Deuterium Tracer Study on Isomerization of Cyclopropane over Thorium Sulfate

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Mechanistic study on the isomerization of cyclopropane into propene was made over $Th(SO_4)_2$ catalyst. With a fresh catalyst, an induction period was observed, disappearing in successive runs. Coisomerization of cyclopropane d_0/d_6 reveals that the reaction involves an intermolecular H(or D) transfer. Nearly random location of the H(or D) atom in the mono-exchanged propene-d_1, and -d_5 indicates that the isomerization proceeds *via* nonclassical carbonium ion in which seven hydrogen atoms are equivalent.

The isomerization of cyclopropane to propene is catalyzed by acidic oxides[1] and crystalline zeolites.[2] Deuterium tracer studies have been made over silica–alumina[3,4] and sodium Y zeolite.[5] On the basis of deuterium distributions in the reactant and product together with the kinetic data over silica–alumina, Hightower and Hall presented the non-classical carbonium ion of cyclopropane as an intermediate in which seven hydrogen atoms are equivalent.[3,4] Bartley *et al.* proposed a different type of nonclassical carbonium ion intermediate in which the hydrogen atom added is not equivalent to the original six hydrogen atoms.[5] They suggested that an intramolecular hydrogen transfer occurs after the ring of the nonclassical carbonium ion is opened, since the reaction partly involves an intramolecular hydrogen transfer.

However, the above discussions are based primarily on the deuterium contents of the reactant and product. The location of deuterium and hydrogen atoms in propene would provide important information as to whether the hydrogen atom added in the intermediate is equivalent to the original hydrogen atoms.

The present study was undertaken to elucidate the intermediate of the isomerization of cyclopropane over an acidic catalyst, thorium sulfate, by deuterium tracer studies. The locations of hydrogen and deuterium atoms in propene were determined by microwave spectroscopy.[6]

Experimental

Catalyst and Reactants. Thorium sulfate was obtained by heating its hydrated form (Wako Pure Chemical Ind., Ltd.) at 500 °C for 3 h in air. Prior to reaction, the catalyst was pretreated with O_2 at 500 °C followed by evacuation at 500 °C for more than 3 h. The BET surface area was 5 m^2/g.

Cyclopropane of 99.8% purity was supplied by Tokyo Kasei Ind., Ltd. Perdeuteriocyclopropane was prepared by repeated exchange reactions of cyclopropane with D_2 over aluminum oxide (Nishio AE 11) at 100 °C.[7] The isotopic purity was higher than 98.0%. The reactants were purified by passage through 4A molecular sieves at −94 °C.

Apparatus and Procedure. A 47 Torr of cyclopropane was allowed to react over 0.1—1 g of catalyst at 80—200 °C in *ca.* 400 ml of a recirculation reactor. The products were separated by gas chromatographic column of VZ-7 (5 m), collected in a liquid N_2 trap, and subjected to mass and microwave spectroscopic analyses in order to determine the deuterium content and the location of deuterium atoms in the product, respectively.

Results and Discussion

Cyclopropane underwent isomerization at 80 °C to yield only propene over a freshly pretreated catalyst with an induction time of 20 min. In the subsequent experiment carried out after brief evacuation at the reaction temperature, isomerization occurred without the induction time, a decrease in rate to some extent being observed (Fig. 1). The isomerization rate was of zero order in cyclopropane. The induction time was prolonged with lowering of reaction temperature. This indicates that the active sites are formed by the interaction of the substrate with a freshly pretreated surface. As observed for the other solid acid catalysts,[3,4] it is suggested that the active sites on $Th(SO_4)_2$ are polymeric residues which supply the protons to act as the Brönsted acid sites.

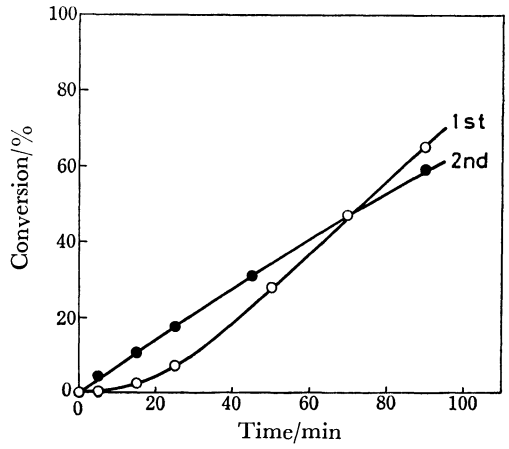


Fig. 1. The time courses of the isomerization of cyclopropane over $Th(SO_4)_2$ at 80 °C in the initial run (○) and in the successive run (●).

Coisomerization experiments were carried out at 100 °C and 200 °C with a mixture containing equal amounts of nondeuterio and perdeuteriocyclopropanes. Isotopic distributions at the two reaction temperatures were similar, those at 100 °C being given in Table 1. The product consisted primarily of non-exchanged isotopic species, d_0 and d_6, and mono-exchanged isotopic species, d_1 and d_5. The numbers of hydrogen atoms

Table 1. Coisomerization of cyclopropane-d_0 and -d_6 over thorium sulfate[a)]

Reaction time, h	Product	% each product	% isotopic species d_0	d_1	d_2	d_3	d_4	d_5	d_5	Atoms exchanged/ molecule[b)]	Ratio of light molecule/ heavy molecule[c)]
0.00	Cyclopropane	100.0	49.5	0	0	0	0	0.9	49.6	0.009	0.980
0.33	Propene	0.7	35.6	14.0	0	0	0	21.3	29.1	0.353	0.984
	Cyclopropane	99.3	50.8	0	0	0	0	1.0	48.2	0.010	1.033
1.00	Propene	2.9	26.7	15.7	0	0	0.5	23.7	33.4	0.404	0.736
	Cyclopropane	97.1	49.5	0	0	0	0	1.3	49.2	0.013	0.980
2.00	Propene	7.7	26.2	17.1	0.3	0	0.7	23.3	32.4	0.424	0.773
	Cyclopropane	92.3	47.6	1.2	0	0	0	1.9	49.3	0.031	0.953
3.00	Propene	12.2	24.5	16.9	0.6	0	0.9	24.0	33.1	0.439	0.724
	Cyclopropane	87.8	48.2	2.1	0	0	0	2.7	47.0	0.048	1.012
6.00	Propene	24.6	22.2	16.9	1.2	0	1.6	25.0	33.1	0.475	0.675
	Cyclopropane	75.4	46.3	5.0	0	0	0	4.5	44.2	0.095	1.053

a) 45.4 Torr of cyclopropane, 100 °C, 150.7 mg of catalyst. b) Calculated from $\sum_{i=0}^{2} i \cdot N_i + \sum_{i=3}^{6} (6-i) \cdot N_i$, N_i; mole fraction of isotopic species containing i deuterium atoms.[3)] c) Calculated from $(\sum_{i=0}^{2} N_i + N_3/2)/(\sum_{i=4}^{6} N_i + N_3/2)$[3)]

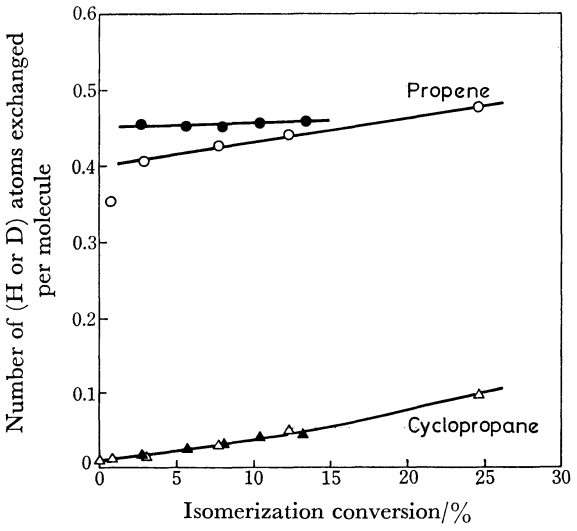


Fig. 2. Exchange concentration curves for coisomerization of cyclopropane-d_0 and -d_6 over $Th(SO_4)_2$. Open symbol: 100 °C, solid symbol: 200 °C.

exchanged per molecule at 100 °C and 200 °C are plotted against conversion in Fig. 2. Hydrogen atoms were exchanged into the unisomerized cyclopropane as well as the product. The superposition of the exchanged concentration curves for cyclopropane at the different reaction temperatures indicates that the activation energy for the exchange process is close to that for isomerization. A similar slope of the curves for cyclopropane and propene indicates that there is little further intermolecular scrambling of hydrogen atom among the propene molecules produced; this is consistent with the limitation of hydrogen exchange mainly to the mono-exchanged isotopic species. The zero conversion intercept of nearly 0.5 for propene demonstrates that one hydrogen atom per molecule is transferred intermolecularly during the course of isomerization.

If the reaction proceeds *via* classical carbonium ions in which no intramolecular hydrogen exchange occurs, the hydrogen atom added would be always left in the product molecule and the original hydrogen atom would be lost on the surface. The intercept for the exchange concentration curve for the product in the coisomerization experiment is expected to be 1/2. On the other hand, if the proton attacks the cyclopropane molecule to form a protonated nonclassical carbonium ion in which seven hydrogen atoms are equivalent, the hydrogen atom added has the same probability of being lost as the original hydrogen atoms when the reaction is completed. As a result, the intercept of the exchange concentration curve will be 6/14. The observed values of 0.45 and 0.40 at 200 °C and 100 °C, respectively, are close to 6/14. The ratio of light molecule (d_0-d_2) to heavy molecule (d_4-d_6) is plotted against conversion in Fig. 3. The zero conversion intercept divided by the initial ratio of light molecule to heavy molecule of reactant gives a kinetic isotope effect. The isotope effect was small or slightly inverse.

The locations of the deuterium atom in propene-d_1

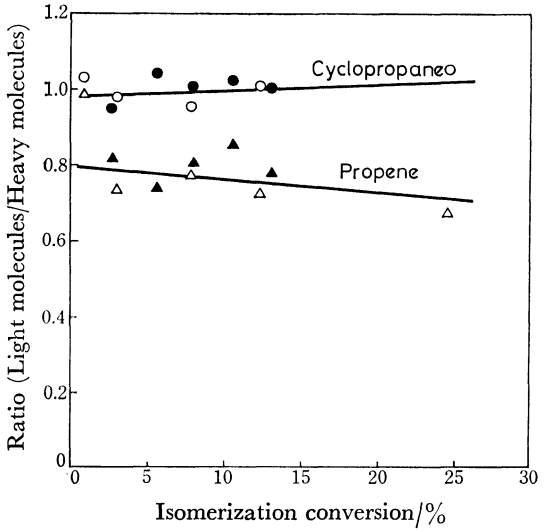
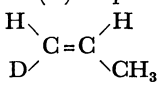
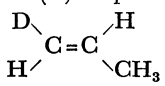
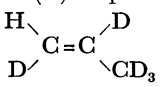
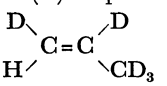


Fig. 3. The ratios of "light molecules" to "heavy molecules" with the conversion in the coisomerization of cyclopropane-d_0 and -d_6 over $Th(SO_4)_2$. Open symbol: 100 °C, solid symbol: 200 °C.

TABLE 2. MASS SPECTROMETRIC AND MICROWAVE SPECTROSCOPIC ANALYSES OF PRODUCTS FORMED IN THE COISOMERIZATION OF CYCLOPROPANE-d_0 AND -d_6 AT 100 °C

	Product	% each isotopic species						
		d_0	d_1	d_2	d_3	d_4	d_5	d_6
3.9% conversion	Propene	28.4	17.2	0.1	0	0.5	22.9	30.9
	Cyclopropane	50.0	0.2	0	0	0	1.1	48.7
	Location of D in propene-d_1	%		Location of H in propene-d_5			%	Random distribution %
	(Z)-1-d_1 a)	14.4		(Z)-1-h_1 a)			—	33.3
	(E)-1-d_1 a)	13.8		(E)-1-h_1 a)			—	
	2-d_1	13.0		2-h_1			—	16.7
	3-d_1	58.8		3-h_1			—	50.0
	Product	% each isotopic species						
		d_0	d_1	d_2	d_3	d_4	d_5	d_6
21.2% conversion	Propene	24.4	17.7	1.1	0	1.4	23.3	32.1
	Cyclopropane	47.9	3.3	0	0	0	3.3	45.5
	Location of D in propene-d_1	%		Location of H in propene-d_5			%	Random distribution %
	(Z)-1-d_1 a)	14.7		(Z)-1-h_1 a)			15.9	33.3
	(E)-1-d_1 a)	15.6		(E)-1-h_1 a)			19.1	
	2-d_1	11.8		2-h_1			9.2	16.7
	3-d_1	57.9		3-h_1			55.8	50

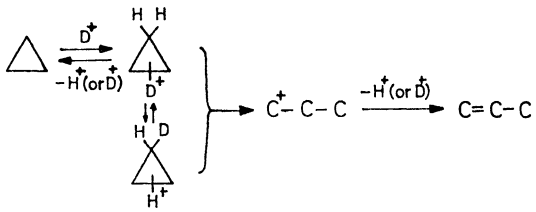
a); (Z)-1-d_1  (E)-1-d_1  (Z)-1-h_1  (E)-1-h_1 

and of the hydrogen atom in propene-d_5 produced in the coisomerization are given in Table 2. The deterium or hydrogen atom was distributed throughout almost all positions instead of being localized at a certain carbon atom. This strongly suggests that the reaction proceeds *via* the nonclassical carbonium ion in which seven hydrogen atoms are equivalent.

If the reaction proceeded *via* classical carbonium ion, the distribution of hydrogen and deuterium atoms might be as follows. 1) A fast intramolecular H transfer occurs after the ring is opened. 2) An intermolecular hydrogen exchange occurs among the propene molecules produced. However, case 1) can be eliminated since the hydrogen transfer should involve the conversion of a stable secondary propyl cation into an unstable primary propyl cation, while in case 2), an extensive hydrogen scrambling among the products should proceed, which was not observed.

Thus, the reaction mechanism is suggested to be as follows: the nonclassical carbonium ion (protonated cyclopropane) is formed by the interaction of cyclopropane with a proton supplied by the surface residue followed by the opening of the ring to yield propene *via* primary propyl cation. The same intermediate, which discharges a proton to the surface and returns to the gas phase without the ring being opened, accounts for the incorporation of hydrogen or deuterium atoms into unisomerized cyclopropane.

This mechanism has been proposed for the reaction over silica–alumina[3,4] without determination of the location of hydrogen or deuterium atom in the product. By analysis of the position of deuterium and hydrogen



atoms in the product by microwave spectroscopy, the proposed mechanism became more plausible.

Neither kinetic isotope effect nor slightly reverse isotope effect appeared for the formation of propene. The cleavage of C–H bond should be fast. The slow step involves either the protonation to cyclopropane or the C–C bond cleavage of the protonated cyclopropane. Since, in both cases, the exchange concentration curves for cyclopropane at different temperatures are on the same line, the energy barriers to cyclopropane and to primary propyl cation from the nonclassical carbonium ion are similar.

References

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