ACID CATALYZED DEHYDRATION USING SUPERCRITICAL WATER WITH CARBON DIOXIDE AS A MILD CATALYST

Kimitaka Minami, Takafumi Sato, Kiwamu Sue and Kunio Arai*
Department of Chemical Engineering, Tohoku University, 07 Aza-Aoba, Aramaki, Aoba-ku,
Sendai, 980-8579, Japan
E-mail: karai@arai.che.tohoku.ac.jp
Fax: +81-22-217-7246

In this study, we examined the dehydration of cyclohexanol to cyclohexene in the much presence of carbon dioxide in supercritical water. At 653 K and 0.5 g cm^{-3} of water density the yield of cyclohexene reached 60 % in the presence of 7.5 mol% carbon dioxide, but in the absence of carbon dioxide the yield of cyclohexene was only 10 %. The yield of cyclohexene tended to increase with increasing the carbon dioxide concentration and water density. Hydration of cyclohexene to cyclohexanol was also studied as a reverse reaction of dehydration of cyclohexanol, it was confirmed that the addition of carbon dioxide accelerated the hydration as well as the dehydration.

INTRODUCTION

High temperature water including the supercritical region has been shown to be advantageous in the acid catalyzed reaction. Without catalyst in high temperature water, dehydration of alcohols, hydration of alkenes, hydrolysis of ethers and sugars, Friedel-Crafts alkylation and acylation of aromatics were proved to occur. For these reactions, however, higher reaction rate and selectivity are required. The addition of acid often accelerates the reaction and achieves high selectivity. Ikushima *et al.* [1] reported that in supercritical water with dilute acid-catalyst (H_2SO_4 and HCl), the Beckmann rearrangement of cyclohexanone oxime into *e*-caprolactam was selectively proceeded and yielded *e*-caprolactam in almost 100 % yield. However, such acid catalyzed reactions require further environmental considerations and post-reaction separation steps.

Carbon dioxide is known to be environmentally benign solvent the same as water. Therefore, we expect that the combined use of water and carbon dioxide improve the development of new environmentally benign and economic processes such as that proposed. At ambient temperatures, water in which carbon dioxide dissolves shows acidity by the formation of carbonic acid. Therefore, carbon dioxide can be worked as an environmentally acceptable acid in its aqueous solution. However, the solubility of carbon dioxide in water is poor. At higher temperatures and higher pressures, the carbon dioxide is readily soluble in water, and therefore the catalytic properties of carbon dioxide in water can be expected to possibly be controlled with changing the more extensive carbon dioxide concentration, temperature and pressure.

Hunter *et al.* [2] examined the catalytic effect of carbon dioxide in water of subcritical condition. They conducted the dehydration of cyclohexanol and alkylation of *p*-cresol with *tert*-butyl alcohol using high temperature water at 523 and 548 K in the presence of carbon dioxide, and reported that these reactions were accelerated further than those in the absence of carbon dioxide. Considering this previous work, we carried out experiments with increasing amount of carbon dioxide for a dehydration reaction. The critical temperature of a mixture of water and carbon dioxide is lower than the critical temperature of water, for example, at 7.5 mol% of carbon dioxide, the critical point of the mixture of water and carbon dioxide is 633.2 K and 28 MPa [3]. Thus the reaction temperature range can be expected to enlarge with the addition of carbon dioxide.

Conditions for mixtures of supercritical water and carbon dioxide can be adjusted to obtain a homogeneous phase [3] which is advantageous for many reactions. After reaction completion, carbon dioxide can be separated from water by decreasing temperature and pressure thus allowing simplified separation of a homogeneous catalyst. However, since water at supercritical conditions has a lower density than that at subcritical conditions, the decrease of the dissociation constant of water and carbonic acid and the reduction of the acidic nature has to be considered. In this study, we conducted the dehydration of cyclohexanol and the hydration of cyclohexene with carbon dioxide in supercritical water at 653 K and evaluated the effects of the concentration of carbon dioxide and the density of water on the reactivities.

I - EXPERIMENTAL

Experiments were carried out with 6 cm^3 stainless steel batch reactors. One port of the reactor served as a K-type thermocouple entrance for measuring the reaction temperature. The other port was connected to high-pressure valve for the loading of gases. Details of the reactor have been reported previously [4]. The reactor was loaded with 0.2 g of cyclohexanol, or cyclohexene and up to 3.3 g of distilled and de-ionized water. The air in the reactor was displaced with carbon dioxide by successive purging and then 0.3 - 1.3 g of carbon dioxide was introduced into the reactor from the bomb. For the experiments in absence of carbon dioxide, the air in the reactor was exchanged with argon gas. The loaded reactors were submerged into a fluidized sand bath that was controlled at 653 K. Heat-up time was about 2 min. After a given amount of time, the reactors were taken out of the sand bath and rapidly quenched in a water bath. Cooling to room temperature required about 1 min. After the reactors were cooled, gases in the reactor were released by bubbling through 20 cm^3 of tetrahydrofuran (THF) solution to collect as much of the liquid products as possible. After that, the reactor washed with 20 cm^3 of THF and THF solution was analyzed with GC-FID.

II - RESULTS & DISCUSSION

Dehydration of cyclohexanol using supercritical water in the presence of CO_2

Figure 1 shows the molar yield of product at 653 K at 0.5 g cm^{-3} of water density with 7.5 mol% of carbon dioxide and without carbon dioxide as a function of reaction time. Carbon yield was defined as the moles of carbon atoms in the product based on the moles of carbon atom of cyclohexanol loaded. The observed product was only cyclohexene and the total carbon yield of recovered cyclohexanol and cyclohexene after every experiment was more than 85 %, which means that the dehydration of cyclohexanol was the main reaction. In the presence of carbon dioxide, the yield of cyclohexene was clearly higher than that in the absence of carbon dioxide. From the results, it was concluded that the dehydration of cyclohexanol in supercritical water was promoted by carbon dioxide.

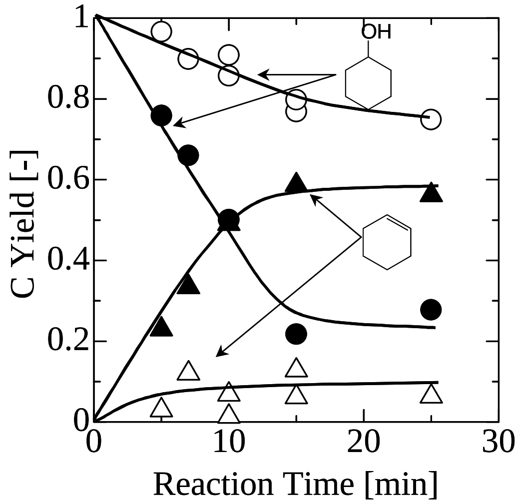

Figure 1. Yield of products of dehydration as a function of reaction time.

Symbols for experimental data 7.5 mol% CO_2 **:** ●, ▲, no CO_2 **:** ○, △

Figure 2 shows the dependence of the conversion of cyclohexanol and the yield of cyclohexene on carbon dioxide fraction at 653 K and 0.5 g cm^{-3} water density for 7 min reaction time. The yield of cyclohexene increased with increasing mole fraction of carbon dioxide. At 15 mol% of carbon dioxide, the yield of cyclohexene reached 73.3 %.

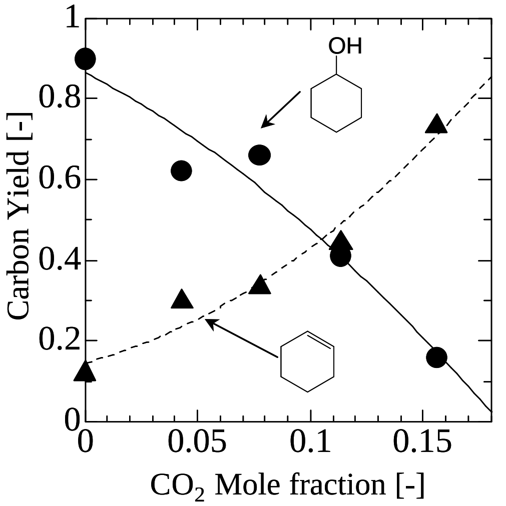

Figure 2. Dependence of the yield of products of dehydration on carbon dioxide fraction.

Table 1. Dependence of product yield on the water density and carbon dioxide mole fraction at 653 K for 7 min of reaction time.

Density/ g cm^{-3}	Mole fraction (mol%)		Yield (%)		[H^{+}]/ 10^{-7} mol kg^{-1}	
H_2O	CO_2	H_2SO_4	$C_6H_{11}OH$	C_6H_{10}	with CO_2 or H_2SO_4	H_2O only
0.00	100	-	90.0	0.4	-	-
0.34	10.8	-	80.5	17.2	4.80	0.0974
0.50	7.5	-	66.0	33.4	129	3.52
0.55	6.9	-	27.2	58.7	239	6.86
0.50	0.0	-	89.9	12.0	-	3.52
0.50	4.1	-	62.1	29.7	87.6	3.52
0.50	7.5	-	66.0	33.4	129	3.52
0.50	10.9	-	41.2	44.2	165	3.52
0.50	14.9	-	16.1	73.3	208	3.52
0.50	-	3.1×10^{-7}	86.9	6.3	130	3.52
0.50	-	3.1×10^{-6}	16.5	67.4	661	3.52

Next, we examined the dependence of water density on the reaction. Table 1 shows the dependence of the molar yield of cyclohexanol and cyclohexene on water density at 653 K in the presence of 0.6 g of carbon dioxide (6.9 – 100 mol%) for 7 min of reaction time. The dependence of these products on the mole fraction of carbon dioxide (data of Figure 2) is also shown in this table. In the absence of water, that is, at 100 mol% carbon dioxide, the yield of cyclohexene was just 0.4 %, which means that dehydration of cyclohexanol hardly occurred without water. However, in the presence of water, the yield of cyclohexene increased with increasing water density.

Since the ion product of water and equilibrium constant vary with water density in supercritical water, this can lead to a change of the concentration of chemical species such as protons. Akiya *et al.* [5] reported that in high temperature water, dehydration of cyclohexanol to cyclohexene occurs via an E2 mechanism and the protons arising from the dissociation of water catalyze dehydration. Hunter *et al.* [2] reported that in high temperature water at 523 and 548 K, the dehydration of cyclohexanol is accelerated by the addition of carbon dioxide. They suggested that protons mainly supplied through the dissociation of carbonic acid, which was formed from water and carbon dioxide, promoted the dehydration reaction. In supercritical water, the augmentation of yield of cyclohexene in the addition of carbon dioxide was probably caused by the formation of carbonic acid.

We estimated the proton concentration at each water density in the presence and the absence of carbon dioxide as shown in Table 1. The proton concentration was calculated by using ion product of pure water [6], the equilibrium constants of carbonic acid (first ionization [7] and second ionization [8]) and the activity coefficient formulation with charge and mass balance constraints [9]. The equilibrium constant of carbonic acid in supercritical condition was calculated by the extrapolation of the literature values in subcritical condition [7,8]. As shown in Table 1, the proton concentration in the presence of carbon dioxide was 25 - 60 times higher than that in the absence of carbon dioxide. In supercritical water, protons are mainly formed by the dissociation of water, and probably the formation of the protons is further promoted by the addition of carbon dioxide. The dehydration of cyclohexanol probably becomes catalyzed with the increase in proton concentration.

To evaluate the dependence on the proton concentration in detail, we conducted the experiments of the dehydration of cyclohexanol in supercritical water with sulfuric acid whose dissociation constant in supercritical water has been reported. The results are shown in the bottom of Table 1. As well as the results in the presence of carbon dioxide, the dehydration of cyclohexanol was promoted with increasing proton concentration. At 0.50 g cm^{-3} of water density, the proton concentration in the presence of 7.5 mol% of carbon dioxide and that in presence of 3.1 × 10^{-7} mol% of sulfuric acid were the same, however, the yield of cyclohexene in carbon dioxide was almost five times higher than that in sulfuric acid. To elucidate the effect, it will be necessary to estimate the local proton concentration around the solute molecule and the effect of the chemical species other than the proton (carbonate anion and hydrated carbon dioxide) by simulation and spectroscopy. However in supercritical water with high concentration of carbon dioxide, the acid catalytic effect appears to be significant.

Hydration of cyclohexene using supercritical water in the presence of CO_2

The hydration of alkenes is commercially a very important reaction. For the hydration of cyclohexene to cyclohexanol, which is a reverse reaction of dehydration of cyclohexanol, the acid catalytic effect of supercritical water in presence of carbon dioxide was examined. Figure 3 shows the dependence of the molar yield of cyclohexanol with time. The condition was 0.5 g cm^{-3} of water density at 653 K in presence of 7.5 mol% of carbon dioxide and in the absence of carbon dioxide. The observed products were cyclohexanol of main product and 1-methyl cyclopentene of sub-product. Akiya *et al.* [5] reported that in supercritical water, some of cyclohexene molecules are protonated to the secondary cyclohexyl carbocation and this carbocation rearranges to form the tertiary methyl cyclopentyl carbocation, which loses a proton to form 1-metyl cyclopentene. These reactions probably afforded with the hydration of cyclohexene in this study. The carbon balances after reaction were 68 – 89 %. One reason for

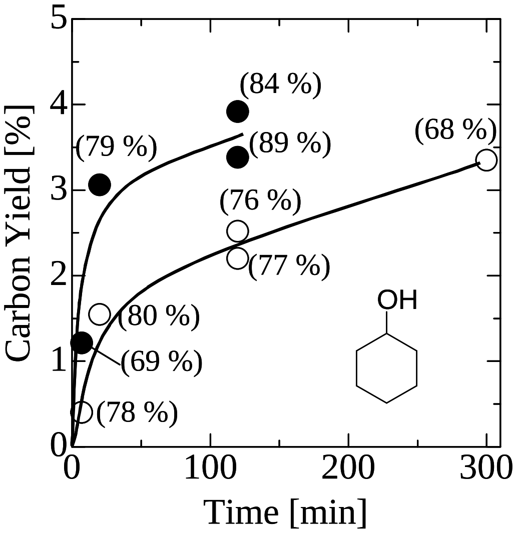

Figure 3. Yield of product of hydration as a function of reaction time.

Symbols for experimental data 7.5 mol% CO_2 **:** ●, no CO_2 **:** ○. Values in parentheses **:** carbon balance.

lower carbon balance values probably was due to high volatility of cyclohexene, which may be evaporated through the loading and recovering. Cyclohexanol, which has low volatility, probably had less fugitive losses in our procedures. In the presence of carbon dioxide, the yield of cyclohexanol was clearly higher than that in the absence of carbon dioxide. From the results, it can be concluded the hydration of cyclohexene was promoted with carbon dioxide in supercritical water.

CONCLUSION

Both the dehydration of cyclohexanol and the hydration of cyclohexene using supercritical water in the presence of carbon dioxide were promoted more efficiently than that in supercritical water alone. The increase in both density of the water and concentration of the carbon dioxide improved the dehydration most likely due to the increase of proton concentration. These results mean that carbon dioxide can function as a non-toxic and effective acid catalyst in supercritical water syntheses and reactions. A further advantage of using carbon dioxide with supercritical water is that the strength of acid can be controlled in a simple fashion by changing carbon dioxide concentration.

REFERENCES :

[1] IKUSHIMA, Y., HATAKEDA, K., SATO, M., SATO, O., ARAI, M., Chem. Comm., Vol. 19, **2002**, p. 2208

[2] HUNTER, S., E., SAVAGE, P., E., Ind. Eng. Chem. Res., Vol. 42, **2003**, p. 290

[3] HICKS, C., P., YOUNG, C., L., Chem. Rev., Vol. 75, **1975**, p. 119

[4] ARAI, K., ADSCHIRI, T., WATANABE, M., Ind. Eng. Chem. Res., Vol. 39, **2000**, p. 4967

[5] AKIYA, N., SAVAGE, P., E., Ind. Eng. Chem. Res., Vol. 40, **2001**, p. 1822

[6] MARSHALL, W., L., FRANCK, E., U., J. Phys. Chem. Ref. Data, Vol. 10, **1981**, p. 295

[7] PATTERSON, C., S., SLOCUM, G., H., BUSEY, R., H., MESMER, R., E., Geochim. Cosmochim. Acta, Vol. 46, **1982**, p. 1653

[8] PATTERSON, C., S., BUSEY, R., H., MESMER, R., E., J. Sol. Chem., Vol. 13, **1984**, p. 647

[9] LVOV, S., N., ZHOU, X., Y., MACDONALD, D., D., J. Electroanal. Chem., Vol. 463, **1999**, p. 146