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Studies of the Hydrogen Held by Solids

IX. The Hydroxyl Groups of Alumina and Silica-Alumina as Sites for the Isomerization of Butene

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The rates of double-bond isomerization of butene-1 and *cis*-butene-2 have been measured over alumina and silica-alumina catalysts as a function of their hydrogen contents (comprised principally of terminal surface OH groups). Changes which occurred as the catalysts "lined-out" are described. The isomerization rate of butene-1 increased with hydroxyl concentration over silica-alumina, but decreased over alumina. Over silica-alumina, the ratio of *cis*- to *trans*-butene-2 was near unity in the initial product; over alumina, higher ratios were obtained. Both the activity and selectivity of alumina were increased by fluoriding. *cis*-Butene-2 and butene-1 isomerized at about the same rate over alumina while the latter was converted much faster than the former over silica-alumina. It was concluded that the mechanism of isomerization, and the intermediates involved, were not the same over alumina as over silica-alumina. Mechanisms consistent with the available literature are considered.

INTRODUCTION

Two problems of current interest to catalytic chemists are the nature of the active sites utilized in the double-bond isomerization of olefins and the cause of the stereoselectivity of the reaction. Various workers have studied the isomerization of the *n*-butenes on catalysts with widely ranging acidity; in every instance, they have observed that the reaction is kinetically controlled. Early workers (*1, 2*) suggested that over acidic catalysts the double-bond isomerization occurred via a secondary butyl carbonium ion. Supposedly, a proton was furnished by the catalyst; release of a proton from another carbon yielded the isomer. Then, Turkevich and Smith (*3*) proposed a "hydrogen switch" mechanism in which the double bond was shifted by simultaneous formation and breaking of carbon–hydrogen bonds. Later, these interpretations were discarded by Lucchesi, Baeder, and Longwell (*4*) and by Haag and Pines (*5*) as inadequate to explain the high selectivities observed. Instead, they proposed that the carbonium ion decomposed through a pi complex. Foster and Cvetanovic (*6*), like Haag and Pines (*7*), found very high ratios of *cis*-2-butene to *trans*-2-butene when 1-butene was isomerized over basic catalysts. These authors (*6, 7*) proposed an allylic carbanion intermediate.

In a comprehensive study using a variety of acid catalysts, Brouwer (*8*) found that the relative rates of isomerization (and selectivities) depended upon the catalyst composition, the extent of surface hydration, and the configuration of the starting olefin. This led Brouwer to suggest that double-bond isomerization proceeded via the "hydrogen switch" mechanism (*3*), and *cis–trans* isomerization via the classical carbonium ion.

Generally, the selectivities found for silica-alumina and alumina have been noticeably different. In studies where the conversion of 1-butene was kept low

($<10\%$), the selectivity (*cis/trans* ratio) observed with silica-alumina was 0.6–1.4 (*6, 8, 11, 12*), the single exception being the work of Lucchesi, Baeder, and Longwell (*4*). Moreover, with mineral acids on inert supports, values of 0.93–1.23 were found (*6*). On the other hand, with a very pure alumina, Haag and Pines (*5*) observed a selectivity of 4.4.

From an infrared study of the adsorption of 1-butene on dehydrated alumina, Peri (*9*) found that "strongly adsorbed" butene resembled liquid *cis*-2-butene. Furthermore, he observed that the rate of isomerization increased as the dehydration temperature was raised from 400° to 800°C. Peri (*10*) and Leftin and Hermana (*11*) offered conflicting proposals for the adsorbed species on silica-alumina. Peri observed that "strongly adsorbed" butene resembled liquid *cis*-2-butene and that this changed to low molecular weight polymer on standing. In addition, he found no evidence for ionic intermediates in the ultraviolet. On the other hand, Leftin attributed a strong band at 3100 Å to an allylic carbonium ion, and provided kinetic and mechanistic evidence that the isomerization of the *n*-butene passed through this intermediate. Recently, Ozaki and Kimura (*12*) examined the reaction over deuterated acid catalysts. They suggested that over silica-alumina, and probably over alumina, the isomerization proceeded through a proton donor–acceptor mechanism, with protons furnished either by Bronsted sites or by carbonium ions formed when olefins react with Lewis acid sites. Our own tracer studies (*13*) revealed, however, that if Bronsted sites were important with silica-alumina, their concentration could be no more than about $3 \times 10^{11}/\text{cm}^2$; with alumina, it was concluded that the mechanism probably did not involve catalyst protons. Nevertheless, Ozaki and Kimura's data are in good general agreement with ours and, in addition, show that the mechanism over alumina differs from that over silica-alumina in some important way.

Previous work (*14*) on the isomerization of cyclopropane and the cracking of 2,3-dimethylbutane over silica-alumina and alumina catalysts showed that the rate of the former reaction increased markedly as the "water content" of the catalysts was increased while the rate of the latter reaction was nearly independent of this variable. The object of the present work was to determine the effect of the catalyst hydration state on the isomerization rates and the stereospecificity of the reaction. It was hoped that these measurements would reveal the nature of the active sites and/or the structure of the intermediates in the transition states.

EXPERIMENTAL

Catalysts. The silica-alumina (Houdry M-46), SA, and alumina, A, were used in a previous study (*14*), as were the procedures used for pretreatment at high temperatures and for "adding-back" water. The surface areas of the SA samples evacuated at 625°, 700°, 800°, and 900°C were determined by nitrogen adsorption (BET). The surface areas of the remaining samples, as well as the hydrogen contents of all samples, were taken from earlier work (*14*). This was valid because occasional redetermination of surface areas and hydrogen contents (*14*) had given good agreement. The fluorided alumina (FA) was furnished by the MK Research & Development Co., Pittsburgh, Pa.; it was made by soaking Catalyst A in 0.035 *M* TransistAR Grade H_2F_2. Acid, equivalent to 1.5% F, was present in the solution; 1.22% was found in the catalyst. Other properties are reported elsewhere (*14*).

Reagents and gases. Helium gas was from Airco (nominal purity, 99.997 mole %). It was passed through a large charcoal trap cooled at −196°C. Linde Oxygen (99.9 mole %) was passed through an activated charcoal trap cooled at −80°C to remove water. Phillips Pure Grade 1-butene (99+ mole %) was passed through Drierite to remove traces of water and then through sodium hydride to ensure quantitative removal of oxygenated impurities. Phillips Pure Grade *cis*-2-butene (99+ mole %) was distilled from −50° to

—196°C and degassed several times before use. Gas-phase chromatographic analyses revealed that the 1-butene contained less than 0.7% 2-butenes, and that the *cis*-2-butene contained no detectable impurities.

Procedure. Aliquots of catalyst were sealed into Pyrex or quartz reactors, which were fitted with stopcocks, and given the selected pretreatment. Fresh samples were used for each experiment. The catalytic activity was evaluated using our semiautomatic microreactor (*15*). Each experiment consisted of three parts carried out in the following order: (a) an experiment in which small slugs of reactant were carried by a helium stream over the catalyst at a constant temperature; (b) an experiment in which a mixed stream of helium and reactant flowed over the catalyst at various temperatures and the tail-gas was analyzed; and (c) a repeat of Part (a) on the poisoned catalyst. In Parts (a) and (c), each dose contained 3.1 cc(NTP) of reactant and the flow rate of the carrier gas was 28 cc(NTP)/min. The pressure in the reactor was about 2 atm. In Part (b), a mixture of 45% reactant and 55% helium was prepared by blending the streams from two capillary flow meters; the total flow rate over the catalyst was 58 cc(NTP)/min and the pressure in the reactor was close to 1 atm. During the tail-gas experiment, the catalytic activity was measured at six temperatures. After each change, the temperature was allowed to stabilize for at least 30 min before the effluent was analyzed. The process was continued in a cyclic manner, and the time required for determination of each activity point was 1 hr. Conversion isotherms were constructed by plotting the fraction reacted vs. time and drawing smooth curves through points corresponding to the same temperature. From the data at any particular reaction time, Arrhenius plots could be made and the apparent activation energy calculated.

The ratios of butenes formed from 1-butene and from *cis*-2-butene were determined at low conversions for several catalysts. Fresh samples were pretreated, but smaller amounts (A $\sim$ 0.05 g; SA $\sim$ 0.1 g) were used. This led to lower conversions than could be obtained in the same temperature range in the standard experiments. Slugs of 1-butene [4.1 cc(NTP)] and *cis*-2-butene [3.6 cc(NTP)] were passed over the samples using the same microcatalytic equipment mentioned above.

Analyses were made by gas chromatography using a 9-m column (¼-inch diam. Cu tubing) containing 25% dimethylsulfolane and 25% ethylene carbonate on 30–60 mesh Fisher Columnpak. The column was operated at 30°C. The three *n*-butenes were completely resolved on the column and isobutene was partially separated from 1-butene. However, isobutene was never present to an extent greater than 1%. In order to effect good separation of the butenes, it was necessary to freeze the sample to be analyzed in a U-tube situated between the reactor and the gas chromatograph. After a suitable period of collection, the trap was rapidly heated. This procedure gave rapid injection and sharp peaks, even in certain slug experiments where desorption of the butene from the catalyst required as long as 15 min.

The relative sensitivities of the *n*-butenes were determined; these were: 1-butene, 1.00; *trans*-2-butene, 1.00; and *cis*-2-butene, 1.07. In the data reported herein, no correction was made for the difference in sensitivities; conversions and product ratios were calculated on the basis of peak area.

Treatment of data. When slugs of gas are passed over a catalyst in a microreactor, the reaction time is a function of both the flow rate and the adsorption equilibrium constant. According to Bassett and Habgood (*16*), neglecting back-reaction, the effective rate constant, kK, for a simple first order reaction can be calculated from the relation

$$kK = -(F^\circ/273RW)\ln(1-x) \quad \text{mole atm}^{-1}\,\text{sec}^{-1}\,\text{g}^{-1} \qquad (1)$$

where k is the kinetic factor, K is the coverage factor, and F° is the flow rate in cc(NTP)/min; R is the gas constant, W the catalyst weight, and x the fraction converted. Since the isomerization of 1-butene is a reversible reaction, this equation must be modified. For the purposes of this study, it was sufficient to assume that the equilibrium can be represented by

$$\text{1-Butene} \underset{k'}{\overset{k}{\rightleftharpoons}} \text{2-Butene}$$

Taking this into account, Eq. (1) can be rewritten as

$$kK = \frac{F^{\circ}}{273\,RW(1 + k'/k)} \ln\left(\frac{1}{1 - x/x_e}\right) \qquad (2)$$

where x_e is the fraction of 2-butene at thermodynamic equilibrium. All thermodynamic data were taken from the work of Rossini *et al.* (*17*).

Obviously, the equilibrium written above is an oversimplification. Because the above equilibrium lies far to the right, however, the error in kK amounts to no more than a few per cent, even at fairly high conversions. This point was checked by substitution of probable rate constants in kinetic equations derived for the three-component system. The values of kK reported in this study were normalized to unit surface area and have units of mole atm^{-1} sec^{-1} m^{-2}. The rate constants for the tail-gas experiments were also calculated from Eq. (2).

RESULTS

Typical conversion isotherms for the Part (a) slug experiments are shown in Fig. 1. The poisoning rate for silica-alumina was much faster than that for alumina. The alumina rate constants, calculated by means of Eq. (2), could be extrapolated to zero slug number. With SA, on the other hand, nearly all the butene in the first slug either was adsorbed irreversibly or polymerized and that which was recovered was nearly equilibrated. Thereafter, the activity declined rapidly with slug number. Accordingly, the sixth slug was arbitrarily selected for comparative purposes.

As will be discussed later, the poisoning during the Part (b) tail-gas experiments was pronounced with alumina, but very slight with silica-alumina. Evidently, most of the loss of activity of the latter occurred during the Part (a) slug experiment (equivalent to only a few minutes of the tail-gas experiment), while the poisoning of alumina was gradual, requiring many hours of the tail-gas experiment to reach a constant activity.

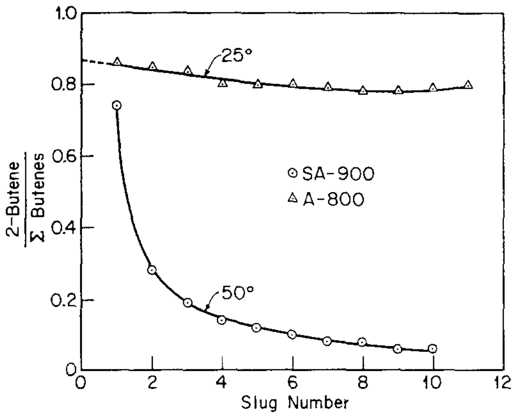


FIG. 1. Conversion isotherms for isomerization of 1-butene over silica-alumina and alumina; slug experiments.

In one of the tail-gas experiments, the effect of flow rate on conversion was measured at a constant temperature. When $-\log(1\text{-}x/x_e)$ was plotted vs. $1/F^{\circ}$ (Fig. 2), the data below 50% conversion fell close to a straight line, but above 50% conversion, deviation occurred. Evidently, the kinetics approximate the first order rate law [Eq. (2)]. The rate constant product, kK, calculated from the highest conversion points, was about 86% that calculated from the low conversion data. If the correction, x/x_e, had not been made, the curvature in Fig. 2 would have been more pronounced. All tail-gas experiments were carried out at $100/F^{\circ} = 1.72$, where most of the conversions were below 50%. In comparing rates of tail-gas and microcatalytic experiments, it should be borne in mind that the microcatalytic rates should be about eight times faster due to a factor of 4 in pressure and a factor of 2 in flow rate.

Representative conversion isotherms from the tail-gas experiments are shown in Figs. 3 and 4. Over SA (Fig. 3), the isotherms were fairly constant with time for all water contents. The behavior of A was quite dif-

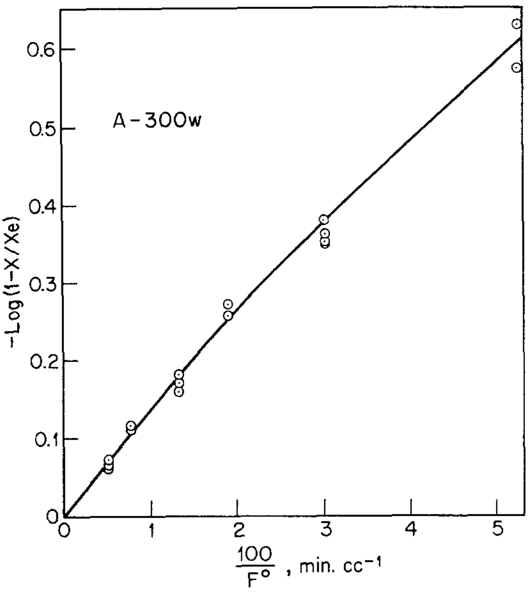


FIG. 2. Rate of isomerization of 1-butene over alumina; dependence on flow rate.

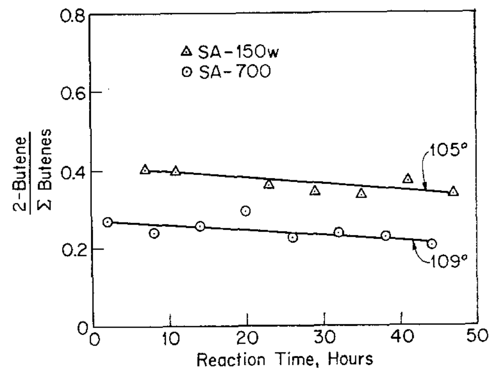


FIG. 3. Conversion isotherms for isomerization of 1-butene over silica-alumina; tail-gas experiments.

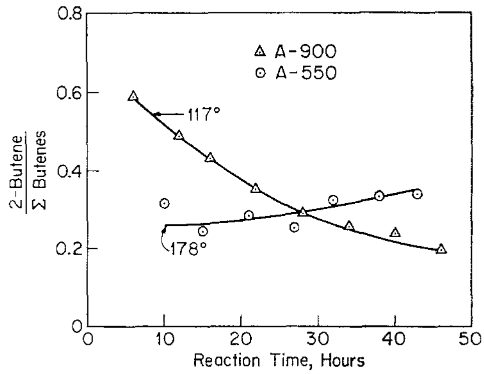


FIG. 4. Conversion isotherms for isomerization of 1-butene over alumina; tail-gas experiments.

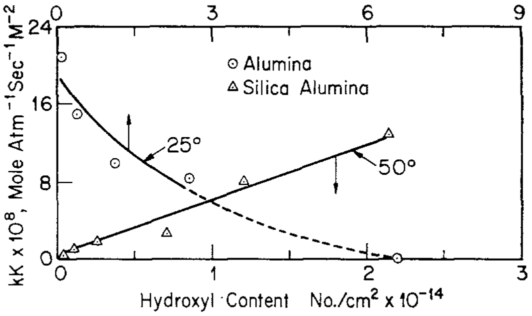


FIG. 5. Dependence of rate of isomerization of 1-butene on the water content of silica-alumina and alumina; slug experiments.

ferent (Fig. 4); for the sample dehydrated at 550°C, the conversion increased slightly with time, but after dehydration at 900°C (and similarly, 700° and 800°C), it decreased markedly. In comparing the relative activities of the SA catalysts and for calculating the activation energies, the data taken after 40 hr were used, although this choice made little difference. On the other hand, the relative activities of the alumina preparations were time-dependent, and it would have been best to compare the initial tail-gas activities by extrapolation to zero time. Unfortunately, the activity of several of the samples declined so rapidly that reliable data could not be obtained until after 20 hr of reaction. Consequently, the rate data were compared at this reaction time. As with SA, the activation energy for A was the same, whether it was calculated from data at 20 or 40 hr of reaction.

The rate constants calculated from the Part (a) slug experiments are plotted as a function of hydroxyl content in Fig. 5. The rates of isomerization increased with the water content of SA and decreased with the water content of A. The rate over SA-150w (water "added-back" at 150°) was immeasurably fast at 25°C. When water was "added-back" to A at 300° (or at 150°), the catalyst had no detectable activity at 25°. With the latter (A-150w), the conversion at 50° was <2% and at 111° it was only 8%. This may be compared with the conversion over A-550 which was 72% at 25°.

A-150w could be made an active catalyst by heating to 550° for 2 hr while helium was flowing over the sample. Following this treatment, which probably removed most of the "added-back" water, the conversion at 25° was 30%. Subsequently, the same sample was given a standard pretreatment at 550°, and additional slugs of 1-butene passed at 25°C. The initial conversion was 85%. This was greater than that obtained with A-550, demonstrating that the activity is a sensitive function of the history of the catalyst.

Qualitatively, the rate constants correlated in the same way with water content for the tail-gas experiments (Fig. 6). Again, the rate increased about linearly with the hydroxyl content of silica-alumina (up to SA-300w), but decreased over alumina, i.e., the rate increased as the water content was decreased, but appeared to reach a maximum at A-800.

Additional results are given in Tables 1 and 2. The apparent activation energies were determined from the Arrhenius equations by plotting $-\log(1 - x/x_e)$ vs. $1/T$. For the SA series, the E_a's were 12 ± 1 kcal/mole (Col. 4), indicating that they were independent of hydroxyl content. In addition, the relative rates of isomerization of 1-butene to *cis*- and *trans*-2-butene were essentially constant at about 1.2 (Col. 6). The data for alumina (Table 2) were not as regular. The apparent activation energies obtained for three samples of A-550 and for A-300w were 16 ± 1 kcal/mole, but were lower by about 5 kcal/mole for alumina dehydrated at higher temperatures. The ratio of *cis*- to *trans*-2-butene is probably meaningful for only A-300w, A-800, and A-900, where 4.0, 3.8, and 3.0, respectively, were obtained. The low values for A-550 and A-700 are too close to equilibrium to be significant. They may be due to a very rapid secondary reaction of the *cis*-2-butene. Generally, the *cis*/*trans* ratio decreased rapidly with increased conversion.

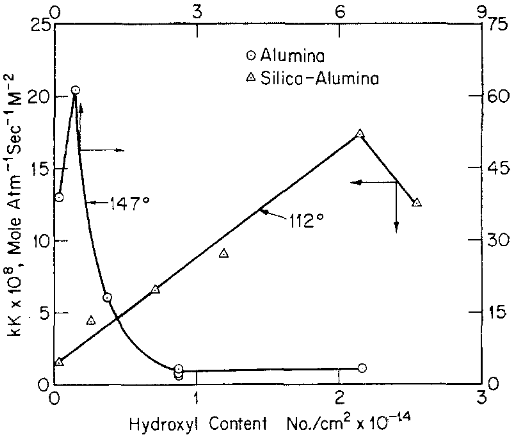


FIG. 6. Dependence of rate of isomerization of 1-butene on the water content of silica-alumina and alumina; tail-gas experiments.

TABLE 1

ISOMERIZATION OF 1-BUTENE OVER SILICA-ALUMINA; TAIL-GAS EXPERIMENTS[a]

Catalyst and pretreatment[b] (°C)	Catalyst weight (g)	Surface area (m^2/g)	E_a (kcal/mole)	Conv. at 112° (%)	$\left(\frac{Cis}{Trans}\right)^c$	$kK \times 10^8$ at 112° (mole atm^{-1} sec^{-1} m^{-2})
SA-150w	1.04	269	11	54	1.2	12.4
SA-300w	1.00	259	13	62	1.2	17.3
SA-550	1.03	265	11	43	1.2	9.0
SA-625	1.02	274	12	34	1.1	6.5
SA-700	1.03	270	11	23	1.1	4.4
SA-800	1.02	257	12	9	1.3	1.5
SA-900	1.02	218	12	8	1.8	1.6

[a] Data after 40 hr reaction; partial pressure of 1-butene (in helium) was 340 mm and its flow rate was 26.7 cc(NTP)/min.

[b] Numbers give temperature at which catalyst was evacuated; w indicates water was added-back before evacuation.

[c] Equilibrium value at 112°C = 0.42; ref. (*17*).

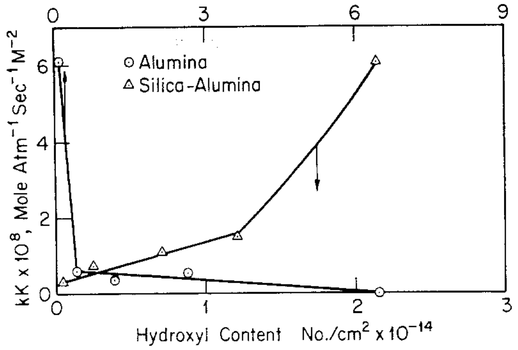


FIG. 7. Dependence of rate of isomerization of 1-butene on the water content of silica-alumina and alumina at 50°; slug experiments on poisoned catalysts.

Some results of the Part (c) slug experiments are depicted in Fig. 7. These data, which were obtained *after* the tail-gas experiments, are equivalent to those one would obtain after passage of an "infinite" number of slugs. For these samples, the conversion was constant with slug number, indicating that the poisoning rate was immeasurably slow. As with fresh samples, the rate increased with water content over silica-alumina and decreased over alumina. The rates over alumina were very low except for A-900; even though the experiments were carried out at 50° (instead of 25° for the fresh samples), the values of *kK* were still well below those for the fresh samples (compare Figs. 5 and 7).

Initial *cis*/*trans* ratios, derived from slug experiments at very low conversions, are collected in Table 3. Lower temperatures and smaller catalyst weights were required to achieve these low conversions. The product chromatographic peaks were magnified by lowering the attenuation on the output of the detector; this substantially increased the accuracy. The data confirm that *cis*- and *trans*-butene-2 are produced initially at nearly equal rates over silica-alumina, whereas *cis*-butene-2 appears to be the primary product over alumina.

The rates of isomerization and selectivities for the isomerization of *cis*-2-butene were determined for some of these same catalysts. Comparison of typical results for the two reactants is made in Table 4. Over alumina, the rates were indistinguishable, but over silica-alumina, 1-butene reacted much faster than *cis*-2-butene. Neither catalyst produced 1-butene and *trans*-2-butene in the equilibrium ratio; 1-butene was always in excess in the initial product. This suggests, but does not prove, that *trans*-2-butene is formed via intermediate 1-butene.

TABLE 2

ISOMERIZATION OF 1-BUTENE OVER ALUMINA; TAIL-GAS EXPERIMENTS[a]

Catalyst and pretreatment[b] (°C)	Catalyst weight (g)	Surface area[c] (m^2/g)	Activation energy (kcal/mole)	Conv. at 147° (%)	$\left(\frac{Cis}{Trans}\right)^d$	$kK \times 10^8$ at 147° (mole atm^{-1} sec^{-1} m^{-2})
A-300w	1.15	145	16	12	4.0	3.5
A-550	1.15	152	16	9	0.6	2.3
A-550	0.90	152	15	9	0.6	3.0
A-550	1.16	143	17	10	0.6	2.6
A-700	1.15	134	9	46	0.9	18
A-800	1.15	133	12	82	3.8	61
A-900	1.15	126	11	60	3.0	39
FA-550[e]	0.97	143	16	15	5.1	5.2

[a] Data after 20 hr reaction; partial pressure of 1-butene (in helium) was 340 mm and its flow rate was 26.7 cc(NTP)/min.

[b] Numbers give temperature at which catalyst was evacuated; w indicates water was added-back before evacuation.

[c] These surface areas were not measured but were assumed to be the same as those determined for the same catalysts used in an earlier study (*14*).

[d] Obtained by extrapolation to zero conversion. However, since the conversion was varied by changing the temperature, these initial selectivities represent values at a variety of temperatures.

[e] Fluorided alumina containing 1.22 wt % F.

TABLE 3

SELECTIVITIES AT LOW CONVERSIONS OF 1-BUTENE; SLUG EXPERIMENTS[a]

Catalyst and pretreatment[b] (°C)	Weight (g)	Reaction temp. (°C)	Fraction converted	$\left(\frac{cis\text{-2-Butene}}{trans\text{-2-Butene}}\right)^c$
SA-150w	0.101	0	0.010	1.4
SA-550	0.102	0	0.012	1.0
SA-700	0.108	0	0.008	1.2
SA-900	0.100	0	0.003	1.9
A-150w	1.149	111	0.08	5
A-550	0.050	0	0.007	4.6
A-900	0.049	0	0.014	3.5

[a] Amount of 1-butene per slug was 4.1 cc(NTP); carrying gas flow rate = 28 cc(NTP)/min.

[b] Numbers give temperature at which catalyst was evacuated; w indicates water was added-back before evacuation.

[c] The value at thermodynamic equilibrium is 0.22 at 0°C and 0.42 at 111°C; ref. (*17*).

TABLE 4

ISOMERIZATION OF *cis*-2-BUTENE OVER ALUMINA AND SILICA-ALUMINA; SLUG EXPERIMENTS[a]

Catalyst	Weight (g)	Temp. (°C)	Surface area[b] (m²/g)	Reactant	Fraction converted	$\left(\frac{\text{1-Butene}}{Trans}\right)^c$	$kK \times 10^8$ (mole atm^{-1} sec^{-1} m^{-2})
A-550	1.149	27	143	*Cis*	0.63[d]	0.09	8.2
A-550	0.050	26	143	*Cis*	~.01	0.3	—
A-550	1.149	25	143	1-Butene	0.72[d]	—	8.4
A-550	0.050	28	143	1-Butene	~.02	—	—
SA-550	1.038	50	265	*Cis*	0.23[e]	0.3	1.0
SA-550	0.102	26	265	*Cis*	~.003	1.0	—
SA-550	1.027	50	265	1-Butene	0.85[e]	—	8.0
SA-550	0.102	26	265	1-Butene	~.07	—	—

[a] The amount of 1-butene per slug was 4.1 cc(NTP); 3.6 cc(NTP) of *cis*-2-butene were used. The carrying gas flow rate was 31 cc/min (at 25°) and the catalyst pretreatment temperature was 550° in all experiments.

[b] Taken from earlier work; ref. (*14*).

[c] Values at thermodynamic equilibrium are 0.04 at 25°C and 0.057 at 50°C.

[d] Extrapolated to zero slug number.

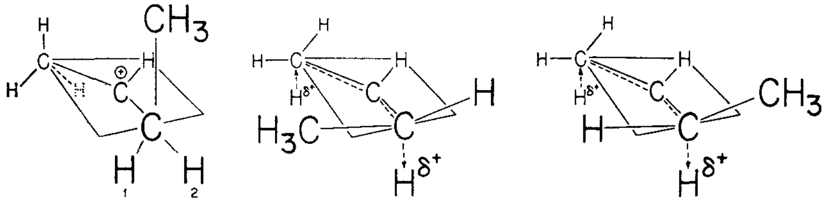
[e] Data for sixth slug.

DISCUSSION

The rate of isomerization varied inversely with the "water content" of alumina and directly with that of silica-alumina. This behavior was followed irrespective of the type of experiment in which the activity was measured. Moreover, the selectivity differed for the two catalysts; the initial ratio of *cis*-2-butene to *trans*-2-butene fell between 1 and 2 for SA and 3.5 to 5 for A. This is in agreement with observations by others (*5, 8, 11, 12*). These differences indicate that the active sites and, consequently the intermediate or transition states, are not the same for the two materials.

Considering first the reaction over silica-alumina, the increase in rate with water content is consistent with the idea that hydroxyl groups are involved in the transition state. Our tracer work (*13*) indicates that the concentration of Bronsted sites, if they are present, must be less than $3 \times 10^{11}/\text{cm}^2$, i.e., no more than 0.2% of the available hydrogen is acidic. It is possible, however, that hydroxyl groups function as co-catalyst (*18, 19*) with butene chemisorbed on Lewis sites as postulated for cyclopropane (*14*). In this case, only hydroxyls adjacent to Lewis sites would count.

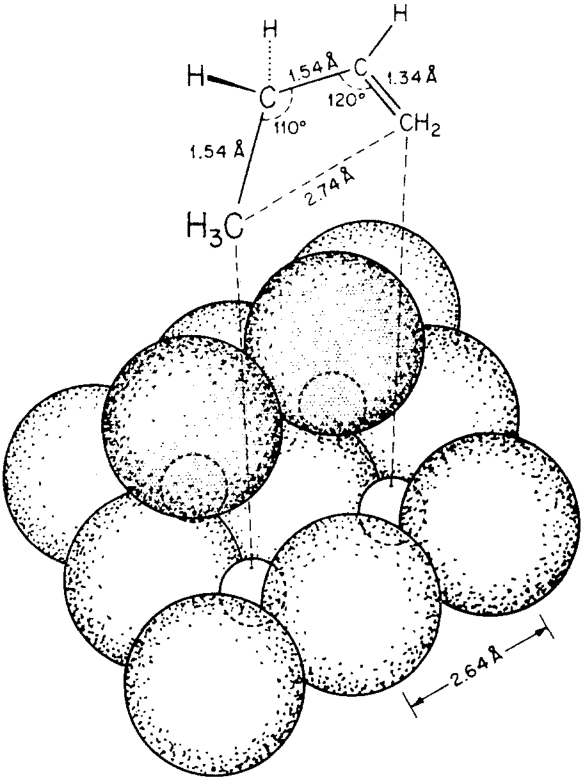
A possible intermediate, formed on a



a. Classical Carbonium Ion Intermediate

b. Gauche Transition State

c. Trans Transition State



d.

Fig. 8. Possible intermediates for butene isomerization.

Bronsted (or dual Lewis-hydroxyl co-catalyst) site, is the classical secondary butyl carbonium ion. As indicated by Ozaki and Kimura (*12*), this ion could also be formed by a bimolecular reaction of olefin with Lewis-bound substrate. As illustrated in Fig. 8(a), butyl carbonium ion would be adsorbed on the catalyst with the trigonal carbon atom, and the atoms surrounding it forming a plane parallel to the surface. Loss of a proton from position 1 would lead to the formation of *cis*-2-butene and from position 2 to *trans*-2-butene. On a statistical basis, one would expect the loss of the two protons to be nearly equally probable so that the *cis*/*trans* ratio would be close to unity.

Another possible reaction is the concerted "hydrogen switch" process (*3*). As illustrated in Figs. 8(b) and (c), the transition state formed on the approach of 1-butene to the surface can have two configurations: the *trans* form, if the methyl group eclipses the hydrogen atom on C-2, and the gauche form, if hydrogen atoms on C-2 and C-3 eclipse one another. On approach of the *trans* rotational isomer to the surface, the "hydrogen switch" would give *trans*-2-

butene and on approach of the gauche form, *cis*-2-butene. The C-3 hydrogen atoms in the *trans* form are equivalent and either can participate in formation of the transition state. There are two equivalent gauche forms, but only the noneclipsed hydrogen on C-3 would be in a favorable position to form the transition state. From these considerations, i.e., a plane of symmetry in the *trans* form and two equivalent gauche forms, one would also predict the selectivity of the "hydrogen switch" process to be close to unity. Leftin and Hermana (*11*) used a similar argument, involving the *trans* and gauche configurations, to argue that the selectivity for *cis*-2-butene would be less than 2 if the reaction occurred via an allylic carbonium ion intermediate. While abstraction of hydride ions to form allylic carbonium ions (or the closely related hydrogen switch) would explain the selectivity observed in the present work, it is difficult to reconcile this process with the increase in rate with water content.

In contrast to silica-alumina, the rate of isomerization over alumina correlated inversely with the hydroxyl content. This behavior suggested that the active centers do not include hydroxyl groups, i.e., that addition of water to form new hydroxyl groups actually decreased the concentration of active sites. Furthermore, the high selectivities obtained with 1-butene (*cis/trans* $\geqslant 3.5$) cannot be explained on a purely statistical basis as discussed above. To be sure, if the gauche rotational isomer of 1-butene adsorbed and desorbed at a faster rate than the *trans* form, the high *cis/trans* ratio could be explained. There is, however, no apparent reason why this should occur. When part of the hydroxyl groups on A-550 were replaced by fluorine, both the rate and selectivity increased. These effects may be attributed to a combination of two factors: a decreased hydroxyl concentration and an increased electropositivity of the surface aluminum ions.

Haag and Pines (*7*) suggested that intermediate allylic carbanions were formed in the isomerization of 1-butene over a Na-alumina catalyst. They explained the high *cis/trans* ratio ($\sim$4) on the basis that the *cis* anion was stabilized by a cyclic intermediate. On pure alumina, a cyclic intermediate conceivably might be formed and stabilized by an aluminum ion in place of the larger sodium ion. It is interesting that Haag and Pines (*5*) observed almost the same selectivities on pure alumina as on Na-alumina (*7*).

Peri (*9*) envisioned the condensation of adjacent hydroxyl groups on the alumina surface, leaving an oxide in the outermost layer and an exposed aluminum ion in the next lower layer. The possibility that these ions function as nucleophilic and electrophilic centers was mentioned by Peri (*9*) and he suggested that either proton or hydride abstraction could occur. Although the formation of a cyclic intermediate was not discussed by Peri, he did suggest that the dual acid-base sites could effect the transient formation of a carbanion during butene isomerization. Moreover, this idea is in accord with his observation that the IR spectrum of "strongly adsorbed" butene on alumina resembled that of *cis*-2-butene.

According to Peri's (*9*) conception of a dehydrated alumina surface, the minimum distance between exposed aluminum ions is 2.64 Å. In Fig. 8(d), the gray circles represent oxide ions in the outer layer and the larger lighter circles, oxide ions in the next lower layer. The small white circles represent exposed aluminum ions in the same plane as the latter oxide ions. If 1-butene (in the *cis* configuration) approached the surface, it could be adsorbed with the terminal carbons (2.74 Å separation) attached to the exposed *pair* of aluminum ions. The strong electrostatic field surrounding these small cations would polarize the carbon–hydrogen bond, affording a means by which the molecule would be "frozen" in the *cis* configuration. Indeed, Pickert, Rabo, Dempsey, and Schomaker (*20*) have proposed that the catalytically active sites in zeolites exchanged with divalent cations are exposed cations, and that the electrostatic field surrounding these cations is sufficient to polarize the carbon–hydrogen bond of an adsorbed hydrocarbon toward the structure C^+H^-. If the molecule were adsorbed in this manner adjacent to an oxide ion in the outer layer, the latter could readily remove a proton from the allylic position of the olefin. The oxide ion, being comparable in size (diam. = 2.64 Å) with the olefin, could then act as a medium for transfer of the relatively small proton to the terminal methylene group. Finally, the olefin would desorb as *cis*-2-butene. This process would, in effect, amount to an intramolecular rearrangement of the olefin. Admittedly, this idea is speculative, but it does account for the following observations:

1. The activity increased with increasing dehydration temperature and, hence, with a correspondingly increased concentration of exposed aluminum ions and upper layer oxide ions.
2. Very high ratios of *cis*-2-butene to *trans*-2-butene were produced from 1-butene.
3. In previous work with deuterated alumina (*13*), the appearance of deuterium in the 2-butenes was small and decreased with increased dehydration temperature. These data were sufficient to rule out all mechanisms involving transfer of catalyst hydrogen to the chemisorbed intermediate.

The heats of adsorption of olefins and hydrocarbons on cationic sites have been measured by Habgood (*21*). Using zeolites as gas chromatographic columns, he measured the retention times of the hydrocarbons as a function of the reciprocal absolute temperature. The heats of adsorption for *n*-butane had values of 9.2–10.2 kcal/mole when the zeolite was charge-balanced with monovalent ions and 7.4–13.9 kcal/mole when divalent ions were used. Similarly, the values for propylene were 7.6–8.4 and 9.6–19 kcal/mole, respectively. Habgood suggested that heats of adsorption of this magnitude could be attributed to quadrupole and ion-induced dipole polarization energies created by the strong electric field surrounding the exposed cation. In like manner, Rabo *et al.* (*20*) observed that the activity of exchanged zeolites toward the cracking of *n*-hexane was greater for divalent cations than for monovalent cations. Furthermore, for a given charge on the cation, the activity increased as the size of the ion decreased. Since the charge density around trivalent cations is even greater, one could expect even larger heats of adsorption with these ions. Although the trigonal aluminum ions in dehydrated alumina would be more effectively shielded than cations in zeolites, they would still be exposed to an appreciable extent, especially where two or three ions lie adjacent to one another. Accordingly, where adjacent aluminum ions are exposed on dehydrated alumina, these electrophilic centers could provide a considerable driving force for the 1-butene to adsorb in the *cis* configuration [Fig. 8(d)].

MacIver *et al.* (*22*), reported that the selectivity of aluminas for *cis*-2-pentene formation in the isomerization of 1-pentene decreased and disappeared as the drying temperature was increased from 250° to 500°. These experiments were carried out at 150° and initial *cis/trans* ratios determined by lowering the conversion by increasing the space velocity. Under these conditions, the most active catalysts were the least selective. MacIver's data for γ- and η-Al_2O_3 dried at 250° and 500° gave *cis/trans* ratios, extrapolated to zero conversion, of about 2.2 and 0.55, respectively. These data were not given for aluminas evacuated at higher temperatures. The selectivities obtained in the present work for A-300w and A-550 (Table 2) show the same decreasing trend with decreasing water content; the *cis/trans* ratios were 4.0 and 0.6, respectively. At higher drying temperatures, the reverse trend appeared, i.e., the more active catalysts were more selective. The present experiments were run differently from MacIver's, i.e., the conversion was lowered by decreasing the temperature. Hence, the more active catalysts were run at lower temperatures than the less active ones. This may have altered the selectivity. This is suggested by the higher values for the slug experiments (Table 3). Evidently, all of the variables have not yet been sorted out, so that it is not yet possible to separate unambiguously the effects of temperature from those of pretreatment.

Joice and Rooney (*23*) suggested that

above equilibrium amounts of *trans*-2-butene are produced on isomerization of *cis*-2-butene when the reaction goes through the classical secondary carbonium ion; high ratios of 1-butene to *trans*-2-butene result when the allylic butenyl ion is intermediate. They presented data suggesting that either process may predominate over $Mg(ClO_4)_2$. Thus, the high initial ratio found for SA-550 (Table 4) supports Leftin's contention (*11*) that the allylic ion is involved over extensively dehydrated silica-alumina. Over A-550, the ratio was too close to the equilibrium value to be unambiguous. No explanation can presently be offered for the close similarity in rates of isomerization of 1-butene and *cis*-2-butene over alumina. Presumably, *cis–trans* isomerization occurs independently of the double-bond shift on this material, if a cyclic intermediate is involved in the latter reaction.

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