

# Beckmann Rearrangement of Cyclohexanone Oxime in a Microchemical System: The Role of SO<sub>3</sub> and Product Inhibition

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*The mechanism of Beckmann rearrangement of cyclohexanone oxime in oleum is investigated with a multiphase microchemical system, which is designed to give good control of the reaction temperature and residence time. The influences of SO<sub>3</sub> and caprolactam concentrations in oleum on the conversion are investigated. The results indicate that SO<sub>3</sub> acts as the catalyst and caprolactam plays a product inhibition role. Based on these results and previous mechanism analysis, an equilibrium relation between protonated caprolactam and caprolactam hydrogen sulfate is proposed and the equilibrium constants at 70, 80, and 90°C are gained. According to the equilibrium, the lowest acid/oxime molar-ratio of 0.5 for sufficient conversion (>99%) at 100°C has been provided. This quantitative mechanism analysis gives the reason for the negative influences of higher caprolactam concentration and lower temperature on the reaction conversion, which is very useful for the optimization and reliable design of Beckmann rearrangement processes. © 2011 American Institute of Chemical Engineers AIChE J, 58: 3156–3160, 2012*

**Keywords:** Beckmann rearrangement,  $\epsilon$ -caprolactam, mechanism, microchemical system

## Introduction

$\epsilon$ -Caprolactam, the monomer for nylon-6, is mainly synthesized by a classical industrial process including Beckmann rearrangement of cyclohexanone oxime (Figure 1), which was first described more than a century ago.<sup>1</sup> This industrial process of caprolactam synthesis usually uses benzene or phenol as starting material and consists of three main steps: the synthesis of cyclohexanone, the ammoximation of cyclohexanone to cyclohexanone oxime, and the Beckmann rearrangement of the oxime to  $\epsilon$ -caprolactam. For the Beckmann rearrangement step, all manufacturers use fuming sulfuric acid (oleum) as the solvent and catalyst.<sup>2,3</sup> Because of the application of this strong acid, ammonia has to be introduced to neutralize sulfuric acid producing ammonium sulfate as byproduct. According to the data from industrial process, nearly 2 tons of ammonium sulfate is produced for the production of 1 ton of caprolactam.

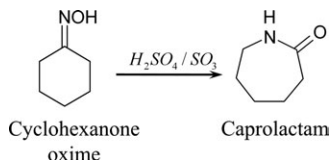
The “rearrangement mixture” is composed of unreacted cyclohexanone oxime, caprolactam, and oleum. The viscosity of the mixture is not measurable with a standard viscosimeter even at 80°C.<sup>4</sup> The reaction process is normally controlled by mass and heat transfer resistances. As the rearrangement is very rapid and highly exothermic,<sup>5</sup> it is difficult to control the temperature of the process. In addition, the reaction is an oleum-based process in which sampling and analysis are not convenient. Hence, although some studies have been devoted to the reaction and a lot of valuable

results have been obtained,<sup>6–8</sup> more progress need to be made to understand the mechanism of the Beckmann rearrangement.

Cavalieri d'Oro et al.<sup>9</sup> investigated the Beckmann rearrangement of cyclohexanone oxime in the solvent of SO<sub>2</sub> at low temperature (−29.4 to −19.3°C). Their results suggested that cyclohexanone oxime and  $\epsilon$ -caprolactam formed four complexes in the reaction process, as shown in Figure 2. A rearrangement mechanism was proposed by Fukumoto<sup>10</sup> based on the fact that cyclohexanone oxime dissolved in sulfuric acid is quickly protonated. The hydrogen ion is thought to be the catalyst and the mechanism includes the protonation of cyclohexanone oxime and the dehydration process. The reaction process is shown in Figure 3. However, the mechanism cannot explain the accelerating effect of excess sulfur trioxide in the Beckmann rearrangement. Fábos et al.<sup>4</sup> investigated the structure of  $\epsilon$ -caprolactam in 97% sulfuric acid and 10% oleum by NMR spectroscopy measurements. Their results suggest that  $\epsilon$ -caprolactam is protonated to form caprolactamium hydrogen sulfate. They also investigated the mechanism of the rearrangement in <sup>18</sup>O-labeled sulfuric acid, revealing that the migration of oxygen atom is intermolecular.

Multiphase microchemical system<sup>11</sup> is an effective tool to investigate the process of the Beckmann rearrangement. Two-phase droplet flow<sup>12</sup> can be created by adding an inert solvent carrying cyclohexanone oxime to contact oleum. The rearrangement reaction is exclusively confined to the acid phase surrounded by the immiscible inert solvent as the continuous phase. The micro-sized droplets dispersed by the immiscible fluid can effectively reduce the transfer limitations.<sup>13</sup> The system can also prevent the viscous rearrangement mixture from direct contact with microchannel walls and thereby eliminate or reduce undesired clogging of

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**Figure 1. The Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam.**

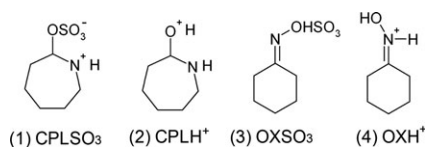
microchannels. The inert solvent is also an effective heat carrier for controlling reaction temperature. Zuidhof et al.<sup>14</sup> designed a microstructured chemical system including a micromixer and a microchannel for controlling the residence time. They dissolved cyclohexanone oxime in cyclooctane and measured the selectivity of the Beckmann rearrangement of cyclohexanone oxime with oleum for various conditions.

In our previous study, a microchemical system was designed to perform the Beckmann rearrangement of cyclohexanone oxime. 100% conversion of cyclohexanone oxime and higher than 99% selectivity of caprolactam were reached with the reaction time less than 40 s and molar ratios of oleum to cyclohexanone oxime as low as 0.8.<sup>15</sup> However, the effect of  $\text{SO}_3$  on the reaction has not been disclosed. To our knowledge, the quantitative interaction between caprolactam and  $\text{SO}_3$  has not been reported, which is very important for reducing the acid/oxime molar ratios and optimizing the parameters of the reaction process. In the study, we set out to tackle these two fundamental questions about the mechanism of the Beckmann rearrangement, namely: (1) the role of  $\text{SO}_3$ ; (2) the influence of caprolactam on the reaction performance. The multiphase microchemical system including a micromixer, the delay loops and a microhydrolyzer was used to control the reaction temperature and the residence time. The solution of cyclohexanone oxime dissolved in *n*-octane and oleum were used as the continuous phase and the dispersed phase respectively. The influence of  $\text{SO}_3$  and caprolactam concentration on the reaction performance has been investigated. An equilibrium relation and a quantitative analysis of molar ratios of oleum to cyclohexanone oxime have been suggested.

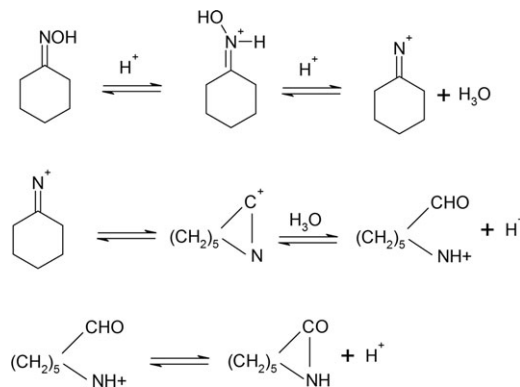
## Experimental

### Equipment

The microchemical system is the same as the system used in our previous work.<sup>15</sup> It consists of a micro-sieve dispersion mixer, a delay loop, and a microhydrolyzer. Cyclohexanone oxime was dissolved in *n*-octane as the continuous phase and oleum as the dispersed phase. The two fluids were delivered by metering pumps (Beijing Satellite Co.) through the pipes immersed in a water bath to control the feeding temperature. The feed pipes and the pump head were warmed by self-regulated electric heating bands (Kete electric heating Co.) to keep the temperature at 70°C and inhibit the precipitation of cyclohexanone oxime due to its low solubility in *n*-octane at room temperature. A delay loop (316 stainless steel) with an inner diameter of 2 mm and an



**Figure 2. The four complexes in the reaction system.<sup>9</sup>**



**Figure 3. The mechanism described by Fukumoto.<sup>10</sup>**

external diameter of 3 mm was connected directly downstream to the micromixer to control the residence time. The reaction time could be controlled accurately by changing the length of the delay loop. Three commercial temperature sensors (PT 100, Japan,  $\phi 2 \times 10$  mm) integrated in the pipeline system and a data acquisition system (Beijing Riubohua Co.) were used to record the temperature online. The samples were collected at the outlet after the microhydrolyzer.

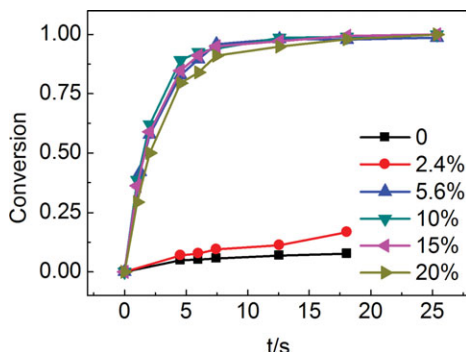
The micromixer and microhydrolyzer used in the microsystem are micro-sieve dispersion mixers (316 stainless steel). The details were described in our previous work<sup>15</sup> and the mixing performance and mass transfer rate have been described in literatures.<sup>16,17</sup> For analysis, the oleum phase has to be hydrolyzed and neutralized. The hydrolyzation step is also a fast and highly exothermic process. In addition, controlling reaction time accurately is difficult in consideration of the fast reaction rate. To achieve the process, a microhydrolyzer was designed to quench the reaction by adding water to the reacting system. A large amount of water was pumped into the microhydrolyzer and oleum would convert quickly to aqueous  $\text{H}_2\text{SO}_4$ . Ogata et al.<sup>18</sup> described the kinetics of the rearrangement reaction in the aqueous phase of  $\text{H}_2\text{SO}_4$ . The rate was found to be first order with respect to the oxime concentration and the reaction rate constant  $k$  is about  $10^{-5}$ – $10^{-4} \text{ s}^{-1}$  at 90°C, which is rather slow. Thus, we can assume that the reaction is completely stopped in the aqueous phase of  $\text{H}_2\text{SO}_4$  at room temperature.

### Analysis

The collected samples were separated into two phases, an organic phase and an aqueous phase. The organic phase was mainly composed of *n*-octane and unreacted cyclohexanone oxime while the aqueous phase of water, caprolactam, cyclohexanone oxime,  $\text{H}_2\text{SO}_4$ , and some undefined byproducts. In the analysis, the two phases were weighed by an electronic analytical balance. Then, the organic phase was diluted and measured by gas chromatography (GC) (HP 6890). The aqueous phase was diluted and neutralized with NaOH solution. Subsequently, the sample was determined by high performance liquid chromatography (HPLC) (Agilent 1100). The cyclohexanone oxime conversion  $C$  and caprolactam selectivity  $S$  were calculated by the following equations

$$C = 1 - \frac{W_{\text{org-ox}} \times M_{\text{org}} + W_{\text{aqu-ox}} \times M_{\text{aqu}}}{M_{\text{ox}}} \quad (1)$$

$$S = \frac{W_{\text{org-cap}} \times M_{\text{org}} + W_{\text{aqu-cap}} \times M_{\text{aqu}}}{C \times M_{\text{ox}}} \quad (2)$$



**Figure 4.** The concentration of cyclohexanone oxime in the organic solutions was 4 wt % and the concentrations of initial SO<sub>3</sub> in oleum were 0, 2, 6, 10, 15, 20 wt %, respectively.

The flow rate of cyclohexanone oxime solution was controlled at 25 mL/min, and the flow rates of oleum were 0.8 mL/min. The molar ratio of acid to cyclohexanone oxime, calculated as  $([H_2SO_4] + [SO_3])/[oxime]$ , was kept about at 2.5–2.7. The residence time was varied by changing the length of the reaction tube. The temperature of the water bath was kept at 70 °C.

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where  $W_{org-ox}$  (%) is the mass fraction of cyclohexanone oxime in the organic phase,  $W_{aqu-ox}$  (%) is the mass fraction of cyclohexanone oxime in the aqueous phase,  $W_{org-cap}$  (%) is the mass fraction of caprolactam in the sample organic phase,  $W_{aqu-cap}$  (%) is the mass fraction of caprolactam in the sample aqueous phase,  $M_{org}$  (g) is the mass of the organic phase,  $M_{aqu}$  (g) is the mass of the aqueous phase and  $M_{ox}$  (g) is the feeding mass of cyclohexanone oxime calculated with the feeding rate of cyclohexanone oxime solution and the sampling time. Most experiments are repeated twice and the average relative errors of replication in conversion and selectivity are 1.3 and 2.4%, respectively.

## Results and Discussion

### The effect of initial SO<sub>3</sub> concentration in oleum on Beckmann rearrangement

Figure 4 shows the reaction rates of the Beckmann rearrangement in the oleum phase with different initial SO<sub>3</sub> concentrations. The concentration of cyclohexanone oxime in the organic phase was restricted to 4 wt % to reduce the heat release in the reaction system and realize a smooth reaction process. The maximum temperature rise of reaction mixture was less than 1 °C in the experiments. So, the change of reaction temperature could be ignored. As shown in Figure 4, when the oleum concentration is above 6 wt %, the reaction can be finished within 20 s in the microchemical system and the reaction rates are nearly independent with the oleum concentration. Also, the caprolactam selectivity is found to be above 99% because of the greatly reduced heat release and the good control of temperature. Correspondingly, when the initial concentration of SO<sub>3</sub> is 2 wt % or lower, the reaction kinetics is rather slow and many byproducts are formed in our experiments, which is also described by Ogata et al.<sup>18</sup>

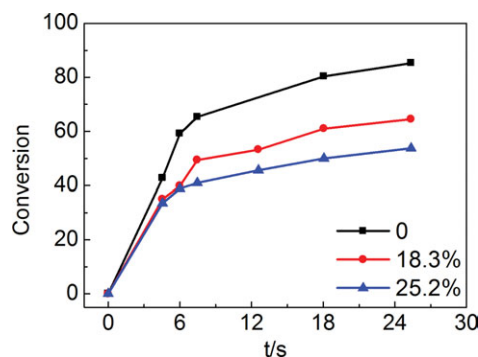
In the mechanism described by Fukumoto,<sup>10</sup> SO<sub>3</sub> acts as the dehydration agent. The added sulfur trioxide is able to bind water and thus forms sulfuric acid, which further catalyzes the ongoing rearrangement. However, this catalytic mechanism cannot well explain the fact that the reaction rate

decreases sharply when the oleum concentration decreases from 6 to 2 wt %. As the acid/oxime molar-ratio (M-ratio) is about 2.5–2.7, SO<sub>3</sub> is always enough to bind water in the system except that it can be consumed by participation in the reaction process. In 2008, Fábos et al.<sup>4</sup> proposed a new reaction path concerned with SO<sub>3</sub>. The attack of oxygen atom of cyclohexanone oxime to sulfur atom of SO<sub>3</sub> may be the reason for the significant rate increase in the presence of sulfur trioxide. When the SO<sub>3</sub> concentration is above 6 wt %, the reaction path concerned with SO<sub>3</sub> carries through quickly and little byproducts are formed. When the SO<sub>3</sub> concentration is low, the new path slows down and the reaction is catalyzed by H<sub>2</sub>SO<sub>4</sub>. The reaction rate becomes slow and the selectivity decreases apparently.

As for nearly the same reaction rates with the oleum concentration above 6 wt %, the most likely reason is that the reaction is a mass transfer controlled process. In the microsystem, cyclohexanone oxime dissolved in octane is transported to the oleum and transforms to caprolactam. The reaction medium, also called the rearrangement mixture, contains the unreacted cyclohexanone oxime and caprolactam in oleum. The mass transfer in the mixture is relatively slow as its viscosity is larger than 500 mPa s even at 80 °C.<sup>4</sup> Accordingly, the reaction process is a mass transfer controlled process even though the oleum droplets diameter in the multiphase system can reach 10–25 μm.<sup>15</sup> To get further conclusion, more work of process intensification has to be done to overcome the mass transfer limitation. This study will be done in our future work.

### The effect of ε-Caprolactam addition in oleum on Beckmann rearrangement

In theory, sulfur trioxide as the catalyst is not consumed. However, it is proved that caprolactam in the oleum phase is not in a free state but in the form of two complexes (CPLH<sup>+</sup> and CPLSO<sub>3</sub>), as shown in Figure 2. It can be assumed that, with the reaction ongoing, the accumulation of caprolactam may bring an adverse effect on the reaction process. To study the effect of caprolactam, a mixture by dissolving

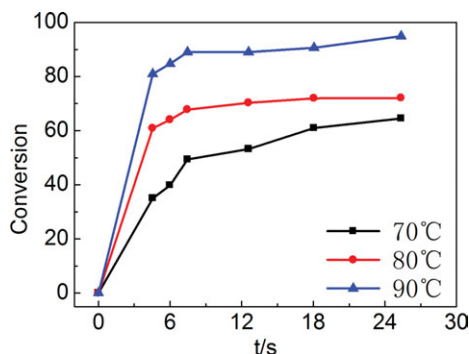


**Figure 5.** The concentration of cyclohexanone oxime in solutions was 4 wt % and the concentrations of caprolactam in oleum were 0, 18.3, 25.2 wt %, respectively.

The flow rate of cyclohexanone oxime solution was controlled at 25 mL/min, and the flow rates of oleum solution were 0.33, 0.29, 0.21 mL/min. The molar ratio of acid to cyclohexanone oxime was kept about at 0.70. The residence time was varied by changing the length of the reaction tube. The temperature of the water bath was kept at 70 °C.

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**Figure 6.** The experimental conditions were selected as 18.3 wt % caprolactam in oleum and 4 wt % cyclohexanone oxime in octane.

The flow rates of cyclohexanone oxime solution and oleum solution were 25 and 0.29 mL/min, respectively. The M-ratio was kept at 0.70. The residence time was varied by changing the length of the reaction tube. The reaction temperature was controlled by the water bath.

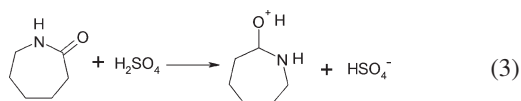
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caprolactam in the oleum was used as the dispersed phase instead of pure oleum. The M-ratio based on the overall feed ratio of cyclohexanone oxime to oleum was restricted to 0.7. The concentration of initial  $\text{SO}_3$  in oleum was 20 wt %.

**The Influence of Caprolactam Concentration on the Reaction Rate.** Figure 5 shows the influence of the caprolactam concentration on the reaction rate. Obviously, the concentration of caprolactam could influence the reaction greatly. In all conditions, the reaction rates are fast at first and come into a “smooth period” in a short time. The smooth period is close to the process when the  $\text{SO}_3$  concentration is below 2 wt %. The process means that reaction rates slow down and many byproducts are formed. With the concentration of caprolactam growing, the reaction rate decreases quickly and lower conversion is reached in the same residence time, indicating that caprolactam has a negative influence on the reaction rate and selectivity.

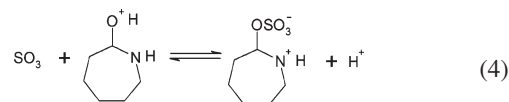
**The Influence of Temperature on the Reaction Rate.** Figure 6 shows the influence of temperature on the reaction rate with the presence of caprolactam in oleum. With the temperature increasing, the reaction rate increases and the conversion can reach higher value in the same residence time. The high conversion of above 90% can be achieved at 90°C even with the M-ratio of 0.7. It can be concluded that the higher temperature is advantageous for improving the reaction rate and reaching high conversion at the low M-ratio. The temperature rise can not affect the dehydration while it improves the reaction rate. The results prove that the added sulfur trioxide acts as the catalyst and participates in the reaction process not only as the dehydration agent.

According to the statement earlier,  $\text{SO}_3$  acts as the catalyst and has an important influence on the reaction rate. The sharp decreasing reaction rates in Figures 4–6 results from low  $\text{SO}_3$  concentrations. The interaction of caprolactam and  $\text{SO}_3$  may be a key point. It has been proved that  $\epsilon$ -caprolactam is protonated to form caprolactamium hydrogen sulfate ( $\text{CPLH}^+$ ) in sulfuric acid

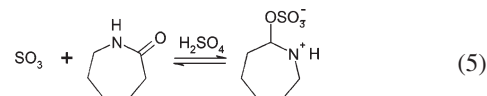


The accumulation of caprolactam brings an adverse effect on the reaction process. Because of the existence of

$\text{CPLSO}_3$ , we conjecture that there is equilibrium between  $\text{CPLH}^+$  and  $\text{CPLSO}_3$



The accumulating caprolactam can bind free  $\text{SO}_3$  and reduce the free  $\text{SO}_3$  concentration. When the  $\text{SO}_3$  concentration reduces to a certain value, the reaction rate may decrease apparently. That is the reason why caprolactam has an adverse effect on the reaction process shown in the Figures 5 and 6. It is assumed that the two reactions are very fast. The total reaction could be written as



The equilibrium constant is defined as

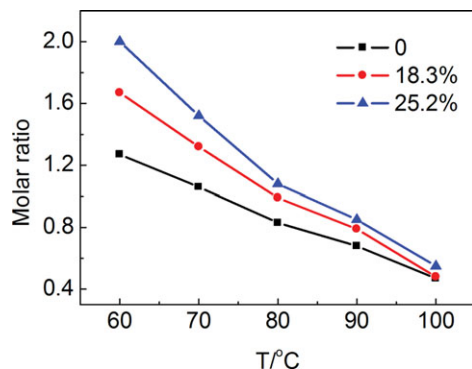
$$K = \frac{c_{\text{CPLSO}_3}}{c_{\text{SO}_3} \times c_{\text{CPL}}} \quad (6)$$

The equilibrium constants are relevant to the oleum concentrations. In our experiments, the concentrations of initial  $\text{SO}_3$  in oleum are 20 wt %, which is adopted in the industry. Higher  $\text{SO}_3$  concentration means high viscosity and decreasing the protonation whereas lower concentration means decreasing the catalyst concentration. As shown in the Figures 5 and 6, the reaction rate decreases apparently at about 7.5 or 12.6 s while the reaction system goes into the “smooth period.” As the reaction mixture containing oleum has strong oxidizability and corrosivity, it is really difficult to directly measure the concentrations of the complexes at the period. We calculated the equilibrium constants according to the experimental data shown in Figures 5 and 6. The free  $\text{SO}_3$  concentration at the smooth period is a value between 2 and 6 wt % as shown in Figure 4. It needs more experiments to determine the value. Here, we assume the value is 2 wt %. The  $\text{SO}_3$  concentration is 20 wt % in the beginning and the concentration of  $\text{CPLSO}_3$  can be obtained. The concentration of caprolactam is calculated according to the conversion of cyclohexanone oxime. The calculated equilibrium constant results are listed in Table 1.

Table 1 shows that the calculated equilibrium constants are nearly the same at 70°C even though the caprolactam concentrations in oleum are different. With the increasing of temperature, the equilibrium constants become smaller. It means that the higher temperature may give out more  $\text{SO}_3$  at

**Table 1.** The Calculated Results of the Equilibrium Constants

Equilibrium constants at 70°C (L/mol)			Equilibrium constants with caprolactam concentration of 18.3 wt % (L/mol)		
Caprolactam concentration	0 wt %	1.663	Temperature	70°C	1.663
	18.3 wt %	1.658		80°C	1.533
	25.2 wt %	1.660		90°C	1.467



**Figure 7.** The concentrations of caprolactam in oleum were 0, 18.3, 25.2 wt %, respectively.

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the same composition and be of benefit for the reaction. The existence of the equilibrium explains the adverse effect of caprolactam and the positive effect of temperature on the reaction well.

According to the equilibrium constants at different temperature, we calculate the reaction heat and the equilibrium constants at other temperatures. The reaction heat is about  $-6.65$  kJ/mol which means the reaction is exothermic. As the  $\text{SO}_3$  concentration at the equilibrium state is an assumed value, we make an error analysis in the calculation of the reaction heat. The reaction heat increases by about 6.4% with the assumed value of 1 wt % while it decreases by about 5.3% with the assumed value of 3 wt %. That means change of the assumed value gives minor impact on the reaction heat. The lowest M-ratio required to achieve 99% conversion (without smooth period) at different temperature and caprolactam concentrations are also calculated. The results are listed in Figure 7. It can be concluded that temperature is a key factor to reduce the M-ratio in the caprolactam production. The higher temperature can decrease the lowest M-ratio at each caprolactam concentration. The M-ratio can reach about 0.5 at the ideal conditions when the temperature is  $100^\circ\text{C}$ , indicating a large decreasing in the consumption of oleum and the production of ammonium sulfate. The results can explain why higher temperature is beneficial at the later rearrangement process. However, the temperature cannot be increased unbounded while the side reactions such as reactant carbonization would arise at high temperature. The quantitative analysis is useful for optimization and reliable design of Beckmann rearrangement processes.

## Conclusions

In this work a multiphase microchemical system has been successfully applied to investigate the mechanism of Beckmann rearrangement of cyclohexanone oxime in oleum. Different reaction rates are measured in several tests with different  $\text{SO}_3$  concentrations of oleum, indicating  $\text{SO}_3$  acts as catalyst for the Beckmann rearrangement process. The influence of caprolactam concentration in oleum phase on the cyclohexanone oxime conversion is studied at low molar ratio of oleum to cyclohexanone oxime, and it is concluded caprolactam plays an adverse role for this reaction. Based on the results, an equilibrium between protonated caprolactam and

caprolactam hydrogen sulfate is proposed and the equilibrium constants are gained at 70, 80, and  $90^\circ\text{C}$ . The existence of the equilibrium explains the fact that high concentration of caprolactam and low temperature have a negative influence on the reaction performance at low acid/oxime molar ratio. According to the analysis, the lowest M-ratio for sufficient conversion ( $>99\%$ ) can reach as low as 0.5 at  $100^\circ\text{C}$  indicating a large decreasing in the production of ammonium sulfate.

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## Literature Cited

- Beckmann E. Zur Kenntniss der Isonitrosoverbindungen. *Chem Ber.* 1886;19:988.
- Ritz J, Fuchs H, Kieczka H, Moran WC. *Caprolactam*. In: *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, 2001.
- Dahlhoff G, Niederer JPM, Hoelderich WF.  $\epsilon$ -Caprolactam: new by-product free synthesis routes. *Catal Rev Sci Eng.* 2001;43:381–441.
- Fábos V, Lantos D, Bodor A, Bálint AM, Mika L, Sielcken OE, Cuiper A, Horváth IT.  $\epsilon$ -Caprolactamium hydrogen sulfate: an ionic liquid used for decades in the large-scale production of  $\epsilon$ -caprolactam. *ChemSusChem.* 2008;1:189–192.
- Wichterle O, Rocek J. Beckmann rearrangement of cyclohexanone oxime. Kinetics of final stages of the reaction I. *Collect Czech Chem Commun.* 1951;16:591–598.
- Jones B. Kinetics and mechanism of the Beckmann rearrangement. *Chem Rev.* 1944;35:335–350.
- Nguyen MT, Raspoet G, Vanquickenborne LG. Mechanism of the Beckmann rearrangement in sulfuric acid solution. *J Chem Soc Perkin Trans 2.* 1997;4:821–825.
- Ronchin L, Bortoluzzi M, Vavasori A. A DFT study on secondary reaction pathways in the acid-catalysed Beckmann rearrangement of cyclohexanone oxime in aprotic solvent. *J Mol Struct Theochem.* 2008;858:46–51.
- Cavalieri-d'Oro P, Bagatin R, Caimi A. Caprolactam from Beckmann rearrangement reaction kinetics and industrial simulation. In: *The International Chemical Engineering Conference*. Germany, 1992.
- Fukumoto O. Studies on the production of  $\epsilon$ -caprolactam.4. On kinetics of Beckmann rearrangement. *Kogyo Kagaku Zasshi.* 1961;64:1285–1289.
- Günther A, Jensen KF. Multiphase microfluidics: from flow characteristics to chemical and materials synthesis. *Lab Chip.* 2006;6:1487–1503.
- Link DR, Anna SL, Weitz DA, Stone HA. Geometrically mediated breakup of drops in microfluidic devices. *Phys Rev Lett.* 2004;92:054503-1-4.
- Song H, Tice JD, Ismagilov RF. A microfluidic system for controlling reaction networks in time. *Angew Chem Int Ed Engl.* 2003;42:768–772.
- Zuidhof KT, de Croon MHJM, Schouten JC. Beckmann rearrangement of cyclohexanone oxime to  $\epsilon$ -caprolactam in microreactors. *AIChE J.* 2010;56:1297–1304.
- Zhang JS, Wang K, Lu YC, Luo GS. Beckmann rearrangement in a microstructured chemical system for the preparation of  $\epsilon$ -Caprolactam. *AIChE J.* 2011. In press.
- Wang K, Lu YC, Xu JH, Gong XC, Luo GS. Reducing side product by enhancing mass-transfer rate. *AIChE J.* 2006;52:4207–4213.
- Zhang JS, Wang K, Lu YC, Luo GS. Characterization and modeling of micromixing performance in micropore dispersion reactors. *Chem Eng Process.* 2010;49:740–747.
- Ogata Y, Okano M, Matsumoto K. Kinetics of the Beckmann rearrangement of cyclohexanone oxime. *J Am Chem Soc.* 1955;77:4643–4646.

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