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Solvent effects in the liquid-phase Beckmann rearrangement of oxime over H-Beta catalyst II: adsorption and FT-IR studies

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Abstract

Solvent effect has been investigated in the liquid-phase Beckmann rearrangement of cyclohexanone oxime over H-Beta catalyst. Co-adsorption of substrate and solvent suggests that the facility of protonation of oxime is primarily dependent upon the competitive adsorption between substrate and solvent. On the other hand, the result of IR study indicates that the N-protonation of oxime is largely preferred to the O-protonation and the 1,2-H-shift is possibly more energy-demanding than the subsequent rearrangement. In addition, it is revealed that there is an interaction between the protonated oxime and a polar solvent. This implies that there exists a quite stable five-membered ring complex which may decrease the energy barrier of the 1,2-H-shift significantly. In this regard, a solvent making a balance between these two competitive factors is considered suitable for the liquid-phase Beckmann rearrangement of oxime over solid-acid catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Beckmann rearrangement; Cyclohexanone oxime; Caprolactam; Adsorption; Solvent effect; Dielectric constant; Zeolite catalyst

1. Introduction

Conventionally, the Beckmann rearrangement of oxime into the corresponding amide employs the concentrated sulfuric acid as a catalyst. Although this procedure is very convenient from the chemical point of view, the large amount of ammonium sulfate formed during the subsequent neutralization process and the corrosion problem due to the fuming sulfuric acid make this process environmentally unacceptable.

To overcome these matters, a zeolite seems to be an excellent candidate to take over the catalytic function, since the use of a zeolite as catalyst is very promising not only from an economical point of view but also from an ecological viewpoint. In fact, after the possibility of the heterogeneously catalyzed reaction was reported [1], considerable attention has been paid to the potential of zeolites to act as a catalyst in the vapor-phase Beckmann rearrangement of cyclohexanone oxime [2–8]. The vapor-phase reaction, however, suffers from its intrinsic features such as the requirement of high temperature above 250°C and rapid deactivation of catalyst due to the coke formation. Moreover, compounds that hardly vaporize or become unstable at high temperature are not suitable for the vapor-phase reaction. On the other hand, the liquid-phase reaction does neither bring about the catalyst deactivation nor any restriction on the choice of a suitable substrate. In this regard, the possibility of using a solid–liquid-phase process at a moderate temperature is worth to be reexamined. These

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arguments are suggestive of conducting the liquid-phase Beckmann rearrangement of oxime over zeolite-based catalyst.

Concerning the solvent effect, it has been reported that the solvent strongly affected the activity, selectivity and stability of zeolite catalysts in the vapor-phase Beckmann rearrangement of cyclohexanone oxime [9–11]. It is suggested that a polar protic solvent such as ethanol is effective in accelerating the reaction rate by assisting the desorption of ε-caprolactam probably due to the effect of OH groups.

It should be noted, however, that there still exists an open question concerning whether the solvent effect reported for the 'vapor-phase' reaction may be extended to the 'liquid-phase' reaction. In contrast to the vapor-phase reaction, it is evident that in the liquid-phase reaction at a moderate temperature, the stronger the adsorption power of a solvent is, the stronger the competition between reactant and solvent for the adsorption sites becomes. Previously, we found that the properties of a solvent significantly affect the catalytic activity and consequently the selection of a suitable solvent is the most important factor enhancing the catalytic activity [12].

In this study, we have carried out the liquid-phase Beckmann rearrangement of cyclohexanone oxime over H-Beta catalyst. In line with our previous work with 4-hydroxyacetophenone oxime [12], it is aimed here to elucidate the role of solvent by adsorption and FT-IR studies. Furthermore, we hope that this work may serve as a guideline to the selection of an appropriate solvent in the liquid-phase Beckmann rearrangement of oxime over a solid-acid catalyst.

2. Experimental

2.1. Catalyst and reagents

The zeolite beta (Si/Al = 11) sample was taken from a commercial batch provided by P.Q. Industries (CP814E-22). Before being used as a catalyst, the material was ion exchanged twice and calcined to yield the catalytically active hydrogen form. For this, 10 g of the catalyst and 100 g of 1N ammonium nitrate solution were thoroughly mixed in a flask at 80°C for 48 h. Afterwards, the catalyst was recovered by filtration, washed with deionized water and dried at 110°C for 4 h. Finally, the material was calcined under air at 550°C for 12 h with a heating rate of 2°C/min. All chemicals were supplied by Aldrich, Acros and Merck and were used without further purification.

2.2. Reaction procedure

The Beckmann rearrangement of cyclohexanone oxime was carried out in liquid-phase at 70°C under nitrogen in a 50 ml three-necked, round-bottomed flask reactor equipped with a reflux condenser and a magnetic stirrer. The reactor was immersed in a thermostatted bath. For the case when methanol was used, the reaction temperature was maintained at the reflux temperature. A typical reaction run was as follows: 100 mg catalyst, pre-calcined in air at 500°C, was suspended in a solution of 1mmol of cyclohexanone oxime in 20 ml solvent which was allowed to equilibrate at the set temperature. The reaction mixture was heated to the reaction temperature and stirred under nitrogen for 5 h. After completion of the reaction, the reaction mixture was filtered and analyzed by using an HP5890 gas chromatography (GC) equipped with an HP-Innowax column.

2.3. Adsorption experiments

Adsorption studies were carried out at 70°C in the same vessel as used for the reaction except for a calcium chloride guard tube for protection against humidity. A volume of 0.25 mmol cyclohexanone oxime and 68 mmol solvent to be tested were added to 30 ml 1,3,5-tri-isopropylbenzene, a bulky solvent incapable of adsorption on the zeolite. After 0.1 g activated H-Beta was added to the solution, samples were taken periodically and analyzed by GC.

2.4. FT-IR study

FT-IR spectroscopy was done with a Nicolet Impact 410. FT-IR spectra of self-supported wafers were recorded between 4000 and 1200 cm^{-1}. In a typical experiment, 10 mg of the zeolite H-Beta were pressed into a self-supported wafer (13 mm diameter). The wafer was fixed by quartz holders and introduced into a horizontal type in situ IR vacuum cell equipped with an external heater and a thermocouple well. The IR cell was fitted with detachable CaF_2 windows which were sealed to the cell through rubber O-ring and brass screw-threaded couplings.

The wafer was first pretreated at 500°C under evacuation for 3 h and cooled down to 60°C, and the parent spectrum was recorded. Then 1% toluene solution of cyclohexanone oxime were allowed to adsorb from a microsyringe onto the zeolite pellet held in the in situ cell, and after evacuation for 1 h, the first spectrum was collected. The result was recorded as a differential spectrum from the parent spectrum. Afterwards, the temperature was raised to the desired value and the spectra were recorded after allowing 15 min for the system to equilibrate at the prescribed temperature.

Cyclohexanone oxime sulfuric acid salt was prepared by the addition of equimolar sulfuric acid in the 10 wt.% oxime solution according to the method reported in [13]. The sample was introduced into the demountable liquid-cell kit equipped with KBr windows, and the spectrum was recorded.

3. Results and discussion

During the reaction, the major product of the reaction is the corresponding amide regardless of the solvent used. The parent ketone was formed only in a trace amount and no other by-products were detected under our reaction conditions. Mass balance of the rearrangement was found to be close to 100%. A blank experiment was also conducted under the same reaction conditions, and no substrate transformation was observed in the absence of catalyst.

3.1. Co-adsorption of oxime and solvent on catalyst

Firstly, we carried out the Beckmann rearrangement with various solvents to investigate the influence of the solvent property on the catalytic activity. As shown in Table 1, the result of solvent screening reveals that the nature of a solvent determines the performance of the reaction. While the reaction did not proceed in the polar protic media, the reaction progressed to a considerable extent in the presence of polar aprotic or non-polar solvents. Obviously, the stronger the solvent–adsorption site interaction, the more difficult the access of a reactant to the active sites, which may lead to a decrease in the catalytic activity.

To elucidate the adsorption site competition between solvent and substrate, we carried out co-adsorption experiment of the substrate and the solvent on zeolite H-Beta from the non-adsorbing medium 1,3,5-triisopropylbenzene. Fig. 1 presents the result of the co-adsorption of cyclohexanone oxime with various solvents. This figure shows that the site competition between solvent and substrate is undoubtedly one of the major factors affecting the performance of the catalytic reaction. It is clear that the predominant adsorption of methanol renders the active center inaccessible to the substrate and consequently brings about the low concentration of the substrate on the catalytic surface. This indicates that the affinity of zeolite H-Beta towards methanol is much higher than that towards the substrate, so the reaction may not occur at all. Other polar protic solvents exhibit the same

Table 1
Properties of solvent candidates and their catalytic performances

Solvent	ε^0 (Al_2O_3)[a]	Dielectric constant[b]	Basicity[c]	Conversion (%)	Amide selectivity (%)
Methanol	0.95	33.0	19.0	–	–
Ethanol	0.88	25.3	19.2	–	–
2-Propanol	0.82	20.18	19.8	–	–
Acetonitrile	0.65	36.64	14.1	27.3	>98
DMSO	0.62	47.24	19.3	35.1	>98
MEK	0.51	18.56	17.4	45.0	>98
THF	0.45	7.52	20.0	11.7	>98
Chlorobenzene	0.3	5.67	–	16.1	>98
Toluene	0.29	2.38	–	14.3	>98

[a] Solvent strength parameter in Snyder's eluotropic series, for silica a good approximation is ε^0 (silica) $= 0.77\varepsilon^0$ (alumina).

[b] Values at 293.2 K.

[c] Donor number (DN, kcal/mol) for solvent basicity devised by Gutmann [24].

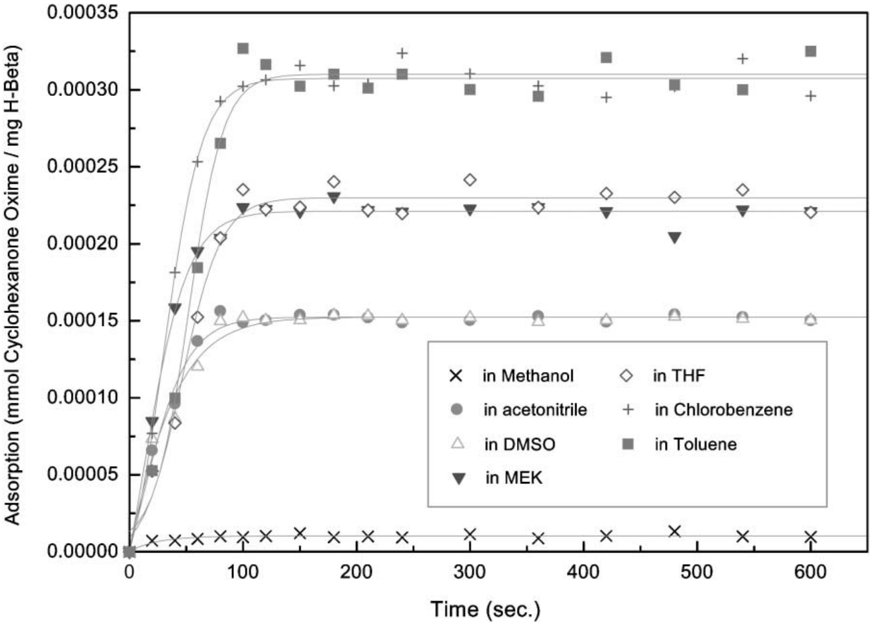


Fig. 1. Temporal variation of the amount of cyclohexanone oxime adsorbed on H-Beta in various solvents.

trend as methanol (not shown here). Co-adsorption experiment on zeolite H-Beta was also conducted for both caprolactam and solvent. According to the results of adsorption experiment, oxime and caprolactam exhibit a similar adsorption characteristics.

In the case of a polar aprotic or non-polar solvent, the amount of adsorbed substrate on the catalyst is found to be substantial. Accordingly, the reaction may readily proceed in polar aprotic or non-polar media in which the chance of the substrate to access the active sites will be considerably higher than that in a polar protic solvent such as methanol. It should be stressed, however, that the difference in reactivity cannot be totally ascribed to the unbalanced adsorption equilibrium between solvent and substrate. Considering the adsorption equilibria alone, one may intuitively expect that a higher conversion of oxime can be obtained in the least polar medium, because the less polar a solvent, the larger the amount of the substrate that is accessible to the active sites. However, this does not hold in this work. Among the solvents tested, methyl ethyl ketone (MEK) is found to be the most effective one for the Beckmann rearrangement of cyclohexanone oxime. This suggests that there must be another factor affecting the performance of the reaction.

3.2. Mechanistic aspect of the Beckmann rearrangement

Regarding the reaction mechanism, it is generally assumed that the rearrangement step from O-protonated oxime to the corresponding nitrilium cation is rate-determining [14,15], although there has been neither kinetic nor spectroscopic supporting evidence. In this regard, we carried out IR study to examine the mechanistic aspect of the Beckmann rearrangement further in detail.

The temperature dependency of the in situ FT-IR spectra of the adsorbed cyclohexanone oxime on zeolite H-Beta was measured and the result is shown in Fig. 2. By adsorption of oxime on catalyst at 60°C, the characteristic peaks of cyclohexanone oxime appear at 1440 and 1450 cm^{-1} assigned for δ (CH_2) and δ $(OH)_{\mathrm{assoc}}$, respectively. By stepwise rise of the evacuation temperature, strong absorption band appears around 1512 and 1638 cm^{-1}, and these are assigned to the characteristic peaks of δ $(N–H)_{\text{in-plane}}$ and ν (C=O), respectively. This implies that the Beckmann rearrangement readily takes place and leads to the production of the corresponding amide. The complete disappearance of δ $(N–H)_{\text{in-plane}}$ and ν (C=O)

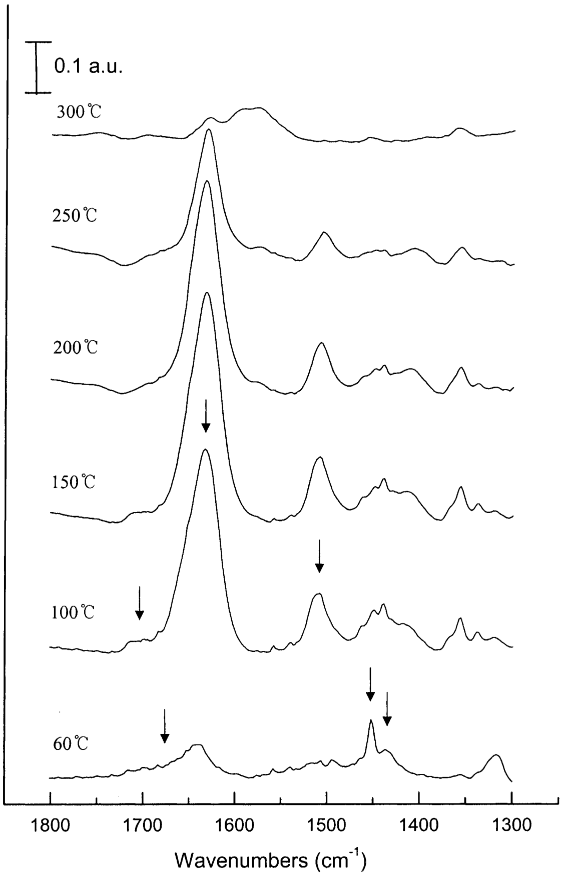


Fig. 2. In situ IR spectra of cyclohexanone oxime adsorbed on H-Beta.

at 300°C indicates the completion of the catalytic cycle.

As far as the Beckmann rearrangement mechanism is concerned, it should be noted that the characteristic peak for ν (C=N) around 1664 cm^{-1} was not observed at all. On the contrary, the appearance of the shoulder around 1685 cm^{-1} for ν (C=N$^+$) [16] indicates that cyclohexanone oxime is already adsorbed and exists as a protonated form, and a strong interaction of acidic silanol with nitrogen atom rather than with oxygen atom of oxime predominates. This means that the initial step of the rearrangement reaction is N-protonation of oxime by the acidic silanol [17].

One may assume that the small shoulder which can be seen around 1720 cm^{-1} for δ (O$^+$–H$_2$)$_{asym}$ vibration [18] is possibly overlapped with the shoulder appeared around 1685 cm^{-1} for ν (C=N$^+$). The appearance of the shoulder may be an evidence for the existence of the O-protonated oxime. This view, however, cannot account for the considerable change that has occurred in the ν (C=N) band upon adsorption. Moreover, the appearance of δ (OH)$_{assoc}$ at 1450 cm^{-1} also strongly supports that the hydroxyl group of oxime does not interact with the Brönsted acid sites and remains intact. This result suggests that the N-protonation of oxime is largely preferred to the O-protonation. Although the formation of O-protonated oxime appears to be indispensable, it is considered to be short-lived. Once the O-protonated species is formed, it can be converted to the corresponding amide.

The changes observed in the IR spectra of cyclohexanone oxime may be a good supporting evidence for the newly proposed postulation [19,20]. They

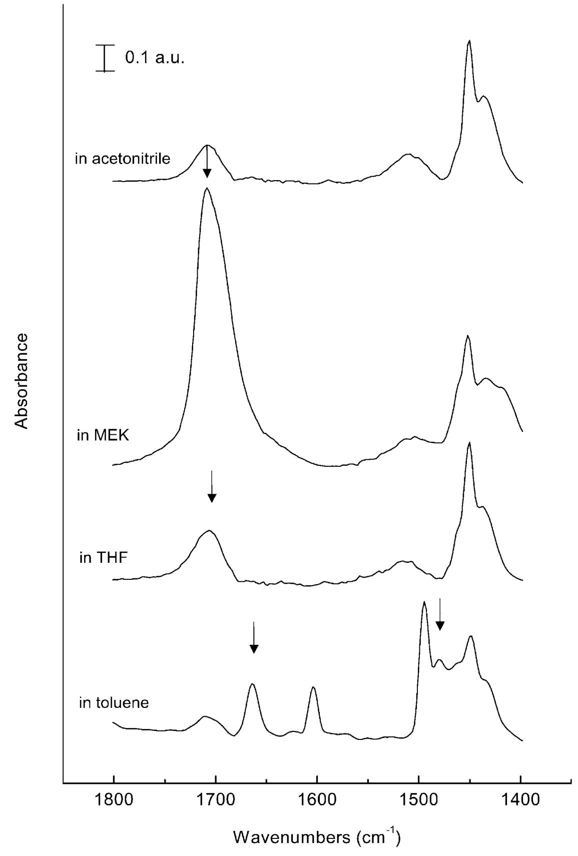


Fig. 3. IR spectra of cyclohexanone oxime salt in various solvents.

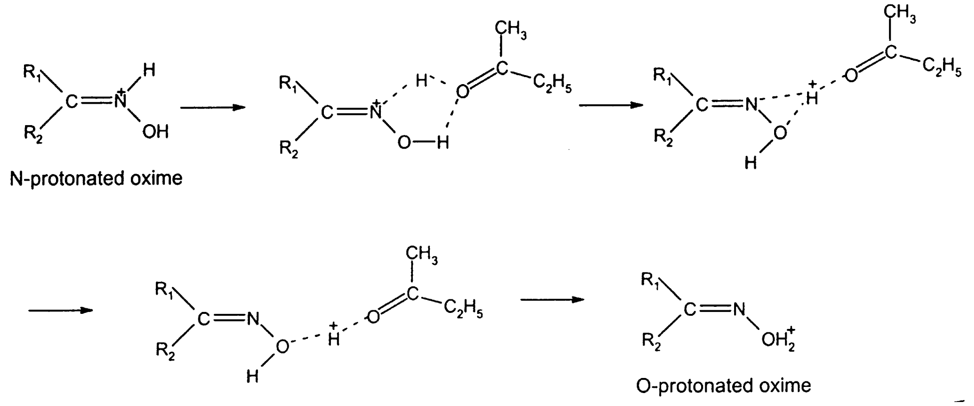
calculated the energy barriers for the individual steps of the Beckmann rearrangement using ab initio MO calculations and proposed that the 1,2-H-shift connecting both N-, O-protonated isomers has a higher activation energy than the subsequent rearrangement and, thus, constitutes the rate-determining step. If the Beckmann rearrangement step at which the O-protonated oxime is converted to the nitrilium cation is the most energy-demanding step, the O-protonated oxime should be observed in the IR spectra. However, the appearance of the N-protonated oxime instead of the O-protonated one in the IR spectra suggests that the 1,2-H-shift connecting both the protonated isomers is possibly more energy-demanding than the subsequent rearrangement.

3.3. Interaction between oxime and polar solvent

To investigate the interaction of the protonated cyclohexanone oxime with a solvent, we observed the change in the IR spectra of the cyclohexanone oxime salt in various solvents and the result is shown in Fig. 3. In polar solvent, the disappearance of ν (C=N) vibration around 1664 cm^{-1} indicates that cyclohexanone oxime exists as a protonated form. The appearance of ν (C=N^{+}) at 1708 cm^{-1} also suggests that the protonation takes place preferentially at the nitrogen atom of cyclohexanone oxime. On the contrary, the existence of the C=N stretching band in the non-polar solvent such as toluene indicates that not all the oxime is protonated.

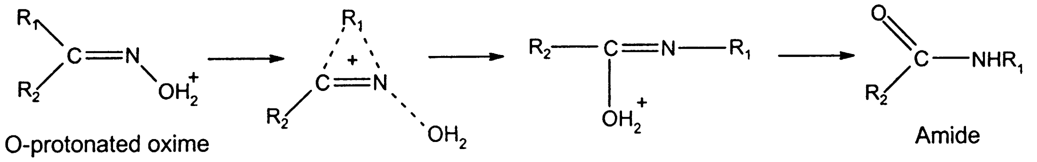
The conspicuous spectra changes of the oxime salt formed in polar solvents is the disappearance of the bending of the associated hydroxyl group of oxime at 1480 cm^{-1} [13] which is clearly present in non-polar medium such as toluene. Presumably, the disappearance of the δ (OH)$_{\text{assoc}}$ band in polar medium is believed to be due to the interaction between the hydroxyl group of oxime and polar solvent. This result may be supported by the fact that the ν (C=O) band of pure MEK shifts from 1712 to 1708 cm^{-1} in the presence of the protonated oxime. The shift of the carbonyl group band may be due to the weakening of the double bonding character of the carbonyl group as a result of the interaction with the N-protonated oxime. In other words, the interaction of carbonyl group of MEK with both the protonated nitrogen and the hydroxyl group of oxime results in the loss of δ (OH)$_{\text{assoc}}$ band of oxime and the band shift of carbonyl group of MEK. This result strongly suggests that there are interactions between the N-protonated oxime and a polar solvent.

On the basis of this result it may be assumed that in the presence of a polar solvent, there exists a quite strong five-membered ring complex formed via a direct interaction between the solvent molecule and the N-protonated oxime. This complex plays a crucial role permitting a preassociation mechanism in which the reactants are oriented in an optimal manner creating the most favorable spatial conditions for proton transfer in a subsequent rapid step [21]. Such a direct action of a solvent molecule to the transition structure is clearly beneficial and reduces the energy barrier dramatically. This implies that the 1,2-H shift, the most energy-demanding step, can be accelerated by the involvement of the solvent in transition state. Thus, the action of a solvent may be regarded as that of a catalyst from the energetic point of view.



It is to be pointed out that the proton affinity of a solvent is an important feature determining the stability of the transition structure. The larger the proton affinity of a solvent, the more stable the five-membered ring complex. This implies that the 1,2-H-shift is accelerated by a solvent having large proton affinity because the solvent reduces the energy barrier of the transition state, leading to an increase in the reaction rate. Since the order of proton affinity is directly related to the dielectric constant of a solvent, it is evident that a solvent having a larger dielectric constant or a larger proton affinity promotes the 1,2-H-shift.

The environment of polar molecules also facilitates the subsequent rearrangement step. In the transformation of O-protonated oxime, the withdrawal of electrons from the nitrogen by OH_2^+ group creates in the N(δ^+)–O(δ^-) bond a dipole with its positive end on the nitrogen atom. Because of the configuration of the O-protonated oxime, the field of this dipole is so oriented as to include the electrons of the bond R_1–C on the far side of the nitrogen atom within its influence rather than those of the bond R_2–C on the near side [15,22,23]. When the molecule already in this state of stress acquires sufficient energy, rearrangement takes place, the group R_1 becoming anchored to the nitrogen atom and OH_2^+ migrating in compensation for the central carbon atom. This emphasizes the importance of the strong electron attraction of the OH_2^+ group which determines the ease of the rearrangement. As the dielectric constant of a solvent becomes larger, the OH_2^+ group exerts stronger attraction for electrons. The more powerful this attraction, the more facile the change.



3.4. The role of solvent in the transition state

One may now speculate that both the strength of adsorption and the dielectric constant of a solvent possibly play central roles in determining the performance of the reaction. From the viewpoint of the accessibility of the reactant to the active sites, a non-polar solvent such as chlorobenzene or toluene is favorable. However, the relatively lower dielectric constants of the non-polar solvents counterbalance the advantage (see Table 1). This means that the 1,2-H-shift of the N-protonated oxime may be more difficult in the non-polar solvents presumably due to the lower ability to stabilize the transition structure or to reduce the energy barrier of the transition state in comparison with other solvents which have larger proton affinities. Moreover, these solvents are also less efficient in assisting the migration of OH_2^+ group from nitrogen to carbon atom, and hence, the promotion of the rearrangement rate by a solvent is smaller.

On the other hand, dimethyl sulfoxide (DMSO) may be regarded as the most favorable reaction medium to accelerate not only the 1,2-H-shift but also the subsequent rearrangement among the solvents tested. The relatively strong adsorption of DMSO, however, may hinder the reactant from approaching the active sites and suppress the reaction. In this regard, a comparison between acetonitrile and DMSO is of particular interest because the adsorption power of acetonitrile is as good as that of DMSO, but its dielectric constant is lower than that of DMSO. The lower catalytic performance of the reaction in acetonitrile suggests that acetonitrile is less efficient than DMSO to promote the 1,2-H-shift and the migration of OH_2^+ group due to its relatively lower dielectric constant in comparison with DMSO.

The highest conversion can be obtained with MEK and consequently MEK is considered as the most suitable solvent in the reaction among the solvents used. MEK is placed in the middle among the representative polar aprotic solvents for both the adsorption power and the dielectric constant. Therefore, it is reasonable that the appropriate balancing between the two competitive factors in MEK gives rise to the best performance of the reaction. It is also interesting to note that with less polar solvents, i.e. THF, chlorobenzene, and toluene, the performance of the reaction is found similar regardless of the solvent used. This result indicates that in the less polar solvent, the positive effect of a solvent in accelerating the reaction rate is substantially reduced, and the accessibility of the reactant to the active sites influences dominantly the performance of the reaction.

In the case of polar protic solvent such as methanol, however, the superiority in lowering the activation energy and in assisting the migration of OH_2^+ group is no longer meaningful because the adsorption of substrate on the active sites is a prerequisite in a heterogeneous reaction. This result strongly suggests that the positive effect of the polar protic solvents in 'vapor-phase' reaction cannot be extrapolated to the 'liquid-phase' reaction.

One may speculate that the basicity of a solvent may play a crucial role in the reaction. If so, the order of activity should be related to the basicity of a solvent. As shown in Table 1, however, the basicity of a solvent cannot account for the result of the catalytic reaction. In other words, if the basicity plays a crucial role, THF should be preferential because it is advantageous in the reactant adsorption aspect and has a higher basicity. But this is not the case here. Although both the dielectric constant as well as the basicity of a solvent may be related to the catalytic activity [22], the result of this study shows that the dielectric constant of a solvent takes a more important role in the reaction.

On the basis of these results, it is clear that the facility of protonation of oxime through the adsorption of substrate on the active site depends on the competitive adsorption between substrate and solvent. On the other hand, a solvent having a higher dielectric constant or a more polar nature is preferred in the two subsequent energy-demanding steps in which a solvent may accelerate the reaction by stabilizing transition structure and also by promoting the migration of OH_2^+ group. This leads to the conclusion that the selection of a suitable solvent balancing the two aspects of adsorption and the dielectric constant is the most important in the liquid-phase Beckmann rearrangement of oxime over solid acid catalyst.

4. Conclusion

The liquid-phase Beckmann rearrangement of cyclohexanone oxime over zeolite H-Beta catalyst has been studied. It is revealed that the performance of the reaction is strongly dependent upon the nature of the solvent. Co-adsorption of substrate and solvent shows that the stronger the solvent–adsorption sites interaction, the less the chance of substrate to approach the active sites. This indicates that the facility of protonation of oxime is primarily dependent upon the competitive adsorption between substrate and solvent.

On the other hand, FT-IR study suggests that the initial step of the rearrangement is not the O-protonation but the N-protonation of oxime and that the 1,2-H-shift connecting the two protonated isomers is possibly more energy-demanding than the subsequent rearrangement. In addition, it is noticed that there is an interaction between the N-protonated oxime and a polar solvent. This may be considered as a supporting evidence for the existence of a quite strong five-membered ring complex formed via the interaction between the solvent molecule and the N-protonated oxime. Such a direct action of a solvent molecule to the transition structure is clearly beneficial and reduces the energy barrier dramatically. This implies that the 1,2-H shift, the most energy-demanding step, can be accelerated by the involvement of the solvent in transition state. In this regard, a solvent having a higher dielectric constant or a more polar nature is preferred in the 1,2-H-shift as well as in the subsequent rearrangement step. Therefore, the choice of a suitable solvent balancing the two aspects of adsorption and the dielectric constant is the most important factor determining the performance of the reaction.

Acknowledgements

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