JOURNAL OF CATALYSIS 76, 48–60 (1982)

The Isomerization and Metathesis of *n*-Butenes

III. Reduced Molybdena–Alumina Catalyst

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Received September 17, 1981; revised January 20, 1982

The isomerization of *n*-butenes was studied over a molybdena–alumina catalyst which had been reduced with hydrogen at 500°C (e/Mo = 1.4 ± 0.1). The rate of *cis–trans* isomerization was found to be much higher than that of double bond isomerization. The initial *trans*-/1-butene ratio was determined as around 10 from data obtained in the recirculation system. Metathesis proved to play a significant role in this reaction (except for the first pulse in the microcatalytic studies). The isomerization was accompanied by extensive H–D exchange when mixtures of C_4H_8 and C_4D_8 were co-reacted and by significant deuterium incorporation when C_4H_8 was reacted in the presence of D_2. The experimental data suggested that, except for *cis–trans* transformation by metathesis, the isomerization proceeds by hydride insertion leading to a sec-butyl intermediate.

INTRODUCTION

Data for the isomerization of *n*-butenes have been reported previously (*1–3*) for our unreduced molybdena–alumina catalyst (8% Mo on γ-Al_2O_3). Over the freshly oxidized catalyst these reactions proceeded by an acidic mechanism. The rate of the acidic-type isomerization decreased during the reaction in a recirculation system and *cis–trans* isomerization via metathesis became the prevailing reaction (*1*). The "turning on" of metathesis activity was accompanied by the slight reduction of the catalyst (*1, 2*).

The isomerization rates of 2-butenes have been reported to be significantly higher over molybdena–alumina catalysts reduced with hydrogen at 550°C for 2 hr than over unreduced catalysts (*4, 5*). A similar increase was observed in the rate of propene metathesis (*5*). The metathesis of propene as well as the cross-metathesis of butenes were suppressed, while the isomerization of butenes was enhanced over the reduced catalyst by H_R (hydrogen adsorbed at high temperature) (*5–7*). These facts raise some interesting questions such as: what is H_R and how does it affect metathesis sites? How important is metathesis in the *cis–trans* isomerization over the reduced catalyst? Can the isomerization reactions be explained in terms of a common intermediate? The latter two questions are addressed herein.

The surface chemistry of reduced molybdena–alumina catalyst (*7–12*) and its relationship to catalyst function (*13–17*) have been of continuing interest here as has the development of butene isomerization as a diagnostic tool for the prediction of the nature of catalytic sites and the characterization of reaction intermediates (*1–3, 18, 19*). The present paper is concerned with the isomerization of butenes over reduced molybdena–alumina catalysts.

EXPERIMENTAL

Catalyst. The same molybdena–alumina catalyst (8% Mo) prepared by impregnation of γ-alumina (Ketjen CK 300) was used as in most of our previous works (loc. cit.). The same charge of catalyst was calcined before each experiment in flowing dry oxygen overnight at 500°C, followed by evacuation for 30 min at the same temperature.

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0021-9517/82/070048-13$02.00/0

The catalyst was then reduced with flowing ultrapure hydrogen (60 cm^3/min) at atmospheric pressure for 1 hr at 500°C, followed by evacuation at the same temperature for 1 hr. The degree of reduction achieved under these conditions (*7*) was $e/Mo = 1.4 \pm 0.1$, as determined by the reoxidation of the catalyst.

Reagents. 1-Butene and *cis*-2-butene were Matheson C.P. grade; before use they were outgassed after freezing with liquid nitrogen, and distilled from a vessel cooled with dry-ice in acetone. The 1-C_4D_8 was from Merck which we determined to have 97 atom % isotopic purity. The *cis*-2-C_4D_8 was prepared by the procedure reported by Larson *et al.* (*20*) and purified by gas chromatography.

Procedure. The experiments were carried out in an all glass recirculation system and in a microcatalytic pulse system. Reactants and products were separated by gas chromatography and the separated fractions were analyzed for the deuterium distribution in individual components by mass spectrometric analysis. A more detailed description of the procedure was given previously (*1*, *2*).

RESULTS

Experiments with *cis*-2-butene were carried out in the recirculation system using 100 mg of catalyst and an initial pressure of *cis*-2-butene of 150 Torr. The changing product distribution with time for a typical experiment (at 40°C) is shown in Fig. 1. The initial ratio of *trans*-2-butene to 1-butene was about 12. Both rates decreased sharply after reacting for a few minutes. Propene and pentene, the products of cross-metathesis between 2-butene and 1-butene, were not observed in the early stages but appeared later on. Pentene was detected by gas chromatography, but was not determined quantitatively because the broadness of the peaks and because the amounts recovered appeared to be less than those of propene.

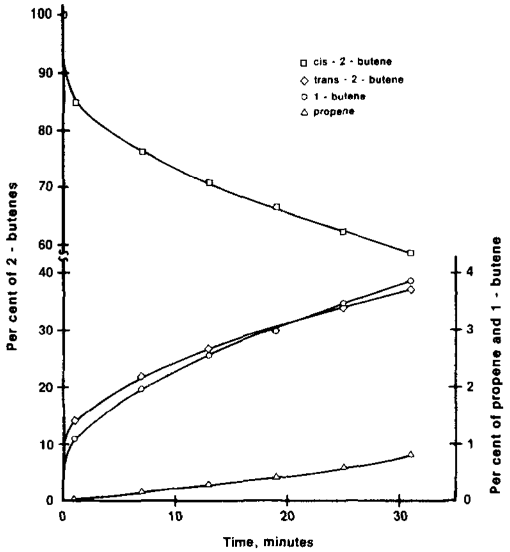

FIG. 1. Isomerization of *cis*-2-butene over reduced (e/Mo = 1.4) molybdena–alumina catalyst at 40°C in the recirculation system. Weight of catalyst: 0.1 g; initial pressure of *cis*-2-butene was 150 Torr.

The reaction of *cis*-2-butene-d_0 + *cis*-2-butene-d_8 was carried out to determine the role of metathesis in the *cis*–*trans* transformation. The microcatalytic pulse system was used for the experiments, the weight of the catalyst being 50 mg and the reaction temperature 60°C. The product distributions are given in Table 1, and the deuterium distributions in 2-butenes in Table 2. In the first pulse about 40% *trans*-2-butene and only about 2% 1-butene were produced. The amount of propene formed indicates that a significant fraction of 1-butene product was consumed in the cross-metathesis. The formation of small amounts of *n*-butane (0.2%) can be explained by the reaction of hydrogen held by the reduced catalyst, even after evacuation for 1 hr at 500°C; note the 8% mass loss from the first pulse.

The deuterium distribution in *trans*-2-butene formed in the first pulse (Table 2) showed that extensive hydrogen scrambling had taken place. Only a little more d_4-species than d_3- and d_5-species was present in the *cis*- and in the *trans*-2-butene. This

TABLE 1

Product Distributions from Isomerization of *cis*-2-C_4H_8 + *cis*-2-C_4D_8 over a Molybdena–Alumina Catalyst Using the Microcatalytic Pulse System at 60°C[a]

Catalyst	Pulse No.	Molecules × 10^{-17}					
		cis-Butene	1-Butene	*trans*-Butene	Propene	*n*-Butane	Mass loss
Reduced[b]	1	49.9	1.9	41.3	2.7	0.2	8.1
	2	55.0	0.4	43.3	5.6	—	—
	3	55.7	0.3	43.6	5.1	—	—
	4[d]	68.9	0.4	43.4	5.9	—	−14.6
Unreduced[c]	1	95.2	1.8	4.7	—	—	2.4
	2	99.9	1.4	2.4	—	—	0.3
	3[d]	103.0	0.2	4.6	0.2	—	−4.0
	4	99.2	0.2	4.4	0.1	—	—

[a] Weight of catalyst, 50 mg (2.5 × 10^{19} Mo); pulse size, 1.04 × 10^{19} molec.; He flow rate, 60 cm^3/min.

[b] Reduction with H_2 (60 cm^3/min) at 500°C for 1 hr (to e/Mo $\simeq$ 1.4), and evacuation at the same temperature for 1 hr.

[c] For further information see Refs. (*1*, *2*).

[d] Before the pulse the catalyst was treated with *cis*-2-C_4H_8 + *cis*-2-C_4D_8 (initial pressure; 200 Torr) for 10 min at 60°C, and flushed with helium at the same temperature for 1 hr.

result suggested that metathesis played a minimal role in the isomerization process, but this was not true with subsequent pulses.[3] In these approximately the same amount of *trans*-2-butene (40%, Table 1) was formed as in the first pulse, but significantly less 1-butene and more propene was produced. No *n*-butane nor mass loss was observed in the second and successive pulses. Extensive hydrogen scrambling still took place (Table 2), but the much higher concentrations of d_4-species compared with the d_3- and d_5-species clearly indicated the significant role that metathesis played in the *cis*–*trans* transformation. The exact determination of the fraction of *trans*-2-butene formed via metathesis was not possible because of the extensive hydrogen scrambling. Part of the d_4-species evidently was formed via an isomerization process involving intermolecular H or D transfer as were part of the d_3- and d_5-species. To further complicate matters, part of the d_3- and d_5-species undoubtedly resulted from metathesis of already exchanged olefins or from secondary exchange with already formed *trans*-2-butene-d_4. From an equimolar mixture of *cis*-2-butene-d_0 and *cis*-2-butene-d_8, the equilibrium ratio of $d_4/(d_0 + d_8)$ is unity. Hence, the product formed by metathesis will be about twice the concentration of the d_4-species. Using this estimation, in the first pulse not more than about 12% of the *trans*-2-butene resulted from metathesis, but in the successive pulses over 50% was formed in this way.

Over unreduced molybdena–alumina catalysts metathesis was not observed in the first pulses of *cis*-2-butene (*1*). Hydrogen scrambling was present, but significantly decreased after conditioning the catalyst by contact with *cis*-2-butene (initial pressure, 200 Torr) for 10 min at 60°C; now *trans*-2-butene was formed almost exclusively via metathesis. No decrease in hydrogen scrambling nor increase in metathesis activity was observed after the same treatment of the reduced catalyst (4th pulse in Tables

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[3] Note that if isomerization of *cis*- to *trans*-2-butene occurred exclusively by metathesis, the deuterium distribution in the latter should be d_0: d_8: d_4 = 1 : 1 : 2. This behavior was approached in the most favorable cases.

TABLE 2

Deuterium Distribution in 2-Butenes from the Isomerization of *cis*-2-C_4H_8 + *cis*-2-C_4D_8 over a Reduced Molybdena–Alumina Catalyst Using the Microcatalytic Pulse System at 60°C[a]

Pulse No.	Butene isomers	Deuterium distribution (%)									Metathesis (%)[b]
		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
0	Reactant *cis*	45.7	0	0	0	0	0	0.8	7.2	46.3	0
1	*cis*	28.1	11.2	3.3	1.3	2.5	1.7	3.2	15.0	33.8	5
	trans	14.3	15.8	6.3	3.9	6.1	5.0	7.2	21.5	20.0	12
2	*cis*	25.3	7.1	2.6	4.1	10.9	5.2	3.6	11.2	29.9	22
	trans	9.2	7.8	5.7	9.4	23.1	10.9	6.8	11.8	15.3	46
3	*cis*	25.4	8.0	2.6	4.1	10.9	5.2	3.1	10.5	30.3	22
	trans	9.2	8.4	5.4	10.0	21.9	11.0	6.1	11.5	16.5	44
4[c]	*cis*	28.0	5.7	2.1	3.7	9.3	4.0	2.5	9.7	35.0	19
	trans	11.1	8.2	5.3	10.1	23.6	9.6	6.2	10.6	15.4	47

[a] Analysis of products for reduced catalyst from experiments of Table 1.

[b] Estimated values, $2N_4$ (see text).

[c] Before the pulse the catalyst was treated with *cis*-2-C_4H_8 + *cis*-2-C_4D_8 (initial pressure: 200 Torr) for 10 min at 60°C, and flushed with helium at the same temperature for 1 hr.

1 and 2), possibly because the first pulse effected the same result (see Fig. 2).

For comparison purposes the reaction of an equimolar mixture of *cis*-2-butene-d_0 and *cis*-2-butene-d_8 was studied in the microcatalytic pulse system over unreduced molybdena–alumina catalyst (50 mg) under the strictly comparable conditions as with the reduced catalyst. The product distribution is given in Table 1, and the deuterium distribution in the product *trans*-2-butene is shown in Fig. 2. Very high selectivity can be achieved in this way (*1*, *21*) but the activity is many times lower than with the reduced catalysts (Table 1). Both in the first pulse, where no metathesis was observed over unreduced catalyst and little over the reduced one, and in 4th pulse, after soaking the catalyst with *cis*-2-butene so that metathesis became the prevailing reaction, the reduced catalyst proved to be at least 10 times more active for *cis–trans* isomerization than the unreduced catalyst.

Since the isomerization of *cis*-2-butene over reduced molybdena–alumina catalyst was accompanied by an extensive hydrogen exchange, the isomerization of *cis*-2-butene-d_0 was studied in the circulation system in the presence of deuterium (18% D_2 in C_4H_8). The results are summarized in Table 3 (Expt. 1); mass spectrometric analysis of the individual butenes was carried out when less than 50% of the initial deuterium was consumed. Formation of only 0.7% butane was observed. It also can be seen that only d_1 isomers were obtained (besides the d_0). This may be accounted for in terms of isomerization, but not metathesis.

A similar experiment was made with a mixture of 1-butene-d_0 and deuterium (Expt. 2). The exchange character was similar to that obtained with *cis*-2-butene. Nearly 25% of the product 2-butenes appeared as d_1 isomers, but the amount of deuterium incorporated into the unconverted 1-butene was much larger (Table 3, Expt. 2). This differed from the result with *cis*-2-butene (Expt. 1) where the incorporation into products (particularly 1-butene) was greater. The rate of hydrogenation (6.4% *n*-butane) was comparable with the

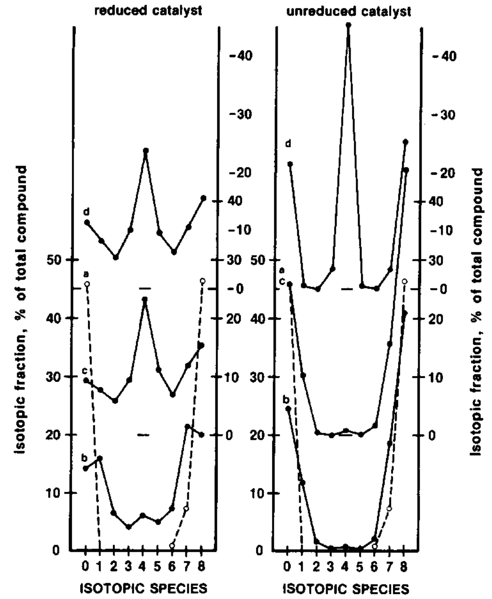


FIG. 2. Deuterium distribution in *trans*-2-butene produced in reaction of *cis*-2-C_4H_8 + *cis*-2-C_4D_8 over reduced and unreduced molybdena–alumina catalyst at 60°C in pulse system. Weight of catalyst: 50 mg reduced at 500°C for 1 hr. (a) Initial deuterium distribution in *cis*-2-butene; (b) 1st pulse; (c) 2nd pulse; (d) 3rd pulse after contact with the catalyst with *cis*-2-C_4H_8 + *cis*-2-C_4D_8 for 10 min at 60°C. Scales for (a) and (b) are on the left; scales for (c) and (d) are on the right and are displaced upward to prevent overlap with (a) and (b), or each other.

rate of double bond isomerization. The possibility that these stepwise exchange processes were taking place on the exposed alumina portion of the surface (*23*) was considered and abandoned (see below).

Sharp differences between the reduced molybdena–alumina on the one hand and γ-alumina, zinc oxide, and microcrystalline chromia catalysts on the other were observed in the concomitant exchange with D_2 during the 1-butene isomerization. The data for the experiments of a mixture of 82% 1-butene and 18% D_2, carried out under the same conditions as with reduced molybdena–alumina, are summarized in Table 3. Whereas in the case of reduced molybdena–alumina, 23 to 24% of the product 2-butenes appeared as d_1 isomers, values for γ-alumina, zinc oxide, La_2O_3, and chromia catalysts were very much lower. Significantly, all of the latter group have been shown to isomerize olefins via the allylic (intramolecular) mechanism (*19, 22, 38*).

Experiments with mixtures of 1-butene-d_0 + 1-butene-d_8 were carried out in the pulse system using 15 mg of molybdena–alumina catalyst; the results are summarized in Table 4. The extensive hydrogen exchange (1.6 H/D atoms exchanged per molecule of product 2-butenes) indicates that multiple exchange took place besides isomerization and this agrees with the results obtained in the recirculation system (Table 3) which indicated that exchange into the 1-butene was much faster than into the *cis*-butene. Isotope effects were insignificant. As with the results for *cis*-2-butene (Tables 1 and 2), double bond isomerization decreased in the 2nd pulse compared with the first. Metathesis, however, increased significantly (see ethene and propene). The change in the character of the catalyst can be described by the M/I ratio, i.e., the ratio of the products of metathesis to the products of isomerization. In this calculation we considered only the products of productive metathesis (twice the amount of ethene) because the cross metathesis depends on the amount of first formed 2-butenes. The amount of propene is equal to the amount of 2-butene consumed in cross metathesis, therefore it has to be counted in the products of isomerization. The M/I ratio increased from 0.1 in the first pulse to 1.6 in the pulse after treating the catalyst with 1-butene.

It has been reported elsewhere (*6*) that both *cis–trans* and double-bond shift isomerization were enhanced by hydrogen either in the gas phase or preadsorbed on the reduced molybdena–alumina catalyst. The same effect of preadsorbed hydrogen was observed in the hydrogen scrambling (Table 4). One pulse of hydrogen was sent over the catalyst immediately before each one of the 1-butene pulses. The metathesis activity of the catalyst was not influenced sig-

TABLE 3

Isomerization of *cis*-2-Butene and 1-Butene in the Presence of D_2 in the Recirculation System

Experiment No.	Reagent	Catalyst	Total conversion (%)	Butene isomers	Percentage butenes in product[j]	Deuterium distribution (%)		
						d_0	d_1	d_2–d_8
1[a]	82% *cis*-2-butene	Reduced	45.9[b]	*trans*	40.9	84.0	16.0	—
	18% D_2	molybdena–alumina		1-but	2.6	66.0	34.0	—
				cis	54.1	96.5	3.5	—
2[c]	82% 1-butene	Reduced	31.5[b]	*trans*	3.7	77.0	23.0	—
	18% D_2	molybdena–alumina		1-but	68.5	83.2	16.8	—
				cis	4.4	75.9	24.1	—
3	82% 1-butene	Microcrystalline	68.6[e]	*trans*	44.9	96.0	4.0	—
	18% D_2	Chromia[d]		1-but	31.2	95.1	4.9	—
				cis	18.2	96.8	3.2	—
3a	18% 1-butene	Microcrystalline	38.5[e]	*trans*	21.0	97.0	3.0	—
	18% D_2	Chromia[d]		1-but	63.0	96.4	3.6	—
				cis	12.8	98.0	2.0	—
4[f]	82% 1-butene	γ-Alumina	21.0	*trans*	8.9	98.8	1.2	—
	18% D_2			1-but	79.0	98.1	1.9	—
				cis	12.1	99.1	0.9	—
5[g]	82% 1-butene	Zinc oxide	23.2[h]	*trans*	4.1	99.0	1.0	—
	18% D_2			1-but	75.0	99.1	0.9	—
				cis	18.9	98.5	1.5	—
6[i]	76% 1-butene	Lanthanum oxide	20.2	*trans*	2.2	99.0	1.0	—
	24% D_2			1-but	79.8	99.3	0.7	—
				cis	18.0	98.9	1.1	—

[a] Molybdena–alumina (0.2 g) reduced with H_2 at 500°C for 1 hr and evacuated at the same temperature for 1 hr; 50 cm^3 (NTP) butene + 11 cm^3 (NTP) D_2. Reaction temperature, 60°C.

[b] Total conversion was calculated on the basis of all products. For *cis*-2-butene: isomerization (*trans* + 1-butene) 43.5%, cross metathesis (propene) 1.7%, hydrogenation (*n*-butane) 0.7%; for 1-butene: isomerization (*cis* + *trans*-butene) 8.1%, metathesis (2 × ethene + propene) 17%, hydrogenation (*n*-butane) 6.4%.

[c] Reaction temperature, 65°C; other experimental conditions are the same as (*a*).

[d] Catalyst (0.5 g) prepared according to Ref. (*22*); activated by flowing H_2 for 14 hr at 500°C and evacuated at the same temperature for 1 hr. Reaction temperature, 60°C; other experimental conditions are the same as (*a*). We are indebted to Professor Gary Haller for this sample of his catalyst.

[e] Two experiments are shown at total conversion given (isomerization 33.8 and 63.1%, hydrogenation 3.0 and 5.7% respectively); data from separate experiments.

[f] γ-Al_2O_3 (0.5 g) same as used in Ref. (*19*), activated by flowing O_2 for 2 hr at 530°C and evacuated overnight at the temperature. Other experimental conditions are the same as (*a*).

[g] ZnO (2.0 g) used in Ref. (*19*), activated by flowing O_2 for 2 hr at 530°C and evacuated for 2 hr at the same temperature. Reaction temperature, 50°C; other experimental conditions are the same as (*a*).

[h] Total conversion given (isomerization 23.0%, hydrogenation 0.2%).

[i] Reaction temperature, 25°C; catalyst weight = 0.04 g. Catalyst activation same as described earlier (*38*).

[j] The difference between 100% and the sum of the butene percentages is largely due to the percentage propene; smaller amounts of butane were also formed.

TABLE 4

Isomerization of 1-Butene-d_0 + 1-Butene-d_8 on Reduced Molybdena–Alumina in Microcatalytic Pulse System at 60°C[a]

Treatment[b]	Pulse No.	Products, molecules × 10^{-17}						Butene isomers	Deuterium distribution (%)									H(D)[d] exchange	Isotope effect[e]
		1-but	*cis*	*trans*	Ethene	Propene	M/I[c]		d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
	0							1-Butene	47.2	—	—	—	—	—	1.5	11.9	39.4		
None	1	70.2	5.1	11.8	1.1	3.6	0.11	1-Butene	22.3	15.6	8.2	2.7	1.2	4.3	10.9	17.4	17.4	0.8	1.1
								2-Butene	10.8	14.9	12.7	9.8	9.1	10.5	13.5	12.9	5.8	1.6	1.2
	2	79.0	2.6	3.1	4.8	4.9	0.90	1-Butene	24.6	12.6	8.7	2.8	1.3	4.7	10.2	13.9	21.2	0.8	1.1
								2-Butene	15.7	12.5	13.7	10.5	9.3	9.8	11.4	10.8	6.4	1.6	1.5
	3[f]	97.0	1.3	1.1	3.3	1.8	1.6	1-Butene	33.4	7.9	6.0	1.5	0.6	2.5	8.4	12.2	27.7	0.7	1.1
								2-Butene	21.7	15.0	11.3	6.7	6.7	6.2	9.3	10.8	12.5	1.2	1.5
H_2	1	56.0	10.2	21.4	0.8	5.4	0.05	1-Butene	17.3	16.5	10.3	3.4	1.6	4.8	13.2	17.8	15.2	1.1	1.0
								2-Butene	8.7	14.7	15.1	10.4	7.6	11.9	14.3	12.5	4.8	1.8	1.2
	2	71.7	3.4	4.7	5.5	8.7	0.66	1-Butene	21.9	12.1	9.1	4.2	1.3	5.4	12.9	13.8	19.3	1.0	1.0
								2-Butene	11.7	15.4	15.8	13.0	9.0	10.3	11.9	8.5	4.4	1.9	1.7
NO	1	89.8	1.1	0.8	1.4	0.3	1.24	1-Butene	33.0	10.8	4.0	1.1	0.5	1.7	5.9	16.2	26.8	0.6	1.1
								2-Butene	33.4	9.4	5.5	5.4	5.4	6.2	6.4	10.6	16.1	1.0	1.5
	2	97.4	1.4	0.7	0.1	0.1	0.14	1-Butene	37.6	4.5	1.8	0	0	1.0	4.0	16.3	34.7	0.4	0.9
								2-Butene	34.5	10.0	4.9	6.0	5.5	6.3	6.2	10.1	15.0	1.0	1.6
CO[g] reduced	1	76.4	1.5	2.0	1.6	1.9	0.3	1-Butene	35.7	9.3	3.5	—	—	0.9	6.1	9.3	35.1	0.6	—
								2-Butene	25.8	15.1	9.0	6.4	4.9	6.0	6.7	11.9	14.0	1.3	1.4
	2	80.1	0.7	0.8	5.1	2.6	1.24	1-Butene	39.1	7.1	1.2	—	—	—	2.1	8.0	42.5	0.2	—
								2-Butene	24.6	16.3	6.0	5.3	4.8	6.0	6.1	12.3	18.6	1.1	1.4

[a] Catalyst 15 mg (7.5 × 10^{18} Mo) reduced with flowing H_2 at 500°C for 1 hr and evacuated at the same temperature for 1 hr. He flow rate, 50 cm³ (NTP)/min; pulses contained 1.04 × 10^{19} molecules.

[b] The catalyst treatment was carried out at 60°C in the pulse system by sending one pulse of H_2 or NO (1.04 × 10^{19} molecules) immediately before each pulse of 1-butene.

[c] The metathesis/isomerization ratio was calculated by taking into account the products of productive metathesis and double bond shift isomerization. M/I = 2 × [ethene]/[2-butenes + propene].

[d] The number of H(D) atoms exchanged per molecules of butene was calculated by using the equation of Hightower and Hall (*23*), viz. $H(D) = \sum_{i=0}^{4} iN_i + \sum_{i=5}^{8} (8 - i)N_i$ where N_i is the mole fraction of the *i*th species (i = number of D atoms/molecule).

[e] The isotope effect was calculated by the method given in Ref. (*23*).

[f] After the 2nd pulse the catalyst was treated with 1-C_4H_8 + 1-C_4D_8 (initial pressure 120 Torr) at 60°C for 10 min and flushed with helium for 1 hr.

[g] Reduced as in (*a*) except with CO instead of H_2.

nificantly, but both the isomerization and the H(D) exchange increased. The response was particularly large with the first pulse.

The coordinative unsaturated sites of the reduced molybdena–alumina catalyst can be effectively poisoned by treatment with NO (*13, 17*). The NO was added in the same way as with hydrogen, i.e., by sending a pulse of NO immediately before each 1-butene pulse (Table 4). The pulse of NO directly preceding the first pulse of 1-butene decreased significantly the total conversion and the extent of hydrogen scrambling. In the first pulse, the metathesis reaction was not influenced by the NO treatment, but after the 2nd pulse of NO, metathesis was almost completely eliminated while the total conversion and extent of scrambling were further reduced. This is not at variance with our earlier report (*17*), where the objective was to determine the smallest amount of chemisorbed NO which would eliminate hydrogenation of propene; these amounts left metathesis activity unaffected.

The *cis*/*trans* ratio and its temperature dependence in the 1-butene isomerization are characteristic for the type of isomerization. Experiments were carried out in the recirculation system with 1-butene as the reagent. By extrapolation of the conversion vs reaction time curves to zero conversion, the ratio of the initial rates for the *cis*- and *trans*-butene formation were determined. As can be seen from Fig. 3, the ratio of the initial rates over the reduced molybdena–alumina catalyst is very close to unity, and nearly independent of the temperature.

For comparison purposes, 1-butene isomerization experiments were made under comparable conditions over lanthanum oxide, γ-alumina, and zinc oxide catalysts. The catalysts and the conditions for pretreatment were identical to those described by Lombardo *et al.* (*19*). Over each of these catalysts (see Fig. 3) the ratio of initial rates for the formation of *cis*- and *trans*-2-butene was >7 at 30°C and the ratio decreased significantly with increasing temperature. For the unreduced molybdena–alumina catalyst the ratio of the amount of *cis*- to *trans*-2-butene determined in the pulse system (*3*) at low conversion was about 3 at 30°C, but it decreased slowly on increasing temperature, as with the reduced catalyst.

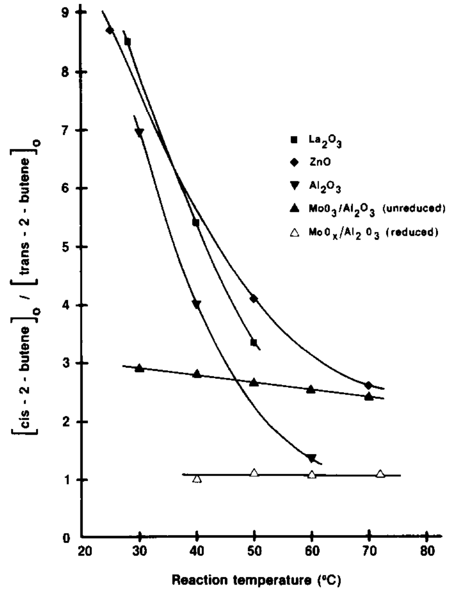


FIG. 3. Temperature dependence of the ratio of initial rates for *cis*-2-butene and *trans*-2-butene formation in 1-butene isomerization over different catalysts. Experiments in recirculation system (except for unreduced molybdena–alumina). For details see text.

The activity for acid catalysis increases with the degree of hydroxylation (*30*); the reverse is true for allylic mechanisms. The reduced molybdena–alumina catalyst was tested in this respect for the isomerization of 1-butene. After the usual reduction and evacuation at 500°C the catalyst was exposed to water vapor at room temperature for 3 hrs. After this, it was partially dehydroxylated by evacuation overnight at different temperatures. To avoid the reoxidation of the catalyst by water vapor, the temperature of the catalyst was raised slowly while pumping. The results are summarized in Table 5; the activity of the catalyst was found to increase with the increase in the temperature of dehydroxylation. Reduction with CO instead of H_2 significantly

TABLE 5

Initial Rate of 1-Butene Isomerization over Reduced Molybdena–Alumina Catalyst Dehydroxylated at Different Temperatures[a]

Temperature of dehydroxylation (°C)	Initial rate of 2-butenes formation molec. g^{-1} s^{-1} $\times 10^{-17}$
400	2.4
450	3.8
500	5.8
500[b]	7.1
500[c]	1.1

[a] Catalyst (0.2 g) reduced in flowing hydrogen at 500°C for 1 hr and evacuated at the same temperature for 1 hr. Then the catalyst was exposed to water vapor at room temperature for 3 hr and evacuated overnight at the given temperatures. Reaction carried out in the recirculation system at 42°C, initial pressure of 1-butene, 150 Torr.

[b] Value for catalyst freshly reduced in H_2.

[c] Value for catalyst freshly reduced in CO.

lowered the isomerization and exchange activity.

DISCUSSION

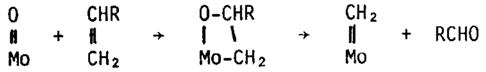
The isomerization of *cis*-2-butene over freshly oxidized molybdena–alumina catalysts in the microcatalytic pulse system was shown (*1*, *3*) to be acid (proton) catalyzed in the first pulses. After the fresh catalyst had been treated with ~100 Torr of *cis*-2-butene, for a few minutes, or when the reaction was carried out in the recirculation system, however, the acidic-type isomerization decreased materially and the *cis–trans* isomerization was found to proceed almost exclusively by metathesis (*1*, *2*). The change in the character of the catalyst by induction in butene was explained by a slight reduction of the catalyst with *cis*-2-butene accompanied by the formation of carbenes.

The activities of the catalysts reduced with hydrogen were found to be much higher for the double-bond isomerization of butene than those for unreduced catalysts (*4*).

A similar increase in activity has been reported for the metathesis of propene and for butene isomerization (*24*) with the extent of reduction of the catalyst with hydrogen. The isomerization of cyclopropane is presumably catalyzed by Brönsted acid sites (*14*, *16*). If so, it is curious that acidity should increase with extent of reduction.

Over reduced molybdena–alumina catalysts, metathesis of 2-butenes was observed in the very first pulse (Tables 1 and 2), but the extent increased substantially in subsequent pulses. This induction effect differed from that observed with unreduced catalysts in that with the latter a slight reduction of the catalyst occurred (*1*, *2*, *25*), without which it proved to be inactive for metathesis; carbene formation may have been concomitant with this reduction as suggested by Rappe and Goddard (*26*) (Scheme a). On the surface of the reduced catalyst, coordinately unsaturated sites suitable for metathesis are already present and in the course of induction the carbene and metallocyclic complexes can develop as suggested by Lombardo *et al.* (*15*) (Scheme b) or alternatively via the allylic route suggested by others (*27–29*) (Scheme c). The much higher activity of the reduced catalyst suggests that a larger number of active sites can be developed on the already reduced surface. Although the role of metathesis was small in the first pulse, about the same conversion of *cis*-2-butene to *trans*-2-butene was achieved in all of the successive pulses (Table 1). This is possible only if the nonmetathetic isomerization decreased as the metathesis activity increased, suggesting that the sites for the former are con-

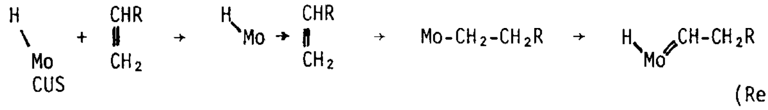
a)



$$\underset{\text{Mo}}{\overset{\text{O}}{\|}} + \underset{\text{CH}_2}{\overset{\text{CHR}}{\|}} \rightarrow \begin{matrix}\text{O-CHR}\\ | \quad \backslash \\ \text{Mo-CH}_2\end{matrix} \rightarrow \underset{\text{Mo}}{\overset{\text{CH}_2}{\|}} + \text{RCHO}$$

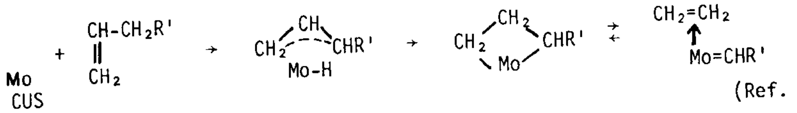
(Ref. 26)

b)



(Ref. 15)

c)



(Ref. 27-29)

verted into sites for the latter. This could happen, for example, if an alkyl intermediate is involved both in isomerization and in the formation of the carbene (Scheme b).

With butene-1 (Table 4), the double-bond isomerization is a nonmetathetic process; it decreased in the second pulse, and further decreased after treatment with 1-butene. The metathesis activity also decreased noticeably after this treatment presumably because of polymerization of butene. The decrease of the activity of the catalyst for the nonmetathetic isomerization was similar to that observed in the acidic isomerization over unreduced catalyst.

Since the role of metathesis proved to be small in the *cis–trans* isomerization in the early stages of the reaction (Fig. 2) we can treat the data for the first pulses as "pure" isomerization and try to use the reaction characteristics as diagnostic tools for mechanistic interpretations with the reduced catalyst. The reaction characteristics for isomerization were as follows:

(a) *Initial cis–trans ratios from the isomerization of 1-butene were very close to unity and temperature independent* (*Fig. 3*). This is typical for carbonium ion chemistry (*18*) where the sec-carbonium ion will yield *cis*- and *trans*-2-butene with equal probability. Although this criterion has been widely used to distinguish acid catalysis from basic catalysis, it should not be forgotten that any common intermediate where the probability of forming *cis*- and *trans*-2-butene is about equal will yield the same results, e.g., a secondary alkyl-intermediate species. The fact that the *cis–trans* ratio is close to unity and temperature independent tends to exclude the possibility of a π-allylic carbanion mechanism, since the initial *cis–trans* ratios for such systems [Al_2O_3, ZnO (*19*) and La_2O_3 (*38*)] are usually high (~8), and since in these systems (because of the nature of the mechanism) the initial *cis–trans* ratios decrease rapidly with increasing reaction temperature (Fig. 3). Although the evidence is tenuous, reduced chromia may be an exception (*22*) (vide infra).

(b) *Small isotope effect* (*Table 4*). The values between 1.2 and 1.7 are similar to those expected for a carbonium ion mechanism (*18*) and disagree with the known literature on π-allylic systems (*19*), where much higher values (~4) are characteristic. However, this serves mainly to eliminate the latter mechanism, not establish acid catalysis.

(c) *Rate of isomerization increased with the extent of dehydroxylation of the surface* (*Table 5*). This characteristic is contrary to expectation for a carbonium ion mechanism, where the rate should increase with extent of hydroxylation (*30*), but is in agreement with a mechanism where vacancies are required for catalytic activity. Mechanisms involving removal of hydrogen from the molecule (allylic intermediates) are unlikely, based on both (a) and (b) above, whereas hydride insertion to form the secondary alkyl may be considered a likely mechanism. Here Mo–H species would be present at coordinately unsaturated isomerization sites which are produced by reduction, poisoned by H_2O, and regenerated by evacuation at increasingly higher temperatures.

(d) *Isomerization as well as hydrogen scrambling were poisoned by NO (Table 4).* When a pulse of 1×10^{19} molecules of NO was passed over 15 mg of the catalyst containing (7.5×10^{18} total molybdenum atoms), the activity for isomerization and exchange was drastically reduced. NO would be expected to be a strong ligand for coordinatively unsaturated molybdenum ions, as is H_2O. Therefore, these are the catalytic centers and not catalyst protons. Proton transfer should be assisted by H_2O co-catalyst and why should a carbonium ion reaction be inhibited by NO?

(e) *Isomerization and hydrogen scrambling were enhanced by H_2 (Table 4).* This is consistent with expectation for a reaction involving a metalloalkyl (a half hydrogenated state) formed by hydride insertion on coordinatively unsaturated sites (*31*).

(f) *Brönsted acidity was not observable in the ir spectra for pyridine on the reduced molybdena–alumina catalyst.* The results of Segawa and Hall (*32*) have confirmed (*33*) the presence of Brönsted acidity on unreduced molybdena–alumina catalysts. It could not be detected, however, after reduction.

(g) *The isomerization reaction is an "add-on" mechanism involving intermolecular transfer of H and D.* Table 3 shows that in the case of known "intramolecular" systems [ZnO, Al_2O_3, La_2O_3 (*38*) and chromia (*22*)] the incorporation of deuterium into the isomerization products is minimal while in the case of reduced molybdena–alumina (Expt. 1 and 2, Table 3) the amount of d_1 product is significantly higher. This supports the notion that some form of H or D must be added onto the olefin in the transition state, i.e., that either a carbonium ion or sec-alkyl mechanism is operative. This is strongly supported by the deuterium distribution shown for the first pulses in Tables 2 and 4. Comparing the deuterium distribution in the products of isomerization of 1-butene and *cis*-2-butene in the presence of 18% D_2 (Reactions 1 and 2 of Table 3), an appreciable amount of d_1 (~17%) was found incorporated into the unreacted 1-butene whereas only 3.5% was introduced into the unreacted *cis*-2-butene. Presumably, the ability of 1-butene to form the primary alkyl, a pathway for exchange but not for isomerization, accounts for this difference. Recent work by Tanaka and Okuhara (*31*) on MoS_2 supports this view. Here it was shown using a mixture of propene-d_6 + propene-d_0 and the microwave technique for the identification of the position of the deuterium in the reacted molecules, that the ratio of propene-1-d_1/propene-2-d_1 was 3/7. This suggested that the σ-alkyl intermediates were about 70% *n*-propyl and 30% isopropyl. Since the MoS_2 system has similarities with our reduced molybdena–alumina catalyst (vide infra), it can be assumed that most of the exchange occurring in the unisomerized 1-butene comes from a primary and not from a secondary intermediate. This obviously supports the hydride insertion mechanism over the carbonium ion, since it is known that the formation of the primary alkyl (which leads only to exchange) is strongly competitive with the sec-alkyl (which can lead to isomerization). Of course, in the carbonium ion the situation would have been exactly opposite. Interestingly, the alkyl reversal, which is not significant with C_2H_4 (*15*), becomes more important with propene and is facile with butene, at least at low D_2 partial pressures.

The data presented indicate that hydrogen scrambling is a stepwise process moderated by metathesis; they suggest that isomerization occurs by a related "add-on" mechanism and the supporting arguments tend to eliminate a carbonium ion mechanism, provided that the origin of the Brönsted acid is the catalyst itself. In fairness, it must be noted that most of these latter arguments would break down (or be seriously weakened) if in some way the catalyst could generate its own protons by some as yet not understood interaction with strongly adsorbed hydrocarbon molecules. There is little to support this notion, however, except some unanswered questions. What is the origin of the Mo–H required for the alkyl mechanism? The catalysts were evacuated at 500°C before use or reduced by CO. Although the latter were significantly less active, they still effected the isomerization of butene (Tables 4 and 5) and cyclopropane (*16*). Intermolecular scrambling of H and D reached equilibrium when equimolar mixtures of cyclopropane-d_0 and -d_6 were passed over the same reduced catalyst in the same temperature range, not only in the propene formed, but in the unisomerized molecules (*16*). How can this be explained other than by acid catalysis? Experiments where a pulse of perdeuterio-hydrocarbon was passed over the freshly reduced catalyst showed little transfer of catalyst-H into product molecules, but when the next pulse of perhydromolecules was passed, nearly 30% of the product molecules contained at least one atom of D. Similar experiments with silica–alumina catalysts yielded analogous results and were interpreted to mean that "residues furnish protons needed for the reaction" (*18*).

One might expect reduced chromia catalysts to isomerize olefins by the same basic chemistry as with reduced molybdena–alumina. Haller and John (*34*) have presented convincing evidence that double-bond isomerization of $CH_3CH{=}CD_2$ is an intramolecular process proceeding via allylic intermediates. Moreover, Burwell and coworkers (*36*) found that isomerization accompanied deuterogenation of 1-hexene, but that the resulting 2- and 3-hexenes were largely free of deuterium. However, Haller and Saint-Just (*22*) found the expected high *cis–trans* ratio which usually accompanies allylic mechanisms for only one of four kinds of preparations; the others were close to unity. The evidence is weak, however, since these data were reported for pulse experiments at unspecified temperature and conversion levels. They attributed the low vs high ratio, and other kinetic differences among the catalysts, to differences in the charge on the allylic intermediate, i.e., carbanion vs neutral or positively charged. Why, then should the chromia preparations be so different from the molybdena–alumina catalysts? The answer may be the following. Catalysts such as ZnO and chromia, which dissociate H_2 heterolytically, form π-allylic carbanions on the same sites by analogous chemistry. When both gases are present, isomerization via the latter is competitive with hydrogenation which takes place via the metal alkyl produced by olefin insertion into the metal hydride bond. The alkyl can only function in isomerization if its formation is readily reversible and if the secondary alkyl can form. Neither of these requirements is met by ZnO (*37*). Both seem to be possible on reduced molybdena–alumina with the butenes, although alkyl reversal was minimal with ethene (*15*) and small but definate with propene (*17*). Thus, the chromia and the molybdena–alumina results may indeed be part of common chemistry, differing only in such matters as strength of adsorption, relative rate constants, and structural features of the surface which may favor or disfavor the formation of the secondary alkyl.

The present work clarifies the role of the changing surface chemistry in dictating mechanism and the nature of products produced. The freshly oxidized catalyst effects acid catalysis (*1*), but this is an unstable situation because slight reduction and carbene formation occur when the catalyst is contacted with olefin (*1–3*). Now, metathesis plays a dominant role; isomerization is suppressed. When the catalyst is reduced extensively before contact with olefin, carbene formation is more extensive than can be achieved with unreduced catalyst, the acid function is eliminated and metallo-organic chemistry becomes possible. Metathesis is again important, but must compete with isomerization involving a sec-butyl metalloalkyl, perhaps having restricted rotation (*6, 31*) thus explaining the high initial *trans*-2-butene/1-butene ratios observed in the present work (Tables 1 and 3). It is of considerable interest that olefin isomerization over reduced chromia catalyst proceeds by proton abstraction via an allylic mechanism (*22, 34*) while reduced molybdena–alumina goes by hydride insertion via an alkyl mechanism with superimposed metathesis.

ACKNOWLEDGMENTS

The authors wish to acknowledge the National Science Foundation Grant (CHE80-19309) for its support in this work, and one of us (J.G.) wishes to thank Consejo nacional de investigacion cientifica y tecnologica de Venezuela for a graduate stipend.

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