

# Investigation of “Rearrangement Step” in classical Beckmann rearrangement mechanism over solid acid by means of $^{18}\text{O}$ isotopic labeling

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Received 14 March 2007; received in revised form 10 May 2007; accepted 11 May 2007  
Available online 18 May 2007

## Abstract

The reaction mechanism of the Beckmann rearrangement over  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and TS-1 in the gas phase has been investigated by isotope labeling approach. The isotopic labeled products were measured by mass spectrometry method. By exchanging oxygen with  $\text{H}_2^{18}\text{O}$  in the rearrangement step, it was found that the exchange reaction between cyclohexanone oxime and  $\text{H}_2^{18}\text{O}$  over  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and TS-1 could only be carried out in some extent. It suggested that the dissociation of nitrilium over solid acids be not completely free as the classical mechanism. A concept of the dissociation degree ( $\alpha$ ) that is defined as the ratio of the dissociated intermediate nitrilium to the total intermediate nitrilium has been proposed. By fitting the experimental values with the calculation equation of isotopic labeled products, it is obtained that  $\alpha$  values for  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and TS-1 are 0.199 and 0.806 at the reaction conditions, respectively.

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**Keywords:** Rearrangement; Reaction mechanisms; Isotopic labeling; Mass spectrometry

## 1. Introduction

In the classical Beckmann rearrangement mechanism (Scheme 1A1), the key step is an intramolecular migration of an alkyl group concurrently with the departing hydroxyl group because this step is irreversible [1], which should be a crucial step for the acid catalysts to give the excellent selectivity to the corresponding amide in a liquid catalysis. In recent years, great research efforts have been paid to the Beckmann rearrangement of cyclohexanone oxime to caprolactam over various solid acids, it aims to avoid the production of a large amount of undesirable by-product of ammonium sulfate and the corrosion of reaction vessels in conventional liquid-phase industrial process [2]. Unfortunately, this process has not been commercialized as yet, which was mainly due to the insufficient catalysts lifetime as well as the low yield to caprolactam over the investigated solid acids. Recently, much attention has been paid to the activation of oxime. Blasco and co-workers [3] found that acetophenone oximes could be initially protonated at the nitrogen atom over Brønsted acid sites but could not be protonated by a weakly acidic silanol group as shown in Scheme 1A2. Nguyen et al. [4–6] also confirmed that the oximes could be initially protonated at the nitrogen atom by means of the ab initio method. Although the above activation process of oxime is different from that in the classical Beckmann rearrangement, an intramolecular migration of an alkyl group and with the departure of a water molecule over solid acid catalysts is still mentioned in the mechanism of the Beckmann rearrangement [3,5,7], as shown in Scheme 1A. Murakami et al. [8] proposed the mechanism without the process of release of a water molecule as shown in Scheme 1B, but they could not offer the direct evidence about their mechanism. Based on the result of RB3LYP calculations, Yamabe et al. [9] thought that cyclohexanone oxime underwent a concerted process to produce protonated caprolactam directly without  $\text{H}_2\text{O}$  releasing. Referring to the above mechanisms, it is concerned that reaction mechanism involves the transfer of a water molecule, but it is not confirmed whether the water molecule can be released from a formed nitrilium

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cation or not. To our knowledge, the real reaction pathway of Beckmann rearrangement is a key point to understand why the lower caprolactam selectivity often appears over the investigated solid acids, and it is of benefit to the development of the new solid catalysts of the Beckmann rearrangement for industrial application. As described in the classical mechanism, a water molecule (intermediate) is released from a formed nitrilium cation, and if the nitrilium cation does not finally capture a water molecule and release  $H^+$  to form an amide tautomer, it will contribute to the ring open and the formation of unsaturated nitriles as by-products [10,11]. The polymerizing of the unsaturated nitriles could be a cause for the formation of coke and consequently lead to the deactivation of the solid acid catalysts [12,13]. Does a water molecule release from the nitrilium or combine with the nitrilium in term of the transition state in the reaction?

In this study, we performed an experimental investigation on the mechanism of Beckmann rearrangement over solid acids by means of isotope labeling and mass spectrometry method, in which whether a water molecule releases from the nitrilium or not can be identified. Two most high selective solid acid catalysts for vapor phase Beckmann rearrangement of cyclohexanone oxime,  $B_2O_3/\gamma-Al_2O_3$  and TS-1 were chosen, and  $H_2SO_4$  was used as a comparison in this investigation.  $H_2^{18}O$  has been added in the feed as a tracer.

## 2. Experimental

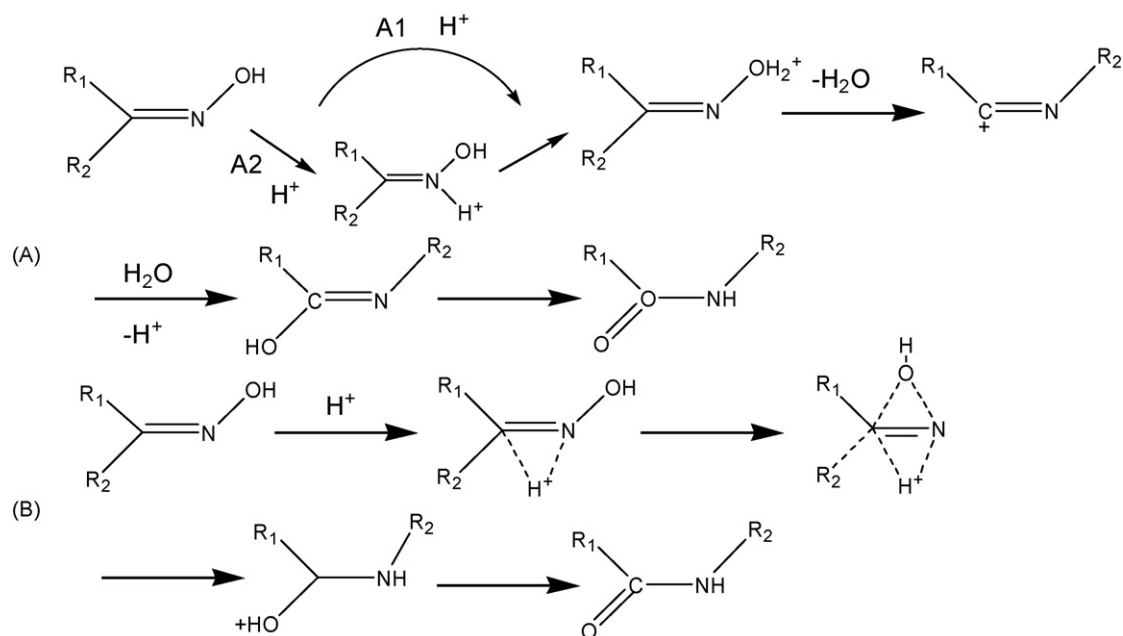
### 2.1. Experimental Principle

Scheme 2 is the sketch on  $H_2^{18}O$  exchange with  $H_2^{16}O$  in the reaction process. In rearrangement step, if an intermediate nitrilium cation is formed with  $H_2^{16}O$  departure and  $R_2$  migration, in turn, the intermediate nitrilium cation ought to have chance to react with  $H_2^{18}O$  or  $H_2^{16}O$  in formation of a rearrangement product. Then  $^{18}O$  will finally appear in the caprolactam product (route A). If a water molecule does not leave from the intermediate, then the final product (caprolactam) should not contain  $^{18}O$  (route B).

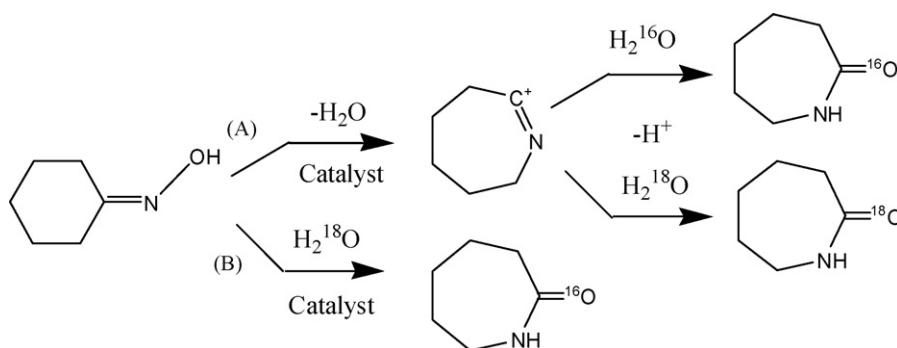
Scheme 3 is a sketch map on  $H_2^{18}O$  exchange process over solid catalysts. The diagram presented here describes the process of  $H_2^{18}O$  exchange with the released water by nitrilium cation over solid acid catalyst. Assume the catalyst has been divided into  $n$  parts of identical regions and the rearrangement and  $H_2^{18}O$  exchange process take place in every region. The exchange process in each region can be presented that  $A/n$  mole of  $H_2O$  exchange with  $D/n$  mole of  $H_2^{16}O$  released by nitrilium cation. If the exchange in each region was added up and at the condition of  $n \rightarrow \infty$ , the final content of  $^{18}O$  in caprolactam was obtained.

Assume the degree of dissociation,  $\alpha$ , was defined as the ratio of the dissociated intermediate nitrilium ( $D$ ) to the total intermediate nitrilium ( $B$ ), i.e.:

$$D = B \times \alpha \quad (1)$$



Scheme 1. Possible Beckmann rearrangement mechanism over solid acid. (A) Classical mechanism with release of a water molecule. (B) Mechanism without release of a water molecule.



Scheme 2. Sketch on  $\text{H}_2^{18}\text{O}$  exchange with  $\text{H}_2^{16}\text{O}$  in Beckmann rearrangement mechanism. (A) If an intermediate nitrilium is formed with  $\text{H}_2^{16}\text{O}$  departure and  $\text{R}_2$  migration, in turn, the intermediate nitrilium can have a chance to react with  $\text{H}_2^{18}\text{O}$  or  $\text{H}_2^{16}\text{O}$  and form a rearrangement product. Then  $\text{O}^{18}$  will finally appear in the caprolactam product. (B) If a water molecule does not leave from the intermediate, then final product (caprolactam) should not contain  $\text{O}^{18}$ . The  $\text{O}^{18}$  proportion in caprolactam is same as the blank value.

The exchange degree,  $E$ , is the proportion of  $^{18}\text{O}$  labeled caprolactam in total of caprolactam, which can also derived from MS data, then:

$$n_{\text{ca.}}(^{18}\text{O}) = \lim_{n \rightarrow \infty} (\delta n_{\text{ca.}}(1) + \delta n_{\text{ca.}}(2) + \delta n_{\text{ca.}}(3) + \cdots + \delta n_{\text{ca.}}(m) + \delta n_{\text{ca.}}(m+1) + \cdots + \delta n_{\text{ca.}}(n)) = \lim_{n \rightarrow \infty} \sum_{m=1}^n \delta n_{\text{ca.}}(m)$$

$$E = \frac{n_{\text{ca.}}(^{18}\text{O})}{n_{\text{ca.}}} = \frac{\lim_{n \rightarrow \infty} \sum_{m=1}^n \delta n_{\text{ca.}}(m)}{n_{\text{ca.}}} \quad (2)$$

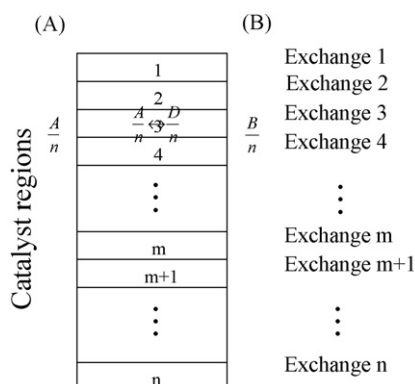
where  $n_{\text{ca.}}(^{18}\text{O})$  is the number of mole of  $^{18}\text{O}$ -caprolactam after reaction;  $\delta n_{\text{ca.}}(m)$  is the number of mole of  $^{18}\text{O}$ -caprolactam produced by the  $m$ th region. With detailed theoretical calculation, the expression of  $E$  versus  $A/B$  and  $\alpha$  is obtained as follows (see Appendix A):

$$E = \frac{A}{B} C (1 - e^{-B\alpha/(A+B\alpha)}) \quad (3)$$

where  $A$  (mole) is the total of number of mole of  $\text{H}_2\text{O}$  that added in raw materials ( $\text{H}_2^{18}\text{O} + \text{H}_2^{16}\text{O}$ );  $B$  (mole) the number of mole of cyclohexanone oxime as raw material of reaction; and  $C$  is the content of number of mole of  $\text{H}_2^{18}\text{O}$  in  $A$  (raw materials).

## 2.2. Catalysts

Twenty-five percent of  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  was prepared by using an incipient wetness impregnation method [14]. The calculated amount of boric acid was dissolved in deionized water, the  $\gamma\text{-Al}_2\text{O}_3$  was impregnated in the solution, then the catalyst was dried at  $110^\circ\text{C}$  overnight and calcined at  $350^\circ\text{C}$  in air for 3 h. The solid was crushed and sieved to 20–40 mesh before carrying out rearrangement reactions.



Scheme 3. Sketch on  $\text{H}_2^{18}\text{O}$  exchange process over solid catalysts.

TS-1 (Si:Ti = 24) was supplied by Research Institute of Petroleum Processing SINOPEC, which was prepared as the method in literature [15]. A clear solution was prepared from tetraethylsilicate (TEOS), tetrabutyl orthotitanate (TBOT) and tetrapropyl ammonium hydroxide (TPAOH) in dry isopropyl alcohol. Then the mixture was stirred to remove the alcohol and the precursor of TS-1 was crystallized statically. After it was washed, dried, then calcined at 500 °C for 10 h to remove the organic template.

### 2.3. Reactions

Concentrated sulfuric acid as the catalyst for Beckmann rearrangement of cyclohexanone oxime in liquid phase was performed as follows: 1.13 g cyclohexanone oxime was dissolved in 3.0 g concentrated H<sub>2</sub>SO<sub>4</sub> (Beijing Yili company ~98%), then 0.2 g 62.8 wt.% H<sub>2</sub><sup>18</sup>O was added in the above solution. The solution was carefully heated until weakly boiled, immediately withdrew from the heater, then, the solution was neutralized by KOH solution to pH 8–10 with the ice bath to keep the temperature below 10 °C, finally, the solution was filtrated off and the product (caprolactam) was extracted from the solution by using chlorobenzene as an extraction reagent.

The vapor phase Beckmann rearrangement of cyclohexanone oxime over B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and TS-1 was carried out in a fixed bed glass reactor with an internal diameter of 8 mm. Before the reaction, the catalyst was heated at 350 °C in N<sub>2</sub> steam for 1 h. Then cyclohexanone oxime in benzene was injected to the reactor by a syringe pump under N<sub>2</sub> flow at 300 °C (B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) or 350 °C (TS-1). At the same time, 62.8 wt.% H<sub>2</sub><sup>18</sup>O (thereafter simplified by H<sub>2</sub><sup>18</sup>O) has been carried by N<sub>2</sub>, the H<sub>2</sub><sup>18</sup>O content in the feed was determined by weight method (weight loss), which was in good agreement with the calculation from saturation vapor pressure of water ( $A = P_{\text{H}_2\text{O}} V_{\text{N}_2} / RT_0$ ). The reactor effluent was collected in a liquid nitrogen-trap and analyzed by GC using a SE-60 capillary column.

### 2.4. Mass spectrometry characterization

The quantitative analysis of the proportion of <sup>18</sup>O labeled caprolactam in products was determined by ESI-MS. Mass spectrometry experiments were performed in positive mode on an LCQ<sup>TM</sup> ion trap mass spectrometer (Finnigan Mat, America) equipped with an ESI source. Nitrogen was used as the drying and nebulizing gas. The spray voltage was set to 5.0 kV. The temperature of capillary was 200 °C. Before analysis, all samples were diluted to 10<sup>-4</sup> mol L<sup>-1</sup> by addition of methanol. The solutions were injected in mass spectrometer by a syringe pump at a flow rate of 5 μL min<sup>-1</sup>. The proportion of <sup>18</sup>O-caprolactam ( $E = \text{PS}_{116} / (\text{PS}_{116} + \text{PS}_{114})$ ) was calculated by the ratio of the peak strength of (M+3, PS<sub>116</sub>) <sup>18</sup>O-caprolactam to the sum of both the peak strength <sup>18</sup>O-caprolactam (M+3, PS<sub>116</sub>) and the peak strength of <sup>16</sup>O-caprolactam (M+1, PS<sub>114</sub>).

## 3. Result and discussion

### 3.1. Effect of reaction time on isotope exchange

Fig. 1 shows the MS data of H<sub>2</sub><sup>18</sup>O exchange with different reaction time, the exchange degree *E* and the conversion and selectivity over various catalysts are summarized in Table 1. As shown in Fig. 1A, the proportion of the <sup>18</sup>O-caprolactam of the blank test (the

Table 1  
Results of isotope exchange over TS-1 and B<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>

Catalyst	<i>t</i> (h)	Conversion (%)	Selectivity (%)	<i>n</i> <sub>H<sub>2</sub>O</sub> / <i>n</i> <sub>oxime</sub>	<i>E</i>
Blank					0.0056
H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>		99.8	99.2	1.36	0.0501
TS-1 <sup>b</sup>	2	98.8	88.6	0.610	0.133
TS-1 <sup>b</sup>	8	99.2	89.2	0.610	0.147
TS-1 <sup>b</sup>	24	99.7	90.4	0.610	0.118
B <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	2	100.0	98.8	0.610	0.0604
B <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	12	98.4	94.2	0.610	0.0891
B <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	24	95.9	91.2	0.610	0.0785
TS-1 <sup>c</sup>	2	100.0	88.0	2.79	0.289
TS-1 <sup>d</sup>	2	100.0	93.2	10.7	0.460
B <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> <sup>c</sup>	12	100.0	92.6	2.79	0.0898
B <sub>2</sub> O <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> <sup>d</sup>	12	100.0	92.7	10.7	0.115

A small quantity of coke is not accounted in the conversion and selectivity data.

<sup>a</sup> Reaction condition: Catalyst charge = 3 g.

<sup>b</sup> Reaction conditions: Catalyst charge = 0.6 g, WHSV = 0.40 h<sup>-1</sup>, cyclohexanone oxime:benzene = 1:9 (wt.%), N<sub>2</sub> = 86 mL min<sup>-1</sup>, T<sub>H<sub>2</sub>O</sub> = 273 K.

<sup>c</sup> Reaction conditions: Catalyst charge = 0.4 g, WHSV = 0.13 h<sup>-1</sup>, cyclohexanone oxime:benzene = 1:49 (wt.%), N<sub>2</sub> = 86 mL min<sup>-1</sup>, T<sub>H<sub>2</sub>O</sub> = 273 K.

<sup>d</sup> Reaction conditions: Catalyst charge = 0.4 g, WHSV = 0.13 h<sup>-1</sup>, cyclohexanone oxime:benzene = 1:49 (wt.%), N<sub>2</sub> = 86 mL min<sup>-1</sup>, T<sub>H<sub>2</sub>O</sub> = 293 K.

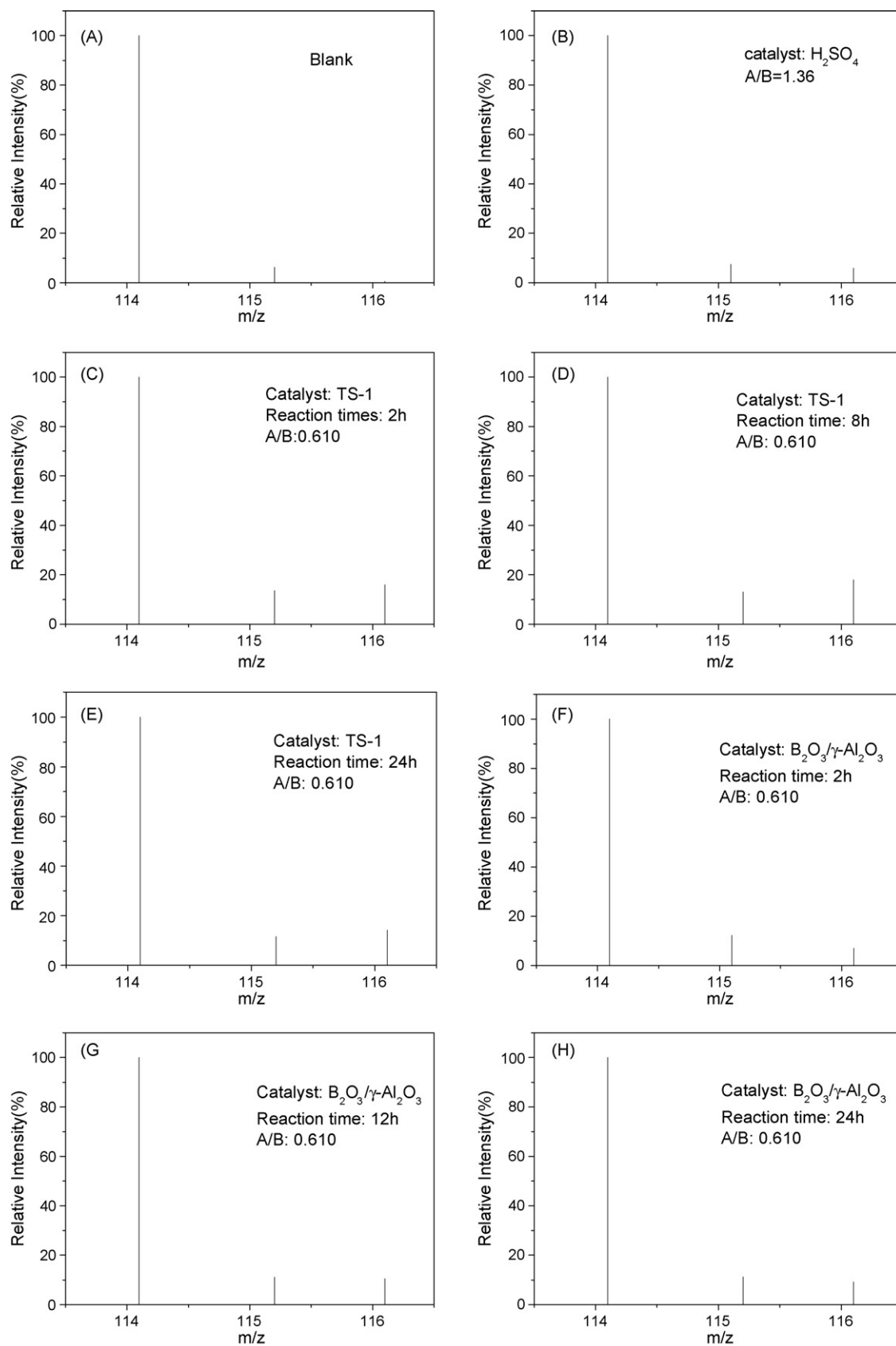


Fig. 1. ESI mass spectrum of  $\text{H}_2^{18}\text{O}$  exchanged production with difference reaction time. (A) Blank, (B)  $\text{H}_2\text{SO}_4$ , (C–E) TS-1 reaction for 2, 8 and 24 h and (F–H)  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  the total  $\text{H}_2^{18}\text{O}$  processing times are 2, 12 and 24 h.

blank sample was prepared by dissolve pure caprolactam in benzene) from MS data was 0.0056, which was almost identical with the value calculated from the H, C, N and O isotope abundance in nature. It was found that there was almost no negative effect on the catalytic performance of  $\text{H}_2\text{SO}_4$  even if the existence of the amount of water as listed in Table 1. In Fig. 1B, the isotope exchange proportion between  $\text{H}_2^{18}\text{O}$  and the intermediate of Beckmann rearrangement was very low as it was only 0.0501, which has subtracted the blank value (thereafter, all data were corrected by subtracting the blank values). It was possible that there existed partially isotope exchange between  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2\text{SO}_4$ , which resulted in the lower proportion of the  $^{18}\text{O}$ -caprolactam in product.

The conversion of oxime and the selectivity of caprolactam change slightly with reaction time and the yields of caprolactam were both in excess of  $\sim 90\%$  over TS-1 and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  as listed in Table 1. It could be affirmed that both solid acid catalysts showed good catalytic performance for Beckmann rearrangement and the conversion and the selectivity were good enough for this investigation.

Because the surface oxygen of solid catalysts could also be exchanged with  $\text{H}_2^{18}\text{O}$  [16], it still existed the probability of some isotope exchange between  $\text{H}_2^{18}\text{O}$  and TS-1,  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ . In order to eliminate the influence of the isotope exchange effect between  $\text{H}_2^{18}\text{O}$  and the solid acid catalysts, the isotope exchange experiments with various reaction time have been carried out as shown in Fig. 1C–H. The proportion of  $^{18}\text{O}$ -caprolactam over TS-1 was 0.133, 0.147 and 0.118 for 2, 8 and 24 h as shown in Table 1, in which the proportion of  $^{18}\text{O}$ -caprolactam was almost the same after 2 h. It could be concluded that the isotope exchange reached the equilibrium between  $\text{H}_2^{18}\text{O}$  and TS-1 after 2 h.

For  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ , however, the lifetime of the catalyst was too short (less than 4 h) to study the isotope exchange between  $\text{H}_2^{18}\text{O}$  and catalyst with various reaction time directly. The catalysts were pretreated by  $\text{N}_2$  flow with  $\text{H}_2^{18}\text{O}$  for a given time before the reaction was carried out, and the product was collected for 1 h from the first hour to the second hour of the run. From Table 1, the proportion of the  $^{18}\text{O}$ -caprolactam over  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  was 0.0604, 0.0891 and 0.0785 for 2, 12 and 24 h. The proportion of the  $^{18}\text{O}$ -caprolactam for 12 h was obviously higher than that for 2 h and was almost identical for 24 h. It indicated that there still some isotope exchange between  $\text{H}_2^{18}\text{O}$  and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  existed and the equilibrium of isotope exchange between  $\text{H}_2^{18}\text{O}$  and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  has completed after 12 h. A little change of the proportion of the  $^{18}\text{O}$ -caprolactam with the reaction time could also result from the conversion change with the reaction time.

### 3.2. Effect of ratio of $\text{H}_2^{18}\text{O}$ to cyclohexanone oxime (mol/mol) on isotope exchange

Fig. 2 shows the MS data of  $\text{H}_2^{18}\text{O}$  exchange with various ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime over two kinds of catalysts. The exchange degree,  $E$ , is also listed in Table 1. From Table 1, the proportion of  $^{18}\text{O}$ -caprolactam over TS-1 obviously increased from 0.133 to 0.460 with an increase of the ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime from 0.61 to 10.7, but it only slightly increased from 0.0891 to 0.115 over  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ .

According to  $E$  values in Table 1, it indicated that the proportion of  $^{18}\text{O}$ -caprolactam over both catalysts obviously increased after  $\text{H}_2^{18}\text{O}$  was added in the feed, which implied that  $\text{H}_2^{18}\text{O}$ , in a certain extent, participated in the rearrangement reaction definitely and exchange with the  $\text{H}_2^{16}\text{O}$  from the host molecules. But it was a great difference in exchange degree between TS-1 and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ , which may be caused by reaction mechanism. As from the commonly accepted classical reaction mechanism, the release of  $\text{H}_2^{16}\text{O}$  from nitrilium is completely free, it means that the exchange degree ( $E$ ) of TS-1 and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  should be identical at the same ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime. To interpret the above results, we suggested that the dissociation degree ( $\alpha$ ), which was defined as the ratio of the dissociated intermediate nitrilium to the total intermediate nitrilium, should be adopted. The dissociation degree ( $\alpha$ ) was obtained by fitting equation:  $E = (A/B)C(1 - e^{-B\alpha/(A+B\alpha)})$  by using several groups of  $A/B$  and  $E$  values, as shown in Fig. 3, in which  $\alpha_{\text{TS-1}}$  and  $\alpha_{\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3}$  were 0.806 and 0.199, respectively.

This result indicated that  $\sim 80.6\%$  water departed from intermediate nitrilium over TS-1 and only  $\sim 19.9\%$  water departed from intermediate nitrilium over  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ .

The above result implied that the classical Beckmann rearrangement mechanism cannot completely express the real reaction pathway over the used solid acids. Yamabe et al. [9] believed that rearrangement of cyclohexanone oxime could be a “concerted process” over a very strong acid. It is easy to understand that when a basic cyclohexanone oxime molecule is adsorbed on a stronger acid site, it will be more difficult for the intermediate molecule to release the formed  $\text{H}_2\text{O}$  and to meet a  $\text{H}_2^{18}\text{O}$  molecule before it transform to a caprolactam. On the other side, a weaker acid site will result in higher exchange of  $^{18}\text{O}$  between oxime with  $\text{H}_2^{18}\text{O}$ . As for the investigated solid acid, the dissociation degree could be attributed to the unhomogeneous acid sites or different acid strength, so we could not affirm completely that  $\alpha$  was the dissociation degree or the dissociation extent of water. Acid type might be a cause to affect dissociation degree of nitrilium over solid acid. However, as for Lewis acid, the reaction mechanism of Beckmann rearrangement was not completely understood till now [17–20]. The effect of the acid type upon the dissociation degree of nitrilium needs to be investigated further. Anyway, our work on Beckmann rearrangement gives the clues of a real mechanism over solid acids.

This concept assumed that the intermediate water molecule leaving from nitrilium was limited in a different degree under the reaction atmospheres over various catalysts. And, the above result showed that the  $\text{H}_2\text{O}$  release in this process was not completely free, which should be contributed to improve the selectivity of caprolactam.

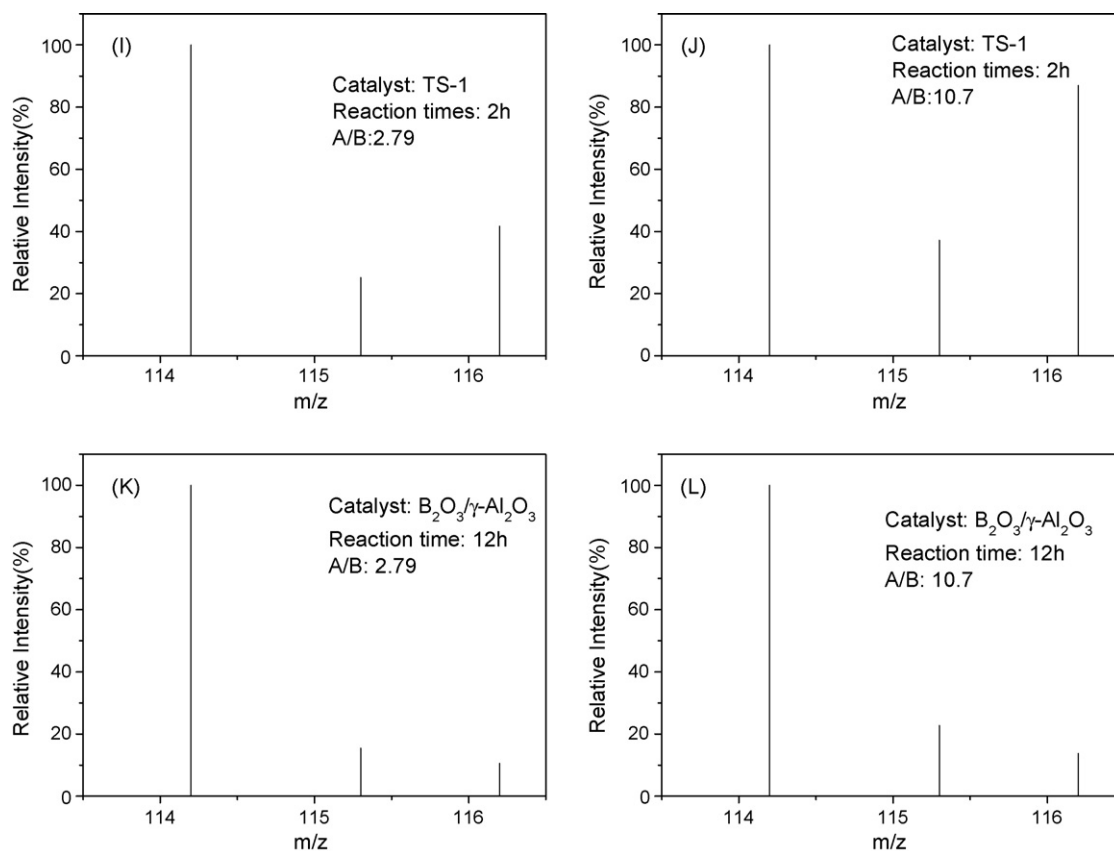


Fig. 2. ESI mass spectrum of  $\text{H}_2^{18}\text{O}$  exchanged production with the change of ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime. (I and J) TS-1 ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime were 2.79 and 10.7. (K and L)  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  ratio of  $\text{H}_2^{18}\text{O}$  to cyclohexanone oxime were 2.79 and 10.7.

### 3.3. Relationship between dissociation degree ( $\alpha$ ) and the caprolactam selectivity

The relationship between the dissociation degree ( $\alpha$ ) and the caprolactam selectivity over  $\text{H}_2\text{SO}_4$ ,  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and TS-1 is shown in Fig. 4. The  $\alpha$  value of  $\text{H}_2\text{SO}_4$  was also calculated by Eq. (3) as the reference. In Fig. 4, the dissociation degree ( $\alpha$ ) increased in order of  $\text{H}_2\text{SO}_4$ ,  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and TS-1, but the selectivity of them decreased in opposite order. It suggested that the dissociation degree ( $\alpha$ ) should be a key factor to affect the selectivity, the larger dissociation degree will lead to the ring open and the formation of unsaturated nitriles as discussed in part 1.

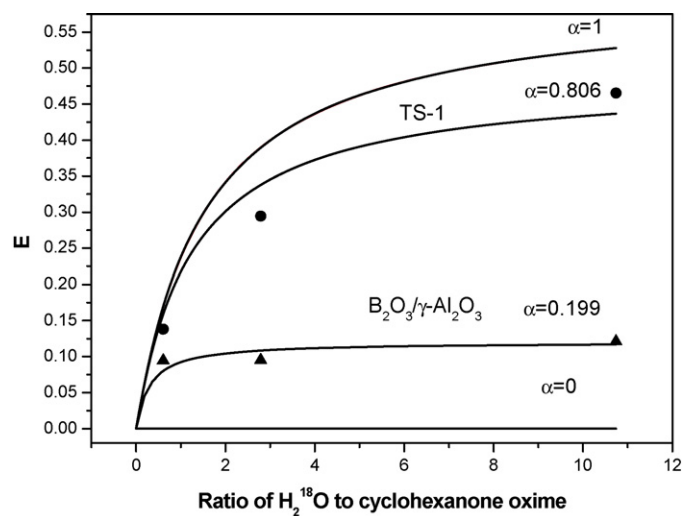


Fig. 3. Dissociation degree ( $\alpha$ ) of TS-1 and  $\text{B}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ . The dissociation degree ( $\alpha$ ) was obtained by fitting equation:  $E = A/BC(1 - e^{-B\alpha/(A+B\alpha)})$  by using several groups of  $A/B$  and  $E$  values.

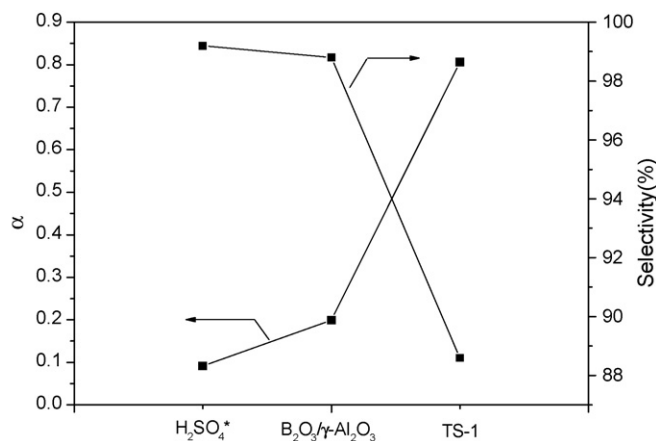


Fig. 4. Relationship between dissociation degree ( $\alpha$ ) and caprolactam selectivity. The  $\alpha$  value of H<sub>2</sub>SO<sub>4</sub> was also calculated by Eq. (3) as the reference.

#### 4. Conclusions

Beckmann rearrangement mechanism has been investigated over two sorts of solid acid catalysts by the means of <sup>18</sup>O isotope labeling. By exchanging oxygen with H<sub>2</sub><sup>18</sup>O in the rearrangement step, it was found that the formed water only partially released or there still some interaction between the formed H<sub>2</sub>O and the nitrilium cation over B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and TS-1. The process without water release is a main route in Beckmann rearrangement over B<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>, which can give the excellent selectivity of caprolactam. The process with water release is a main route in Beckmann rearrangement over TS-1, which cannot give the excellent selectivity of caprolactam. The dissociation degree might be a key factor to affect the selectivity of catalysts. The reaction pathway proposed herein might be contributed to the preparation of the high selectivity, long lifetime catalysts and better understanding the realistic mechanism on Beckmann rearrangement.

#### Acknowledgements

We thank the Ministry of Science and Technology of China (973 program 2003CB615805) and the National Natural Science Foundation (20573103) for the support of this research.

#### Appendix A. The detailed theoretical calculation

Assume the conversion of cyclohexanone oxime and selectivity to caprolactam over solid acid catalysts are both 100%, then after the first exchange:

Before entering the second region, the content of number of moles of O<sup>18</sup> in caprolactam produced by the first region ( $C_{ca.(1)}$ ):

$$C_{ca.(1)} = \frac{(A/n)C}{(A/n) + (D/n)} = \frac{A}{A + D}C \quad (2.1)$$

The number of mole of <sup>18</sup>O-caprolactam produced by the first region ( $\delta n_{ca.(1)}$ ):

$$\delta n_{ca.(1)} = \frac{D}{n} \frac{A}{A + D}C \quad (2.2)$$

The number of mole of <sup>18</sup>O in water (A) after exchanged by the first time ( $n_{wa.(1)}$ ):

$$n_{wa.(1)} = AC - \frac{D}{n} \frac{A}{A + D}C \quad (2.3)$$

The content of number of mole of <sup>18</sup>O in water (A) after exchanged by the first time ( $C_{wa.(1)}$ ):

$$C_{wa.(1)} = \frac{AC - (D/n)(A/(A + D))C}{A} = \left(1 - \frac{1}{n} \frac{D}{A + D}\right)C \quad (2.4)$$



After the second exchange:

Before entering the third region, the content of number of moles of  $^{18}\text{O}$  in caprolactam produced by the second region ( $C_{\text{ca.}(2)}$ ):

$$C_{\text{ca.}(2)} = \frac{(A/n)(1 - (1/n)(D/(A + D)))C}{(A/n) + (D/n)} = \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right) C \quad (2.5)$$

The number of mole of  $^{18}\text{O}$ -caprolactam produced by the second region ( $\delta n_{\text{ca.}(2)}$ ):

$$\delta n_{\text{ca.}(2)} = \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right) C \quad (2.6)$$

The number of mole of  $^{18}\text{O}$  in water (A) after exchanged by the second time ( $n_{\text{wa.}(2)}$ )

$$n_{\text{wa.}(2)} = A \left(1 - \frac{1}{n} \frac{D}{A + D}\right) C - \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right) C \quad (2.7)$$

The content of number of moles of  $^{18}\text{O}$  in water (A) after exchanged by the second time ( $C_{\text{wa.}(2)}$ ):

$$\begin{aligned} C_{\text{wa.}(2)} &= \frac{A(1 - (1/n)(D/(A + D)))C - (D/n)(A/(A + D))(1 - (1/n)(D/(A + D)))C}{A} \\ &= \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^2 C \end{aligned} \quad (2.8)$$

After the third exchange:

Before entering the fourth region, the content of number of mole of  $^{18}\text{O}$  in caprolactam produced by the third region ( $C_{\text{ca.}(3)}$ ):

$$C_{\text{ca.}(3)} = \frac{(A/n)(1 - (1/n)(D/(A + D)))^2 C}{(A/n) + (D/n)} = \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^2 C \quad (2.9)$$

The number of mole of  $^{18}\text{O}$ -caprolactam produced by the third region ( $\delta n_{\text{ca.}(3)}$ ):

$$\delta n_{\text{ca.}(3)} = \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^2 C \quad (2.10)$$

The number of moles of  $^{18}\text{O}$  in water (A) after exchanged by the third time ( $n_{\text{wa.}(3)}$ ):

$$n_{\text{wa.}(3)} = A \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^2 C - \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^2 C \quad (2.11)$$

The content of number of mole of  $^{18}\text{O}$  in water (A) after exchanged by the third time ( $C_{\text{wa.}(3)}$ ):

$$\begin{aligned} C_{\text{wa.}(3)} &= \frac{A(1 - (1/n)(D/(A + D)))^2 C - (D/n)(A/(A + D))(1 - (1/n)(D/(A + D)))^2 C}{A} \\ &= \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^3 C \end{aligned} \quad (2.12)$$

Supposing the content of number of mole of  $^{18}\text{O}$  in water (A) after exchanged by the  $m$ th time ( $C_{\text{wa.}(m)}$ ):

$$C_{\text{wa.}(m)} = \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^m C \quad (2.13)$$

The number of moles of  $^{18}\text{O}$ -caprolactam produced by the  $m$ th region ( $\delta n_{\text{ca.}(m)}$ ):

$$\delta n_{\text{ca.}(m)} = \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^{m-1} C \quad (2.14)$$

Then after the  $m + 1$ th exchange,

Before entering the  $m + 2$ th region, the content of number of mole of  $^{18}\text{O}$  in caprolactam produced by the  $m + 1$ th region ( $C_{\text{ca.}(m+1)}$ ):

$$C_{\text{ca.}(m+1)} = \frac{(A/n)(1 - (1/n)(D/(A + D)))^m C}{(A/n) + (D/n)} = \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^m C \quad (2.15)$$

The number of moles of  $^{18}\text{O}$ -caprolactam produced by the  $m + 1$ th region ( $\delta n_{\text{ca.}}(m + 1)$ ):

$$\delta n_{\text{ca.}}(m + 1) = \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^m C \quad (2.16)$$

The number of moles of  $^{18}\text{O}$  in water (A) after exchanged by the  $m + 1$ th time ( $n_{\text{wa.}}(m + 1)$ )

$$n_{\text{wa.}}(m + 1) = A \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^m C - \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^m C \quad (2.17)$$

The content of number of moles of  $^{18}\text{O}$  in water (A) after exchanged by the  $m + 1$ th time ( $C_{\text{wa.}}(m + 1)$ ):

$$\begin{aligned} C_{\text{wa.}}(m + 1) &= \frac{A(1 - (1/n)(D/(A + D)))^m C - (D/n)(A/(A + D))(1 - (1/n)(D/(A + D)))^m C}{A} \\ &= \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^{m+1} C \end{aligned} \quad (2.18)$$

So, it was proved that the content of number of moles of  $^{18}\text{O}$  in water (A) after exchanged by the  $n$ th ( $C_{\text{wa.}}(n)$ ):

$$C_{\text{wa.}}(n) = \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^n C \quad (2.19)$$

The number of mole of  $^{18}\text{O}$ -caprolactam produced by the  $n$ th region ( $\delta n_{\text{ca.}}$ ):

$$\delta n_{\text{ca.}}(n) = \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^{n-1} C \quad (2.20)$$

Then the total number of mole of  $^{18}\text{O}$ -caprolactam produced by  $n$  regions ( $n_{\text{ca.}}(n)$ ):

$$\begin{aligned} n_{\text{ca.}}(^{18}\text{O}) &= \sum_{m=1}^n \left[ \frac{D}{n} \frac{A}{A + D} \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^{m-1} C \right] = (D/n)(A/(A + D))C \frac{1 - (1 - (1/n)(D/(A + D)))^n}{1 - (1 - (1/n)(D/(A + D)))} \\ &= AC \left[ 1 - \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^n \right] \end{aligned} \quad (2.21)$$

The total number of mole of  $^{18}\text{O}$ -caprolactam produced by  $n$  regions when  $n \rightarrow \infty$

$$\begin{aligned} \lim_{n \rightarrow \infty} AC \left[ 1 - \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^n \right] &= \lim_{n \rightarrow \infty} AC \left[ 1 - \left(1 - \frac{1}{n} \frac{D}{A + D}\right)^{-n(1/((A+D)/D)(-D/(A+D))} \right] \\ &= AC(1 - e^{-D/(A+D)}) \end{aligned} \quad (2.22)$$

Then the proportion of  $^{18}\text{O}$  labeled caprolactam in total of caprolactam ( $E$ ):

$$E = \frac{A}{B} C(1 - e^{-D/(A+D)}) \quad (2.23)$$

After substitution Eq. (1) into Eq. (2.23), the expression of  $E$  versus  $A/B$  and  $\alpha$  would have the following form:

$$E = \frac{A}{B} C(1 - e^{-B\alpha/(A+B\alpha)}) \quad (3)$$

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