

[AMT13] Photodimerization and photocycloaddition of 2-cyclohexenone in confined space of cation-exchanged Y zeolites

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Introduction

Zeolite Y was used in this research. The structure of FAU zeolite is cubic and built from sodalite cage connected via the double 6-membered ring. It forms a three-dimensional network of nearly spherical supercages of about 1.3 nm in diameter connected tetrahedrally to four other supercages through 0.74 nm windows. The charge-compensating cations are mobile and distributed among several types of sites. The supercage concentration in zeolite Y with Na⁺ ions as charge-compensating cation (NaY) is estimated to be approximately 6×10^{-4} mol/g on the basis of the crystal structure (Hashimoto, 2003).

The synthetic utility of intermolecular photodimerization of cyclic enones and the cycloaddition to unsymmetrical alkenes can be limited by the formation of the mixtures of the head-to-head (HH) and head-to-tail (HT) regioisomers. HT regioisomers are always formed in much larger amount compared to HH isomer in solution reaction (Corey *et al.*, 1964; Wagner *et al.*, 1969). The regioselectivity of the photoproducts in the photodimerization of 2-cyclohexenone (CH) (1) and photocycloaddition of CH (1) to vinyl acetate (VA) (2) within the confined space of various cation-exchanged Y zeolites were reported in this paper.

Materials and Methods

Chemicals and Instrumentations

NaY zeolite (CBV100) was purchased from Zeolyst International and used as received. Cation-exchanged Y zeolites were obtained by exchanging the NaY zeolite with its corresponding nitrate solutions and termed as MY zeolite (M = Li, K, Rb, and Cs). Exchange levels of the zeolites as measured by flame photometry are as follows: NaY = 100 %, LiY = 84.2 %, KY = ~ 99 %, RbY = 75.7 % and CsY = 71.3 %. CH, VA, and hexane were obtained from Fluka. JEOL Ultraviolet

radiation (ES-USH 500 Hg lamp) was used as UV source. GC chromatograms were taken using the Hewlett-Packard chromatography (Model 6890). The MS spectra were taken using coupled GC-MS Agilent Technologies spectrometer Model G 1540 N (GC) and G 2579 A (MS).

Photodimerizations of CH(1)

(a) Homogenous reactions: Solution of CH (1) (10.0 mg/mL) in hexane (5 mL) was UV-irradiated in pyrex tube for 5 h in continuous stirring and inert condition. Photoreaction was also conducted in open-air condition as control experiment. The concentrated solution was analyzed with GC and GC-MS. Conversion rate was determined with acetophenone as external standard. (b) Solid state reactions: Activated MY zeolites (M = Na, Li, K, Rb, and Cs) (300.0 mg) were stirred in hexane solutions of CH (1) (15.0 mg) for 3 h. The hexane layer was analyzed with GC to detect the absent of CH (1). The MY zeolites containing CH (1) (CH-MY) were dried under vacuum (10^{-4} Torr) for 2 h. The magnetically stirred dried powder samples were irradiated for 5 h in a pyrex tube in vacuum condition. The treatment of the irradiated zeolites with HCl acid (1 N) and EtOAc gave the photoproducts which were then analysed using GC and GC-MS. (c) Reactions in zeolite-hexane slurry: The CH-MY samples (15 mg CH/ 300 mg MY) were irradiated as translucent slurries for 2 h under inert condition. The photoproducts were extracted and analyzed as the above.

Photocycloadditions of CH(1) to VA(2)

(a) Homogenous reactions: A continuously stirring hexane solution (10 mL) of CH (1) (0.01 mol) and vinyl acetate (VA) (2) (0.15 mol) was irradiated for 5 h in a pyrex tube in inert condition. The concentrated solution was then analyzed using GC and GC-MS. (b) Reactions in zeolite-hexane slurry: MY zeolites (500.0 mg) containing CH (1) (5.0 mg) and VA (2) (64.0 mg) in hexane (CHVA-MY-

hexane-slurries) were irradiated for 5 h under inert condition. The treatment of the irradiated zeolites with HCl acid (1 N) and EtOAc gave the photoproducts which were analysed using GC and GC-MS.

Results

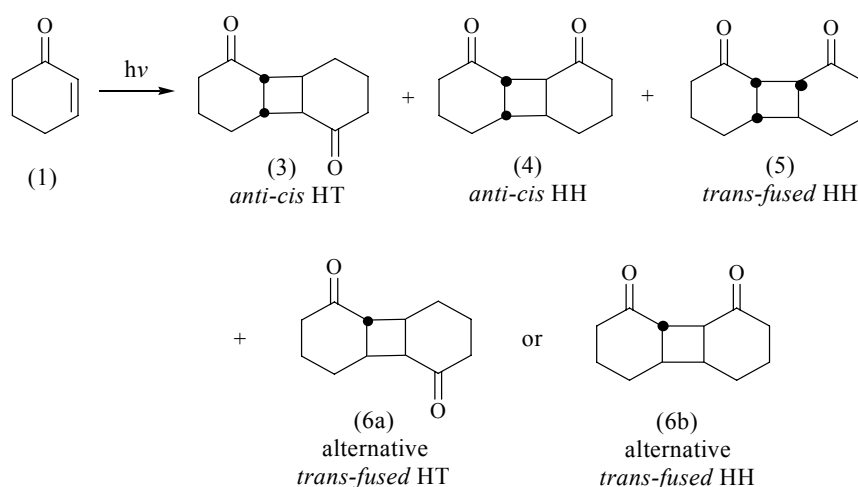
Photodimerizations of CH(1)

The GC analysis of the photoproducts in the photodimerization of CH (1) in homogenous reaction showed the presence of four peaks, each with R_t values of 23.40, 23.60, 23.89, and 24.12 minutes. The mass spectra of all the four peaks gave the same molecular ion peaks at m/z 192. Which was in agreement with a molecular formula of $C_{12}O_2H_{16}$. The fragmentation pattern of this compound was matched with the fragmentation pattern of CH dimer. The peak 2 (R_t 23.60 minutes) and peak 4 (R_t 24.12 minutes) were further confirmed to be anti-*cis* HT(3) and HH(4) and peak 1 (R_t 23.40 minutes) and peak 3 (R_t 23.89 minutes) were assigned to either dimer (5) or (6) with the comparison of literatures (Wagner *et al.*, 1969; Lem *et al.*, 1993; Lam *et al.*, 1967). SCHEME 1 shows the correspondence photoproducts of the photodimerization of CH. The products ratios were calculated using the peak area in GC chromatograms. TABLE 1 shows the HT(3)/HH(4) dimers ratios. Dimer (5) and (6) were classified under "other products". From the table, It was observed that the ratio of (3)/(4) is independent from the % of conversion. The

existence of oxygen molecules did not inhibit the photoreaction but will slow the rate of the reaction.

The ratio of *anti*-dimers HT(3) and HH(4) was also reported in the function of both the solvent and the concentration of starting material CH (1). In non-polar solvent, the photodimerization of CH gives predominantly the HT photodimer (in n-hexane, ratio HT/HH 5.21:1), but the regioselectivity switched in favor of the HH photodimer in polar solvent (in acetonitrile, ratio HT/HH 0.5:1). Irradiation of 0.5 M and 3.0 M CH in benzene gave the HT/HH ratio of 2.50:1 and 1.52:1 respectively and photodimerization of the neat ketone gave the dimer ratio 1.06:1 (Wagner *et al.*, 1969; Lem *et al.*, 1993; Lam *et al.*, 1967).

Chromatograms of the mixture of the photodimerization of CH in solid state MY zeolites gave 7 peaks instead of 4 peaks in homogenous reaction with the extra peaks at R_t 24.54, 25.66 and 25.87 minutes. Peaks with R_t 24.54 and 25.66 minutes also gave ion peaks at m/z 192 in their MS spectra. Their fragmentation patterns were further matched with the fragmentation patterns of CH dimer, but their regio-structures could not be identified. While peak at 28.57 minutes gave the ion peak at m/z 207. Its MS pattern is similar to CH dimers. It is believed that these unknown products are CH dimer with a methyl substitution. The product ratios were calculated based on the peak areas of these 7 peaks in GC chromatogram and are shown in TABLE 2.



SCHEME 1 Photodimerization of CH (1).

TABLE 1 Products ratio of the photodimerization of CH (1) in n-hexene.

Condition	Conversion	HT(3) ^a	HH(4)	(3)/(4)	Other products
Inert	67%	0.61	0.16	3.81	0.23
Open air	10%	0.65	0.17	3.82	0.28

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 3\%$

TABLE 2 Products ratio in solid state photodimerization of CH in MY zeolites

M+Y	HT(3) ^a	HH(4)	(3)/(4)	Other products	Total products/ (CH+ Total products)
LiY	0.10	0.50	0.20	0.40	0.37
NaY	0.15	0.31	0.48	0.54	0.81
KY	0.11	0.71	0.15	0.14	0.96
RbY	0.05	0.81	0.06	0.15	0.63
CsY	0.05	0.80	0.06	0.15	0.98

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 2\%$

Discussion

There is a great increase in the formation of HT(3) relative to HH(4) dimers from NaY (0.48) to CsY (0.06). The greatest reversal in the regiochemistry from HT to HH dimer in RbY and CsY is due to the smallest supercage volume and weakest electrostatic interaction of ion in the zeolites (Lem *et al.*, 1993; Turro *et al.*, 1991; Ramamurthy *et al.*, 1992). Although polar solvent can result in high HH product (ratio HT/HH 0.63), but such low ratio in RbY and CsY has never been achieved in the homogenous reaction. It was suggested the complexing effect of the charge compensating cation and the size constriction factor always play a role in controlling the regiochemistry of products (Lem *et al.*, 1993; Ramamurthy *et al.*, 1991). In the case of RbY and CsY, the constriction factor most probably is the dominant factor. Even at very low loading levels there are supercages with double occupancies (Liu *et al.*, 1989). Thus, the formation of high HH in RbY and CsY are caused mainly by the confined space. While in the case of LiY, the relatively large effect of Li⁺ (strong van der Waals) are expected to provide strong interaction/binding between the carbonyl group of CH with the zeolite surface (Ramamurthy *et al.*, 1991; Pitchumani *et al.*, 1998). LiY has been reported to give the greatest enhancement of Norrish Type I products in the photolysis of macrocyclic ketone within zeolites (Ramamurthy *et al.*, 1991). Lithium ions have

been suggested to exert a large effect due to their small size, give rise to high charge density (Ramamurthy *et al.*, 1999). The factor of strong electrostatic field in LiY can suggest why LiY gives the higher HH product compared to NaY with smaller supercage volume.

In most of the zeolites, the minor (other) products are formed in comparable amounts with the yield from the solution reaction (compare TABLE 1 and TABLE 2). In NaY and LiY they were the prominent products. In NaY, these products formed (54 % of total products) more than HT(3) and HH(4) dimers. It further proved the solid state photodimerization of CH can result in totally different product selectivity. Dimer ratios also did not change when the dimers were allowed to remain within the zeolite for up to 24 h after irradiation before workup.

It has been shown that the product distribution obtained upon UV irradiation of organic molecules included in zeolite-solvent slurries is distinctly different from conventional dry powder photolysis. The difference in the product distribution obtained between zeolite-solvent slurry and a homogenous solution is often higher than that between the dry powder zeolites and homogenous solution (Corbin *et al.*, 1991). Solvent present within the supercages of zeolite X and Y was reported to provide constraint on the mobility of the included guest molecules, thus one might be able to modify the photoreactivity of the guest molecules. The result obtained in the photolysis of

acenaphthylene in a RbY-hexane slurry gave a high yield of *cis* dimer compared to solid state reaction and it was believed the migration of acenaphthylene between cages was blocked or inhibited by the solvent hexane, thus dimerization preferentially occurred from doubly occupied cages (Corbin *et al.*, 1991). In order to study the effect of solvent on the HT(3)/HH(4) ratio, the reactions were carried out in zeolite-hexane slurry. Since the adsorption of CH is achieved by the same process (stirring in hexane) both for dry (hexane evaporated off) and slurry (hexane left within zeolite) irradiations, we may assume that the distribution pattern remains the same for both the dry and slurry samples.

Most of the chromatograms obtained from the dimerization conducted in zeolite-hexane slurries provided similar pattern with those obtained in dry powder (solid state) reaction, except in the NaY and LiY zeolite-slurry systems. These systems showed a significant increase of background peaks at the R_t 20-23 minutes, which were not observed in the solid state systems. These peaks are believed to be caused by impurities. Thus, solid state reaction provided a "clearer" reaction compared to slurry system. An extra peak with the R_t 26.93 minutes was observed in LiY, NaY and KY-slurry systems compared to dry powder systems. This peak gave ion peak at m/z 277 in the MS

analysis. Its fragmentation pattern did not match with any compound as cited in the GC-MS database system. However, this unknown compound formed an important portion (12 %) of total products in LiY-slurry system. The product distributions are calculated based on the peak areas of these 8 peaks in the GC chromatogram. TABLE 3 shows the calculated results.

In LiY, NaY and KY-slurry systems, the formations of HT(3) became lesser, thus provided lower HT(3)/HH(4) value compared to solid state systems (TABLE 2). However, the formations of HT(3) and HH(4) decreased in NaY-slurry system, the "other products" become the main portion (78%) and Peak 1 (*trans*-fused photodimers (5) or (6)) is the prominent compound (28 %). Except for the KY-system, all the formations of HH(4) are lesser compared to solid-state reactions. The zeolite-slurry system gave rise to more "other products" compared to HT(3) and HH(4). There was no significant change in the HT(3)/HT(4) for the KY, RbY and CsY systems. Generally, conversion of starting material to products is higher in zeolite-slurry compared to dry powder. It can be observed on the value of total products/(CH + total products). All the zeolite-slurry systems gave a value greater than 0.9 even in a shorter irradiation time (3 h shorter compared to the solid state reaction).

TABLE 3 Products ratio of the photodimerization of CH in zeolite-hexane-slurries.

MY zeolites	HT(3) ^a	HH(4)	(3)/(4)	Other products	Total products/ (CH+ Total products)
LiY	0.05	0.32	0.16	0.63	1.00
NaY	0.06	0.16	0.38	0.78	0.94
KY	0.06	0.74	0.08	0.20	0.92
RbY	0.06	0.71	0.08	0.23	0.91
CsY	0.05	0.69	0.07	0.26	0.97

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 2\%$

Photocycloaddition of CH (1) to VA(2)

GC analysis of the product showed the presence of five significant peaks, each with R_t values of 19.58, 19.71, 19.83, 19.94, and 20.10 minutes. All these five peaks gave similar fragmentation patterns and the ion peaks at m/z 158, and other fragment ions at m/z 139, 122, 111, 97, and 43 in the GCMS analysis. Its fragmentation pattern was matched with the cyclohexane-cyclobutene adduct (8) or (9)

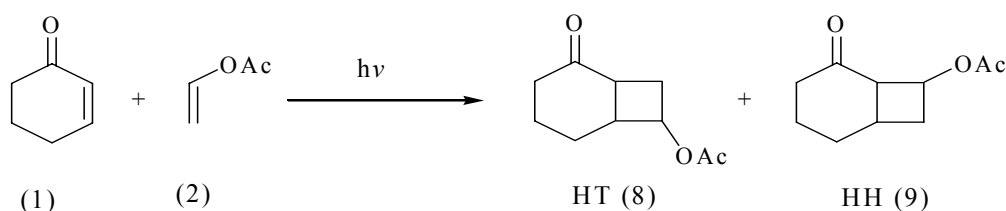
(SCHEME 2) which has a molecular formula of $C_{10}H_{14}O_3$ (M^+ , 182). The ion peak at m/z 122 confirmed the loss of $HOCOCH_3$ from the molecular ion. Small amounts of CH dimer were also detected in this reaction. Although we are not able to determine the stereochemistry of these cycloadducts, we hope to compare the different of product distribution between solution reaction and reaction in confinement space of zeolite. These cyclobutene adducts

were then named as (P1)-(P5). TABLE 4 shows the resulted product ratios in different mediums.

Similar photocycloaddition products were obtained within zeolite-slurries system. However, distinctly difference of product selectivity was observed as compared to the homogenous reaction. There are drastically decrease of product portion of (P2) and increase of the ratio of (P3). Surprisingly, all the MY zeolites provided a similar pattern of product distributions. There is no significant change of product ratios from LiY to CsY. LiY and KY systems almost provided a same product distribution. RbY system gave the highest yield of (P1) while CsY system provided (P5) as the largest portion in the products mixture. We also tried to increase the loading level of CH for better confinement effect, however the obtained results provided a high yield of CH dimer, indicated that photodimerization reaction was

more prominent than the photocycloaddition of VA.

A zeolite reaction cavity has been characterized to be "active" when the interaction between a guest molecule and the cavity is attractive or repulsive. While there is no significant interaction, it is considered to "passive" (Ramamurthy, 2000). Thus, we tried to reason the failure of cation to vary the selectivity in this reaction is caused by the "passive" cavity. VA ($\text{CH}_2=\text{CHOCOCH}_3$) molecule has two polar groups, C-O and C=O which can compete with the C=O group in the CH molecule to interact electrostatically with the surface cations. Because the VA molecules are presence in a large amount in the supercage, it may also shielded and weaker the electric field created by the cations.



Scheme 2 Photocycloaddition of CH (1) to VA (2).

TABLE 4 Product ratios obtained in photocycloaddition of CH to VA in different mediums.

Medium	(P1) ^(a)	(P2)	(P3)	(P4)	(P5)	Total products/ (CH+ Total products)
Hexane	0.30	0.18	0.08	0.15	0.29	1.00
LiY	0.21	0.05	0.28	0.08	0.38	0.97
NaY	0.25	0.06	0.24	0.09	0.36	1.00
KY	0.21	0.05	0.29	0.08	0.37	0.83
RbY	0.34	0.05	0.21	0.05	0.35	0.70
CsY	0.21	0.06	0.25	0.06	0.42	1.00

^aNumbers reported are the average of at least two measurements. Error limit of the analysis is $\pm 2\%$

Conclusion

In conclusion, solid state and slurry photodimerization of CH in alkali metal cation-exchanged Y zeolites has successfully gaining favorable result in controlling the regio and stereoselectivity of the photodimer.

The selectivity of the photoproducts is due to combine factors of size constriction effects and the complexing ability of the charge-compensating cation of the zeolites. The presence of solvent molecules in the system did not give big different in the ratio of HT

(3)/HH (4). The study of regioselectivity in the photocycloaddition of 2-cyclohexenone to vinyl acetate in zeolite slurries showed drastically change of product yield compared to homogenous reaction. We reasoned the fail of cation to vary the selectivity was due to the passive cavity effect.

Acknowledgements

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