of strong acid and harmful solvent is expected to be limited, however, as more emphasis is placed on Green Chemistry.

Water is an inexpensive and environmentally acceptable solvent in harmony with the philosophy of Green Chemistry. High temperature water has a great potential as a reaction media. The various organic reactions occur in high temperature water because of high ion product [1]. Alkylation of phenol with alcohol occurs without catalyst in water at 523 K [2]. On the other hand, alkylphenols were stable at 523 K in high temperature water [3].

When water is heated above its critical temperature, water becomes supercritical region. The high temperature condition allows alkylphenols to decompose. For example, the dealkylation of alkylphenols occurs at about 700 K in supercritical water [4]. Further, density of water can greatly change by manipulating temperature and pressure in supercritical water, which follows the change of the reaction rate and equilibrium.

In supercritical water, both organic syntheses through bond formation such as Diels-Alder reaction and decomposing organics through bond cleavage such as hydrolysis occurs [5]. Based on these findings, it is highly possible that forward and reverse reactions such as bond formation and bond cleavage reactions can be manipulated in supercritical water. The possibility of controlling reversible reactions such as alkylation and dealkylation with solvent properties can be one of the new characteristics of organic reactions in supercritical water.

In this paper, we will first show that alkylation of phenol with 2-propanol proceed in supercritical water without catalyst and evaluated the effect of water density on reaction rate. Next, the dealkylation of 2-isopropylphenol was examined and the effect of water density was also evaluated. Finally, the effect of temperature and water density on the reaction rate of both alkylation and dealkylation will be discussed.

EXPERIMENTAL

Reactions were carried out in 6 cm³ stainless steel batch reactors as reported previously [6]. In some cases, we used the reactor whose one port was connected to high-pressure valve for gas analysis. The reactor was loaded with certain amount of 2-propanol and phenol, or 2-

isopropylphenol and up to 3.6 g of distilled water. Air in the reactor was displaced with argon with successive purgings. After the reactor had been loaded, the reactor was submerged into a fluidized sand bath that was controlled at the reaction temperature (613 -713 K). After a given amount of time including the heat-up time, the reactor was removed from the sand bath, and the reaction was rapidly quenched in a water bath.

After being cooled, the reactor was opened and gas products were recovered to syringe through the sampling loops attached to two GC-TCDs that have a molecular sieve SA and Porapak Q column, respectively. The composition of gas products was analyzed with these GCs. After that, the reactor washed with THF and THF solution was analyzed with GC-FID equipped with an HP-S column and GC-MS with an HP-S MS column. The concentration of products was determined by GC-FID with naphthalene as internal standard.

RESULTS

Alkylation of phenol with 2-propanol

We conducted the reaction of phenol with 2-propanol in supercritical water at 673 K and 0-0.5 g/cm³ of water density. The initial concentration of phenol and 2-propanol loaded were 1.65 and 0.33 mol/L, respectively. Figure 1 shows the yield of products (mols of 2-propanol loaded basis) with reaction time. The yield of propene was evaluated from carbon balance because propene was main gas product under the present conditions. Within 10 minutes, 2-propanol decreased corresponding to the increase of propene, which means that the dehydration of 2-propanol to propene rapidly occurred in supercritical water. Next, propene decreased while ortho-isopropylphenol was produced, and then 2-isopropylphenol decreased corresponding to the formation of 2-propylphenol. Alkylation of phenol with propene and rearrangement of alkyl side chain occurred without catalyst in supercritical water. Further, the molar ratio of ortho substituents and para substituents were over 94 %, which indicates that the alkylation in supercritical water was high ortho selectivity.

Figure 2 shows the yield of IPP with reaction time at various water densities and 673 K. The yield of IPP increased with increasing water density. Alkylation was promoted with increasing water density. The increase of water density probably promoted the local

dissociation of hydroxy group and stabilized the reaction intermediate to enhance alkylation [6].

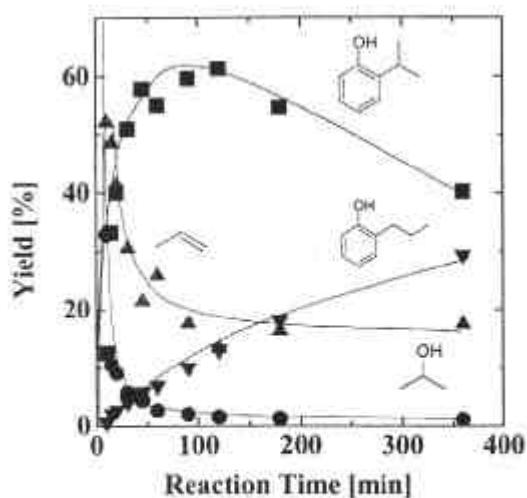


Figure 1 Yield of products with reaction time at 673 K and 0.5 g/cm^3 of water density

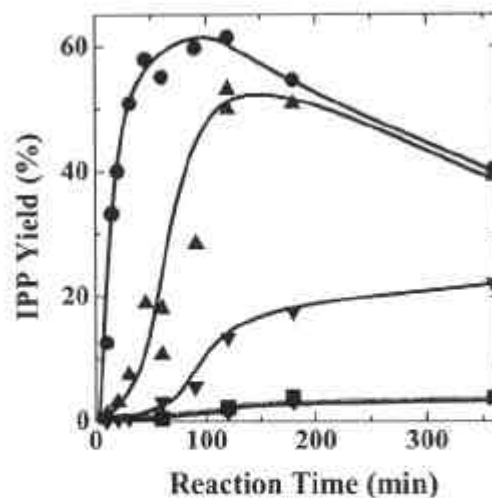


Figure 2 Yield of IPP with reaction time at various water densities and 673 K.
 ● : 0.5 g/cm^3 , ▲ : 0.4 g/cm^3 , ▼ : 0.3 g/cm^3 , ◆ : 0.2 g/cm^3 , ■ 0 g/cm^3 .

Dealkylation of 2-isopropylphenol

We conducted the decomposition of 2-isopropylphenol (IPP) in supercritical water at 613-713 K and 0.5 g/cm^3 of water density. The decomposition of IPP yielded propene and phenol, and 2-propylphenol (PP). Both dealkylation and rearrangement of alkyl side chain occurred in supercritical water. The yield of phenol increased with increasing water density and the yield of PP was almost constant regardless of water density. The dealkylation was enhanced with increasing water density, whereas rearrangement was not influenced by the water density. The reaction rate constant was evaluated using the data of initial stage of reaction. The rate constant of dealkylation was in proportional to water density.

Reaction rate of alkylation and dealkylation

From the experiment of alkylation and dealkylation, the reaction pathway of this reaction can be expressed as Figure 4. We examined the reaction of phenol and 2-propanol at each

initial concentration of 0.33 mol/L and 613-713 K. The rate constant of dealkylation (k_{deal}) and rearrangement (k_r) was reported previously [7]. We determined the alkylation rate constant (k_{al}) and dehydration rate (k_{deh}) by considering the reaction pathways. We fit models to experimental data of 2-propanol, propene and IPP at each temperature and water density and evaluated the reaction rate constant of dehydration (k_{deh}) and alkylation (k_{al}) each condition. Dehydration and alkylation

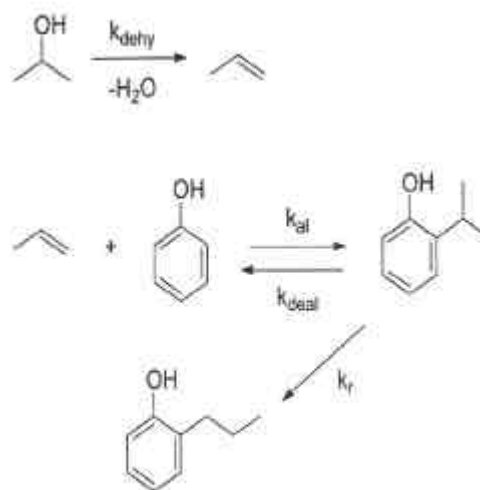


Figure 4 Main reaction pathway

at

were assumed to be first order in 2-propanol, propene and phenol. We evaluated alkylation rate and dealkylation rate with k_{al} and k_{deal} as equation 1 and 2

$$\text{Alkylation rate} = k_{\text{al}}[\text{propene}]_o[\text{phenol}]_o \quad (1)$$

$$\text{Dealkylation rate} = k_{\text{deal}}[\text{IPP}]_o \quad (2)$$

where $[\text{propene}]_o$, $[\text{phenol}]_o$ and $[\text{IPP}]_o$ are the initial concentrations of each compound.

Here, the initial concentrations were set equal to at the experimentally ideal values of 0.33 mol/L. Figure 5 shows the initial reaction rates of alkylation and dealkylation. As a whole, in the high temperature and low water density region, dealkylation rate was larger than the alkylation rate. The alkylation became predominant in the low temperature and high water density region. This dependence of alkylation

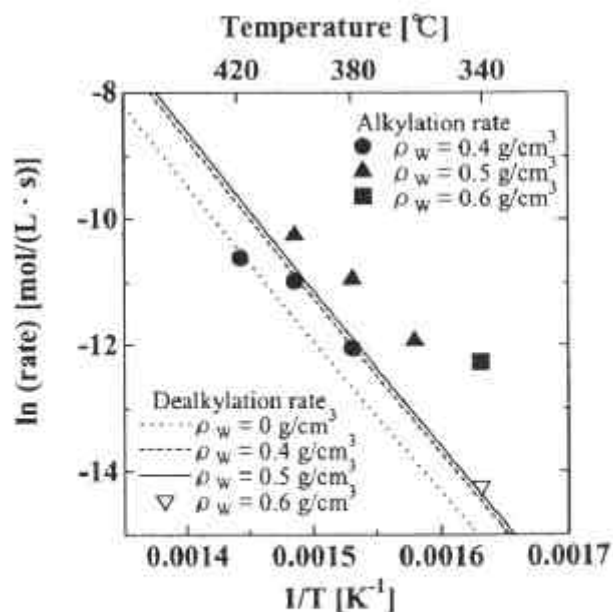


Figure 5 Reaction rate of alkylation and dealkylation.

and dealkylation rate on temperature and water density shows that

the reversible reaction could be shifted to alkylation or dealkylation side by manipulating temperature and water density (reaction pressure).

CONCLUSION

The reaction of phenol and 2-propanol yielded propene by dehydration and then propene reacted with phenol by alkylation in supercritical water. The dealkylation and rearrangement of 2-isopropylphenol also occurred in supercritical water. Both alkylation and dealkylation rate increased with increasing water density. The low temperature and high water density region, alkylation rate was larger than the dealkylation rate.

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