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Catalytic Isomerization of Ethylenic Hydrocarbons

XII. Isomerization of 2-Butenes Selectively Deuterated in the Allylic and Vinylic Positions Over Alumina and Silica–Alumina

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The isomerization of 2,3-d_2- and 1,4-d_6-*cis*-butenes was carried out on alumina and silica–alumina catalysts. Over both catalysts, double-bond shift is closely related to exchange between the allylic hydrogens of the reactant and the catalyst. On the other hand, it becomes apparent from the reported data that *cis–trans* isomerization proceeds through two different paths: a mechanism (I) involving exchange between the catalyst and the vinylic hydrogens of the reactant and an "intramolecular" mechanism (II) without any exchange between the reactant and the catalyst. It is shown that both double-bond shift and *cis–trans* reaction by mechanism I can occur on the two catalysts by a stereospecific carbonium ion mechanism while mechanism II is not fully understood.

INTRODUCTION

We have already studied the isomerization over alumina (*1*) and silica–alumina (*2*) of ethylenic hydrocarbons of about 10 different skeletal structures. Over both catalysts, the relative rate measurements were consistent with a mechanism involving single-adsorbed carbonium ions. However, the isotope effects measured on these catalysts during the isomerization of selectively labeled *cis*-butenes do not comply exactly with this view (*3*). On both catalysts, the isotope effects obtained for *cis–trans* isomerization were small, compared to those observed in the course of double-bond shift. This result led us to conclude that if C–H bond-breaking is very likely to occur in the rate-determining step of double-bond shift, it does not seem to be the same in the case of *cis–trans* isomerization. Thus, as already suggested, over alumina (*4–6*) both reactions might not wholly proceed through the same mechanism.

To make this point clearer, we determined the isotope distributions of the products formed by isomerization from 2,3-d_2- and 1,4-d_6-*cis*-butene. These results, together with the measured isotope effects, are discussed and the mechanisms consistent with our data are considered.

I. EXPERIMENTAL METHODS

The experimental procedure and materials have been partly described elsewhere (*3*).

Apparatus and Analysis

The microcatalytic pulse technique (Fig. 1) was used with nitrogen as carrier gas (3–12 liters/hr). The reagents were purified by gas chromatography on a 4-m column

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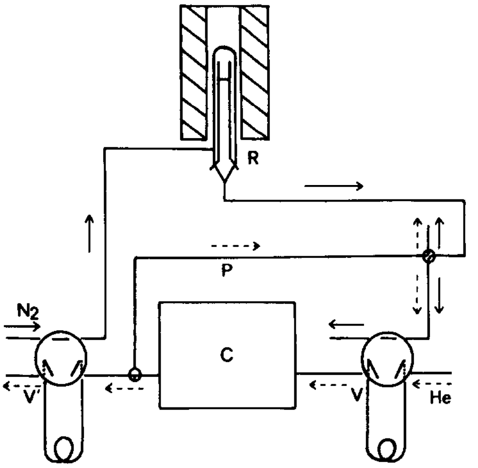


FIG. 1. Schematic diagram of apparatus. C, chromatograph; P, way for further purification of the products; R, reactor; V, V': six-port switching valves.

(1/8 in.; hexamethylphosphoramide, 30%; dimethyl-sulfolane, 10% on chromosorb W; 1 liter/hr helium; 0°C), then trapped and flash-evaporated in the reactor. The reaction mixture was frozen before being evaporated for analysis in the chromatograph. All three butenes were completely resolved and collected separately for mass spectral analysis (Thomson-Houston THN 206; 11 eV).

In one case (that of d_6-*cis*-butene isomerization) the D-position in the product d_6-*trans*-butene was analyzed by NMR spectroscopy of the corresponding dibromide. For that purpose, the *trans*-butene formed in about 20 successive pulses was collected in a mixture composed of bromine, carbon tetrachloride, and tetramethylsilane.

Procedure

To prevent a possible isotopic dilution of the hydrogen atoms present on the surface, each pulse (about 0.5 cm^3) was included in a larger slug of ethylene (10 cm^3). This gas was chosen for its volatility in preference to 3-methyl-1-butene, previously used for isotope effects measurements (*3*). Furthermore, between two consecutive pulses the catalyst was swept with an additional 10-cm^3 pulse of ethylene. This treatment proved to be effective as shown by the absence of highly exchanged species in the products.

Both catalysts exhibited a deactivation period during which the conversion decreased more or less rapidly from one experiment to the next before finally reaching a stable and reproducible activity. All experiments were performed under normal working conditions, i.e., after deactivation of the catalysts.

II. RESULTS

1. Isotope Distributions in the Isomerization Products of d_2- and d_6-cis-Butene

Some results obtained at low conversion over alumina at 250°C and silica–alumina at 85°C are reported, respectively, in tables 1 and 2.

When 2,3-d_2-*cis*-butene is used as a reactant, the products contain mainly d_1- and d_2-species and few or no heavier d_3- and d_4-species. When 1,4-d_6-*cis*-butene isomerization is carried out, it is principally d_5- and d_6-species that are detected; d_7-species are found in small amounts even at a 15% conversion (pulse V in Table 1). This means that most of the protonic sites, if they intervene, are not deuterium exchanged or that ethylene plays its role correctly in restoring these sites. Similarly highly exchanged species, i.e., d_0 from d_2-*cis*-butene and $d_{i<5}$ from d_6-*cis*-butene are not formed in appreciable amounts and exchange, when it does occur, is always single- stepped.

The amount of deuterium in the products was followed in relation to the extent of the isomerization. Figures 2 and 3 give two examples of the development of the d_i-species in 1-butene and *trans*-butene formed, respectively, from d_6- and d_2-*cis*-butene over alumina. Extrapolation near zero *cis*-butene conversion in such dia-

TABLE 1
ISOMERIZATION OVER ALUMINA AT 250°C

Experiments	Products: %	Isotope distribution (%)									Number D per mole
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
Starting material 2,3-d_2-*cis*-butene		0.75	2.7	96.1	0.5						1.96
I	1-butene :1.45	2.7	3.3	93.5	0.4						1.915
	trans-butene :2.05	3.2	23.1	73.3	0.4						1.71
	cis-butene :96.5	1.3	2.6	95.8	0.3						1.95
II	1-butene :2.8	2.2	3.7	93.4	0.7						1.93
	trans-butene :3.8	1.0	26.1	72.7	0.2						1.72
	cis-butene :93.4	1.4	3.8	94.5	0.3						1.94
III	1-butene :4.6	1.5	5.9	91.8	0.7						1.915
	trans-butene :6.4	1.8	29.4	68.6	0.2						1.67
	cis-butene :89.0	1.4	5.1	93.4	0						1.92
Starting material 1,4-d_6-*cis*-butene				0.05	0.1	0.95	10.7	88.3			5.87
IV	1-butene :1.2	0.5	0.6	0.7	1.4	9.9	84.0	2.7	0.2		4.83
	trans-butene :2.4	0.1	0.2	0.2	0.2	0.8	11.4	86.3	0.8		5.85
	cis-butene :96.4	0.1	0.1	0.1	0.2	1.1	10.2	87.9	0.2		5.85
V	1-butene :4.6	0.4	0.4	0.5	1.4	11.6	83.2	2.3	0.1		4.82
	trans-butene :9.6	0.1	0.1	0.1	0.2	1.4	13.9	83.6	0.6		5.82
	cis-butene :85.8		0.1	0.1	0.3	1.4	11.4	86.4	0.2		5.84

TABLE 2
ISOMERIZATION OVER SILICA-ALUMINA AT 85°C

Experiments	Products: %	Isotope distribution (%)									Number D per mole
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
Starting material 2,3-d_2-*cis*-butene		0.75	2.7	96.1	0.5						1.95
I	1-butene :1.6	4.1	4.7	89.4	1.8						1.90
	trans-butene :1.8	5.3	55.8	38.5	0.4						1.34
	cis-butene :96.6	1.1	3.5	95.2	0.2						1.945
II	1-butene :3.1	1.5	8.2	87.1	3.2						1.92
	trans-butene :3.7	3.5	61.9	34.2	0.4						1.31
	cis-butene :93.2	1.2	6.1	92.7							1.915
III	*trans*-butene :1.2	2.0	51.0	46.3	0.7						1.46
	cis-butene :97.65										
Starting material 1-4 d_6-*cis*-butene		—	—	0.05	0.10	0.95	10.7	88.3			5.87
IV	1-butene :0.8	1.2	1.2	1.2	1.3	10.3	82.7	1.9	0.2		4.74
	trans-butene :1.9	0.1	0.2	0.2	0.2	1.4	12.9	84.0	0.9		5.82
	cis-butene :97.3	—	—	0.1	0.2	1.0	10.5	87.7	0.5		5.87
V	1-butene :1.1	0.5	0.5	0.5	1.3	10.4	82.8	3.8	0.3		4.80
	trans-butene :3.1	0.2	0.2	0.3	0.3	1.0	10.9	85.5	1.5		5.84
	cis-butene :95.8	—	—	0.2	0.2	0.7	11.5	88.2	0.2		5.92

TABLE 3
ISOTOPE DISTRIBUTION (EXTRAPOLATED VALUES) AND ISOTOPE EFFECTS

Alumina 250°C		Isotope effects (3)[a]
2,3-d_2-*cis*-butene → 1-butene	100% d_2	1.0
1,4-d_6-*cis*-butene → 1-butene	100% d_5	2.0 (2.0)
2,3-d_2-*cis*-butene → *trans*-butene	25% d_1 75% d_2	1.2
1,4-d_6-*cis*butene → *trans*-butene	100% d_6	1.4 (1.6)
Silica alumina 85°C		
2,3-d_2-*cis*-butene → 1-butene	100% d_2	1.0
1,4-d_6-*cis*-butene → 1-butene	100% d_5	2.9 (2.7)
2,3-d_2-*cis*-butene → *trans*-butene	50% d_1 50% d_2	1.3
1,4-d_6-*cis*-butene → *trans*-butene	100% d_6	1.3 (1.35)

[a] Values in parentheses obtained with d_6-*cis*-butene of higher purity (5.87 D) than in Ref. (3).

grams leads to the values reported in Table 3. In the following discussion we shall talk mostly about initial isotope distribution.

In the course of double-bond shift, *cis*-butene undergoes H-exchange in the allylic position: 1,4-d_6-*cis*-butene leads to almost pure d_5-1-butene (after correction for d_5 impurities in the starting *cis*-butene), whereas vinylic hydrogens are not removed; 2,3-d_2-*cis*-butene yields 1-butene without any deuterium loss.

On the other hand, *cis–trans* isomerization occurs without exchange of allylic hydrogens with the catalysts: 1,4-d_6-*cis*-butene gives only d_6-*trans*-butene. Furthermore the *trans*-isomer retains the vinylic hydrogens in part; 2,3-d_2-*cis*-butene yields about 25% d_1-*trans*-butene and 75% d_2-*trans*-butene over alumina at 250°C (about 0.25 D-loss); over silica–alumina at 85°C d_1- and d_2-species in *trans*-butene are formed in equal amounts (about 0.5 D-loss) (Table 3). This last result is unexpected, given the usual mechanisms of olefin isomerization (this point will be discussed later).

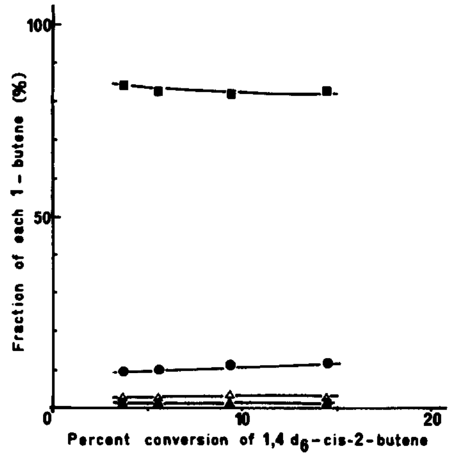


FIG. 2. Isomerization of 1,4-d_6-*cis*-butene over alumina at 250°C. Isotope distribution in 1-butene (d_3 (▲); d_4 (●); d_5 (■); d_6 (△).

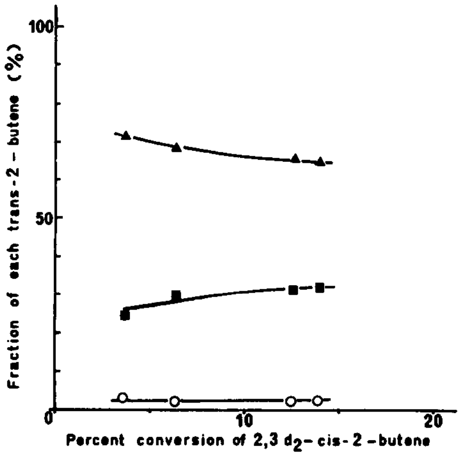


FIG. 3. Isomerization of 2,3-d_2-*cis*-butene over alumina at 250°C. Isotope distribution in *trans*-butene; d_0 (○); d_1 (■); d_2 (▲).

TABLE 4

d_1-*trans*-BUTENE TO d_2-*trans*-BUTENE RATIO IN 2,3-d_2-*cis*-2-BUTENE ISOMERIZATION

		Temperature (°C)		
		60	85	120
Silica alumina	d_1-*trans*-butene/d_2-*trans*-butene	1.5	1.0	0.65
		Temperature (°C)		
		175	250	302
Alumina	d_1-*trans*-butene/d_2-*trans*-butene	0.5	0.33	0.17

2. *NMR Analysis of the Trans-Butene Formed in the Isomerization from 1,4-d_6-cis-Butene over Alumina and Silica–Alumina*

The NMR spectrum of the corresponding dibromide shows only one singlet near 4.1 ppm ascribed to "vinylic" hydrogen. No signal was detected at the expected shift for "allylic" protons (1.9 ppm). Geometric isomerization thus occurs without any hydrogen transfer from the vinylic to the allylic position in the molecule.

3. *Effect of Reaction Temperature on the Formation of d_1- and d_2-trans-Butene from 2,3-d_2-cis-Butene*

The ratio d_1-*trans*-butene/d_2-*trans*-butene increases with decreasing temperature (Table 4). On both catalysts, the difference of activation energy for the formation of the two species is about 4 kcal/mole.

III. DISCUSSION

Double-Bond Shift

On both catalysts, 1-butene formed from *cis*-butene shows that double-bond shift implies exchange of a hydrogen atom with the catalyst, H-abstraction occurring from the allylic position in the reactant. It should also be stated (*3*) that, from the large isotope effect due to the allylic deuterium atoms (Table 3), the C–H (or C–D) bond-breaking occurs in the rate-determining step of the reaction. These results agree with most of the mechanisms proposed up to now, be they associative or dissociative, and provide further evidence that the reaction proceeds intermolecularly as stated recently (*7*).

Whatever the mechanism may be, it becomes evident that protonic sites exist on the surface of the catalysts, either initially or formed in the course of the reaction. According to the structural effects established previously (*1,2*), it seems very likely that the reaction proceeds through carbonium ions formed on Brønsted sites by an associative mechanism.

Cis–trans Isomerization

The data are more difficult to account for.

(a) 1,4-d_6-*cis*-Butene only yields d_6-*trans*-butene but with a kinetic isotope effect of 1.6 over alumina and 1.35 over silica–alumina (Table 3). However, the NMR spectrum of the d_6-*trans*-butene shows that intramolecular shift of allylic hydrogen does not take place. The isotope distribution is that expected with a carbonium ion mechanism; however, the isotope effects observed, particularly over alumina, seem too important to be ascribed to secondary effects. If these effects are primary, it means that the *cis–trans* isomerization involves an allylic C–H

(C–D) bond-breaking. This is in disagreement with the carbonium ion mechanism postulated for double-bond shift.

(b) The more interesting feature is that 2,3-d_2-*cis*-butene leads to a mixture of d_1, and d_2-*trans*-butene species (Table 3), the corresponding isotope effect being rather low. This isotope distribution is in contradiction with the carbonium ion mechanism, at least if we suppose that isomerization proceeds stereospecifically. This last assumption has often been postulated in heterogeneous catalysis for such reactions as hydrogenation (*8*) or dehydration (*9,10*). Kibby *et al.* (*11*) even suggest that the most typical feature of surface-catalyzed reactions must be the *cis*-stereospecificity as opposed to the nonstereospecificity of reactions occurring in homogeneous media. That means, in our case, that the addition of the proton to the olefin to form the *s*-butyl carbonium ion and the abstraction of another proton to yield the geometric isomer occur on the side of the molecule facing the catalyst. We reported in a previous paper a result which supports this idea: we showed, in the case of *cis*- and *trans*-3,4-dimethyl, 3-hexenes, that the reaction proceeded stereospecifically: the two isomers did not convert into each other over alumina (*12*) and silica–alumina (*2*) whereas this transformation should take place if the addition and abstraction of protons occured on both faces of the adsorbed molecule.

By a stereospecific carbonium ion mechanism d_2-*cis*-butene should yield exclusively d_1-*trans*-butene, a proton from the catalyst allowing the carbonium ion formation at the C_2 and a subsequent release of a deuteron from the C_3, leading to the d_1-*trans*-butene after rotation (120°) around the C_2–C_3 bond (Fig. 4). This expected result is observed neither on alumina nor on silica–alumina where d_2-*trans*-butene forms in large amounts.

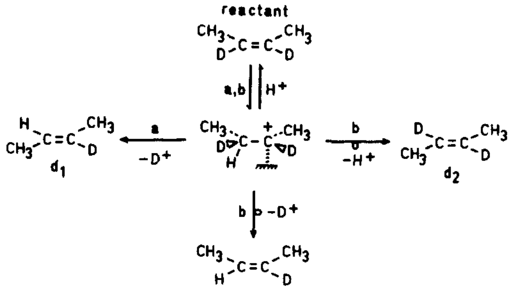


FIG. 4. Carbonium ion mechanism; *cis*-reaction (→) and *trans*-reaction (⇝) relative to the surface. (a) Example of a stereospecific process; (b) example of a nonstereospecific process.

But if a nonstereospecific carbonium ion mechanism were involved, d_2-*cis*-butene would yield, besides 1-butene and d_1- and d_2-*trans*-butenes, a mixture of d_1- and d_2-*cis*-butene (Fig. 4). In fact d_1-*cis*-butene is not a primary product of the isomerization of d_2-*cis*-butene as one can see from Fig. 5 or, by extrapolating to zero conversion, the selectivity for d_1-*cis*-butene calculated from Tables 1 and 2. This result supports the idea that a nonstereospecific carbonium ion mechanism is not suitable.

All our results can be better explained by two simultaneous mechanisms. Indeed one can add to the conventional carbonium ion mechanism postulated for double-bond shift, a mechanism which allows *cis*-*trans* isomerization with D-retention. As it proceeds in a stereospecific way, the former will only lead to d_1-*trans*-butene

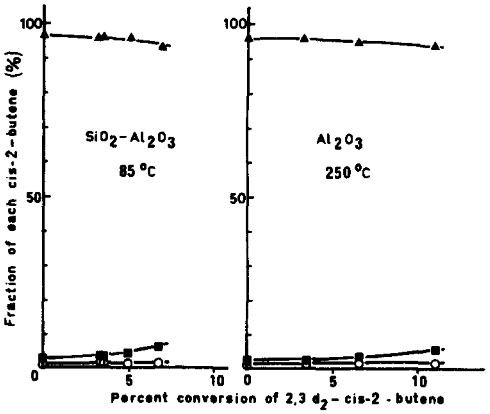


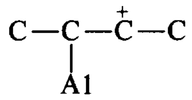
FIG. 5. Isomerization of 2,3-d_2-*cis*-butene over silica–alumina at 85°C and alumina at 250°C. d_0 (○); d_1 (■); d_2 (▲).

from d_2-*cis*-butene, while the second, which we might call "intramolecular," would allow the isomerization of d_2-*cis*-butene into d_2-*trans*-butene, that is without D-exchange. Such a reaction, namely intramolecular, has already been considered possible by others (*4,6*) to account for *cis–trans* isomerization over alumina.

The difference in activation energy which is about 4 kcal/mole larger for d_2-*trans*-butene than for d_1-*trans*-butene formation corroborates the existence of two mechanisms for *cis-trans* isomerization. At high temperature the reaction would be exclusively "intramolecular" whereas at room temperature it would proceed only through the carbonium ion mechanism.

The isotope effects obtained in the geometric isomerization of d_2- and d_6-*cis*-butene can be discussed within this framework: in the case of 2,3-d_2-*cis*-butene, one can suppose that, since the intramolecular *cis–trans* isomerization takes place without exchange, it produces no isotope effect and that the isotope effects obtained in the overall process only arise from the parallel carbonium ion reaction. If this is the case, the relative amounts of d_1- and d_2-*trans*-butene in the products together with the experimental value of the overall isotope effects allow us to estimate the part played by each mechanism in the absence of isotope effects (light butene isomerization). It is found that over alumina at 250°C the reaction would proceed 63% intramolecularly and 37% with exchange, whereas on silica-alumina at 85°C the reaction is only 38% intramolecular.

In the isomerization of 1,4-d_6-*cis*-butene, on the other hand, no primary isotope effect is to be expected from the carbonium ion mechanism. The lowering in reaction rate may be ascribed either to secondary isotope effects in any of the two mechanisms or to primary isotope effects in the intramolecular mechanism. In the former case, if the intramolecular reaction occurs without any C–H bond-breaking, it can be assumed that it takes place on Lewis sites. The molecule would then be linked to the catalyst by a C–Al bond as in the case of Webb's carbonium ion: C—C—C—C (*13*)



$$C-\underset{\underset{Al}{|}}{C}-\overset{+}{C}-C$$

or of the protonic residue of Ozaki and Kimura (*14*).

But if we consider that primary effects do intervene, which is very likely, at least over alumina where the overall effect is 1.6, it appears that the intramolecular mechanism involves an allylic C–H bond-breaking in the reactant. Given the part played by this process in the overall reaction, we can estimate the magnitude of the isotope effect arising in that intramolecular reaction. Values of about 2 and 3 are found, respectively, for alumina and silica–alumina. Both are close to the experimental values obtained in double-bond shift and are of the order of magnitude to be expected for primary effects.

Besides allylic C–H bond-breaking in the rate-determining step of the reaction, this intramolecular mechanism has the important characteristic of allowing only geometric isomerization. None of the allylic mechanisms described in the literature (*15,16*) appear to meet these two requirements exactly. For instance, the σ-allylic species mentioned on zinc oxide (*17*) could make *cis–trans* isomerization possible without exchange. But it would be necessary to assume that they could not allow the intramolecular transfer of hydrogen that would lead to double-bond shift, and the reason for such an assumption is not clear.

In order to obtain further information on this point and on the nature of active sites we are currently studying d_2- and d_6-*cis*-butene isomerization in terms of the following parameters: pretreatment and deactivation state of the catalyst and selective poisoning of active sites.

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