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Tracer Study of Conversion of Alkanes Catalyzed by Solid Super Acid

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Coisomerization of pentane-d_0/d_{12}, 2-methylbutane-d_0/d_{12}, 2-methylpropane-d_0/d_{10}, and cyclohexane-d_0/d_{12} were carried out to study the reaction mechanisms over the solid super acid, SbF_5–SiO_2–Al_2O_3. The methyne H atom of 2-methylbutane was rapidly exchanged among the molecules. 2-Methylpropane extensively exchanged all H atoms among the molecules before yielding 2-methylbutane. For all skeletal isomerizations, an intramolecular H (or D) transfer was involved in the rearrangements of the carbon skeletons. It is suggested that all the reactions proceeded by carbenium ion mechanisms in which the reactions were initiated by abstraction of an H^- from the reactants.

INTRODUCTION

In the preceding papers (*1*), we reported the preparation of solid super acids and their catalytic nature for alkane reactions. Metal oxides treated with SbF_5 exhibited the super acidic character in the sense that skeletal isomerization of alkanes easily occurred at room temperature. Distinct differences were observed between solid and liquid super acid. With liquid super acids, the reactions of alkanes are initiated by the protonation of alkanes to form carbonium ions, followed by production of carbenium ions and hydrogen and/or smaller alkanes (*2–4*). On the other hand, with solid super acids, the reactions of alkanes which possess a secondary or a tertiary C–H bond can proceed, and it was assumed that the reactions are initiated by abstraction of an H^- from the reactants by Lewis acid sites on the surface to form carbenium ion directly. However, the reaction mechanisms over solid super acids were not investigated in detail.

In this paper, the reaction mechanisms over solid super acid were investigated by a tracer study using D atom as a tracer. A coisomerization method of nondeutero- and perdeutero-reactants has been developed by Hightower and Hall (*5–6*) for butene isomerization. Since this method is quite useful for a study of the reaction mechanisms, we applied this method to the reactions of alkanes over solid super acid.

EXPERIMENTAL METHODS

Catalyst. The catalyst used in the tracer study was SbF_5–SiO_2–Al_2O_3 (II). The preparation of the catalyst is described in the preceding paper (*1*). However, the treatment with SbF_5 was performed at 0°C both for adsorption and for evacuation.

Preparation of perdeuterio-compounds. For preparation of perdeutero-2-methylpropane, first, butene was repeatedly exchanged with D_2 over the MgO catalyst that had been outgassed at 600°C, and then deuterated at 200°C over the MgO catalyst that had been outgassed at 700°C. The resulting perdeutero-butane was isomerized at room temperature over the SbF_5–SiO_2–Al_2O_3 catalyst. Perdeutero-pentane was prepared by repeated exchange of pentane with D_2 over Al_2O_3 catalyst at 200°C. For preparation of perdeutero-2-methylbutane, 2-methyl-1,3-butadiene was deuterated and exchanged with D_2. The perdeutero-2-methylbutenes produced were deuterated at room temperature over Ni/SiO_2 catalyst. All perdeutero-com-

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pounds were separated from other products by a preparative gas chromatographic column. Perdeutero-cyclohexane was obtained from Merck, Sharp and Dohme, Canada, Ltd.

Those compounds were purified by the freeze–thaw method, followed by passage through 4A or 5A molecular sieves.

Reaction procedure. A closed recirculation reactor having a volume of 324 ml was employed for all reactions. In most experiments, coisomerization was used. A mixture containing equal amounts of nondeutero and perdeutero compounds was allowed to react. Reaction products were periodically withdrawn from the reaction system and separated by a gas chromatographic column. Each product was collected in a liquid nitrogen trap and subjected to mass spectrometric analysis. Corrections were made for fragmentation and naturally occurring carbon-13.

RESULTS

The time dependence of composition for the coisomerization of pentane-d_0/d_{12} is shown in Fig. 1. Isotopic distribution of the products at different reaction times is given in Table 1. At low conversion, 2-methylbutane consisted of about equal amounts of monoexchanged isotopic species, d_1 and d_{11}, and nonexchanged ones, d_0 and d_{12}. Hydrogen scrambling in pentane and 2-

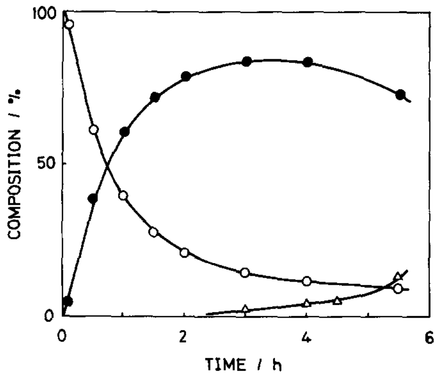


FIG. 1. Time dependence of composition in the coisomerization of pentane-d_0/d_{12} at 0°C. Catalyst, 0.2 g, initial pressure 36.8 Torr; ○, pentane; ●, 2-methylbutane; △, 2-methylpropane.

TABLE 1

Coisomerization of Pentane-d_0/d_{12} at 0°C[a]

Time (min)	0	5		90		
Product	C_5	C_5	2-MB[b]	C_5	2-MB	2-MP[c]
(%)	100	95.4	4.5	27.4	72.1	0.4
Isotopic distribution (%)						
d_0	51.0	49.3	27.4	15.0	14.4	75.0
d_1		1.1	19.0	14.2	22.9	8.6
d_2			3.1	6.1	13.1	2.1
d_3			0.8	1.4	4.1	5.7
d_4					0.6	5.0
d_5						3.6
d_6						
d_7						
d_8				0.1	1.1	
d_9				2.6	6.9	
d_{10}			9.7	9.3	11.2	
d_{11}	6.9	8.0	23.9	23.4	17.6	—
d_{12}	42.1	41.5	16.1	28.0	8.1	—

[a] Catalyst, 0.2 g, initial pressure 36.8 Torr.
[b] 2-Methylbutane.
[c] 2-Methylpropane.

TABLE 2

Coisomerization of 2-Methylbutane-d_0/d_{12} at 0°C[a]

Time (min)	0	5	30		60	
Product	2-MB	2-MB	2-MB	C_5	2-MB	C_5
(%)	100	99.7	95.2	4.7	92.4	7.3
Isotopic distribution (%)						
d_0	49.5	19.4	18.0	24.7	9.5	15.3
d_1		19.4	22.0	19.1	18.3	18.6
d_2		3.3	16.1	7.7	12.7	11.7
d_3			1.0	2.0	4.3	4.5
d_4				0.5		0.8
d_5						0.5
d_6						
d_7						0.5
d_8				0.4		1.1
d_9			2.2	1.7	4.2	4.3
d_{10}		10.7	9.2	7.3	17.8	11.3
d_{11}	5.1	24.8	18.6	20.0	21.5	16.5
d_{12}	45.3	25.7	13.6	19.5	11.6	14.9

[a] Catalyst 0.2 g, initial pressure, 24.5 Torr.

methylbutane gradually extended as the reaction proceeded. The ratio of "light molecules" to "heavy molecules" of 2-methylbutane was close to 1. As the ratio represents the isotope effect when extrapolated to zero conversion, the isotope effect for the isomerization was small.

The isotopic distribution of 2-methylpropane was quite different from those of pentane and 2-methylbutane. In 90 min, when 0.4% of 2-methylpropane was produced, the 2-methylpropane consisted only of the isotopic species containing 0 ~ 5 D atoms and no isotopic species containing more than six D atoms were produced. In 180 min, small amounts of d_9 and d_{10} species were produced, and maxima were observed at d_0, d_3, and d_6 isotopic species.

The isotopic distributions of the products in the coisomerization of 2-methylbutane-d_0/d_{12} are given in Table 2. In 5 min, almost equal amounts of nonexchanged and monoexchanged isotopic species were observed in the reactant. The isotopic distribution of pentane produced was similar to that of 2-methylbutane.

In Table 3, the isotopic distributions in two successive runs are given. In the first run, perdeutero-pentane was used as a reactant. In 120 min, the reaction system

TABLE 3

Reaction of Perdeuteropentane in the First Run and Reaction of 2-Methylbutane in the Subsequent Run at 0°C[a]

Time (min)	0	30		120	
Product	C_5	C_5	2-MB	C_5	2-MB
(%)	100	56.3	43.6	15.1	84.4
d_{12}	85.9	87.3	82.9	86.7	85.4
d_{11}	14.1	12.7	17.1	13.3	14.6
d_{10}					

Time (min)	0	30		120		
Product	2-MB	2-MB	C_5	2-MB	C_5	2-MP
(%)	100	94.7	4.7	87.4	8.4	2.8
d_0	100	97.4	96.7	89.6	89.5	80.8
d_1		2.6	3.3	9.0	9.2	11.4
d_2				1.4	1.3	5.5
d_3						1.9
d_4						0.3

[a] Catalyst 0.2 g, initial pressure of C_5–d_{12}, 22.5 Torr; 2-MB-d_0, 21.5 Torr.

TABLE 4

Coisomerization of 2-Methylpropane-d_0/d_{10} at 0°C[a]

Time (min)	0	150	
Product (%)	2-MP 100	2-MP 99.35	2-MB 0.65
Isotopic distribution (%)			
d_0	52.2	1.6	9.2
d_1		3.6	10.9
d_2		8.2	3.5
d_3		13.5	3.3
d_4		17.5	6.5
d_5		20.5	6.5
d_6		17.3	8.7
d_7		9.9	7.6
d_8	2.2	4.8	3.7
d_9	14.6	2.2	3.9
d_{10}	31.1	1.0	4.4
d_{11}	—	—	17.0
d_{12}	—	—	14.8

[a] Catalyst 0.48 g, initial pressure 19 Torr.

was evacuated for 10 min at 0°C, and the second run was performed, in which nondeutero-2-methylbutane was used as a reactant. In the first run, substantially no H atoms were incorporated into either pentane or 2-methylbutane. In the second run, considerable amounts of D atoms were incorporated into 2-methylbutane, pentane, and 2-methylpropane.

The isotopic distributions of the products in the reaction of 2-methylpropane-d_0/d_{10} are given in Table 4. Extensive scrambling of H atoms in 2-methylpropane was observed even at the low conversion level of 0.65%. For 2-methylbutane, a rather flat isotopic distribution with small maxima at d_1, d_6, and d_{11} was obtained.

The isotopic distributions in the coisomerization of cyclohexane-d_0/d_{12} are given in Table 5. The isotopic distributions of cyclohexane and methylcyclopentane were similar at any conversion levels, and methylcyclopentane consisted substantially of nonexchanged isotopic species, d_0 and d_{12}, at low conversion levels. These demonstrate that the isomerization of cyclohexane to methylcyclopentane involves an intramolecular H(or D) transfer. Scrambling of H atoms in both the reactant and the product extended as the reaction proceeded.

TABLE 5

Coisomerization of Cyclohexane-d_0/d_{12} at 0°C[a]

Time (min)	0	2		5		10	
Product (%)	CH[b] 100	CH 99.3	MCP[c] 0.7	CH 97.6	MCP 2.4	CH 96.0	MCP 4.0
Isotopic distribution (%)							
d_0	47.2	41.1	53.6	30.8	35.7	22.9	14.8
d_1		6.1	3.9	9.4	8.6	11.4	15.8
d_2		2.0		4.5	3.5	6.8	11.0
d_3		1.1		2.5	2.1	4.2	7.2
d_4				1.4	1.0	2.5	4.1
d_5				0.9	1.0	1.6	2.5
d_6				0.7	0.8	1.4	1.9
d_7				0.8	1.0	1.5	2.5
d_8				1.6	1.2	2.5	3.6
d_9		1.0		2.4	1.8	4.0	5.8
d_{10}		1.2		4.0	2.5	6.3	8.6
d_{11}	3.6	6.8	3.7	9.8	7.2	11.5	11.5
d_{12}	49.2	40.7	38.8	31.1	33.3	23.3	10.6

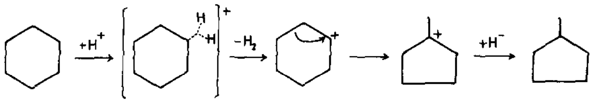
[a] Catalyst 0.2 g, initial pressure 29.5 Torr.

[b] Cyclohexane.

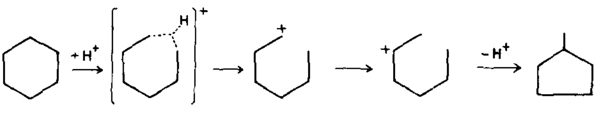
[c] Methylcyclopentane.

DISCUSSION

In the isomerization of cyclohexane to methylcyclopentane, neither an intermolecular H transfer nor an intermolecular CH_3 transfer was involved. If the reaction were initiated by addition of an H^+ to the reactant, the following reaction schemes could be drawn.



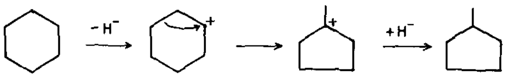
SCHEME I



SCHEME II

The H^- ion that attacks in the last step in Scheme I is considered to originate from another molecule. The H^+ ion that is added in the first step in Scheme II could not be distinguished from other H atoms attached to the same carbon atom. An intermolecular H transfer would be observed if the reaction were initiated by the addition of an H^+ according to Scheme I or II. This was not the observed result.

On the other hand, if the reaction is initiated by the abstraction of an H^- from the reactant, the reaction would proceed by Scheme III.

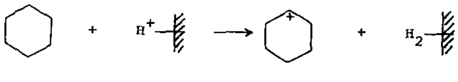


SCHEME III

Provided that the H^- that is abstracted from the reactant returns to the same molecule in the last step, an *intramolecular H transfer* would be involved in the reaction. This was the observed result. Thus, it is concluded that the isomerization of cyclohexane to methylcyclopentane is initiated by the abstraction of an H^- from the reactant.

There are three possibilities for the surface sites that abstract the H^- ion from the reactant. They are (i) surface carbenium ion, (ii) surface H^+ ion, and (iii) Lewis acid site. If surface carbenium ion abstracts the H^- ion, it should be a tertiary carbenium ion, because secondary or primary carbenium ion may return the H^- ion other than the H^- ion abstracted from the reactant. Since any hydrocarbons that possess a tertiary carbon atom could not be observed in a gas phase except methylcyclopentane in the isomerization of cyclohexane to methylcyclopentane, the possibility of the abstraction of the H^- ion by the surface carbenium ion is not high, although the possibility cannot be ruled out.

In case (ii), where the surface H^+ abstracts the H^- ion from the reactant,

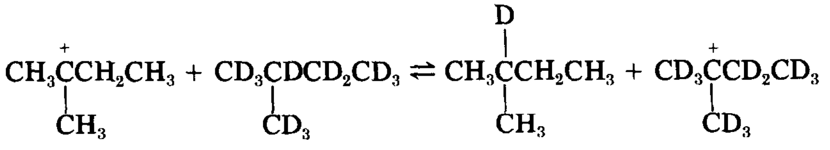


the probability that the H^- ion abstracted from the reactant is incorporated into the product is 1/2 unless the H^- can be distinguished from the original H atom on the surface. Therefore, case (ii) is not plausible.

Finally, if the aprotic Lewis acid site

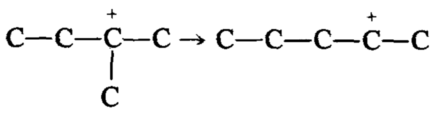
abstracts the H^- ion from the reactant (case (iii)), the H^- ion will return to the carbenium ion in the last step in Scheme III. Thus, case (iii) is most plausible in the isomerization of cyclohexane to methylcyclopentane.

In the isomerization of 2-methylbutane, one H atom of 2-methylbutane was rapidly exchanged among the molecules. The H atom must be the methyne H. This suggests that the chain transfer reaction occurred very rapidly.



$$\mathrm{CH_3\underset{CH_3}{\overset{+}{C}}CH_2CH_3 + CD_3\underset{CD_3}{C}DCD_2CD_3 \rightleftarrows CH_3\underset{CH_3}{\overset{D}{C}}CH_2CH_3 + CD_3\underset{CD_3}{\overset{+}{C}}CD_2CD_3} \qquad (1)$$

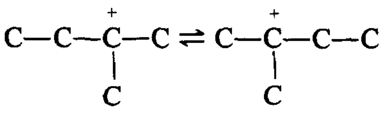
The tertiary carbenium ion rearranges to the secondary carbenium ion.



$$\mathrm{C{-}C{-}\underset{C}{\overset{+}{C}}{-}C \rightarrow C{-}C{-}C{-}\overset{+}{C}{-}C} \qquad (2)$$

A similar isotopic distribution of pentane to that of 2-methylbutane indicates that an intramolecular H transfer was involved in the carbenium ion rearrangement (Eq. (2)).

The rearrangement of the tertiary carbenium ion



$$\mathrm{C{-}C{-}\underset{C}{\overset{+}{C}}{-}C \rightleftarrows C{-}\underset{C}{\overset{+}{C}}{-}C{-}C} \qquad (3)$$

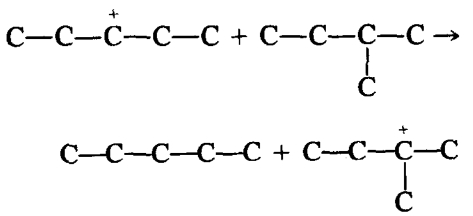
should not be fast, compared with the rearrangement of Eq. (2). If the rearrangement, Eq. (3), were fast, three H atoms of 2-methylbutane would have exchanged rapidly.

A small isotope effect observed for the formation of pentane suggests that the carbenium ion rearrangement is a slow step, and that the formation of the carbenium ion by abstraction of an H^- from the reactant is fast. The fast abstraction of an H^- from the reactant is in accordance with the fast chain transfer by Eq. (1).

The isomerization of pentane to 2-methylbutane should proceed by the reverse route of the isomerization of 2-methylbutane to pentane for miscroscopic reversibility. The reverse route explains the isotopic distribution for the coisomerization of pentane d_0/d_{12}. Secondary carbenium ion may be produced by the chain transfer.

$$\mathrm{CH_3CH_2CH_2CH_2CH_3 + CD_3CD_2\overset{+}{C}DCD_2CD_3 \rightarrow CH_3CH_2\overset{+}{C}HCH_2CH_3 + CD_3CD_2CDHCD_2CD_3} \qquad (4)$$

This reaction is not so fast since the H exchange among pentane molecules was not prominent in the initial stage of the reaction. As the reaction proceeded and a considerable amount of 2-methylbutane became produced, the chain transfer between the secondary carbenium ion and 2-methylbutane occurred.



$$\mathrm{C{-}C{-}\overset{+}{C}{-}C{-}C + C{-}C{-}\underset{C}{C}{-}C \rightarrow C{-}C{-}C{-}C{-}C + C{-}C{-}\underset{C}{\overset{+}{C}}{-}C} \qquad (5)$$

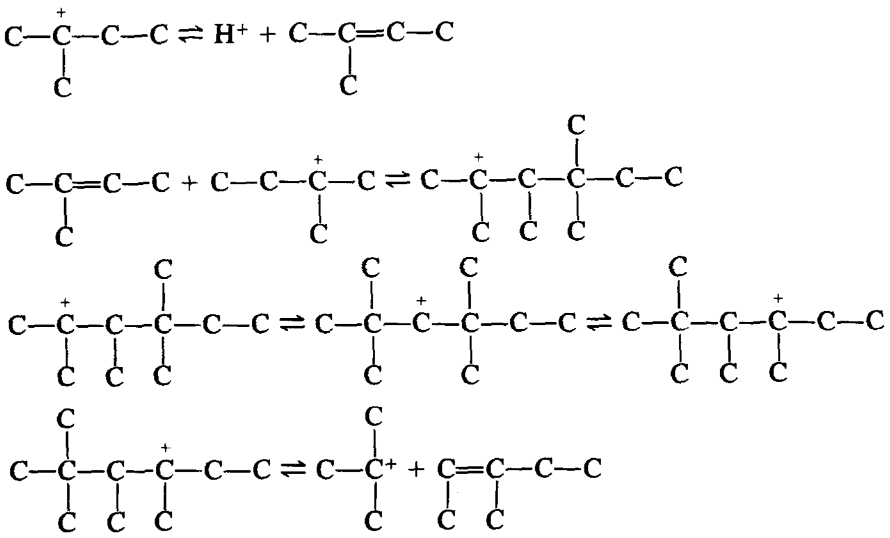
The H exchange into pentane molecules was extended. The production of about equal amounts of nonexchanged and monoexchanged 2-methylbutane at low conversion can be explained as follows. The secondary carbenium ion rearranges to the tertiary carbenium ion by the reverse process of Eq. (2), in which an intramolecular H transfer is involved. The tertiary carbenium ion undergoes fast chain transfer which produces equal amounts of nonexchanged and monoexchanged isotopic species of 2-methylbutane.

For the formation of the surface carbenium ions by interaction of the reactant with fresh catalyst surface, either surface H^+ ion or Lewis acid site is considered to be associated. No surface H atoms were incorporated either into the reactant or into the product in the reaction of perdeuteropentane. This indicates that the surface H atoms do not participate in the formation of surface carbenium ions. This is in accordance with the suggestion in the preceding paper (*1*) that the Lewis acid sites abstract an H^- ion from butane molecules to initiate the reaction.

When the catalyst was used for the reaction of perdeuteropentane, the surface may be covered with perdeuterospecies. The surface species exchanged H atoms with the reactant and product in the subsequent run. The monotonic decrease in the isotopic distribution of the reactant and products and nonformation of the isotopic species containing more than five D atoms suggest that the surface species serve H atoms but were not desorbed from the surface. Since these species would be desorbed from the surface if they were carbenium ions of carbon number of five, the surface species are considered to be polymeric compounds. Whether or not the H exchange of the surface species with the reactant and product is included in the isomerization path is uncertain.

In the reaction of 2-methylpropane, an extensive H exchange among the molecules was observed in 150 min, even though only 0.65% of 2-methylbutane was produced. This is in contrast to the limited exchange of one H atom in the reaction of 2-methylbutane. This may be simply because the rearrangement of the *t*-butyl cation to the *s*-butyl cation is slow compared with the H exchange of a methyl H, while the rearrangement of the *t*-amyl cation (Eq. (2)) is faster than the H exchange of a methyl or methylene H.

The isotopic distribution of 2-methylpropane which was formed in the coisomerization of pentane-d_0/d_{12} is difficult to explain. It is reported that pentane isomerization with aluminum halide-HX is accompanied by a disproportionation reaction that produces mainly 2-methylpropane and hexane. The proposed mechanism is



$$\mathrm{C{-}\underset{C}{\overset{+}{C}}{-}C{-}C \rightleftharpoons H^+ + C{-}\underset{C}{C}{=}C{-}C}$$

$$\mathrm{C{-}\underset{C}{C}{=}C{-}C + C{-}C{-}\underset{C}{\overset{+}{C}}{-}C \rightleftharpoons C{-}\underset{C}{\overset{+}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{C}{C}}{-}C{-}C}$$

$$\mathrm{C{-}\underset{C}{\overset{+}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{C}{C}}{-}C{-}C \rightleftharpoons C{-}\underset{C}{\overset{C}{C}}{-}\overset{+}{C}{-}\underset{C}{\overset{C}{C}}{-}C{-}C \rightleftharpoons C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{+}{C}}{-}C{-}C}$$

$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\underset{C}{\overset{+}{C}}{-}C{-}C \rightleftharpoons C{-}\underset{C}{\overset{C}{C^+}} + C{=}\underset{C}{C}{-}C{-}C}$$

The above mechanism involves abstraction of an H^+ from the carbenium ion. If this step is slow, a large isotope effect would be observed. An olefin produced by abstraction of an H^+ may predominantly consist of "light molecules." This explains why only the 2-methylpropane molecules containing $0 \sim 5$ D atoms were produced in the initial stage of the reaction.

An alternative explanation could be as follows. The reactant is cracked into methylene and methyl groups on the surface. These species accumulate on the surface as the reaction proceeds. Four of these species combine to produce a tertiary carbenium ion. Since CH_2 and CH_3 groups are more easily formed on the surface than CD_2 and CD_3 groups, CH_2 and CH_3 groups predominate on the surface. This may result in the formation of only "light 2-methylpropane" in the initial stage of the reaction.

The catalytic behavior of the SbF_5–SiO_2–Al_2O_3 catalyst for the reactions of alkanes has much in common with those of metal halides. However, the SbF_5–SiO_2–Al_2O_3 catalyst differs from metal halide in a few points. One of the differences is that no promoters are required for the SbF_5–SiO_2–Al_2O_3 catalyst to act as isomerization catalyst, whereas certain promoters are necessary for metal halides. In the latter case, the presence of promoters makes it possible for metal halides to abstract an H^- from alkanes by the chain transfer reaction to form carbenium ions. On the other hand, the surface Lewis acid sites of the SbF_5–SiO_2–Al_2O_3 catalyst can directly abstract an H^- from alkanes as an initiation step.

Another difference is observed in the relative reactivities of hydrocarbons. With metal halides, the hydrocarbons having a methyne H react faster than the hydrocarbons having a methylene H. For instance, the isomerization of 2-methylbutane is much faster than the isomerization of cyclohexane. Over the SbF_5–SiO_2–Al_2O_3 catalyst, however, the general tendency does not hold as shown by a faster isomerization of cyclohexane than 2-methylbutane. This is probably because abstraction of an H^- from alkanes may be a slow step for metal halides, but not a slow step for the SbF_5–SiO_2–Al_2O_3 catalyst.

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