Catalysis Letters 63 (1999) 185–188

Promotive effect of isopentane on cyclohexane isomerization catalyzed by sulfated zirconia

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Received 25 May 1999; accepted 22 September 1999

Cyclohexane isomerization to methylcyclopentane over sulfated zirconia is markedly enhanced in the presence of isopentane which acts as a hydride transfer agent to facilitate the slow step of hydride transfer from cyclohexane to isopropyl cation. This was revealed by deuterium tracer studies.

Keywords: sulfated zirconia, cyclohexane isomerization, effect of solvent

1. Introduction

Hydride transfer is important in acid-catalyzed reactions proceeding by carbenium ion mechanisms. In liquid superacidic media, solvents of high hydride transfer ability accelerate acid-catalyzed reactions with great efficiency [1,2]. However, there have been few reports on the effects of hydride transfer agents on skeletal isomerization of alkanes over solid acid catalysts. The only reported example has been for heptane isomerization over sulfated zirconia catalyst where addition of adamantane markedly increases the rate of isomerization [3,4].

We wish to report in this communication the effects of hydride transfer agents on the rate of cyclohexane isomerization to methylcyclopentane, as determined by a kinetic measurement combined with a tracer study in which deuterium was used to locate the number and position of D (or H) incorporated in the products and reactant.

2. Experimental

2.1. Catalyst preparation

Sulfated zirconia was prepared by soaking zirconium hydroxide with 1 N sulfuric acid, followed by drying and then, finally, calcining at 550 °C for 3 h in air. The zirconium hydroxide was prepared by hydrolysis of zirconium oxide chloride with aqueous ammonia at pH 7.90. The preparation method has been described in more detail elsewhere [5].

2.2. Reaction procedures

The isomerization of cyclohexane (Wako Chemical, Inc., $>99\%$) to methylcyclopentane was carried out in a stainless-steel autoclave (150 ml) at 100 or 250 °C under hydrogen pressure (1.8–5.5 MPa). Pentanes (isopentane, n-pentane, and neopentane) were $>99\%$ pure. These reagents were dried with molecular sieves 3 Å $1/8$ (Wako Chemical, Inc.) before use. The sulfated zirconia (diameter: 355–600 μm, surface area: 157 m^2/g) was pre-treated at 350 °C for 20 min under vacuum before reaction. Pretreated sulfated zirconia (0.5–1.0 g) in cyclohexane (1.5–3.0 g) together with one of the pentanes (5.5–11.0 g) were placed in the cooled autoclave. The reaction mixture under hydrogen pressure (1.8–3.6 MPa) was heated to either 100 or 250 °C at 3.5–4.0 °C/min and held at these temperatures under autogenous pressure. The reaction temperatures were held at 100 °C for 15 min or held at 250 °C for 60 min. After the reaction, the contents of the autoclave were separated from the solid catalyst by pressure through a 0.2 μm pore size filter. d_{12}-cyclohexane (Isotec, Inc., 99.6%) was also used for the isomerization reaction under N_2 pressure.

2.3. Characterization of products

The products were analyzed using a gas chromatograph (HP 5890). Products with ^{13}C-labeled content were analyzed with an HP 5971A gas chromatograph/mass spectrometer to measure the H/D exchange and a ^{1}H-NMR (Jeol Lambda 500 NMR) was used to measure the H/D distribution (in $CDCl_3$ solvents, using tetramethylsilane as an internal standard).

3. Results

3.1. Cyclohexane isomerization with sulfated zirconia

Percent conversions of cyclohexane (d_0-cyclohexane) in reaction times of 60 min at 250 °C and 15 min at 100 °C

Table 1
Isomerization conversion of cyclohexane in various solvents at 250 or 100 °C.[a]

	Conversion (%)	
	250 °C	100 °C
Isopentane	46 (41)[b]	3.9
n-pentane	28	1.1
Neopentane	0	0
None	32	2.4

[a] Cyclohexane/pentanes = 35.7 mmol/149 mmol/g-catalyst, H_2 (initial pressure) = 3.5 MPa. Reaction times: 250 °C, 60 min and 100 °C, 15 min.

[b] d_{12}-cyclohexane, N_2 (initial pressure) = 3.5 MPa.

with different pentanes are given in table 1. Compared to the reaction without addition of pentanes, the conversion was greatly accelerated in the reaction with isopentane, while the conversion was suppressed in the reaction with n-pentane. No reaction was observable in the reaction with neopentane. The conversion percentages of d_{12}-cyclohexane at 100 °C for 15 min with different pentanes were in the same order as those obtained by cyclohexane at a reaction temperature of 250 °C for 60 min.

3.2. d_{12}-cyclohexane isomerization

Conversion percentages of d_{12}-cyclohexane in a reaction time of 15 min at 100 °C, and the isotopic distributions in cyclohexane, isopentane, n-pentane and neopentane for the reactions of d_{12}-cyclohexane with d_0-pentanes are given in table 2. Note that H/D exchange took place between d_{12}-cyclohexane and pentanes even at 100 °C, except for neopentane. The level of H/D exchange of pentanes was correlated with isomerization conversion. The extent of D atoms exchanged into pentanes was higher for isopentane than for n-pentane. During the reaction, 0.4% of the n-pentane was isomerized to isopentane and the level of H/D exchange of the produced isopentane was 12.0%, which was higher than the 5.2% of n-pentane. However, essentially no D atoms were incorporated in neopentane. The number of D atoms incorporated into an isopentane molecule was mostly 1. The content of H atoms in methylcyclopentane was the largest when d_{12}-cyclohexane was reacted with isopentane, and the number of H atoms incorporated into a methylcyclopentane molecule was mostly 1 or 2. The number of H atoms incorporated into cyclohexane molecules was much lower than that of methylcyclopentane. By ^{1}H-NMR, we determined that tertiary deuterium in the produced methylcyclopentane was exchanged with about 77% of the tertiary H atoms incorporated into methylcyclopentane. The percentage of methylcyclopentane incorporating 2 or 3 H atoms in the reaction with n-pentane was comparatively higher than those of the reaction with isopentane.

3.3. ^{1}H-NMR characterization

Isotopic distributions in methylcyclopentane for the reaction of d_0-methylcyclopentane with d_{10}-isopentane are given in table 3. One H atom in d_0-methylcyclopentane rapidly exchanged with one D atom in d_{10}-isopentane. The H (or D) atom was a tertiary H (or D) atom in both methylcyclopentane and isopentane, as confirmed by ^{1}H-NMR.

4. Discussion

Cyclohexane undergoes skeletal isomerization to methylcyclohexane via a cyclohexyl cation and methylcyclopentyl cation, as illustrated in scheme 1 [6]. Although a controversy exists about the formation of the cyclohexyl cation at the beginning of the reaction (pentacoordinated carbonium ion followed by dehydrogenation vs. dehydrogenation followed by protonation), it is generally accepted that two

Table 2
d_{12}-cyclohexane isomerization with d_0-pentanes over sulfated zirconia.[a]

		H$^-$ transfer agent		
		Isopentane	n-pentane	Neopentane
Conversion (%)		3.9	1.1	0
Isotopic distribution				
Pentane	d_0	87.8	94.8 (88.0)[b]	100
	d_1	12.2	5.2 (12.0)[b]	0
	d_2–d_{10}	0	0	0
Methylcyclopentane	d_{12}	7.0	23.8	–
	d_{11}	73.1	45.4	–
	d_{10}	17.5	22.0	–
	d_9	0.8	8.8	–
	d_8	1.7	0	–
	d_7–d_0	0	0	–
Cyclohexane	d_{12}	89.2	98.2	100
	d_{11}	10.8	1.8	0
	d_{10}–d_0	0	0	0

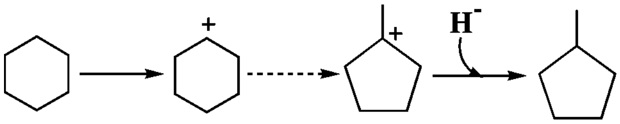
[a] Methylcyclopentane/d-isopentane = 17.5 mmol/73 mmol/0.5 g-catalyst, N_2 (initial pressure) = 3.5 MPa, reaction temperature = 100 °C, reaction time = 15 min.

[b] In parentheses: the level of H/D exchange of isopentane produced from n-pentane during reaction. Its isomerization conversion was 0.4%.

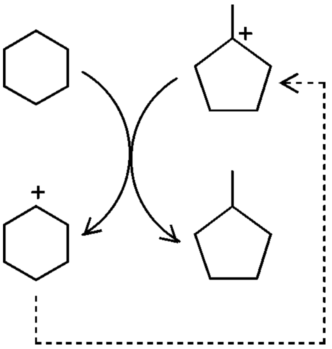
Table 3
H/D exchange between d_0-methylcyclopentane and d_{10}-isopentane over sulfated zirconia.[a]

Methylcyclopentane	d_0	23.9
	d_1	76.1
	d_2	0

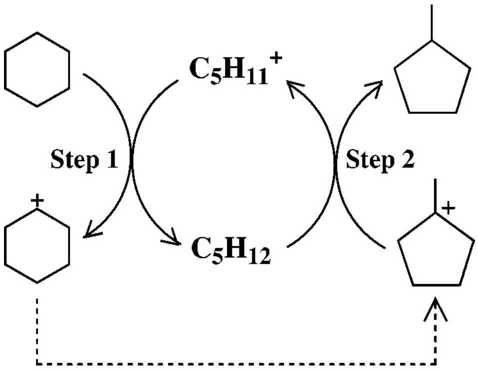
[a] Methylcyclopentane/d-isopentane = 17.5 mmol/73 mmol/0.5 g-catalyst, N_2 (initial pressure) = 3.5 MPa, reaction temperature = 100 °C, reaction time = 15 min.



Scheme 1.



Scheme 2.



Scheme 3.

hydride (H^-) transfer steps are involved in the catalytic isomerization of cyclohexane: H^- transfer to a methylcyclopentyl cation to yield methylcyclopentane and from cyclohexane to form a cyclohexyl cation [7]. The methylcyclopentyl cation as an intermediate must obtain a hydride ion from its surroundings to stabilize. The hydride ion donating abilities of isopentane, n-pentane and neopentane decrease in this order because their heterolytic bond dissociation energies are 968.2, 1021.7 and 1101.6 kJ/mol, respectively. The dissociation energies were calculated from the enthalpies of formation of their cations by releasing hydride ions [8].

In the absence of an H^- transfer agent other than the reactant, the reactant plays the role of H^- transfer, as illustrated in scheme 2. Cyclohexane acts as a hydride source agent as well as the reactant. The cyclohexyl cation is a secondary carbenium ion like n-pentane, and is thus capable of giving a hydride to the methylcyclopentyl cation. The resulting cyclohexyl cation after hydride transfer would rearrange to become a methylcyclopentyl cation.

In the presence of an H^- transfer agent other than the reactant, for example pentane, the H^- transfer agent acts as shown in scheme 3. The promotive effect of isopentane on the rate of cyclohexane isomerization would be caused by the contribution of H^- transfer involving isopentane, as shown in scheme 3. The H/D exchange between methylcyclopentane and isopentane presumably proceeds via the forward and reverse reactions of step 2 in scheme 3. Rapid H/D exchange between d_0-methylcyclopentane and d_{10}-isopentane suggests that both the forward and reverse reactions of step 2 are fast, indicating that the H^- transfer from isopentane to methylcyclopentane is not a rate-limiting step. On the other hand, incorporation of H atoms into cyclohexane in the reaction of d_{12}-cyclohexane with d_0-isopentane, which would have occurred via the forward and reverse reactions of step 1 in scheme 3, is slow. Since the slowest step in the mechanisms leading to the product is the reverse reaction of the rate-determining step, it is suggested that the forward reaction is the rate-determining step.

Now it becomes clear that the promotive effect of isopentane on the rate of cyclohexane isomerization is caused by the high ability of isopentane for hydride transfer as compared to that of cyclohexane. Isopentane donates hydrides to methylcyclopentyl cations forming a high concentration of isopentyl cations accompanied by the formation of the isomerized product of methylcyclopentane. The isopentyl cation abstracts a hydride from cyclohexane (scheme 3, step 1) to form isopentane accompanied by the formation of a cyclohexyl cation, which is an intermediate of the isomerization. This is a slow step in the isomerization. Facilitating this step results in the promotive effect.

We attribute the suppressive effect of n-pentane to its low ability of hydride transfer compared to that of cyclohexane, as well as its retarding of hydride transfer from cyclohexane to methylcyclopentyl cations by dilution of cyclohexane. During the reaction, 0.4% of n-pentane was isomerized to isopentane, and the level of H/D exchange of the produced isopentane was higher than that of n-pentane. This result indicated that sulfated zirconia contributed to promotion of cyclohexane isomerization by the isomerization from n-pentane to isopentane as well as by abstraction of hydride from cyclohexane mainly in the initial reaction stage, as previously described. In contrast, neopentane was not isomerized to isopentane or n-pentane, and no H/D exchange was observed. Consequently, the reason for complete retardation of cyclohexane isomerization in the presence of neopentane can probably be ascribed to the difficulty of isomerizing neopentane and it having the lowest hydride donor ability.

5. Conclusion

Cyclohexane isomerization to methylcyclopentane over sulfated zirconia is markedly enhanced in the presence of the solvent isopentane. As revealed by deuterium tracer studies, isopentane acts not only as a hydride transfer agent to facilitate the slow step of hydride transfer from cyclohexane to isopropyl cations, but also as a co-catalyst. Compared to the reaction without addition of pentanes, the conversion was greatly increased in the reaction with isopentane, while the conversion was suppressed in the reaction with n-pentane. No reaction was observable in the reaction with neopentane.

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