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The Effective Site on Acid Catalysts Revealed in *n*-Butene Isomerization

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1-Butene isomerization experiments were carried out at near room temperatures with deuterated acid catalysts such as silica-alumina, silica-magnesia, silica-zirconia, nickel oxide-silica, alumina, alumina-boria, and nickel sulfate-on-silica, as well as with nondeuterated catalysts in the presence of deuterated propylene or other hydrocarbons. Reaction mixtures were separated by gas chromatographic column and analyzed for deuterium distribution by mass spectrometry.

The exchange behavior revealed in the experiments was remarkably dependent on the evacuation temperature of the deuterated catalysts. For the evacuation temperatures near 100°C, most of the deuterated catalysts gave deuterated products, the deuterobutene concentrations found in product 2-butenes being much larger than in unreacted 1-butene. However the larger deuterobutene concentrations in 2-butenes decreased with a rise in the evacuation temperature of the deuterated catalysts, down to negligible concentration for the evacuation at 500°C, whereas the conversions of reactant increased with rise in the evacuation temperature above 100°C.

On the other hand, with most of the nondeuterated catalysts evacuated at 500°C, 1-butene isomerization in the presence of deuteropropylene revealed an essentially identical behavior of hydrogen exchange with that on the deuterated catalysts evacuated at 100°C.

These results suggest that *n*-butene isomerization on these catalysts proceeds at least partly through a proton donor-acceptor mechanism with either Bronsted acids on the surface or the carbonium ions formed by adsorption of olefins on Lewis acid sites serving as proton donors, although the conclusion is open to question in the case of alumina.

I. INTRODUCTION

It is generally accepted that the double-bond isomerization of *n*-butene is catalyzed by acid catalysts such as silica-alumina at a comparatively low temperature, and that the catalytic activity can be correlated with the acidity of the catalyst, whereas the nature of the effective acid site has been an unsettled problem.

Several suggestions have been made for the isomerization. These include the carbonium ion theory proposed by Whitmore (*1*), and the hydrogen switch or prototropy mechanism proposed by Turkevich and Smith (*2*), and Horiuti (*3*). In recent years Haag and Pines (*4*) and Lucchesi (*5*) have proposed, (modifying the classical theory) that the isomerization proceeds through an intermediate pi-complex of olefin and proton. Brouwer (*6*) suggested the necessity of different intermediates for *cis–trans* and double-bond isomerization. Any one of the above mechanisms, however, assumes proton addition to the olefin double bond accompanied by subsequent or simultaneous proton elimination from another part of the carbonium ion thus formed.

On the other hand, Peri (*7*) found that the rate of isomerization on a deuterated alumina was much faster than that of extinction of infrared absorption by deuteroxyl on the catalyst. Consequently it was suggested that nonprotonic acid or Lewis acid is the active site, but as Brouwer *(6)* pointed out, the evidence is inconclusive because the catalytically effective deuteron might be consumed with a small amount of reactant.

If the proton on the catalyst, that is, Bronsted acid, is the real active site for the isomerization, as has been supposed, the existence of proton-donating and proton-accepting action of the catalyst should be detected in the reaction process on a deuterated catalyst by measuring the deuterium distribution among the products. While separation of isomeric *n*-butenes has been facilitated by gas chromatography, a complete experimental verification of this prediction has not been reported. Hence it is of interest to study the reaction by means of deuterium tracer and to find which is the true active site for the various acid catalysts.

II. EXPERIMENTAL

1. *Materials*

Catalysts. Silica-alumina, containing 15 wt % alumina, was prepared by cogelation of silicic acid and aluminum hydroxide from a mixed aqueous solution of aluminum nitrate, sodium silicate, and sulfuric acid. Silica-magnesia-1 containing 30 wt % magnesia which was obtained from Hara Laboratory of this Institute, was reportedly prepared by the gel-mixing method. Silica-magnesia-2 was prepared by cogelation. Nickel oxide-silica-1, -2, -3, -4, and -5 were prepared by ammonia precipitation of nickel hydroxide from nickel nitrate solution on silica gel so as to contain 30, 40, 50, 30, and 30 wt % nickel oxide, respectively. The catalysts, $NiO\text{-}SiO_2$-1, -2, and -3 showed a deep black color after calcination at 500°C, while $NiO\text{-}SiO_2$-4 and -5 were dark green. Silica-zirconia containing 20 wt % zirconia was prepared from aqueous zirconium oxychloride solution by the same method as for nickel oxide-silica. Alumina (Neobead MS-C) was supplied by Mizusawa Kagaku Co. Alumina-boria of 24 wt % boria was prepared by impregnating hydrous alumina gel with hot aqueous solution of boric acid. Nickel sulfate-on-silica was prepared by impregnating calcined silica gel with an aqueous solution of nickel sulfate.

Reagents. Heavy water was supplied by Showa Denko Co. and the hydrogen was reported by them to be 99.65% deuterium.

Pure *n*-butenes were obtained from commercial cylinders. The purity of any butene was above 99.7%. Three samples of deuteropropylene, A, B, and C, were prepared by exchange reaction between heavy water and propylene over a platinum-asbestos catalyst at 150°C. The values of fractional deuterium concentration, on atom basis f_D, of samples A, B, and C were 0.91, 0.67, and 0.80, respectively. Sample A was contaminated with about 7% propane whereas only a trace amount of propane was present in both B and C. Deuterobutane ($f_D = 0.47$) was prepared by the addition of deuterium to deuterobutene obtained by the exchange method as described above. Deuteroacetylene was prepared by reaction of calcium carbide with heavy water. Deuterobenzene, obtained from the Ikeda Laboratory of this Institute, was reportedly prepared by trimerization of deuteroacetylene over Ziegler catalyst.

2. *Procedures*

Apparatus. The apparatus used for the experiments was a simple vacuum system equipped with a reactor and various reservoirs. The reactor was a small bulb with a stopcock, the dead volume of which was minimized in order to eliminate the contribution of unadsorbed reactant to the analytical data. The actual dead volume was within 5 cc for 2.5 g of catalyst.

Treatment of catalyst. Deuteration of the catalyst was performed as follows. A 2.5- to 3.0-g portion of catalyst, after evacuation at 500°C, was soaked *in situ* overnight at room temperature in heavy water of the same apparent volume, and then evacuated at the indicated temperature for 1 hr at 10^{-5} mm Hg. Such a treatment seemed to be satisfactory for the deuteration because the hydrogen exchange between hydroxyls proceeds rapidly and because the amount of heavy water used was at least 50 times the water content of the catalyst. The water content of the NiO-SiO_2-1 and -4 catalysts evacuated at 500°C was measured by the method of deuteration followed by protium analysis of recovered water. The observed values were 450 and 700 μmole/g catalyst for NiO-SiO_2-1 and -4, respectively, which were in agreement with those obtained by the weight loss on ignition at 1000°C.

Reaction. The reactant was admitted into the reactor under a pressure of 40 to 50 mm Hg. After the indicated reaction time, during which in most cases the pressure decreased to a few mm Hg, reactant remaining in the gas phase outside of the reactor was quickly pumped out. Successively, reaction mixture in the reactor was transferred to a liquid nitrogen trap, while the catalyst was kept at reaction temperature. The transfer continued for 1 to 3 hr, giving a longer time for the lower reaction temperature. The reactant was predominantly adsorbed in the catalyst, and reactant in the gas phase in the reactor was less than 5% of the recovered reactant.

1-Butene isomerization in the presence of deuteropropylene was carried out both by using the prepared mixture of 1-butene with deuteropropylene and by way of preadsorption of deuteropropylene before 1-butene was introduced. Experiments in the presence of other deuterohydrocarbons were carried out by the latter methods.

Analysis. Analyses and separations of the mixture recovered from the catalyst surface were made by gas chromatography using a 5-meter dimethylformamide (40%)-alumina column placed in an ice bath. Deuterium concentrations of isolated isomers were determined by mass spectrometry with the ionization voltage of 10 v and 80 v. The concentrations based on 80-v spectra, for which the contribution of fragment peaks was considered, were in good agreement with those based on the parent peaks of 10-v spectra. It was ascertained that the deuterium concentration was unaffected by gas chromatographic separation.

III. Results

1. *1-Butene Isomerization with Deuterated Acid Catalysts*

The results of 1-butene isomerization over various deuterated catalysts evacuated at close to 100°C are given in Table 1. Reaction temperature and reaction time were chosen according to the isomerization activity of each catalyst to obtain comparatively low conversion, and thus to avoid reverse reaction. No product other than *cis*- and *trans*-2-butene was detected. The deuterium concentration F_D of butenes given in Table 1 is the mole fraction of the deuterobutene. From Table 1, it may be seen that all the catalysts tested, except some nickel oxide-silica catalysts, gave deuterated products. The F_D values of *cis*-butene and *trans*-butene are, in general, considerably higher than that of the reactant 1-butene, which is close to zero. The deuterium distribution shown in the seventh column indicates that more than 80% of the deuterobutene is monodeuterobutene.

Black nickel oxide-silica (NiO-SiO_2-1, -2, and -3) gave deuterated products, whereas green nickel oxide-silica (NiO-SiO_2-4 and -5) gave little deuterated product. The black catalyst changed to dark green when contacted with hydrogen at 200°C. This had a lower isomerization activity and it was unable to deuterate butene, as shown in the experiment No. 12. The original properties of black catalyst were, however, regained by treating the hydrogen-rated catalyst with oxygen at 500°C, as shown in experiment No. 13.

In the experiments No. 4 and No. 11, *cis*-2-butene was used as the reactant, to examine the reactivity differences among the isomeric butenes. It is clearly shown again that the products were more heavily deuterated than the reactant.

Experiments Nos. 1, 2, and 3 were made

TABLE 1

1-Butene Isomerization with Various Deuterated Catalysts

			Reaction condition		Butene composition				D distribution[a]					
No.	Catalyst	Evacuation temp. (°C)	Temp. (°C)	Time (min)	1-	*trans*-	*cis*-	Reacted butene (μmole/g cat)	d_0	d_1	d_2	d_3	d_4	F_D
1	SiO$_2$–Al$_2$O$_3$	80	0	5	93			13	99.0	1.0	0	0	0	0.01
						3			53.9	42.8	3.3	tr.	0	0.46
							4		32.7	62.8	4.5	tr.	0	0.67
2	SiO$_2$–Al$_2$O$_3$	80	0	64	70	12	18	40	*44.3	49.9	5.5	0.3	0	0.56
3	SiO$_2$–Al$_2$O$_3$	80	0	120	21	36	43	177	*43.9	46.3	9.5	0.3	0	0.56
4[a]	SiO$_2$–Al$_2$O$_3$	100	0	4	4			41	50.9	41.3	6.5	1.3	0	0.49
						10			52.8	35.6	9.3	2.3	tr	0.47
							86		92.4	6.4	1.2	tr.	0	0.08
5	SiO$_2$–MgO–1	100	19	47 hr	92			15	99.0	1.0	0	0	0	0.01
						3			63.5	34.0	2.3	0.2	0	0.37
							5		49.5	47.5	2.8	0.2	0	0.50
6	SiO$_2$–MgO–1	100	55	3 hr	68			66	96.2	3.8	tr.	tr.	0	0.04
						9	23		*33.0	60.8	5.7	0.5	tr.	0.67
7	SiO$_2$–MgO–2	100	20	20	96			8	99.1	0.9	tr.	0	0	0.01
						2	2		*63.0	35.9	1.1	0	0	0.37
8	SiO$_2$–ZrO$_2$	110	25	20	89			23	97.9	2.1	tr.	tr.	0	0.02
						5	6		*54.5	44.1	1.1	0.3	0	0.45
9	NiO–SiO$_2$–1	70	0	5	75			43	97.9	2.1	tr.	0	0	0.02
						9	16		*69.0	27.7	2.9	0.4	0	0.31
10	NiO–SiO$_2$–2	75	0	7	82			24	98.5	1.5	tr.	0	0	0.02
						6			57.6	37.2	5.2	tr.	0	0.42
							12		58.4	38.3	3.3	tr.	0	0.42
11[b]	NiO–SiO$_2$–2	80	0	5	4			28	46.8	48.3	4.9	tr.	0	0.53
						15			61.0	36.5	2.4	0.1	0	0.39
							81		94.7	5.1	0.2	0	0	0.05
12[c]	NiO–SiO$_2$–2	100	0	50	93	3	4	24	*95.4	4.6	tr.	0	0	0.05
13[d]	NiO–SiO$_2$–2	80	0	8	75	8	17	34	*65.0	32.1	2.9	tr.	0	0.35
14	NiO–SiO$_2$–3	80	0	11	84			23	98.4	1.6	tr.	0	0	0.02
						6			55.7	39.7	4.6	tr.	0	0.44
							10		55.4	41.8	2.8	tr.	0	0.45
15	NiO–SiO$_2$–4	100	0	30	82			35	99.8	0.2	0	0	0	tr.
						10	8		*99.8	0.2	0	0	0	tr.
16	NiO–SiO$_2$–5	100	0	30	74			51	100.0	tr.	0	0	0	tr.
						15	11		*100.0	tr.	0	0	0	tr.
17	Al$_2$O$_3$–B$_2$O$_3$	100	0	19	96			9	99.7	0.4	tr.	0	0	tr.
						2	2		*76.2	22.5	1.3	tr.	0	0.24
18	NiSO$_4$ on SiO$_2$	110	0	3.5	60			40	96.6	3.3	tr.	0	0	0.03
						20			79.0	19.9	1.1	tr.	0	0.21
							20		77.4	20.7	1.9	tr.	0	0.23

[a] Lines of data preceded by asterisk give values for the *cis–trans* mixture.

[b] The reactant was *cis*-2-butene in these experiments.

[c] Catalyst was treated with hydrogen at 200°C.

[d] Catalyst already treated with hydrogen at 200°C was then treated with oxygen at 500°C.

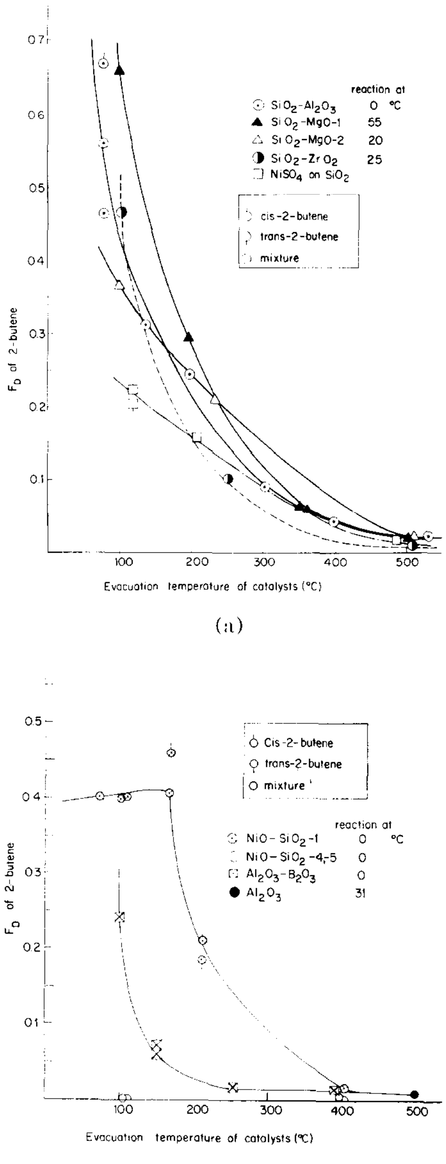
to examine the available deuterium content of deuterated silica-alumina catalyst. The amount of reacted butene was varied from 13 to 177 μmole/g catalyst by adjusting the extent of conversion. In experiment No. 1 an average F_D value of 0.58 was obtained for 2-butene, which was close to the 0.56 obtained in experiments 2 and 3. This suggests that, under the reaction conditions, available deuterium on the catalyst surface was only partially consumed during the reaction.

The F_D value for *cis*-butene is nearly equal to or a little more than F_D for *trans*-butene.

2. *Effect of Heating the Catalyst under Vacuum*

The effect on F_D of the temperature at which the deuterated catalysts were heated under vacuum is shown in Fig. 1. In this series of experiments, some of the catalysts evacuated at higher temperatures were so active that the conversion exceeded 80%, in spite of efforts to keep it at a low level. Nevertheless it is clear that the F_D's of 2-butene decrease generally with a rise in the evacuation temperature and finally reach almost zero at 500°C. The F_D's of reactant 1-butene were negligible at any evacuation temperature except with the black nickel oxide-silica (NiO-SiO_2-1) evacuated at 150°C. In the latter case it seems likely that the catalyst was too active to avoid the effect of the reverse reaction, as the conversion attained 90% in 5 min at 0°C. Hence the exceptionally large value of 0.15 for 1-butene may be attributed to the reverse reaction. Even in this case, however, the F_D of 1-butene was significantly less than the value 0.41 of *trans*-butene and 0.46 of *cis*-butene. Greenish nickel oxide-silica (NiO-SiO_2-4 and -5) gave no exchange throughout the evacuation temperature range, irrespective of reactant or product.

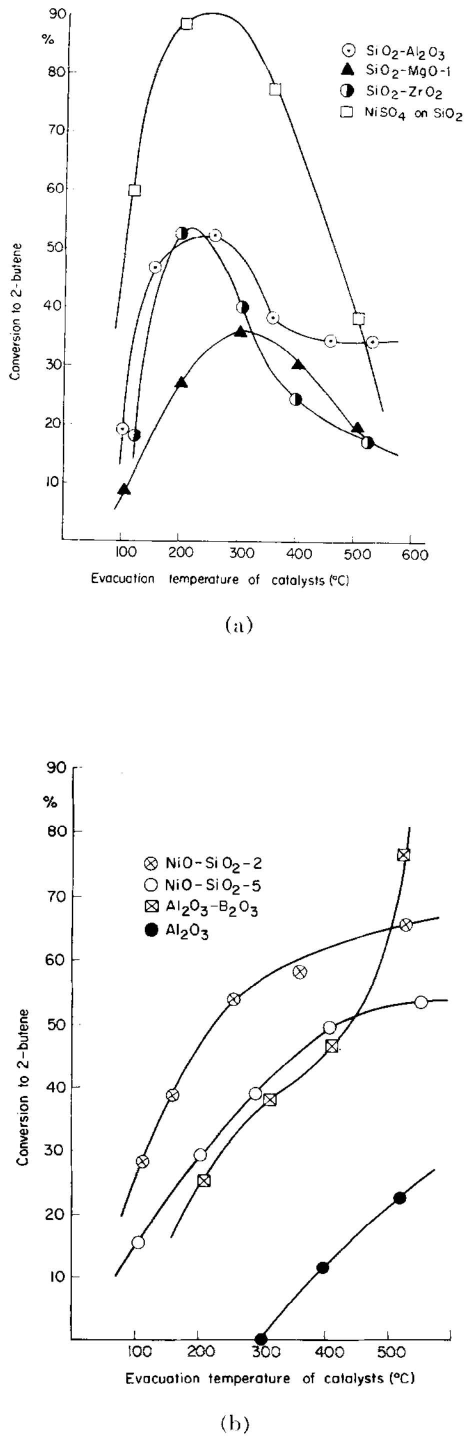
On the other hand, Fig. 2 shows the variation of conversion with the evacuation temperature. A comparison of isomerization activities of various catalysts should not be made directly from the conversions shown in Fig. 2, because the reactions were carried out under different reaction conditions depending on their individual activity. As shown in Fig. 2 the conversions sharply increase in the evacuation temperature range where the F_D's of 2-butene sharply decrease. The maximum conversion



(a)

(b)

FIG. 1. 1-Butene isomerization at indicated temperatures with various deuterated catalysts.



(a)

(b)

FIG. 2. Variation of 1-butene conversion with the evacuation temperature.

was attained with silica-alumina, silica-magnesia, silica-zirconia, and nickel sulfate-on-silica [Fig. 2(a)] by evacuation at 200° to 300°C, while the conversion using nickel oxide-silica and alumina-boria showed no maximum in the temperature range tested [Fig. 2(b)]. Alumina catalyst was activated for isomerization by heating under vacuum above 300°C, but it gave little deuterium in both the reactant 1-butene and the product 2-butene.

In brief, the F_D of 2-butene decreases with the rise in the evacuation temperature of catalysts even as the conversion of butene increases, and the F_D obtained with active catalyst evacuated at 500°C shows little hydrogen exchange between butene and the catalyst.

3. *1-Butene Isomerization in the Presence of Deuteropropylene*

In order to explain the effect of evacuation temperature described above, another series of experiments was carried out in the presence of deuteropropylene. In these experiments catalysts were, of course, nondeuterated and evacuated at about 500°C where the exchange of catalyst hydrogen with butene had already proved to be negligible, as shown in Fig. 1. The same exchange with propylene was separately ascertained to be negligible on silica-alumina.

The results are shown in Table 2. Lower conversions were obtained in the presence of deuteropropylene than with butene alone. With the exception of the results on alumina, the F_D's of product 2-butene were again significantly larger than those of reactant 1-butene, which were negligibly small in the case of low conversion. Hence the behavior of hydrogen exchange in this series is essentially identical with that using deuterated catalysts evacuated at low temperature. However, small or trace amounts of polydeuterated butenes up to d_8 were detected in both the reactant and the products with most of the catalysts.

It should be noted that even green nickel oxide-silica, which was shown in the above section to give little hydrogen exchange

1-Butene Isomerization in the Presence of Deuteropropylene

No.	Catalyst	Evacuation temp. (°C)	Reactant		Reaction condition		Butene composition			D distribution[a]									F_D
			Mixed ratio d-C'_3/1-C'_4	d-C'_3 used	Temp. (°C)	Time (min)	1-	*trans-*	*cis-*	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
1	SiO_2–Al_2O_3	500	1.50	(A)	0	2.5	52			98.4	2.6	tr.	tr.	0	0	0	0	0	0.03
								22	26	*74.7	21.9	2.9	0.5	tr.	0	0	0	0	0.25
2[a]	SiO_2–Al_2O_3	500	0.61	(B)	0	5.5	36			98.0	2.0	tr.	tr.	tr.	tr.	0	0	0	0.02
								37		84.6	13.7	1.7	tr.	tr.	tr.	tr.	0	0	0.15
									27	84.6	13.6	1.4	0.4	tr.	tr.	tr.	0	0	0.15
3	SiO_2–MgO–1	510	1.42	(C)	65	60	88			99.5	0.5	tr.	tr.	0	0	0	0	0	0.01
								11	11	*84.8	11.8	1.0	0.6	0.6	0.6	0.6	tr.	tr.	0.15
4	SiO_2–ZrO_2	500	1.42	(C)	28	35	72			97.2	2.8	tr.	tr.	tr.	0	0	0	0	0.03
								13	15	*80.0	15.6	1.5	0.4	0.4	0.4	0.4	0.3	tr.	0.20
5	NiO–SiO_2–1	500	1.50	(A)	0	1.5	14			77.8	16.0	4.6	1.1	0.5	0	0	0	0	0.22
								57	29	*60.1	29.3	8.5	2.1	tr.	tr.	tr.	0	0	0.40
6	NiO–SiO_2–2	510	1.42	(C)	0	1.5	37			86.0	11.5	2.1	0.4	tr.	tr.	tr.	tr.	tr.	0.14
								40	23	*61.2	30.8	6.6	1.1	0.3	tr.	tr.	tr.	tr.	0.39
7	NiO–SiO_2–5	500	1.50	(A)	0	20	68			91.5	7.5	1.0	tr.	tr.	tr.	0	0	0	0.08
								16	16	*61.6	33.9	3.9	0.6	tr.	tr.	0	0	0	0.38
8	NiO–SiO_2–5	100	1.42	(C)	0	55	96			99.2	0.8	tr.	0	0	0	0	0	0	0.01
								2	2	*71.8	20.3	2.7	1.2	0.8	0.8	0.8	0.8	0.8	0.28
9[b,c]	NiO–SiO_2–5	500	1.62	(C)	0	5	1			65.2	24.5	3.1	2.5	1.2	1.0	1.0	1.0	0.5	0.35
								5		66.7	21.2	2.7	2.7	2.5	1.4	1.3	1.3	0.2	0.33
									94	98.5	0.6	0.3	0.2	0.2	0.1	0.1	tr.	tr.	0.01
10	Al_2O_3–B_2O_3	515	1.42	(C)	0	4	12			89.5	7.6	2.2	0.7	tr.	tr.	tr.	tr.	tr.	0.10
								50	38	*61.3	27.5	8.0	2.6	0.6	tr.	tr.	tr.	tr.	0.39
11	$NiSO_4$ on SiO_2	520	1.42	(C)	0	55	60			93.8	5.7	0.5	tr.	tr.	tr.	tr.	tr.	0	0.06
								17		79.5	18.9	1.6	tr.	tr.	tr.	tr.	tr.	tr.	0.20
									23	81.6	16.5	1.9	tr.	tr.	tr.	tr.	tr.	0	0.18
12	Al_2O_3	510	1.42	(C)	31	60	52			49.5	31.2	18.8	0.5	tr.	0	0	0	0	0.50
								25		28.4	40.2	23.7	6.8	0.9	tr.	tr.	tr.	tr.	0.72
									23	17.9	39.3	34.5	6.6	1.7	tr.	0	0	0	0.82
13	Al_2O_3	520	1.80	(C)	31	55	69			26.0	38.1	25.8	8.5	1.3	0.1	0.1	0.1	tr.	0.74
								15	16	*17.7	35.8	33.2	12.7	0.6	tr.	0	0	0	0.82
14	Al_2O_3	310	1.42	(C)	31	30	100	0	0	99.5	0.5	tr.	tr.	tr.	tr.	tr.	tr.	tr.	0.01

[a] Lines of data preceded by asterisks give values for the *cis*–*trans* mixture.

[b] Deuteropropylene was preadsorbed.

[c] The reactant was *cis*-2-butene in this experiment only.

with butene at any evacuation temperature, brought about an appreciable exchange in 2-butene. An exceptional result was also obtained for alumina catalyst. A substantial amount of deuterated species was found in both the reactant and the products in experiment Nos. 12 and 13, whereas little deuteration or isomerization was detected in experiment No. 14, where the alumina was evacuated at 310°C. Other cases in which relatively large F_D's were obtained for 1-butene are with black nickel oxide-silica catalyst shown in experiments 5 and 6, and with alumina-boria in experiment No. 10. These larger values of F_D for the reactant may be attributed to the higher conversions attained, which should be accompanied by some reverse reaction.

It is to be noted that the exchange behavior appears independent of how the deuteropropylene was added, as shown in experiment No. 2. This experiment showed that with preadsorbed deuteropropylene, the F_D of the unreacted 1-butene was also significantly smaller than those of the products, as in the case of premixed gas.

The reactivity difference among the isomeric butenes was further examined using *cis*-2-butene as the reactant. Experiment No. 9 confirms that the products, i.e. 1-butene and *trans*-2-butene, were more heavily deuterated than the reactant.

4. *1-Butene Isomerization in the Presence of Other Deuterohydrocarbons*

1-Butene isomerization experiments in the presence of deuterobutane, deuteroacetylene, and deuterobenzene were carried out to find out whether hydrocarbons other than olefin have the same intervening effect as propylene. The results are given in Table 3. The F_D's of both 1-butene and 2-butene were very small compared with those using deuteropropylene, even though there was a smaller ratio of deuterohydrocarbon to reactant (1-butene) and a smaller deuterium concentration in the deuterohydrocarbons. With alumina and silica-alumina preadsorbed by deuteroacetylene, isomerization was undetectable, and the F_D of reactant 1-butene was 0.01. Slightly higher values of F_D were obtained for both 1-butene and 2-butene with alumina catalyst preadsorbed by deuterobenzene. Thus with all the hydrocarbons tested none showed the intervening effect described.

IV. Discussion

1. *Hydrogen Exchange between Catalyst and Butene in Isomerization*

The following three processes may be considered as the reaction path by which deuterium may appear in the product butene on deuterated catalyst: (1) rapid exchange of the reactant before the isomerization; (2) the exchange involved in the process of isomerization itself; (3) preferential exchange in the product butene after the isomerization. Process (3) assumes a substantial difference in exchange reactivities among the isomeric butenes.

If process (1) were to prevail, one would expect relatively high concentrations of deuterobutene in both unchanged reactant and product. If process (3) were the case, the product should contain more deuterium than the reactant. However, the result must be substantially affected by altering the type of the reactant used.

Therefore the following condition is required if process (2) is to prevail; the product should contain more deuterium than the unreacted starting material in the mixture recovered from the catalyst surface after the reaction, regardless of the isomeric type of reactant. This last condition is seemingly fulfilled in the results shown in Table 1, except for experiments 12, 15, and 16, that is, in general the F_D's of the products were much larger than that of the reactant, regardless of the type of reactant, 1-butene or *cis*-2-butene, being used. Furthermore the F_D of the reactant was very small, indicating negligible contribution of processes (1) and (3). Thus it is clear that *n*-butene isomerizes over silica-alumina, silica-magnesia, silica-zirconia, black nickel oxide-silica, alumina-boria, and nickel sulfate-on-silica, evacuated at close to 100°C, through process (2), and that these catalysts have, on their surface, active hydrogen taking part in the isomerization. Since

TABLE 3

1-Butene Isomerization in the Presence of Other Deuterohydrocarbons

No.	Catalyst	Evacuation temp. (°C)	Reactant: Deutero-hydrocarbon	Reactant: Ratio d-H.C./1-C'_4	Reaction condition: Temp. (°C)	Reaction condition: Time (min.)	Butene composition: 1-	Butene composition: *trans-*	Butene composition: *cis-*	F_D
1	SiO_2–Al_2O_3	530	*d*-Butane	1.67	0	2.5	43			—
								29	28	0.01
2	Al_2O_3	550	*d*-Butane	0.70	31	55	62			0.01
								20	18	0.01
3	NiO–SiO_2–5	530	*d*-Butane	0.75	0	30	32			—
								52	16	tr.
4	SiO_2–Al_2O_3	520	*d*-Benzene	0.70	0	2	44			tr.
								29	27	0.01
5	Al_2O_3	520	*d*-Benzene	0.70	31	30	87			0.07
								6	7	0.08
6	NiO–SiO_2–5	530	*d*-Benzene	0.68	0	40	74			—
								16	10	0.02
7	Al_2O_3	520	*d*-Acetylene	0.93	32	75	100			0.01
								0	0	—

it is generally accepted that hydrogen atoms are combined with the oxide surface of acid type, forming hydroxyl groups (the hydrogen being more or less protonic), the exchange conforms with the Bronsted acid postulate of active sites. Such an active proton seems to be effective not only in double-bond migration but also in *cis–trans* isomerization, because the above finding was independent of the isomeric type of reactant.

Some irregularities were observed in nickel oxide-silica catalysts. The greenish catalysts, NiO-SiO_2-4 and -5, appear to have few active protons, whereas they are highly active in the isomerization. The active protons of the black nickel oxide-silica, considering its disappearance by hydrogen treatment at 200°C and its reoccurrence by subsequent oxygen treatment at higher temperature, appear to be related with nickel "peroxide," which is known to have a darker color than ordinary nickel oxide.

2. *Decrease of the Amount of Active Proton on the Catalyst with Rise in Evacuation Temperature*

Since the contributions of processes (1) and (3) to the F_D of the reaction products can be considered as negligible, as shown above, the value of F_D of the products should reflect the number of active protons available on the catalyst surface. Hence the decrease of F_D in the product gas, may be interpreted as a decrease in the number of active protons on the surface, and the results in Fig. 1 suggest that the number of active protons on the catalysts decreases with a rise in evacuation temperature.

On the other hand, the isomerization activity did not only decrease in parallel, but, in most cases, increased as the evacuation temperature was raised from 100° to 200°C. There were but few active protons present on catalysts evacuated at 500°C and on greenish nickel oxide-silica (NiO-SiO_2-4 and -5) evacuated at 100°C and above, whereas their isomerization activities were high. Hence there must be an alternative isomerization mechanism independent of the proton originally involved in the catalyst in operation.

Since the catalysts evacuated at lower temperature, with the exception of the greenish nickel oxide-silica, involve Brönsted acid sites, the effect of higher temperature in the evacuation process is likely due to the dehydration of these Brönsted acid sites to the Lewis acid sites, as suggested by Haldeman and Emmett (*8*). Thus either one or both Brönsted and Lewis acid sites are present on the catalysts evacuated at lower temperature, e.g.

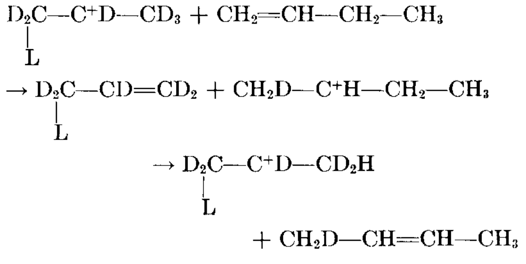
100°C, and both may be responsible for the isomerization. However more and more Brönsted acid is transformed into Lewis acid as the evacuation temperature increases. When this temperature reaches 500°C most of the Brönsted acid is expected to be converted and isomerization takes place essentially on the Lewis acid sites. On the basis of the present interpretation, the F_D value in Table 1 is indicative of the fractional contribution of Brönsted acid sites.

3. *The Catalytic Action of Lewis Acid Sites*

The action of Lewis acid sites in the catalytic reaction of olefin on solid acid catalysts has been interpreted in terms of carbonium ion formed with the adsorption of olefin as follows: $-CH{=}CH- + L^+ \rightarrow -CHL{-}C^+H-$, where L^+ denotes the Lewis acid site. This type of carbonium ion has been suggested on the evidence of ultraviolet absorption by adsorbed olefin on silica-alumina (*9*) and nickel oxide-silica (*10*). It is generally accepted that the carbonium ion is reactive, therefore, it may isomerize through rearrangement of the intermediate carbonium ion on a Lewis acid site. However, isomerization through rearrangement of the carbonium ion on Lewis acid does not necessarily involve hydrogen exchange except the simple exchange which is not involved in the reaction path. The reactivities of isomeric *n*-butenes in the simple exchange are more or less comparable because the alteration of the reactant from 1-butene to *cis*-2-butene gave no significant change in the exchange behavior. Polydeuterated butenes up to d_8 observed in butene-deuteropropylene experiments may be attributed to simple exchange; but as only minor or trace amounts were detected, its contribution to the F_D is not significant. Accordingly it is difficult to interpret the result (that the deuterium was concentrated in 2-butene, which was formed by isomerization of 1-butene in the presence of deuteropropylene using catalysts incapable of exchanging their hydrogen with either propylene or butene) on the basis of the rearrangement mechanism alone. An alternative "proton donor–acceptor mechanism," to be discussed below, appears in operation.

4. *The Mechanism of Isomerization*

The presence of deuterobutene in product 2-butene indicates that an exchange of hydrogen atoms between butene and propylene must be involved in the reaction path of the isomerization. As generally accepted the carbonium ion may be a proton donor and act as a Brönsted acid. The experimental results in the presence of deuteropropylene can be interpreted on the concept of carbonium ion acid as follows: A Lewis acid formed by the dehydration of catalyst reacts first with the reactant olefin to form a carbonium ion. The carbonium ion so formed may act as an active site in the isomerizaiton by donating a proton to the butene molecule to form a protonic carbonium ion which in turn acts as the isomerization intermediate. Particularly in the presence of deuteropropylene, two kinds of active sites, C_4H_8-L and C_3D_6-L, may be involved, and the product 2-butene produced on the latter site may contain deuterium. This mechanism may be expressed by the following equations:



$$\underset{\substack{| \\ L}}{D_2C}{-}C^+D{-}CD_3 + CH_2{=}CH{-}CH_2{-}CH_3$$
$$\rightarrow \underset{\substack{| \\ L}}{D_2C}{-}CD{=}CD_2 + CH_2D{-}C^+H{-}CH_2{-}CH_3$$
$$\rightarrow \underset{\substack{| \\ L}}{D_2C}{-}C^+D{-}CD_2H$$
$$+ CH_2D{-}CH{=}CH{-}CH_3$$

It may be concluded from the above discussion that the Lewis acid sites with adsorbed olefins could act as Brönsted acids. The Brönsted acids thus produced may have an activity different from that originally possessed by the catalyst. Thus a proton donor–acceptor mechanism seems to be involved in the *n*-butene isomerization on all the catalysts tested except alumina. Both the intrinsic Brönsted acid on the catalyst surface and the carbonium ion acid brought out by the adsorption of olefin on Lewis acid may serve as proton donors. Which one of the acids acts as the active site in the isomerization may depend on the type and the treatment condition of the catalysts.

One of the following three reaction steps may constitute the rate-determining step in the over-all proton donor–acceptor mechanism:

(a) formation of carbonium ion,

$$R + H^+ \rightarrow RH^+$$

(b) hydrogen switching reaction,

$$R + H^+ \rightarrow R' + H^{+\prime}$$

(c) reaction of preformed carbonium ion,

$$RH^+ \rightarrow R' + H'^+$$

where R and R′ denote the reactant and the product, respectively.

If (a) or (b) is the rate-determining step, then when the deuterium tracer was applied, deuterium may be expected to concentrate in the product. The catalysts tested here, except for alumina, seem to belong to these cases. With alumina, nearly equal concentrations of deuterium in the product and in the reactant were obtained, so alumina may belong either to case (c) or deuterium might be introduced by the simple exchange which is not directly concerned with the reaction. However, recalling the observation that the hydrogen exchange of 1-butene with the alumina was negligible when the isomerization activity did not appear because of the low evacuation temperature, the former possibility appears to be probable. This speculation may be tested spectroscopically because the reaction intermediate may be detected from the spectrum of adsorbed species in the case of (c), although this may not always be possible in cases (a) or (b), where the concentration of the intermediate may be too low for spectroscopic observation.

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