

The Isomerization and Metathesis of *n*-Butenes

## I. Unreduced Molybdena-Alumina Catalysts

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A significant change in the catalytic characteristics of an unreduced molybdena-alumina catalyst occurred at room temperature with increasing duration of contact with the reactant *cis*-2-butene. Butene isomerization over the fresh catalyst was effected by an acidic mechanism with the concomitant intermolecular transfer of H and D. The chief diagnostic characteristics for this mechanism were maintained throughout pulse experiments, but changed to those characteristic of isomerization by metathesis after soaking in butene for 15 min or when a static recirculation reactor was used, i.e., with increasing contact time, the acidic character of the catalyst decreased and the activity for metathesis increased. Thus, in the later stages of the reaction, equimolar mixtures of *cis*-2-butene  $d_0$  and  $d_8$  isomerized to produce *cis*- and *trans*- $C_4H_4D_4$ ,  $C_4H_8$ , and  $C_4D_8$  in ratios of 2:1:1 without other hydrogen scrambling.

## INTRODUCTION

For several years we have been interested in the use of tracer butenes as diagnostic tools for the assay of surfaces. Different mechanisms (acidic, basic, metathetic, etc.) reflect different kinds of surface sites, intermediates, and chemistry. Recently, our attention in this regard has been focused on the molybdena-alumina surface and the changes which occur on reduction (1-7). The present paper describes some interesting effects brought about by "reduction" of the catalyst by contact with butene gas at room temperature.

In early work on cyclopropane isomerization, a facile reaction in the presence of a strong Brønsted acid, it was shown (4, 5) that the conversion increased with the extent of reduction, and that metathesis of the propylene produced by the isomerization reaction correlated with the anion vacancies formed by reduction. Recent data (7)

using propylene as the reactant showed that the metathesis activity was nearly invariant with the extent of reduction. This observation is in disagreement with data published by Nakamura *et al.* (9), Henrici-Olivé *et al.* (10), and Engelhardt (8), where the activity of the catalyst for metathesis of propylene increased with the extent of reduction.

On reduction, molybdena-alumina also became active for olefin hydrogenation (6, 7) and olefin polymerization (6). This study indicated that ethylene hydrogenation, polymerization, and metathesis could all be accounted for by a common intermediate (adsorbed alkyl) formed on the same coordinative unsaturated sites (CUS). Later studies (7), however, showed that CO and NO were effective poisons for hydrogenation of olefins and exchange with  $D_2$ , but not for isomerization of cyclopropane or metathesis of propylene. Moreover, studying the effect of a high-temperature form of chemisorbed hydrogen on the reduced catalyst ( $H_R$ ) Engelhardt (11) concluded that the metathesis of propylene is effected by different surface sites than those required for the oligomerization of ethylene and the isomerization of *n*-bu-

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tenes. There are, therefore, conflicting data and the resulting interpretations which obviously deserve further investigation.

Our previous work with cyclopropane (7) suggested that the unreduced molybdena-alumina catalyst is not very acidic, relative to reduced catalysts. On the other hand, the experiments of Kiviat and Petrakis (12) demonstrated the presence of Brønsted acidity on the unreduced catalyst. In the present work, the isomerization of *n*-butenes was used to investigate the acidic characteristics of these catalysts and to determine whether or not these data would correlate satisfactorily with the results for cyclopropane isomerization. It was found that the fresh unreduced catalyst did initially catalyze these isomerizations by a Brønsted acid mechanism, but that a second mechanism later became dominant.

Metathesis as a mechanism for *cis-trans* isomerization of olefins has been reported earlier for certain homogeneous tungsten catalysts by Basset *et al.* (13, 14) and for a molybdenum oxide-titanium oxide catalyst by Tanaka *et al.* (15-17).

## EXPERIMENTAL

### Catalyst Pretreatment

The catalyst used in this work was the same molybdena-alumina catalyst (8% Mo) used previously. Dry O<sub>2</sub> was passed over the catalyst overnight at 500°C to condition it. It was then evacuated for 30 min at the same temperature before use.

The "butene-pretreatment" consisted of circulating 20 cm<sup>3</sup> (NTP) of *cis*-2-butene over the catalyst for 15 min or else leaving the catalyst in contact with 200 Torr of *cis*-2-butene for 10 min in the pulse system; both methods had the same effect. The color of the catalyst changed from white to light brown as a result of these treatments, suggesting that a mild reduction had occurred.

### Reactants

The three butenes were Matheson research grade. Although no impurities

were detected by gas chromatography, they were nevertheless outgassed using a freeze-pump-thaw technique before use. Helium carrier gas used in the microcatalytic pulse experiments was passed over anhydrous CaCl<sub>2</sub>, MgClO<sub>4</sub>, and finally over activated charcoal thermostated at -195°C. *cis*-C<sub>4</sub>D<sub>8</sub> and 1-C<sub>4</sub>D<sub>8</sub> were prepared by the procedure reported by Larson *et al.* (19), and the *cis*-C<sub>4</sub>D<sub>2</sub>H<sub>6</sub> (CH<sub>3</sub>-CD=CD-CH<sub>3</sub>) was the same as that used in Ref. (18).

### Procedures

(i) *Circulation system.* Reactions were carried out at 30°C in an all-glass recirculation system. The pumping speed was about 200 cm<sup>3</sup>/min and the system volume was about 300 cm<sup>3</sup>. The catalytic rates were not seriously limited by pumping speed under our experimental conditions. The gases were pumped over a catalyst and into a mixing chamber which contained about 87% of the system volume. The exit stream from this could be sampled for gas chromatographic analysis. About 1% of the circulating gas was removed for each analysis. The column used was described earlier (7) and a thermal conductivity cell was used for detection purposes. The conversions were calculated on the basis of area of chromatographic peaks and the sensitivity factor for each chemical species.

(ii) *Microcatalytic pulse system.* Pulses of *n*-butene were injected into the pure helium carrier gas using a 1.15 cm<sup>3</sup> doser and were passed over the catalyst at 1 atm of total pressure. The products emerging from the catalyst were collected in a -195°C trap for 30 min and then flashed into the chromatographic column. The separation of the product mixture was made on a 4m × 0.25-in. (o.d.) column, containing 20% dibenzilamine on Chromosorb P (60/80 mesh) thermostated at 0°C; the detector was a thermal conductivity cell.

(iii) *Mass spectrometric analysis.* Provisions were made to trap and recover the individual products at the exit of the gas

TABLE 1

Reaction of 1-C<sub>4</sub>H<sub>8</sub> over an Unreduced Molybdena-Alumina Catalyst (8% Mo) in the Microcatalytic Pulse System<sup>a,b</sup>

Pulse No.	Product composition, molecules $\times 10^{-17}$			Mass loss (molec. $\times 10^{-17}$ )	Ratio <i>cis/trans</i>
	1-C <sub>4</sub> H <sub>8</sub>	<i>cis</i> -C <sub>4</sub> H <sub>8</sub>	<i>trans</i> -C <sub>4</sub> H <sub>8</sub>		
1	58.5	22.3	11.2	11.1	1.9
2	75.6	14.7	5.8	7.6	2.5
3	78.1	12.5	4.8	8.2	2.6
⋮					
14	86.0	8.7	2.3	6.5	3.7

<sup>a</sup> Amount of catalyst: 50 mg;  $2.5 \times 10^{19}$  Mo atom; He flow rate, 50 cm<sup>3</sup> (NTP)/min; pulse size  $103.6 \times 10^{17}$  molecules. The temperature was at 60°C.

<sup>b</sup> Neither ethene or propene appeared in the products.

chromatographic column for mass spectrometric analysis. Blank tests showed that no detectable isotopic mixing occurred on the column. The different compounds were analyzed at low ionization voltage (11 eV); more details are given elsewhere (5).

## RESULTS

### Isomerization of 1-Butene

About 50 cm<sup>3</sup> (NTP) 1-butene was circulated over the catalyst at 30°C; the data for the changing product distribution using the

recirculation system are summarized in Fig 1. During the initial stages of the reaction, the products of the double bond shift were present in comparatively large amounts, but as time elapsed the products from cross-metathesis (propene) and 1-butene metathesis (ethene) became dominant, the first at the expense of *cis*- and *trans*-2-butene.

The results obtained from the reaction of 1-butene at 60°C using the microcatalytic pulse system are presented in Table 1.

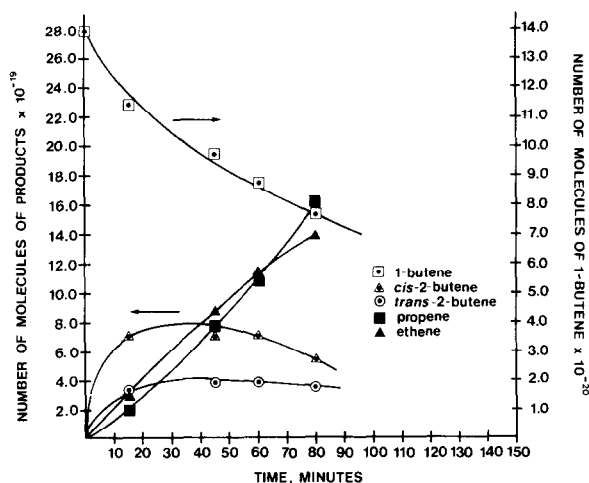


FIG. 1. Product distribution for the reactions of 1-butene over 0.5 g unreduced molybdena-alumina catalyst (8% Mo) at 30°C in the recirculation system. [The right-hand scale corresponds to the reactant (1-butene) and the left-hand scale to the other reaction products.]

TABLE 2

Reaction of *cis*-2-Butene over an Unreduced Molybdena-Alumina Catalyst (8% Mo) at 60°C in the Microcatalytic Pulse System<sup>a</sup>

Pulse No.	Amount of catalyst (mg)	He flow rate (cm <sup>3</sup> /min)	Product composition, molecules $\times 10^{-17}$				Mass loss ( $\times 10^{-17}$ molec)	Ratio <i>trans</i> -C <sub>4</sub> H <sub>8</sub> /1-C <sub>4</sub> H <sub>8</sub>
			<i>cis</i> -C <sub>4</sub> H <sub>8</sub>	<i>trans</i> -C <sub>4</sub> H <sub>8</sub>	1-C <sub>4</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>		
1	50	50	90.7	5.5	1.9	—	5.4	2.9
2			97.5	2.7	1.2	—	2.2	2.4
3			97.9	2.7	1.1	—	2.0	2.4
12			99.8	1.7	0.7	—	1.5	2.4
1	500	60	28.7	39.1	5.1	1.5	29.1	7.6
2			56.7	34.0	7.9	1.7	3.2	4.3
3			57.9	33.9	7.8	1.7	2.3	4.4
4		400	89.1	6.7	3.3	0.11	4.3	2.0

<sup>a</sup> Same as for Table 1 except as noted.

Significantly, neither propene nor ethene was detected in the reaction products.

#### Isomerization of *cis*-2-Butene

The distribution of products from the reactions of *cis*-2-butene in the recirculation system is given in Fig. 2. The *cis*-*trans* interconversion was extremely rapid compared with the double bond shift. The latter could be detected only by the appearance of propene, the product of cross-metathesis of 2-butene with 1-butene (which was not observed directly).

The results obtained in the microcatalytic system were again noticeably different (Table 2) from those obtained in the recirculation system. At low conversion (50 mg catalyst) the ratio of *trans*-butene to 1-butene was  $\sim 2.5$  and neither propene nor ethene were detected. The conversion was lower than when 1-butene was the reactant, but decreased with pulse number in a similar fashion. In both cases, a substantial loss from the mass balance occurred with the first pulse as a polymeric material formed which continued to grow with successive pulses on the catalyst surface. This became more noticeable when larger amounts of

catalyst were used (see second experiment of Table 2). Moreover, small amounts of propene began to appear in the products. This was evidently due to a longer bed length as it could be very much reduced by

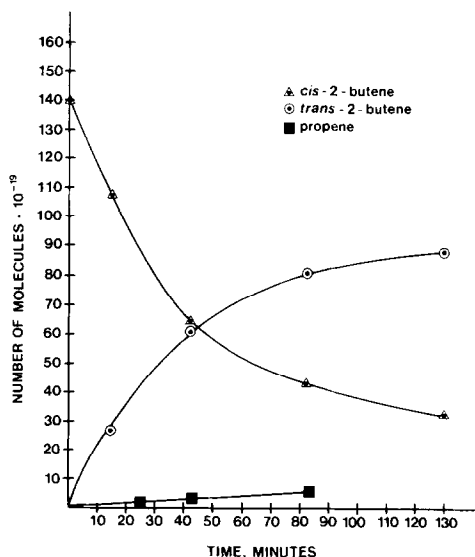


FIG. 2. Product distribution from reaction of *cis*-2-butene over 0.5 g of unreduced molybdena-alumina catalyst (8% Mo) at 30°C in the recirculation system—no 1-butene was observed.

decreasing the contact time (increasing the carrying gas flow rate).

#### Isomerization of Deuterium-Labeled Butenes

The very high *trans*-2-butene to 1-butene ratio (no 1-butene was detected when *cis*-2-butene was isomerized in the recirculation system) was unusual, suggesting the necessity for a special explanation, i.e., *cis*- to *trans*-2-butene transformation must occur by a mechanism other than that responsible for double bond shift. Tracer experiments were carried out in both the recirculation and the pulse system to clarify this point.

The features of the *cis*-2-butene, 2, 3- $d_2$  + *cis*-2-butene- $d_8$  reaction in the recirculation system are shown in Table 3. The isotopic distributions in both the *cis*- and the *trans*-2-butene products can be best explained as the result of olefin metathesis. The last row of the table shows the result calculated on the basis that metathesis is the sole reaction. The calculated normalized isotopic distribution agreed very well with the actual (normalized) distribution for

the *trans*-2-butene species (13% conversion).

Similar experiments were made by the microcatalytic pulse method with mixtures of *cis*- $C_4H_8$  + *cis*- $C_4D_8$  at 60°C. The first experiment in Table 4 shows the isotopic distribution for the three isomers. Serious differences appeared with respect to the recirculation system data, not only in the product selectivity as noted before (Table 2), but also in the isotopic distribution. The data for the first two experiments show the isotopic distribution is similar in the *trans*-2-butene and the 1-butene products; the distributions suggested a stepwise intermolecular mixing process as expected for acid catalysis. The concentration of the  $d_4$ -isomer was small; it would have been a significant indicator were metathesis a major contributing factor. After Expt. 2, the reactor was removed from the pulse system and moved to the recirculation system, where *cis*-2-butene was circulated over the evacuated catalyst for 15 min at 30°C. It was then moved back to the pulse system, flushed with He for 1 hr at 60°C and re-

TABLE 3

Isotopic Distribution in Products from Isomerization of a Mixture of *cis*-2-Butene, 2,3- $d_2$  and *cis*-2-Butene- $d_8$  over an Unreduced Molybdena-Alumina Catalyst<sup>a</sup>

Species	% Converted	Deuterium distribution, %								
		$d_0$	$d_1$	$d_2$	$d_3$	$d_4$	$d_5$	$d_6$	$d_7$	$d_8$
<i>cis</i> -	0	1.7	3.1	38.5	1.4	1.0	0	0	5.3	49.0
<i>trans</i> -	13.0	1.0	2.5	17.6	2.7	3.3	40.1	2.9	4.6	25.3
<i>cis</i> -		0.8	3.4	27.9	2.0	2.8	23.1	1.4	4.5	34.1
<i>trans</i> -	49.0	0.4	3.7	19.8	1.8	4.7	35.1	3.4	4.7	26.4
<i>cis</i> -		0.4	2.6	22.4	1.7	6.3	33.5	2.2	4.1	26.8
<i>trans</i> <sup>c</sup>	13.0	—	—	21.2	—	—	48.4	—	—	30.4
calculated value <sup>d</sup>	—	—	—	20.0	—	—	49.5	—	—	30.5

<sup>a</sup> Recirculation system, 20 cm<sup>3</sup> (NTP) of mixture,  $T = 30^\circ\text{C}$ , weight of catalyst = 0.5 g.

<sup>b</sup> Percentage conversion was calculated as 100 multiplied by the fraction of *trans*-2-butene + *cis*-2-butene.

<sup>c</sup> *trans*-2-Butene isotopic distribution was calculated to values which would be present if only - $d_2$ , - $d_5$ , and - $d_8$  species were present, i.e., if all the *cis*-2-butene reactant were - $d_2$  and - $d_8$ .

<sup>d</sup> Isotopic distribution expected were metathesis the sole reaction.

TABLE 4

Isotopic Distribution for the Isomerization of *cis*-2-C<sub>4</sub>H<sub>8</sub> + *cis*-2-C<sub>4</sub>D<sub>8</sub> over Unreduced Molybdena-Alumina Catalyst in the Microcatalytic Pulse System at 60°C<sup>a</sup>

Expt. No.	Weight of catalyst	He flow rate (cm <sup>3</sup> (NTP)/min)	Butene Isomers	Amount of Isomers (molec. × 10 <sup>-17</sup> )	Deuterium distribution, %									
					<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>5</sub>	<i>d</i> <sub>6</sub>	<i>d</i> <sub>7</sub>	<i>d</i> <sub>8</sub>	
1	50	38	<i>cis</i> - <sup>b</sup>	103.6	47.1									
			<i>cis</i> -	87.8	55.8	9.1	1.2	0.4	0.8	0.3	1.1	5.9	45.9	
			<i>trans</i> -	6.3	28.3	18.6	3.2	1.1	2.2	0.6	3.4	18.6	24.2	
			1-but.	3.0	30.2	23.6	4.3	1.0	0.7	1.0	4.7	16.6	17.9	
2	500	80	<i>cis</i> -	63.7	22.6	16.0	5.0	1.1	1.2	1.3	6.3	18.8	27.7	
			<i>trans</i> -	33.5	20.7	19.3	5.4	1.5	1.9	2.0	8.5	22.4	18.2	
			1-but.	8.4	22.7	28.0	11.0	3.1	1.2	2.7	5.9	16.4	9.0	
3/1 <sup>c</sup>	500	80	<i>cis</i> -	77.6	36.2	3.0	0.6	1.8	20.1	1.0	0.8	3.9	32.5	
			<i>trans</i> -	21.0	34.6	2.7	0.7	3.6	34.3	1.9	0.6	3.0	18.6	
			1-but.	0.49										
3/2 <sup>d</sup>	500	80	<i>cis</i> -	65.0	28.3	1.9	0.6	2.0	28.3	1.5	0.7	3.7	33.1	
			<i>trans</i> -	31.4	26.6	1.7	0.7	3.1	38.9	2.3	0.5	2.9	23.3	
			1-but.	0.4	59.5	7.1	2.4	2.4	9.5	2.4	2.4	4.8	11.9	
4 <sup>e</sup>	500	80	<i>cis</i> -	61.1	26.8	2.1	0.7	2.5	32.9	1.7	0.9	4.4	28.1	
			<i>trans</i> -	41.3	24.6	1.7	0.6	3.3	44.4	2.2	0.6	3.9	18.7	
			1-but.	0.4										
—					22.5	—	—	3.8	46.7	—	0.1	2.8	24.1	

<sup>a</sup> Pulse size: 103.6 × 10<sup>17</sup> molecules.

<sup>b</sup> Deuterium distribution in initial *cis*-2-butene.

<sup>c</sup> Catalyst pretreated with *cis*-2-butene at 30°C for 15 min in the circulation system.

<sup>d</sup> Catalyst pretreated as 3/1 and evacuated at 60°C for 2 h.

<sup>e</sup> Catalyst pretreated with 200 Torr of *cis*-2-butene at 60°C for 10 min without recirculation.

<sup>f</sup> Isotopic distribution calculated on the basis of metathesis being the sole reaction.

tested. The results (Expts. 3/1 and 3/2) showed that now metathesis had become the dominant reaction. Note the significant reduction in the production of 1-butene and the sudden appearance of large amounts of *d*<sub>4</sub> species at the expense of the *d*<sub>1</sub> and *d*<sub>7</sub> products (ideally acid catalysis should produce equal amounts of *d*<sub>0</sub>, *d*<sub>1</sub>, *d*<sub>7</sub>, and *d*<sub>8</sub> species in the *trans*-2-butene and 1-butene products from the isomerization of *cis*-2-butene).

Similar change in the character of the catalyst was achieved by soaking it with 200 Torr of *cis*-2-butene at 60°C for 10 min without recirculation as by the pretreatment in recirculation system (Table 4, Expt. 4).

To check for the possible involvement of catalyst hydrogen, successive pulses of *cis*-2-butene-*d*<sub>8</sub> and *cis*-2-butene-*d*<sub>0</sub> were passed over the catalyst. The results (shown in Table 5) show that the number of

butene molecules which could have exchanged with surface hydroxyl groups was very small when butene-*d*<sub>8</sub> was passed over a fresh sample of catalyst which had not previously been contacted with a deuterated species (Expt. 1). The results resembled those of Hightower and Hall (20) with silica-alumina catalysts. By reasonable estimates, no more than about 1% of the surface OH group present could have been involved. Again as observed previously (20), the situation was quite different when the second pulse was passed (Expt. 2). There was a substantial exchange (about 10%) between the butene-*d*<sub>0</sub> second pulse and the residue (adsorbed "heavy" molecules) left from the first pulse. It is possible that these residues furnish the protons for acid catalysis.

The isotopic distribution pattern from the reaction of 1-butene-*d*<sub>8</sub> + 1-butene-*d*<sub>0</sub> is shown in Fig. 3. The reaction had been

TABLE 5

Isotopic Distribution in Products from Successive Pulses of Isotopic *cis*-2-Butene and Other Hydrocarbons Passed over an Unreduced Molybdena-Alumina Catalysts<sup>a</sup>

Expt. No.	Product composition, mole%	Starting material	Product	Deuterium distribution, %								
				<i>d</i> <sub>0</sub>	<i>d</i> <sub>1</sub>	<i>d</i> <sub>2</sub>	<i>d</i> <sub>3</sub>	<i>d</i> <sub>4</sub>	<i>d</i> <sub>5</sub>	<i>d</i> <sub>6</sub>	<i>d</i> <sub>7</sub>	<i>d</i> <sub>8</sub>
1 <sup>c</sup>	—	<i>cis</i> - <i>d</i> <sub>8</sub> <sup>b</sup>		—	—	—	—	—	—	2.0	11.1	86.9
	45.3		<i>trans</i>	—	—	—	—	—	—	2.8	13.2	84.0
	5.7		1-but.	—	—	—	—	—	—	2.1	11.8	86.1
	49.1	<i>cis</i> - <i>d</i> <sub>8</sub>	<i>cis</i> -but.	—	—	—	—	—	—	2.3	12.0	85.7
2 <sup>d</sup>	40.9		<i>trans</i> - but.	80.4	19.6	—	—	—	—	—	—	—
	6.3		1-but.	77.9	22.1	—	—	—	—	—	—	—
	52.9	<i>cis</i> - <i>d</i> <sub>0</sub>	<i>cis</i> -but.	87.0	13.0	—	—	—	—	—	—	—
3 <sup>e</sup>	100	propene- <i>d</i> <sub>0</sub>	propene	96.2	3.8	—	—	—	—	—	—	—
4 <sup>f</sup>	99.1	C-C <sub>3</sub> H <sub>6</sub>	Δ	96.6	3.4	—	—	—	—	—	—	—
	0.9		propene	—	—	—	—	—	—	—	—	—

<sup>a</sup> Weight of catalyst = 0.5 g, *T* = 60°C, He flow rate = 80 cm<sup>3</sup>/min, pulse size = 1.1 × 10<sup>19</sup> molecules.<sup>b</sup> Isotopic composition of the initial *cis*-2-butene-*d*<sub>8</sub>.<sup>c</sup> First pulse was *cis*-2-butene-*d*<sub>8</sub>.<sup>d</sup> Second pulse was *cis*-2-butene-*d*<sub>0</sub>.<sup>e</sup> First pulse was *cis*-2-butene-*d*<sub>8</sub> as above; second pulse (data shown) was propene-*d*<sub>0</sub>.<sup>f</sup> Same as <sup>e</sup>, except second pulse was cyclopropane-*d*<sub>0</sub>.

carried out at 30°C in the recirculation system and the analysis was made at low conversion (6%), where the isomerization prevails (Fig. 1). The number of hydrogen atoms exchanged per molecule isomerized was 0.6, and there was a small isotope effect (1.2) for production of either *cis*- or *trans*-2-butene, these quantities being calculated as in Ref. (20).

Figure 4 compares schematically the results obtained from the reaction of an equimolar mixture of *cis*-butene-*d*<sub>0</sub> and *cis*-butene-*d*<sub>8</sub> in the microcatalytic pulse system over the unreduced catalyst (Table 4, Expt. 2) and over the same catalyst after pretreatment with 200 Torr of *cis*-2-butene-

*d*<sub>0</sub> at 60°C for 10 min (Table 4, Expt. 4). The dashed lines represent the calculated amount of isomer that is produced exclusively by metathesis. The calculation was made as follows. From the initial composition of *cis*-2-butene, the equilibrium isotopic distribution for metathesis can be calculated by taking into account all the alkylidene units present. The calculated isotopic distribution is given in Table 4 in the last row. All the *d*<sub>4</sub> species obtained after pretreatment with *cis*-2-butene were considered to be exclusively due to metathesis. This approximation is based on the fact that the amount of *d*<sub>2</sub> and *d*<sub>6</sub> species were small, so that the amount of *d*<sub>4</sub> species

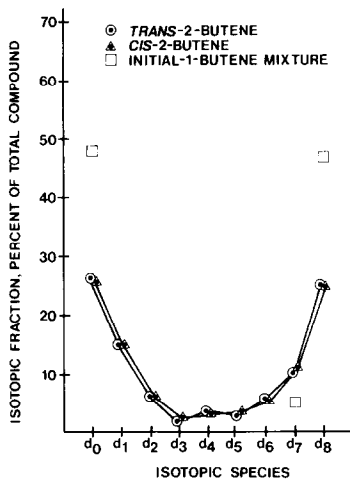


FIG. 3. Isotopic distribution for the reaction of a 50% 1-butene  $d_0$  + 50% 1-butene- $d_8$  in the recirculation system. The initial amount of gas was 15 cm<sup>3</sup> (NTP); the temperature was 30°C and the weight of the catalyst was 0.5 g. The data were taken at a total conversion of 6%. Calculations showed that the atoms exchanged/molecule was 0.6 (calculated as in Ref. (20)) and the isotope effect for both *cis*-2-butene and *trans*-2-butene was 1.2 (calculated as in Ref. (20)).

produced by stepwise hydrogen exchange should be even smaller. With the assumption that the ratio of isotopic components in the experimental mixture is the same as at equilibrium, the fraction of each species that is exclusively due to metathesis was calculated by normalizing the experimental  $d_4$  concentration with the value calculated for equilibrium. Figure 4 shows that the *trans*-2-butene can be regarded almost exclusively as the product of metathesis, and the *cis*-2-butene (reactant) isotopic distribution is not far from that calculated for equilibrium.

Table 6 summarizes the effects of the *cis*-butene pretreatment. Isomerization of cyclopropane was carried out under the same conditions as the *cis*-2-butene isomerization and at 180°C in microcatalytic system. The conversion of cyclopropane was much lower than that of *cis*-2-butene. At 180°C, where the conversion was readily measurable, it appeared to decrease with pretreatment with butene. With *cis*-2-butene, the

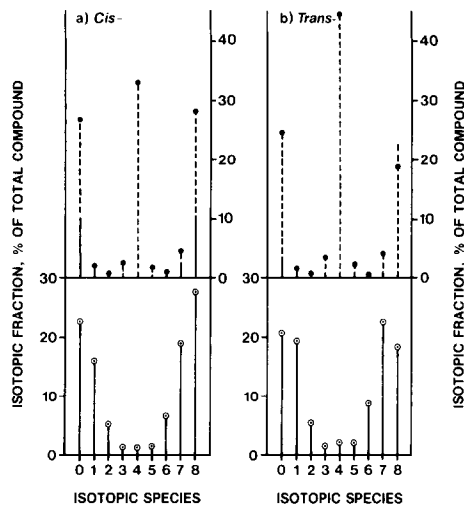


FIG. 4. Isotopic distribution in (a) *cis*-2-butene and (b) *trans*-2-butene produced from an equimolar mixture of *cis*-2-butene- $d_0$  and - $d_8$  over a fresh unreduced molybdena-alumina catalyst (○) and over a catalyst after treatment with *cis*-2-butene (●) in microcatalytic pulse experiments at 60°C. Dashed lines represent the amount of isomers produced via metathesis (see text); solid lines represent the difference between the total (experimental) amount and that produced via metathesis.

amount of 1-butene decreased significantly with the pretreatment and so did the number of hydrogen atoms exchanged per molecule in the product butenes. The latter was calculated using the equation given by Hall and Hightower (20) modified by subtracting the fraction of isomers due to metathesis from the total.

#### DISCUSSION

It has been known for some time that molybdena-alumina, tungsta-alumina and rhenia-alumina catalysts become active for metathesis after a reductive pretreatment. Kobylinski and Swift (21) were first to point out the advantages of an induction with butene at 200°C for this purpose; not only did molybdena-alumina become active for metathesis, but double bond isomerization was suppressed so that much higher selectivity to tetradecene and ethylene could be obtained from the metathesis



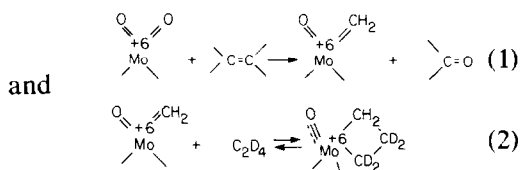
of octene-1. That reduction had occurred was evidenced by the appearance of the EPR signal for  $\text{Mo}^{+5}$ .

The salient feature of the present work was the effectiveness (and definition) of a very mild treatment of our molybdena-alumina catalyst with butene for "turning-on" metathesis activity and "turning-off" double bond isomerization. Very different results were obtained depending upon whether the reactions of butenes were carried out in a static recirculation reactor (Figs. 1 and 2) or in a microcatalytic pulse system (Tables 1 and 2). In both cases, a freshly oxidized catalyst was used. Metathesis products were immediately evident with the former, but neither ethene nor propene appeared in the products when 1-butene was isomerized in the pulse system. This behavior could be abruptly changed to the other by soaking the catalyst in the recirculation system with butene for a few minutes, at 30°C, or in 200 Torr of butene at 60°C for 10 min. In both cases, double bond isomerization was repressed.

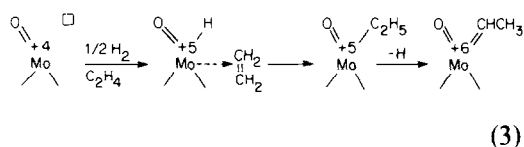
The color of the catalyst changed to a tobacco-colored brown on olefin treatment, rather than black, suggesting that the extent of reduction was low (similar colors were exhibited when the catalyst was reduced in  $\text{H}_2$  or CO to  $0.2 < e/\text{Mo} < 0.4$ ). This deduction was substantiated by setting a lower limit of  $e/\text{Mo} < 0.04$  from the EPR spin density of  $\text{Mo}^{+5}$  generated by this treatment and an upper limit of  $e/\text{Mo} < 0.3$  from the amount of butene adsorbed irreversibly after butene treatment (assuming each such molecule provided two electrons by dehydrogenation, i.e., one  $\text{H}_2\text{O}$  molecule). These findings are supported by the work of Olsthoorn and coworkers (22, 23), who demonstrated that reduction of completely oxidized molybdena-alumina and rhenia-alumina catalysts with subatmospheric pressures of light olefins occurred at 65°C concomitant with the formation of OH bonds in the infrared spectra of their catalysts attributable to chemisorbed  $\text{H}_2\text{O}$ .

When it is recalled that molybdena-alu-

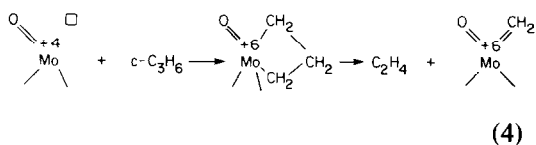
mina and particularly tungsta-alumina catalysts are relatively difficult to reduce with  $\text{H}_2$  or CO (temperatures above 350°C are required to initiate reaction), it seems likely that the valence state of the active metathesis sites must be high, i.e.,  $\text{Mo}^{+5}$  or  $\text{Mo}^{+6}$ . Moreover, since carbene and metallocyclic complexes are recognized as the crucial intermediates for metathesis, tetrahedrally coordinated  $\text{Mo}^{+6}$  species of the parent catalyst are probably involved. Such sites (1, 2) together with the favored reaction pathway deduced by Rappé and Goddard (24) from their calculations of the stabilities of possible intermediates for metathesis formed from  $\text{Cl}_2\text{MoO}_2$ , lead to the following chemistry:



The calculations suggest that the oxygen of the oxycarbene and oxymetallocycle is intimately involved in the catalytic process, providing ballast capacity for electrons. Whereas, this picture provides a satisfactory explanation for many of the present results, we have previously suggested two ways that the oxycarbene may be formed from  $\text{Mo}^{+4}$  CUS, viz., from the metal-alkyl (6) by:



and by the reaction of cyclopropane with the same center (4, 5) following Gassman and Johnson (25):



The  $\text{Mo}^{+4}$  CUS are presumed to be formed

by reductive elimination of  $H_2O$ . It is of considerable interest that the same intermediate species can be formed from either the oxidized or the reduced state of the catalyst. Note, however, that double bond isomerization of olefins will be a competitive side reaction when  $Mo^{+4}$  CUS are present, but need not be if the oxycarbene forms from Eq. (1). The spectroscopic observation of water formation (22, 23) on treatment with olefin suggests that carbene formation by Reaction 1 cannot be entirely specific, although double bond isomerization may be repressed. Moreover, Olsthoorn *et al.* (22, 23) reported that the catalysts became active for ethene polymerization as well as for metathesis. As shown earlier (6) the two reactions may be expected on the same set of sites.

Some confusion exists as to the poisoning of sites by NO. Hall and Millman (26) found that NO became strongly chemisorbed in small but increasing amounts as the extent of reduction was increased. Dini-

trosoyl species were formed on a few percent of the Mo-sites and selectively poisoned the chemisorption of  $H_2$  and, hence, acted as a very selective poison for olefin hydrogenation, but not for metathesis (7). Olsthoorn *et al.* (22, 23) on the other hand reported that NO poisoned metathesis. Their spectra strongly suggest dinitrosyl species, although this was not recognized. The chief difference appears to be (their text is ambiguous on this point) that they observed poisoning of metathesis and polymerization in the presence of excess (gaseous) NO, whereas our experiments were designed to determine the lethal dose which would "kill" hydrogenation. Also, longer exposure times under these conditions could lead to selective reoxidation of the metathesis sites together with formation of  $N_2O$ .

The catalytic properties of the oxidized surface before metathesis is turned-on by self-reduction are of interest. The finding of Kiviat and Petrakis (12), that pyridinium ion

TABLE 6

Effect of Pretreatment with *cis*-2- $C_4H_8$  on the Different Reactions over Molybdena-Alumina Catalyst<sup>a</sup>

	Amount of hydrocarbon molecules $\times 10^{-17}$	
	before treatment with <i>cis</i> -2-butene	after treatment with <i>cis</i> -2-butene
1-butene produced from <i>cis</i> -butene	8.4	0.4
<i>trans</i> -butene produced from <i>cis</i> -butene	34.	41.
Products of metathesis <sup>b</sup>		
in <i>cis</i> -butene	0	45.
in <i>trans</i> -butene	0	40.
Number of H(D) atoms exchanged <sup>c</sup> per molecule		
in <i>cis</i> -butene	0.44	0.057
in <i>trans</i> -butene	0.29	0.034
Propene produced from cyclopropane (percent of pulse)		
at 60°C	0.2	0.5
at 180°C	23.	18.

<sup>a</sup> Microcatalytic pulse system, He flow rate = 80 cm<sup>3</sup>/min, temperature = 60°C, weight of catalyst = 0.50 g.

<sup>b</sup> Calculated from the amount of butene- $d_4$  isomers (see text).

<sup>c</sup> Calculated from the amount of butene- $d_1$ , - $d_2$ , - $d_3$ , - $d_4$ , - $d_5$ , - $d_6$ , - $d_7$  isomers (see text).

is formed on such molybdena-alumina catalysts, provides strong presumptive evidence for a carbonium ion mechanism. The data generated in the microcatalytic pulse experiments (Tables 1, 2, 4, and 5) are in general agreement with this view. The exchange patterns are stepwise, as expected for an "add-on" mechanism, the isotope effects and exchange effects with "residues" are similar to those reported by Hightower and Hall (20) for silica-alumina. Clearly, metathesis is absent. Two pieces of data do not, however, agree exactly with expectation based on earlier work. First the *cis/trans*-2-butene ratios (Table 1) are higher than usual for carbonium ion isomerization. Usually these are temperature independent and close to unity. Yamaguchi *et al.* (27) also reported high ratios for similar tungsta-alumina preparations shown to be acidic by Hammett indicator tests. A brief study (28) showed that our catalyst conformed well to a model where the difference between the energy barriers of any two isomers controlled the selectivity for the process, but with the barrier to form *cis*-lower than that to form *trans*-2-butene, i.e., the *cis/trans* ratio was temperature dependent. A second feature which deserves closer scrutiny was the relatively low activity of the unreduced catalyst for isomerization of cyclopropane (Table 6), both with respect to the same catalysts when reduced (4) and with respect to aluminum-silicates (29). Evidently, the Brønsted acidity is quite weak or else moderated by "residue" (Table 5). These features will be the subject of future research.

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