

Noncatalytic Beckmann Rearrangement of Cyclohexanone-Oxime in Supercritical Water

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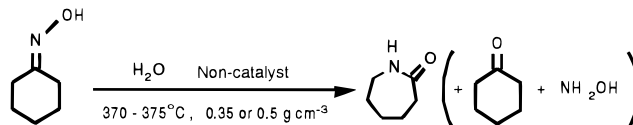
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Introduction

Much attention has been recently drawn to organic syntheses in supercritical fluids.¹ Supercritical carbon dioxide has played a key role as a reaction medium or a reactant in several organometallic reactions,² while in supercritical water very few organic syntheses have been done so far.³ Nonpolar organic compounds are very soluble or miscible in supercritical water,⁴ and "aqueous-phase" organic syntheses is possible for materials that are insoluble at ambient conditions. In addition, in the near-critical region the strength of the hydrogen bonding weakens uniquely, where dimers or monomers are predominant.⁵ The monomers, in part, are further broken into protons near the critical point because dynamic changes in the "local" water structure are liable to induce the evolution of protons.^{5a} If the proton cannot escape, the "local" proton concentration would be high and might have a significant influence on reactivities. The research groups of Antal and Eckert reported important results on organic reactions in superheated and supercritical water. Antal et al. studied such reactions as biomass pyrolysis and they demonstrated that the supercritical water can catalyze the dehydration.^{6a,b} Eckert et al. investigated alkylation reactions such as Friedel–Crafts acylation by using a Lewis acid as catalyst.^{6c} Furthermore, effective decomposition of polymers or cellulose in supercritical water medium could be taken to imply acidic behavior of supercritical water.^{6d,e} In this study, we

Scheme 1. Beckmann Rearrangement



report Beckmann rearrangement of cyclohexanone-oxime in the absence of any acid catalysts as a first organic synthetic reaction in supercritical water and its interesting reactivity in the near-critical region.

Beckmann rearrangement of cyclohexanone-oxime into ϵ -caprolactam is a commercially important reaction for the production of synthetic fibers. This reaction process is very selective for producing ϵ -caprolactam but it has the disadvantages of using highly concentrated sulfuric acid as a catalyst and forming ammonium sulfate as a product of low commercial value.⁷ However, as an environmentally friendly alternative route heterogeneously catalyzed rearrangement has not been commercialized so far, because of problems such as short catalyst lifetime for industrial application.⁸ In this work, a Beckmann rearrangement of cyclohexanone-oxime for producing ϵ -caprolactam without acid catalysts has been attempted in supercritical water. One can expect that the ability of water to accept a proton decreases significantly due to the breakdown of the tetrahedral configurations, promoting the Beckmann rearrangement (Scheme 1).

Results and Discussion

Figure 1 shows ¹H NMR spectra of purified chief product attained by the above supercritical water reaction at 385 °C and a density of 0.35 g cm⁻³ as well as of the authentic ϵ -caprolactam. The NMR spectrum is in fair agreement with that of the authentic sample. The analytical results obtained by GC and GC-MS are also in accord with those of the authentic sample. Thus, Beckmann rearrangement of cyclohexanone-oxime into ϵ -caprolactam was first confirmed to proceed in the absence of any acid catalysts in supercritical water medium. This suggests the evolution of protons from supercritical water medium itself.

Figure 2 shows the rate of the formation of ϵ -caprolactam and the amount of residual cyclohexanone-oxime with temperature at a fixed density of 0.50 g cm⁻³. The rate of reaction is expressed by the amount of ϵ -caprolactam produced in a unit time per 1 mol of water. No products, other than ϵ -caprolactam and cyclohexanone as hydrolysis product of cyclohexanone-oxime, have been detected. The conversion of cyclohexanone-oxime was accelerated with increasing temperature, especially near the critical temperature of water (374.1 °C), while the cyclohexanone obtained by the hydrolysis of cyclohexanone-oxime decreases markedly above the critical tem-

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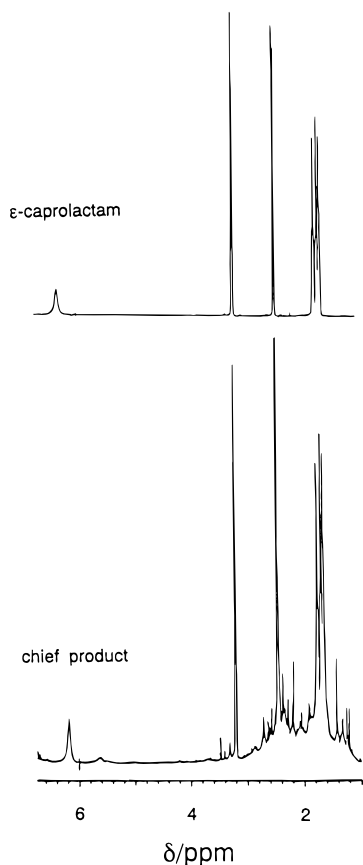


Figure 1. ^1H NMR spectra of the authentic ϵ -caprolactam (a) and of chief product (b) attained by supercritical water reaction at 385°C and a density of 0.35 g cm^{-3} measured in heavy chloroform.

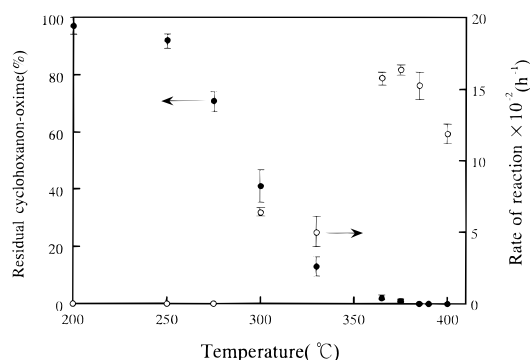


Figure 2. Rate of reaction (open symbols) in the synthesis of ϵ -caprolactam and amount of residual cyclohexanone-oxime (filled symbols) as a function of temperature at a fixed density of 0.50 g cm^{-3} showing errors on data points. The reaction time is 3 min.

perature. Furthermore, one can see an interesting temperature dependence of the formation of ϵ -caprolactam. In this Beckmann rearrangement the ϵ -caprolactam is found to be synthesized peculiarly in the limited temperature range between 300 and 400°C , where the rate of reaction significantly increases, reaches a maximum of $16.3 \times 10^{-2}\text{ mmol h}^{-1}$ per 1 mol of water at 370°C , and then sharply decreases with increasing temperature. To our knowledge, such a temperature dependence showing a maximal rate of reaction at a particular temperature is the first finding for reactions in supercritical water. The specific increase in the rate may be

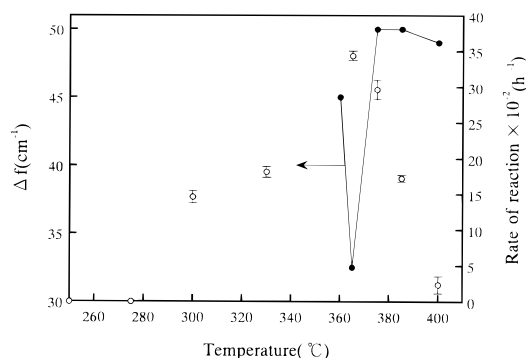


Figure 3. Relationship between the deviation, Δf (filled symbols), of the maximum frequency relative to the monomer frequency and the rate of reaction (open symbols) showing errors on data points as a function of temperature at a fixed density of 0.35 g cm^{-3} . The reaction time is 3 min.

due to a marked increase in the proton concentration around the critical temperature.

The change in the rate of reaction with temperature at a fixed density of 0.35 g cm^{-3} is depicted in Figure 3. The temperature dependence is similar to that at 0.50 g cm^{-3} in Figure 2, where the cyclohexanone decreases to about 20%, and the rate goes up to a maximal value of $34.3 \times 10^{-2}\text{ h}^{-1}$ at the critical temperature, and then decreases with temperature.

In Figure 3 the deviation of the Raman frequency of the OH symmetric stretching mode (ν_1) of water, $\Delta f(T)$, at a certain temperature, T , from the frequency of the monomer structure (3657 cm^{-1})⁹ is represented as well.^{5a} It is well-known that the band shifts of the vibration modes are due to the strong $\text{H}_2\text{O}-\text{H}_2\text{O}$ interactions prevailing in the phase and the existence of an O-H-O bridge weakens partially the covalent O-H stretching (red shifting the frequency). Therefore, the $\Delta f(T)$ is the decreased stretching frequency relative to the monomer structures as an internal reference, and the value of Δf implies the strength of the hydrogen bonding. At the near-critical temperature, the Δf value shows a minimal value and it is significantly lower compared with other super- or subcritical conditions. This evidently implies that the extent of the hydrogen bonding weakens uniquely in the near-critical region, where water is no longer structured and dimers or monomers are predominant,⁵ but monomers, in part, are further broken into protons due to large fluctuations of the structure of water.^{5a} The organization of 4–10 molecules is required to solvate the transferred proton,¹⁰ and the water structure near the critical point becomes less able to accommodate the ejected protons. That is, the most marked loss in the ability of water to accept a proton occurs near the critical point. The ion product of bulk supercritical water near the critical point is similar to the values at ambient conditions (10^{-14}),¹¹ and microscopically dynamic behavior would be more important in discussing the reactivity. The “local” proton concentration is further extremely high when the transferring proton cannot escape. Therefore,

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the rate of reaction in the above Beckmann rearrangement is considerably enhanced and has a maximum near the critical point.

It is possible to mention another factor that may be related to the maximum rate of reaction observed in the near-critical region. Needless to say, we cannot deny the possible role of the proton from the organic reactant, and we are going to try other substrates and this will be helpful for the discussion of the origin of products. It has been further noted that the local concentration of organic solute in supercritical carbon dioxide becomes maximized in the near-critical region,¹² where the rate of reaction significantly is larger.¹³ For example, in noncatalytic esterification of phthalic anhydride and methanol in supercritical carbon dioxide, the rate of reaction was markedly enhanced with an increase in the local concentration of phthalic anhydride molecules around a methanol molecule.^{13b} In the present noncatalytic Beckmann rearrangement in supercritical water, in addition to the local proton concentration as described above, the "local" concentration of cyclohexanone-oxime around protons would be very large at a limited temperature range near the critical point, resulting in the promotion of the reaction.

In summary, noncatalytic Beckmann rearrangement of cyclohexanone-oxime into ϵ -caprolactam was confirmed to be significantly promoted near the critical temperature in subcritical or supercritical water. A marked loss in the ability of water to accept a proton near the critical point leads to a high "local" concentration of protons. An increase in the local concentration not only of protons around a cyclohexanone-oxime molecule but of cyclohexanone-oxime around protons might induce the enhancement in the rate of reaction. The supercritical water reaction described above can be applied to other acid-

catalyzed reactions and is of significant importance from industrial and scientific points of view.

Experimental Section

Supercritical Water Reactions. We performed the Beckmann rearrangement in supercritical water at temperatures of 250–400 °C at fixed densities of 0.35 and 0.50 g cm⁻³. Cyclohexanone-oxime of guaranteed reagent grade was purchased from Wako Chemical Co. Inc. Triply distilled high-purity water was used and degassed by N₂ gas prior to use. The experiments were conducted by using a batch reactor system. The reactor vessel was made from a piece of SUS 316 tubing, providing an internal volume of 10 cm³. A predetermined amount of reactant solution (cyclohexanone-oxime, 0.44 mmol, and water, 0.20 or 0.28 mol) was first loaded into the reactor in N₂ atmosphere. The reactor vessel was immersed and vigorously shaken in a fluidized molten salt bath. The heat-up time to raise the reactor temperature from 20 to 200–400 °C was within 30 s and the temperature was controlled within ± 2 °C. After a preselected reaction time of 3 min, the reactor was withdrawn from the molten salt bath and then quenched in a water bath. All of the products extracted from the reactor vessel by chloroform were qualitatively identified by using ¹H NMR and GC-MS, and each concentration was determined by a gas chromatograph equipped with a FID.

Raman Spectroscopy. A Raman spectroscopic experiment of supercritical water has been described elsewhere.^{5a,b} An optical cell withstanding severe conditions has the body fabricated from a monoblock of Inconel 718. Optical access is given by way of three sapphire windows which are sealed to the cell with gold-plated metal foil. The sample temperature was determined at the point of 3 mL from the focal point of the cell and the uncertainty of the measured temperature was below 1 deg above 300 °C. Pressure control was achieved by a back pressure regulator within ± 0.1 MPa. The light source for Raman scattering was a 150 mW Ar⁺ ion laser operating at 488 nm. A 90° scattering geometry was used, the cell being illuminated from below. The detector was a cooled CCD at -120 °C and the exposure time was 10 s. Microcomputers were used for controlling the detector and triple monochromator, recording the Raman spectra.

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