Isomerizations of cycloheptane to methylcyclohexane and cyclooctane to ethylcyclohexane catalyzed by sulfated zirconia

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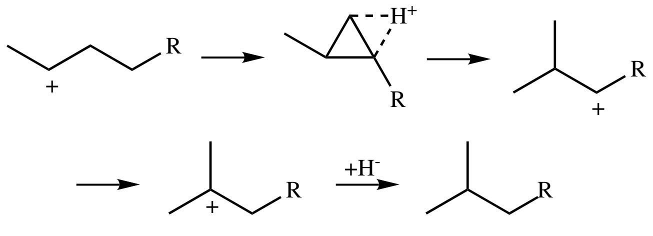
Reactions of cycloheptane and cyclooctane were performed over the superacid of sulfated zirconia in liquid phase at 50 °C; a main product was methylcyclohexane from cycloheptane through a protonated bicyclo[4.1.0]heptane and ethylcyclohexane from cyclooctane via a protonated bicyclo[4.2.0]octane. Cyclodecane was dehydrogenated into decalines; cyclododecane was converted into many products, more than 30 species.

KEY WORDS: sulfated zirconia; isomerization; cycloheptane; cyclooctane; cyclodecane; monomolecular; cyclopropane intermediate; cyclobutane intermediate.

The isomerization of alkanes over superacidic catalysts at low temperature is their characteristic action; the reaction proceeds through a protonated cyclopropane intermediate after the formation of a carbenium ion, converting into an alkane with the same number of carbons as the reactant, as shown in scheme 1 (monomolecular mechanism) [1].

Another reaction, the bimolecular mechanism, has been proposed; the process occurs through the formation of a bimolecular intermediate by the reaction of a carbenium ion with an alkene produced during reaction, with the successive migration of alkyl groups followed by its β-scission to form an isocarbenium ion and an alkene as shown in scheme 2. In such a case, a main product is isobutane together with disproportionated materials such as propane and pentanes, whose number of carbons is different from that of the reactant [2].

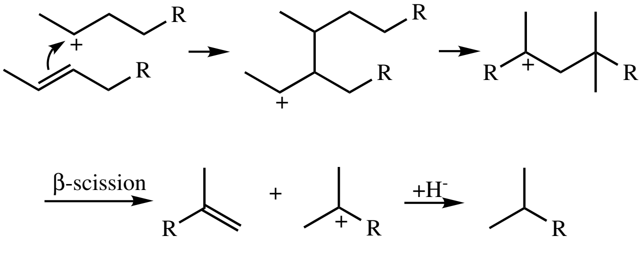
In the isomerization of alkanes over sulfated zirconia (SO_4/ZrO_2), an induction period is observed in the beginning of the reaction. The monomolecular reaction proceeds in the beginning and induction period to form isopentane selectively when the reactant is pentane; afterward, the reaction changes to the bimolecular mechanism with time to produce isobutane by the reaction of carbenium ions with alkenes [3].



Scheme 1. Monomolecular mechanism.

The reaction mechanism of cyclic alkanes is different from that of open-chain alkanes. A known example is the reversible isomerization between cyclohexane and methylcyclopentane, with preservation of the cyclic structure [4,5]. In fact, cyclohexane was converted into only methylcyclopentane over SO_4/ZrO_2. Methylcyclohexane was also converted into dimethylcyclopentane over Pt-SO_4/ZrO_2 [6]. It appears that the skeletal isomerization of cycloalkanes is not based on the bimolecular process but on the monomolecular reaction.

The isomerization of open-chain alkanes with the number of carbons greater than six is capable of giving a main product of isobutane together with disproportionated materials even though the reaction proceeds by the monomolecular mechanism [7]. On the other hand, for cyclic alkanes the monomolecular process with preservation of the cyclic structure seems to be the most probable judging from the results of cyclohexane. The absence of isobutane in the products indicates the reaction path without going through open-chain intermediate species. Therefore, it is of interest to try cycloalkanes greater than cyclohexane for clarification



Scheme 2. Bimolecular mechanism.

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of the reaction mechanism along with the catalytic action of SO_4/ZrO_2.

The SO_4/ZrO_2 catalyst was prepared as described elsewhere [8,9]. The liquid–solid reactions of cycloalkanes were performed in a glass-made apparatus connected to a vacuum apparatus. After 0.05 g of the catalyst was pretreated *in vacuo* at the desired temperature, 150–450 °C, for 3 h, cycloalkanes, 0.15 mL (0.12 g for cyclododecane), were led to reaction at 50 °C. After reaction, the reaction mixture was analyzed by a GC with an FID detector through a 50-m CP-Al_2O_3/KCl capillary column (25-m OV-1701 bonded for cyclododecane).

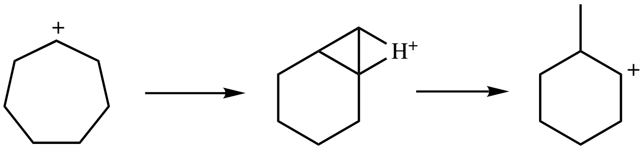
First, the effect of pretreatment of the SO_4/ZrO_2 catalyst on the reaction of cycloalkanes was investigated; the catalysts evacuated at 150–450 °C for 3 h were examined in the reaction of cycloheptane. The maximum activity was observed on evacuation at 200 °C, and the selectivities of products were not varied with the catalysts treated at 150–450 °C. Since the number of Brönsted sites over sulfated zirconia is reduced when it is pretreated at elevated temperatures [10], the results indicate that the isomerization proceeds on the Brönsted sites.

The reaction of cycloheptane was carried out at 50 °C for 30 min over SO_4/ZrO_2 pretreated at 200 °C; the results are shown in table 1. A main product was methylcyclohexane with a selectivity of 97% in addition to small amounts of four dimethylcyclopentanes and ethylcyclopentane. The reaction of methylcyclohexane under the conditions indicated its conversion into the latter five compounds, and the system reached its equilibrium state after 90 min of reaction. The absence of isobutane in the products indicates the monomolecular process with preservation of the cyclic structure. Thus, the conversion of cycloheptane into methylcyclohexane via a protonated bicyclo[4.1.0]heptane intermediate is shown in scheme 3. Ethylcyclopentane was largely isomerized to methylcyclohexane under the conditions, indicating the formation of a protonated cyclopropane intermediate.

The reaction of cyclooctane was carried out over SO_4/ZrO_2 pretreated at 450 °C; the results are shown in table 2. The catalyst treated at 200 °C was exceedingly active for cyclooctane. A main product was ethylcyclohexane with a selectivity of 93% in addition to small amounts of five dimethylcyclohexanes and methylcycloheptane. The reaction of ethylcyclohexane under the conditions indicated its conversion into the other products.

Table 1
Reaction of cycloheptane at 50 °C for 30 min over SO_4/ZrO_2 pretreated at 200 °C

Product	Yield (%)	Selectivity (%)
Methylcyclohexane	53	97
trans-1,2-dimethylcyclopentane	0.7	1.3
trans-1,3-dimethylcyclopentane	0.4	0.7
1,1-dimethylcyclopentane	0.3	0.4
cis-1,3-dimethylcyclopentane	0.2	0.3
Ethylcyclopentane	0.2	0.3



Scheme 3. Intermediate for the isomerization of cycloheptane into methylcyclohexane.

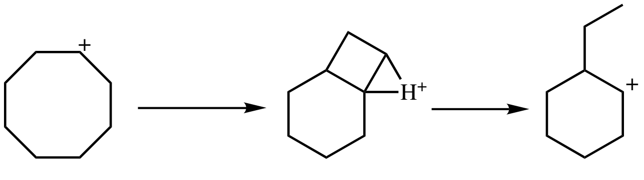
Table 2
Reaction of cyclooctane at 50 °C for 30 min over SO_4/ZrO_2 pretreated at 450 °C

Product	Yield (%)	Selectivity (%)
Ethylcyclohexane	57	93
trans-1,2-dimethylcyclohexane	2.1	3.3
Methylcycloheptane	1.1	1.7
cis-1,3-dimethylcyclohexane	1.0	1.3
trans-1,4-dimethylcyclohexane	0.2	0.3
1,1-dimethylcyclohexane	0.1	0.2
trans-1,3-dimethylcyclohexane	0.1	0.2

The formation of methylcycloheptane shows the reaction process through a protonated cyclopropane intermediate analogous to scheme 3. On the other hand, the production of ethylcyclohexane, which is the main product, indicates the formation of a protonated cyclobutane intermediate, protonated bicyclo[4.2.0]octane, as shown in scheme 4. In this case, the reaction is energetically more advantageous, 31 kcal/mol lower than the former [11]; this is also shown by the large difference in product amounts between the two. The formation of 2,3-dimethylbutane from *n*-hexane catalyzed by H-β zeolites is explained by the isomerization via a protonated cyclobutane intermediate [12].

The reaction of cyclodecane over SO_4/ZrO_2 pretreated at 200 °C led to dehydrogenation into the bicyclic compounds, *cis*- and *trans*-decalines, with the evolution of a dihydrogen as shown in table 3; no isomerization occurred. The SO_4/ZrO_2 catalyst pretreated at 200 °C mainly consists of Brönsted sites; the intermediate species on the sites are shown in scheme 5.

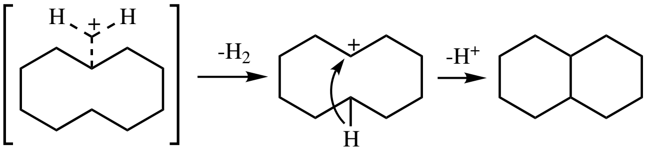
Cyclododecane was tryed over the catalyst (pretreated at 200 °C) at 65 °C, and the products, more than



Scheme 4. Intermediate for the isomerization of cyclooctane into ethylcyclohexane.

Table 3
Reaction of cyclodecane at 50 °C for 180 min over SO_4/ZrO_2 pretreated at 200 °C

Product	Yield (%)	Selectivity (%)
trans-decaline	14	82
cis-decaline	3	18



Scheme 5. Intermediate for the reaction of cyclodecane into decaline.

30 species, were observed. The analysis of GCMS indicated the reaction processes of isomerization, dehydrogenation and cracking.

In the superacid-catalyzed isomerization of alkanes, sulfated zirconia is examined in the reactions of cyclic alkanes greater than cycloheptane because of the possibility in the cracking processes for open-chain alkanes greater than heptane. (1) The reaction results of cycloheptane and cyclooctane indicate the monomolecular process with preservation of the cyclic structure without forming isobutane through protonated cyclopropane and cyclobutane intermediates, respectively. (2) The cyclic structure has a large effect on the reaction; no isomerization is observed with cyclodecane, converting into decalines by dehydrogenation, and cyclododecane is converted into the products, more than 30 species, by rearrangement, dehydrogenation and cracking.

References

[1] J. Sommer, R. Jost and M. Hachoumy, Catal. Today 38 (1997) 309.

[2] X. Song and A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.

[3] H. Matsuhashi, H. Shibata, H. Nakamura and K. Arata, Appl. Catal., A: Gen. 187 (1999) 99.

[4] D. Farcasiu, J.Q. Li and A. Kogelbauer, J. Mol. Catal., A: Chem. 124 (1997) 67.

[5] D. Farcasiu and J.Q. Li, Appl. Catal., A: Gen. 175 (1998) 1.

[6] F. Figueras, B. Coq, C. Walter and J.-Y. Carriat, J. Catal. 169 (1997) 103.

[7] A. Sassi and J. Sommer, Appl. Catal., A: Gen. 188 (1999) 155.

[8] T. Tatsumi, H. Matsuhashi and K. Arata, Bull. Chem. Soc. Jpn. 69 (1996) 1191.

[9] K. Satoh, H. Matsuhashi and K. Arata, Appl. Catal., A: Gen. 189 (1999) 35.

[10] K. Arata, Adv. Catal. 37 (1990) 165.

[11] L. Radom, J.A. Pople, V. Buss and P.V.R. Schleyer, J. Am. Chem. Soc. 94 (1972) 311.

[12] H.Y. Chu, M.P. Rosynek and J.H. Lunsford, J. Catal. 178 (1998) 352.