Beckmann Rearrangement of Cyclohexanone Oxime to ε-Caprolactam in a Modified Catalytic System of Trifluoroacetic Acid

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Abstract A catalytic system, including trifluoroacetic acid and organic solvent additives, was applied to carry out the Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. High conversion (100 %) and high selectivity to caprolactam (>99 %) have been successfully obtained using acetonitrile as the additive. The effect of several organic solvents on the reaction was investigated, and the catalyst composition was optimized. The results indicate that the catalytic system with 10 wt% of acetonitrile can give the fastest reaction rate. An immiscible two-phase system was proposed to study the side reaction of oxime hydrolysis which determines the selectivity. Based on the results, a simplified reaction process was suggested and a mathematical kinetic model was developed. The performance of the catalytic system is much better than the classic process. Neutralization agent and ammonium sulfate by-product are both completely avoided.

Keywords Beckmann rearrangement · ε-Caprolactam · Trifluoroacetic acid · Model · Kinetics

1 Introduction

ε-Caprolactam (CPL), the monomer for nylon-6, is mainly produced via the classical Beckmann rearrangement of cyclohexanone oxime (COX), which was first described more than a century ago [1]. Conventionally, this process employs the fuming sulfuric acid (oleum) as the solvent

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and catalyst [2, 3] since it is generally accepted that this reaction requires strongly acidic and dehydrating media to prevent the side reactions such as oxime hydrolysis. However, this results in difficult product separation from the catalyst solution due to the strong interaction between acid catalyst and caprolactam. As a consequence, large amounts of ammonia have to be used to neutralize sulfuric acid producing ammonium sulfate as the by-product. Nearly 2 tons of ammonium sulfate per ton of product are produced in the rearrangement step [4, 5].

With the growing concern for the environmental impact of chemical industry, great efforts have been made to develop the ammonium sulfate-free processes. A large variety of solid-acid catalysts have been tested for the Beckmann rearrangement of COX both in the liquid and gas phase, such as zeolites [6, 7], oxides [8, 9] and mesoporous materials [10–12]. However, these processes are suffering from the problems such as the low caprolactam yield and rapid catalyst deactivation. Noncatalytic Beckmann rearrangement has also been achieved in supercritical water near the critical point with a short reaction time [13, 14]. However, the reaction conditions are too rigorous to be used in an industrial application. Ionic liquids are also potential medium for the Beckmann rearrangement reaction in which many promising results have been obtained [15–17]. Therefore, to develop an efficient catalytic system without producing the by-product of ammonium sulfate is still highly desired.

Although strong inorganic acids is commonly accepted in the Beckmann rearrangement of COX [18, 19], the use of weak organic acid can be a promising approach to an ammonium sulfate-free process. On one hand, the organic acid can convert the oxime to more reactive ether or ester intermediates. The intermediates, compared with the oxime, have a lower electronic density at the nitrogen

induced by the electron withdrawing effect of the acid group and thus can even undergo spontaneous rearrangement without Brønsted acids [20, 21]. On the other hand, caprolactam is more facile to be obtained by distillation or solvent extraction due to its weak interaction with the acid. In the early studies, acetic anhydride and acetyl chloride have been employed as promoters in the oxime rearrangement [22]. Recently, progresses have been made on the homogeneous Beckmann rearrangement using organocatalysis, such as cyanuric chloride [23, 24], sulfamic acid [25], and trifluoroacetic acid [26, 27]. Excellent conversion and selectivity were obtained. In particular, trifluoroacetic acid (TFA) can be a promising catalyst for its low boiling point (345.5 K) and its facile separation with amides by distillation [26, 27]. However, the low selectivity (83–95 %) and slow reaction rate (1.2×10^{-5} mol L^{-1} s^{-1}, 343 K) compared with the industrial process still present a significant challenge.

In our previous work, microreactors have been applied to carry out the Beckmann rearrangement of COX with oleum as the catalyst [28, 29]. 100 % conversion of COX and higher than 99 % selectivity to CPL were reached with the reaction time less than 40 s and molar ratios of acid to COX as low as 0.8. It is much lower than the industrial value of 1.2–1.7. However the side product of ammonium sulfate has not been avoided completely. In this work, a modified catalytic system, in which TFA acts as the catalyst and solvent and organic solvents act as the additives, was employed in the Beckmann rearrangement of COX to CPL. The effect of different organic solvent and catalyst composition on the reaction rate and the selectivity to CPL were investigated. In addition, an immiscible two-phase system was proposed to study the side reaction of oxime hydrolysis which determined the selectivity. Based on the results, a simplified reaction process was suggested and a mathematical kinetic model was developed to represent the reaction process. The reaction rate constants and activation energy of the kinetic model were given.

2 Experimental

2.1 Materials

Reagents (COX, CPL and TFA) were purchased from J&K Scientific Ltd. (Beijing). All the organic additives (hexane, toluene, Dichloroethane, Benzonitrile, acetonitrile, DMSO) were HPLC grade without further purification.

2.2 Apparatus and Analysis

The experiments were performed in a well-stirred (1000 rpm) glass vial (20 mL) which was placed on a heated magnetic stir-plate (IKA RCT basic). The vial is closed by a bottle cap which has a cushion for sampling. The hermetical environment can approximately ensure a constant system pressure and the vapor phase composition during the reaction process. TFA as the catalyst and solvent has a majority of the reaction mixture and the volatilization of TFA would bring nearly no effect on the reaction. The TFA and additives (total about 15 mL) were first mixed in the glass vial and then heated to the reaction temperature. The COX was then added into the vial and the reaction time was recorded with a stopwatch. Small amounts of the reaction mixtures (80 μL) were drawn at different time and immediately diluted by large amounts of acetonitrile (1 ml). Ronchin et al. [27] described the kinetics of the rearrangement by TFA in acetonitrile at 90 °C. The conversion of COX reached only 15 % with the reaction time of 50 min and TFA concentration of 1 mol L^{-1}. Thus we can figure out that the reaction in the mixtures (TFA concentration: 0.9 mol L^{-1}) is stopped after the dilution of acetonitrile at room temperature. All the samples were measured by gas chromatography (Shimadzu GC-2014) with a flame ionization detector under following conditions: the injection temperature, 260 °C; the column temperature, 140–260 °C, 30 °C min^{-1}; the detector temperature, 280 °C. The sample volume for all analysis was 1 μL. Dimethyl terephthalate was used as the internal standard. The concentrations of cyclohexanone (main side product, CYC), COX and CPL could be determined by this internal standard method within the measurement errors of 0.8, 1 and 0.5 %, respectively. The ester intermediates (including trifluoroacetyl COX and trifluoroacetyl caprolactam) concentrations could not be quantified due to the high interaction with TFA and they were calculated by the mass balance. By this method, the concentration of esters was determined within a measurement error of 1.5 %.

3 Results and Discussion

3.1 Modified Catalytic System Based on TFA

#### 3.1.1 The Influence of Additive on the Reaction Rate and Selectivity

It was concluded that the reaction rate increases with the increase of TFA (as the catalyst) concentration in the previous paper [27]. To improve the catalytic system, it first occurs to us that TFA is employed as the catalyst and solvent.

Table 1 shows influence of some organic solvents on the reaction rate and selectivity. Pure TFA without any organic solvents was first examined (entries 1 and 2). However, COX conversion and CPL selectivity were 27 and 85 %

Table 1 The influence of additive on the reaction rate and selectivity

| Entry	Additive	t (min)	COX Con (%)	CPL Selectivity (%)	r_0 (10^{-5} mol L^{-1} s^{-1})
1	None	20	27	85	–
2	None	120	27	85	–
3	Hexane	60	20	78	–
4	Hexane	120	20	78	–
5	Toluene	120	28	87	0.28
6	Dichloroethane	120	29	85	0.34
7	Benzonitrile	120	96	>99	1.87
8	Acetonitrile	120	100	100	6.20
9	DMSO	120	76	97	1.15

Reaction conditions: 333 K; the additive content in TFA: 7 wt%; COX: 0.16 mol/L
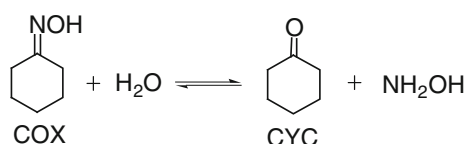
Scheme. 1 The hydrolysis of COX with water

respectively at 120 min and could not be improved at a longer reaction time. This result indicates that the organic solvent may play an important role in the rearrangement. As a result, some organic solvents were used as the additives. When non-polar solvent such as hexane was added into the TFA, similar result was obtained and COX conversion was only 20 % at 120 min (entries 3 and 4). When weak polar solvents such as toluene and dichloroethane were employed (entries 5 and 6), a little improvement has been observed, and the COX conversion increased to 28 and 29 % respectively. But the initial reaction rate was extremely slow. Excellent reaction rate and selectivity were both obtained when polar solvents such as benzonitrile, acetonitrile and DMSO (entries 7–9) were used as the additives. Specially for acetonitrile, 100 % conversion of COX and nearly 100 % selectivity to CPL were obtained at 120 min and the initial reaction rate was the largest reaching 6.2×10^{-5} mol L^{-1} s^{-1} while the value was only 4.1×10^{-6} mol L^{-1} s^{-1} at 333 K in the literature [27]. The confusing and large influence of additive on the reaction rate and selectivity indicate that reaction path is quite complex with which both the TFA and the additive are involved.

3.1.2 Concentration Profile

In the rearrangement, CYC is the main side product, which is produced by the hydrolysis of COX with water as shown in Scheme. 1. During the experiments with acetonitrile as the additive, the selectivity to CPL was nearly 100 % and CYC even could not be detected at 120 min. Compared
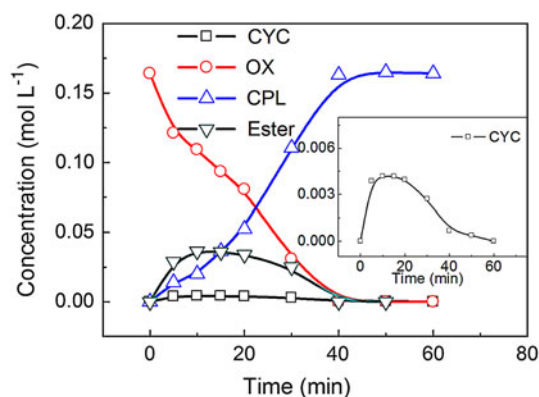
Fig. 1 A typical concentration profile for rearrangement process. Run conditions: T 333 K, COX concentration 0.16 mol L^{-1}, acetonitrile in TFA: 7 wt%

with the selectivity of 83–95 % in the literature [27], it is a great improvement. To figure out the reason, the rearrangement process was carefully investigated.

A typical concentration profile of the Beckmann rearrangement in TFA with acetonitrile as the additive is reported in Fig. 1. For CPL, an initial period of low reactivity is followed by a steady rise until approximately 30 percent of the oxime has been rearranged to CPL, and then a rapid reactivity at almost constant speed is maintained until the 100 % conversion of COX is complete. The concentration of COX decreases fast at an initial period and then decreases at a slower constant rate until all the COX are consumed. The ester intermediates increase fast to a constant value until 20 min and then decrease to zero. The trend of CYC is similar to that of ester intermediates and has a decrease until zero. However, in the previous work [27] CYC increases fast to a value and keeps constant in the following time. This is the reason why the selectivity in the modified catalytic system is nearly 100 %.

For the decease of CYC, The possible reason is that hydrolysis of COX to CYC is a reversible process in the modified catalytic system. It was commonly accepted that
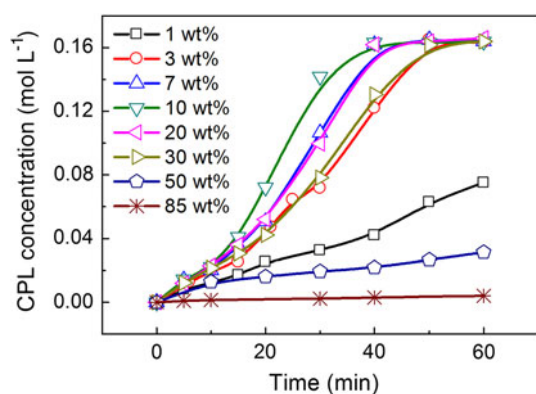
Fig. 2 The influence of additive concentration on the reaction rate. Run conditions: T 333 K, COX concentration 0.16 mol L^{-1}

Table 2 The influences of temperature and TFA concentration on the oxime hydrolysis

Entry	T (°C)	t (min)	TFA (mol L^{-1})	CYC/COX in aqueous phase
1	20	20	0	0
2	20	5	0.13	0.46
3	20	20	0.13	0.46
4	20	20	0.26	0.46
5	50	20	0.13	0.73
6	60	20	0.13	0.81
7	70	20	0.13	0.92

hydrolysis of COX to CYC in aqueous solutions was reversible [30]. Due to the weaker interaction of TFA and hydroxylamine, the reaction of CYC and hydroxylamine in the TFA can proceed which has been verified in our experiments. In the rearrangement, due to the esterification of COX producing water, trace amount of COX hydrolyzes with water to CYC and hydroxylamine reaching an equilibrium state. With the rearrangement undergoing, COX and the ester are converted to CPL and corresponding water decreases too. With the decrease of water and COX, the hydrolysis equilibrium moves towards the COX until all the CYC is consumed. That means the selectivity to CPL is getting larger with the increase of the conversion of COX as shown in Table 1. Hydroxylamine (alkaline material) is unstable which would easily decompose especially in hot water. TFA as an acid can combine hydroxylamine and then form a more stable complex compound like hydroxylamine hydrochloride. In the modified catalytic system, the reaction time is short and the high TFA concentration can keep hydroxylamine stable while the reaction time is long and hydroxylamine may easily be destroyed in a low TFA concentration system. As a result, the equilibrium cannot move back to COX and the selectivity decreases. This may be the reason why high selectivity is obtained in the modified catalytic system.

3.1.3 The Influence of Catalyst Composition on the Reaction Rate

The previous results indicate that both the TFA and solvent have a large influence on the reaction. To obtain the best catalytic activity, a set of experiments was carried out with the additive mass fraction ranging from 1 to 85 wt%. Fig. 2 shows the influence of catalyst composition on the reaction rate. We can find that when the mass fraction of acetonitrile in TFA is 10 wt%, the reaction rate is fastest. The rate decreases when the mass fraction is above or below 10 wt%. However, the rate maintains a high level when the

acetonitrile mass fraction in TFA is between 3 and 30 wt% and decreases greatly when the acetonitrile concentration is beyond the range. When the acetonitrile mass fraction increases to 85 wt% (the concentration adopted in the literature [27]), the reaction rate is extremely slow and only about 2.5 % of oxime has been converted to CPL at 60 min. It is easily understood that the high TFA concentration is favorable for rapid reaction rate as the TFA acts as the catalyst. For the effect of acetonitrile, it may play an important role on aiding the hydrogen transfer in the rearrangement of the ester [31]. However, to draw any further conclusions, more work has to be done.

3.2 The Side Reaction of COX Hydrolysis

It can be concluded that the side reaction of oxime hydrolysis is fast from the fact that CYC appears at the very start and change with the trend of esters as shown in Fig. 1. As a result, it is difficult to directly study the side reaction. To overcome the problem, an immiscible two-phase system is proposed to study the oxime hydrolysis. Water, as aqueous phase, contains the oxime and TFA while octane, as the organic phase, can extract COX and CYC. Due to the extremely low concentration of TFA, rearrangement of oxime is almost stopped and CPL cannot be detected in the experiments. The concentration in octane can be determined by GC and the hydrolysis reaction in water is then quantified by the octane-water partition coefficients of COX and CYC.

Table 2 shows the influence of temperature and TFA concentration on the oxime hydrolysis. COX, in the absence of TFA, was quite stable as expected and nearly no CYC has been produced (entry 1). The results indicate that the oxime hydrolysis is an acid-catalyzed process. The molar ratio of CYC/COX in aqueous phase remained a constant value from 5 min even at 20 °C (entries 2 and 3). The results verify the fact that the side reaction of oxime hydrolysis is fast and a chemical equilibrium exists between COX and CYC. With the increase of TFA
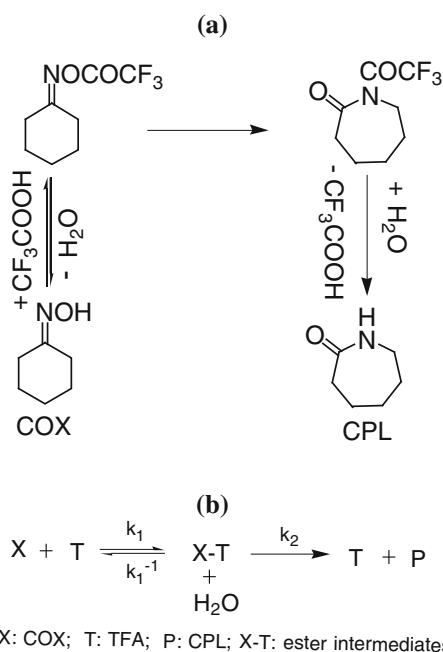
Scheme. 2 aThe rearrangement mechanism in TFA; b the schematic overview for the rearrangement mechanism

concentration, the molar ratio of CYC/COX has not changed which indicates that the acid concentration has no effect on the hydrolysis equilibrium. When the temperature was increased, more CYC was produced. The result indicates that high temperature is advantageous for the oxime hydrolysis (entries 5–7).

3.3 Modeling

3.3.1 The Reaction Model

Mechanism of the rearrangement by TFA has been proposed in earlier papers [26, 27]. The rearrangement path includes three main steps: COX esterification with TFA to COX ester and the rearrangement of COX ester to CPL ester and the hydrolysis of CPL ester to CPL. The process is shown in Scheme. 2a. It is verified that the hydrolysis of CPL ester is quite fast compared with the other two processes and the CPL ester concentration is much lower than the COX ester. As a result, a simplified model was proposed to describe the rearrangement process as shown in Scheme. 2b. X-T was employed to represent the COX and CPL ester and the latter two steps were combined in one step. The reactant X (COX) and T (TFA) combined in a reversible way to form an ester X-T which decomposed into the product P and the catalyst T. The decomposition rate of X-T was described as $k_2 c_{X-T}$. Water concentration was not concluded in the rate as it was mainly involved in the fast hydrolysis of CPL ester.

The evolution of the reagent concentrations with respect to the residence time can be written as

$$\frac{dc_X}{dt} = -k_1 c_X c_T + k_1^{-1} c_{X-T} c_{H_2O} \tag{1}$$

$$\frac{dc_{X-T}}{dt} = k_1 c_X c_T - k_1^{-1} c_{X-T} c_{H_2O} - k_2 c_{X-T} \tag{2}$$

$$\frac{dc_P}{dt} = k_2 c_{X-T} \tag{3}$$

$$\frac{dc_T}{dt} = -k_1 c_X c_T + k_1^{-1} c_{X-T} c_{H_2O} + k_2 c_{X-T} \tag{4}$$

$$\frac{dc_{H_2O}}{dt} = \frac{dc_{X-T}}{dt} \tag{5}$$

The reaction rate constant depends on the temperature according to the Arrhenius equation.

$$k_i = k_{i0} \exp(-E_i/RT) \tag{6}$$

Where k_{i0} is the pre-exponential factor, E is the activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature.

3.3.2 The Parameter Estimation

The experiments were performed with acetonitrile mass fraction in TFA of 10 wt% giving a best performance. The software MATLAB was applied for parameter estimation by integrating concentration curves along the reaction time using the least squares method. The kinetic model was fitted to the experimental data at different temperatures. The experimental data and the model predictions are shown in Fig. 3. The results show that the model can predict the reagents concentrations versus time well at different temperatures except for that at high CPL concentration. A deviation has been observed between predicted and measured CPL concentrations at high CPL concentration. This is probably due to the simplified assumption that the latter two steps are combined in one step.

Table 3 presents the estimated activation energy and pre-exponential factor of the kinetic model. The activation energy of k_1 is comparable with the values reported by L. Ronchin [27], which is 94 kJ mol^{-1}. The activation energy of k_2 is much lower, only 64 kJ mol^{-1}. The activation energy of k_1^{-1} is as high as 129 kJ mol^{-1} indicating that the equilibrium concentration of ester X-T would decrease at higher temperature. Table 4 presents the corresponding rate constants of the kinetic model at different temperatures. According to the results, the value of k_1 is lower by more than an order of magnitude than the other two. However, due to the high TFA concentration (about 9.5 mol L^{-1}) in the modified catalytic system, it can be concluded that the three steps all determine the reaction

Fig. 3 Comparison of predicted and measured concentrations versus time at different temperatures. **a** 50 °C; **b** 60 °C; **c** 70 °C. Run conditions: COX concentration 0.16 mol L^{-1}, acetonitrile in TFA: 10 wt%
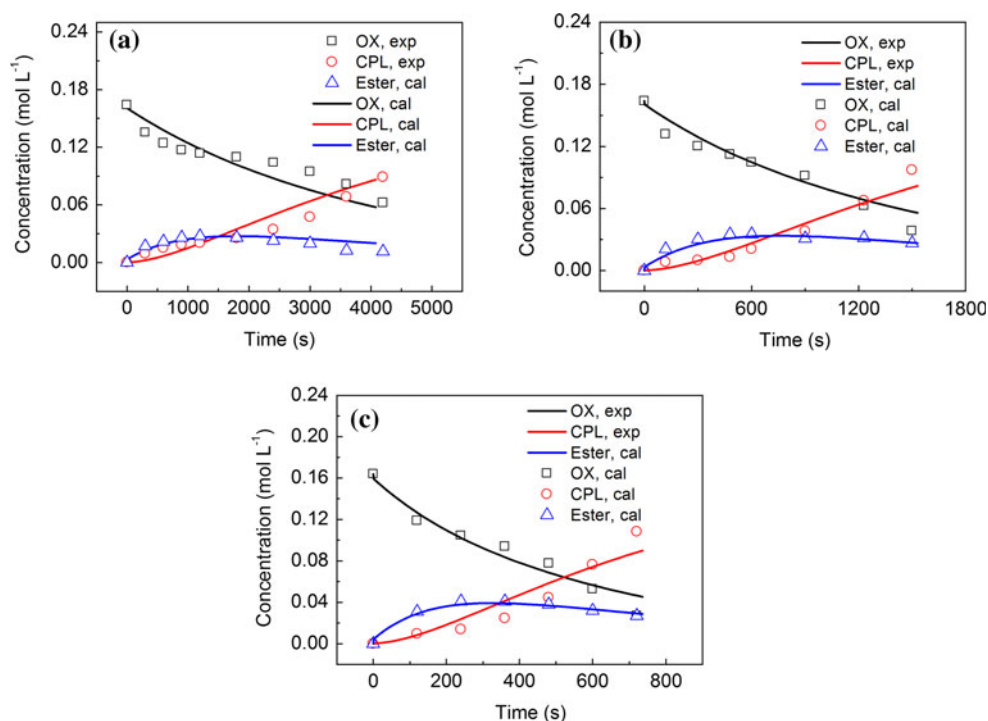

Table 3 Estimated activation energy and pre-exponential factor of the kinetic model

	k_1	k_1^{-1}	k_2
E (kJ mol^{-1})	94	129	64
k_0	4.0×10^{10}	9.0×10^{17}	2.5×10^7

Table 4 Estimated rate constants of the kinetic model at different temperature

Temperature (°C)	k_1 (L mol^{-1} s^{-1})	k_1^{-1} (L mol^{-1} s^{-1})	k_2 (s^{-1})
50	2.7×10^{-5}	1.1×10^{-3}	9.2×10^{-4}
60	7.8×10^{-5}	4.6×10^{-3}	1.9×10^{-3}
70	2.1×10^{-4}	1.8×10^{-2}	3.8×10^{-3}

Table 5 Estimated rate constants of the kinetic model at different solvent concentrations (60 °C)

Solvent concentration (wt%)	k_1 (L mol^{-1} s^{-1})	k_1^{-1} (L mol^{-1} s^{-1})	k_2 (s^{-1})
1	7.7×10^{-5}	4.2×10^{-3}	8.8×10^{-4}
3	7.5×10^{-5}	4.0×10^{-3}	1.7×10^{-3}
20	8.2×10^{-5}	6.2×10^{-3}	2.8×10^{-3}
30	8.0×10^{-5}	5.8×10^{-3}	2.8×10^{-3}

rate. Also, it reveals the importance of the increase of TFA concentration to increase the reaction rate.

Then the model was applied to fit the data of other acetonitril concentrations at 60 °C. Table 5 presents the estimated rate constants of the kinetic model at different solvent concentration (60 °C). With the increase of solvent concentration, the values of k_1 and k_1^{-1} nearly do not change while that of k$_2$ increases until the mass fraction of acetonitril reaches 20 wt%. It can be concluded that the solvent is mainly involved with the second step and the first step of esterification is mainly affected by TFA concentration. The results are consistent with the conjecture that the solvent may play an important role on aiding the

hydrogen transfer in the rearrangement of the ester [31]. Although it has some limitations, such as the poor fitting at higher CPL concentration, the model is helpful to understand the reaction process and also useful for optimization and reliable design of rearrangement process in the future.

A performance comparison between the modified catalytic system and previous catalytic system is presented in Table 6. Although both two catalytic systems are based on the TFA and acetonitrile, the performances are greatly different. A best additive mass fraction is determined to be 10 wt% in this work due to the complex effect of TFA and acetonitrile on rearrangement reaction. The initial reaction rate increases to a high value of 7.9×10^{-5} mol L^{-1} s^{-1} at 333 K, approximately 20 times of the rate in the previous catalytic system. Nearly all the oxime can be converted into the product of CPL because of the reverse hydrolysis equilibrium in the modified catalytic system while the selectivity is only 83–95 % in the previous catalytic system. In addition, TFA does not form stable salts with caprolactam and

Table 6 Comparison of modified catalytic system and previous catalytic system

Catalyst type	Reference	Solvent mass fraction (wt%)	Initial reaction rate (333 K, 10^{-6} mol L^{-1} s^{-1})	Selectivity (%)
Modified catalytic system	This work	10	79	99+
Previous catalytic system	Ref [26, 27]	85	4.1	83–95

there is no need of neutralization step. As a result, the organic acid and the additive can be easily reused by distillation without producing any ammonium sulfate [26]. In conclusion, it is a promising process which may lead the synthesis of CPL to a more efficient and economical route.

4 Conclusions

In this work a catalytic system has been successfully applied to carry out the Beckmann rearrangement of COX to ε-caprolactam. High conversion (100 %) and high selectivity to caprolactam (>99 %) can be easily obtained using acetonitrile as the additive. The effect of several organic solvents on the reaction was investigated, and the catalyst composition was optimized. The results indicate that the catalytic system with 10 wt% of acetonitrile can give the fastest reaction rate. An immiscible two-phase system is proposed to study the side reaction of oxime hydrolysis. The results show that the oxime hydrolysis is fast and a chemical equilibrium exists between COX and CYC. Based on these results, a mathematical kinetic model is developed to represent the reaction process. Using the catalyst, neutralization agent and ammonium sulfate by-product are both completely avoided. The establishment of this process may lead the synthesis of CPL to a more efficient and economical route.

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