ELSEVIER

Journal of Molecular Catalysis A: Chemical 160 (2000) 377–381

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Energetic study of diastereoselective thio-Claisen rearrangement

Lijun Wang [a], Baohui Li [a], Qinghua Jin [a], Zhenya Guo [a], Shixiong Tang [b], Datong Ding [a,*]

[a] Department of Physics, Nankai University, 94 Weijin Road, Tianjin 300071, People's Republic of China
[b] Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received 18 January 2000; accepted 13 April 2000

Abstract

Molecular simulation is applied to explain the diastereoselective thio-Claisen rearrangement results of various *S*-allyl γ-hydroxy ketene dithioacetals. We show that the experimental results of Sreekumar et al. in the absence and in the presence of zeolite catalyst can be rationalized in terms of the energetics of the steric of the reactant and the transition-state structure and of the non-bonding interactions of zeolite–reactant and zeolite–transition-state structure. The procedures used can successfully identify optimum products for a given diastereoselective thio-Claisen rearrangement. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Diastereoselective thio-Claisen rearrangement; Steric energy; Non-bonding interaction

1. Introduction

Most zeolite structures are achiral. It is very difficult trying to synthesis zeolite with chiral structure. When performing an asymmetric reaction with a zeolite catalyst, there are numerous ways in which the chirality can be brought into the system, such as introducing asymmetry via auxiliary, a ligand around a metal center, a chiral reactant and the zeolite framework itself [1].

Asymmetric catalysis with zeolite is a relatively new field. When chiral reactants are confined within the micropores of the zeolite, enantioselectivities can be induced or enhanced. When zeolites are involved in chiral reaction system, it is not bound to produce new products, but rather endowing the catalysts with additional features.

These kinds of reactions take advantages of the adsorption and shape-selective property of zeolites. The chiral reaction with zeolite is explained qualitatively as follows:

1. Reactant molecules are located in the zeolite cave, so only one conformation is more suitably accommodated than the other [2].
2. The reactant molecule can be adsorbed comfortably inside the channels of zeolite in such a way that bulky groups are away from the catalyst surface [3].

---

[*] Corresponding author.
E-mail address: dingdt@sun.nankai.edu.cn (D. Ding).

PII: S1381-1169(00)00255-7

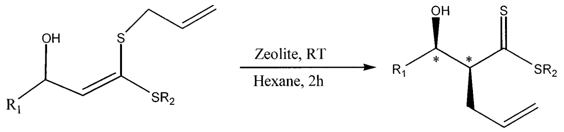

Fig. 1. Thio-Claisen rearrangement over zeolite catalysts.

To quantitatively explain asymmetric reaction results of racemic butan-2-ol over modified Y zeolite, S. Feast et al. [4] used computer simulation. Their calculated results show that reactant (s) butan-2-ol, whose reaction activity (Yield %) is higher, has lower non-bonding interaction energy with modified Y framework, i.e., there is a good correlation between the non-bonding interaction energy and reaction activity.

Recently, R. Sreekumar and R. Padmakumar [3] studied the diastereoselective thio-Claisen rearrangement of various *S*-allyl γ-hydroxy ketene dithioacetals in the absence and in the presence of zeolite catalysts. The reaction equations are shown in Fig. 1. The reaction activity (Yield %) [3] are listed in Table 1. It shows that in the absence of catalyst, the major product is syn-α-allyl β-hydroxy dithioesters (syn isomer), whereas in the presence of zeolite catalysts, anti-α-allyl β-hydroxy dithioesters (anti isomer) is the only product.

In the present paper, we calculated the steric energies of guest molecules (reactant with different conformations or their transition-state structure) and the non-bonding interaction energies between guest molecules and zeolite framework (host). We demonstrated that those energies are crucial for quantitative interpretation the results of thio-Claisen rearrangement of γ-hydroxy ketene dithioacetals in the absence and in the presence of zeolite catalysts.

2. Energetic studies of guest molecule — zeolite framework

The brief steps of energetic analysis of guest molecule and zeolite framework are listed as follows.

2.1. Guest molecule conformations

Two kinds of conformations (A and B) of reactant molecules are presented, where conformation A is favor to produce anti isomer product, conformation B is favor to produce syn isomer product. They are shown in Fig. 2. The initial conformations of A and B are formed randomly using Chem3D software [5]. A molecular dynamic (MD) trajectory for the reactant molecules in the gas phase initial temperature, 2000 K, is used to generate a library of reactant conformations, each of which is then energy minimized with MM2 force field. The conformation of each transition-state structure is also formed using Chem3D software. The above procedures allow us to determine the steric energy of each conformation.

Table 1
Thio-Claisen rearrangement of γ-hydroxy ketene dithioacetals over different zeolite catalyst

Entry	R1	R2	Yield (%)[a]				
			HY	HEMT	H beta	HZSM-5	Uncatalysed
1	Me	Me	88	81	78	84	68 (11:1)[b]
2	Et	Me	84	76	72	68	47 (14:1)[b]
3	Pr	Me	78	69	64	70	49 (15:1)[b]
4	*t*-But	Me	83	71	57	80	40 (19:1)[b]
5	Ph	Me	76	61	55	65	38 (8:1)[b]

[a] Isolated pure Anti isomer products.

[b] Syn:anti ratio.

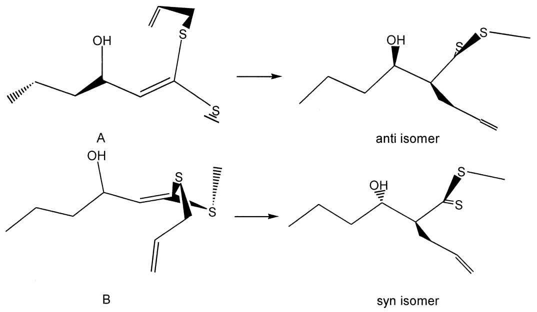

Fig. 2. The conformation relationship between the reactants and product.

Table 2
The potential parameters for non-bonding energy

Atom	R_i^* (Å)	ε (kcal/mol)
Si	2.250	0.140
Al	2.698	0.200
O	1.740	0.050
S	2.110	0.202
C	1.900	0.044
H (−C)	1.500	0.047
H (−O)	0.950	0.036

2.2. Zeolite coordinates

Among the zeolites used by R. Sreekumar and R. Padmakumar [3], we select two typical zeolites Y and ZSM-5 to perform energy calculations. Zeolite Y belongs to space group $Fd\bar{3}m$ (No. 227), and its coordinates are taken from Ref. [6]. Zeolite ZSM-5 belongs to space group *Pnma* (No. 62), and its coordinates are taken from Ref. [7]. In zeolite Y, the framework Si, Al distribution are considered in terms of random substitution of Si by Al atoms (according to Löwenstein's rule) due to its high Al content (Si/Al = 2.5). Whereas in zeolite ZSM-5, the framework Si, Al distribution are considered as pure siliceous due to its low Al content (Si/Al = 30).

2.3. Non-bonding interaction energy between guest molecules and zeolite framework

In the calculation of non-bonding interaction energy between Y, ZSM-5 and guest molecules, we use the following exponent equation [5]:

$$E_{\text{vdw}} = \sum_i \sum_j \varepsilon_{ij}\left(290\,000\mathrm{e}^{-12.5R_{ij}} - 2.25R_{ij}^{-6}\right) \tag{1}$$

At short distances, the above equation favors repulsive over dispersive interactions. To compensate for this at short distances, it is replaced with:

$$E_{\text{vdw}} = 336.176\sum_i \sum_j \varepsilon_{ij} R_{ij}^{-2} \tag{2}$$

where $R_{ij} = (r_{ij})/(R_i^* + R_j^*)$, $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, r_{ij} the actual distance between atom i and atom j, and R_i and R_j the vdw radius of atom i and atom j. The parameters are listed in Table 2 [5].

2.4. Optimized position and orientation of guest molecules in zeolite channel

We put each of guest molecules into zeolite channel randomly. Zeolite framework size in the calculation is $40 \times 26 \times 40$ Å^3 for ZSM-5 and $74 \times 74 \times 74$ Å^3 for zeolite Y.

The initial interaction energy between the zeolite framework and guest is well defined by the coordinates of the guest (with its given conformation) relative to the framework. Energy minimization of each crudely docked configuration is performed using simulated annealing algorithm. The minimum energy structure for a given host–guest pair is obtained by selecting the configuration with the lowest interaction energy.

3. Results and discussion

3.1. Results without catalyst

In the absence of catalyst, conformer A or B can directly undergo thio-Claisen rearrangement into anti or syn product, respectively. The calculated lowest steric energies of each conformer and that of each transition-state structure are list in Table 3.

Table 3
The lowest steric energy of each conformer and that of each transition-state structure in free space

R1	Me	Et	Pr	*t*-But	Ph
R2	Me	Me	Me	Me	Me
E_A	5.669	9.920	12.490	21.950	−18.260
E_B	−8.519	−4.900	−2.425	5.461	−29.520
E_A^T	390.499	508.090	394.589	416.641	469.368
E_B^T	389.841	512.277	395.498	414.116	475.399

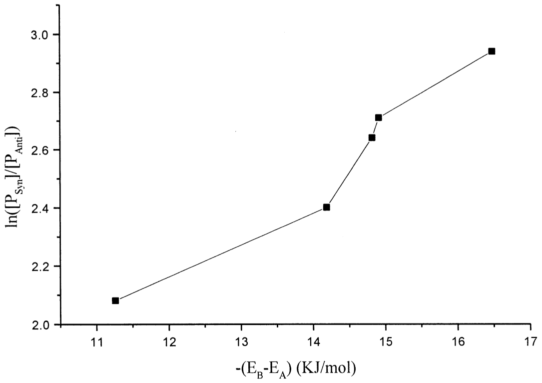

Fig. 3. The plot of $\ln([P_{\mathrm{syn}}]/[P_{\mathrm{anti}}])$ against $-(E_B - E_A)$.

Table 3 shows that the steric energy of conformer B is all lower than that of corresponding conformer A. It shows that conformer B is more stable than conformer A in free space. Therefore, we can infer that the population of conformer B is larger than that of conformer A in free space. The Curtin–Hammett principle [8] declares that the product ratio is dependent upon the conformational equilibrium constant and the rate ratio of the individual conformer, i.e.,

$$\frac{[P_{\mathrm{syn}}]}{[P_{\mathrm{anti}}]} = K\frac{k_B}{k_A}$$

where $K = [C_B]/[C_A] \propto \exp[-(E_B - E_A)/kT]$ and $(k_B)/(k_A) \propto \exp[-(E_B^T - E_A^T)/kT]$. k is the Boltzmann constant and T the reaction temperature. Therefore,1

$$\frac{[P_{\mathrm{syn}}]}{[P_{\mathrm{anti}}]} \propto \exp[-(E_B - E_A)/kT] \times \exp\left[-\left(E_B^T - E_A^T\right)/kT\right]$$

Since the relative differences in steric energy of the two corresponding transition-state structures are all so small that we can ignore the contribution of the rate ratio of the individual conformer to the product ratio. Therefore, the product ratio will be a reflection of the conformer population of the reactants. Plot of $\ln([P_{\mathrm{syn}}]/[P_{\mathrm{anti}}])$ against $-(E_B - E_A)$ is shown in Fig. 3. It is seen that the larger the steric energy difference of conformer A and B, the larger the value of $\ln([P_{\mathrm{syn}}]/[P_{\mathrm{anti}}])$, and, hence, the larger the syn isomer population in the product mixture is. This conclusion can explain why in the absence of catalyst, the major product is syn isomer.

3.2. Results with zeolite as catalyst

In the presence of zeolite catalysts, conformer A or B, firstly, is adsorbed to the chan-

Table 4
The non-bonding energies of isomer A or B and their transition-state conformers with zeolite Y or ZSM-5 (kJ/mol)

Reactant type	R1	Me	Bt	Pr	*t*-But	Ph
	R2	Me	Me	Me	Me	Me
In zeolite Y	E_A	−101.06	−106.51	−119.44	−130.67	−24.93
	E_B	−89.06	−87.60	481.42	51.97	437.94
	E_A^T	−97.73	−92.81	−94.42	347.25	424.15
	E_B^T	1410.78	9021.40	13 717.81	12 294.28	1269.50
In zeolite ZSM-5	E_A	4430.4	5658.4	6704.6	12 665.6	8659.8
	E_B	5667.9	9442.2	10 837.5	15 241.3	11 915.0
	E_A^T	5684.4	7698.7	9718.0	18 157.9	12 050.4
	E_B^T	9326.4	12 852.3	16 369.4	30 455.9	33 635.6

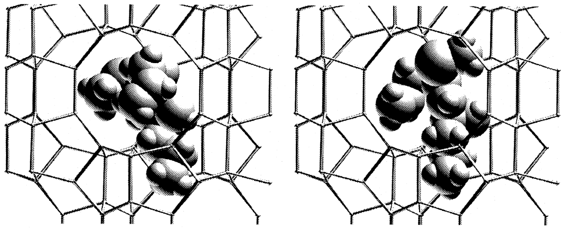
(a) A in HZSM-5 (b) B in HZSM-5

Fig. 4. Position relationship of reactants in the HZSM-5 cave.

nel of zeolites, then rearrangement goes on. Constrained by the shape and size of zeolite channel, conformers A and B have different interaction energies. The non-bonding interaction energies of each conformer and each transition-state conformer with zeolites Y and ZSM-5 are listed in Table 4.

Table 4 shows that the interaction energy of conformer A with zeolites is all lower than that of conformer B. Therefore, conformer A is more favored in energy than conformer B to be adsorbed to the zeolite channel. Table 4 also shows that the interaction energy of the transition-state structure of conformer A with zeolite is all much lower than that of the transition-state structure of conformer B. From the Curtin–Hammett principle, we can therefore infer that the population of anti isomer product is much larger than that of syn isomer product. This results can explain why in the presence of zeolite catalyst anti isomer is the only product. When R1 is Pr, the optimized configures of isomer A or B in ZSM-5 is expressed in Fig. 4.

4. Conclusion

In the absence of catalyst, the steric energy difference of reactant conformers is the major factor that affects the product ratio, which can explain the experimental results, that syn isomer is the major product. Whereas in the presence of zeolite, the interaction energy difference of transition-state structure with zeolites is the major factor that affects the product ratio, which can explain the experimental results that in zeolite mediated rearrangement, anti isomer is the only product. The methodologies described in this paper, although containing many simplifications, can determine the relative populations of the two product isomers in the diastereoselective thio-Claisen rearrangement with and without zeolite catalysts.

References

[1] M.E. Davis, Microporous Mesoporous Mater. 21 (1998) 172.

[2] M. Leibovich, G. Olovsson, G. Sundarabau, V. Ramamurthy, J.R. Scheffer, J. Trotter, J. Am. Chem. Soc. 118 (1996) 1219.

[3] R. Sreekumar, R. Padmakumar, Tetrahedron Lett. 38 (1997) 2413.

[4] S. Feast, D. Bethell, P.C.B. Page, F. King, C.H. Rochester, M.R.H. Siddiqui, D.J. Willock, G.J. Hutchings, J. Chem. Soc., Chem. Commun. (1995) 2409.

[5] CS Chem3D Pro software: MM2 atom type parameters, Cambridge, ver. 4.0, 1997.

[6] H. Baur, Am. Miner. 49 (1964) 697.

[7] H. van Kaningsveld, H. van Bekkum, J.C. Jansen, Acta Crystallogr., Sect. B 43 (1987) 127.

[8] N.S. Isaacs, Physical Organic Chemistry, Longman, New York, 1987.