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A Tracer Study of the Metathesis of Simple Olefins over Molybdena–Alumina Catalysts

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Metathesis of perdeuterio- and perhydroethene, propene, 1-butene, and their mixtures with *cis*-2-butene was studied over a molybdena–alumina catalyst using recirculation and pulse systems. No metathesis was observed over a fresh unreduced catalyst, but after pretreatment with *cis*-2-butene the reactivity of olefins in metathesis reactions increased in the sequence of ethene $\ll$ 1-butene $<$ propene $<$ *cis*-2-butene. The activity was higher for the metathesis of propene or 1-butene after the catalyst was pretreated with the corresponding olefin instead of *cis*-2-butene, but no metathesis was induced by ethene. Metathesis of *cis*-2-butene was suppressed by the addition of equal amounts of olefins in the sequence: ethene $\ll$ 1-butene $<$ propene. Studies of mixtures revealed that the rate of *cis*- to *trans*-2-butene isomerization by metathesis $\simeq$ the rate of degenerate metathesis of 1-butene or the cross metathesis of 1-butene with 2-butene.

INTRODUCTION

Molybdena–alumina catalysts are of great current interest in hydrocarbon chemistry because of the wide range of reactions to which they can be applied and because of their tolerance to sulfur compounds. During the past several years, work in this laboratory has been directed toward defining the surface chemistry of these catalysts and relating it to catalytic functions (*1–7*). Both *cis–trans* and double-bond shift isomerization of *n*-butenes have been shown to be enhanced by reduction of molybdena–alumina catalysts with H_2 (*8, 9*). Very high rates of isomerization were achieved on reduced catalysts in the presence of hydrogen preadsorbed at the temperature of reduction (H_R).

The results of a study of *n*-butene isomerization over an unreduced molybdena–alumina catalyst were presented in a previous paper (*7*). Microcatalytic pulse experiments revealed that over fresh catalyst both *cis–trans* and double-bond shift isomerization proceeded via an acidic mechanism. After contacting the catalyst with butenes, however, the rate of acidic isomerization decreased and the rate of geometrical isomerization via metathesis increased. Moreover, when reactions were carried out in a recirculation system at 30°C, disregarding data from the earliest stages of the reaction, almost all of the *trans*-2-butene formed on isomerization of *cis*-2-butene was actually produced via metathesis. Subsequently, we shall call treatment of the unreduced catalyst by simply contacting it with olefin for a few minutes, *induction.*

We observed that the rate of *cis–trans* isomerization over inducted molybdena–alumina catalyst was significantly higher than the double-bond shift when the reactant was *cis*-2-butene. This rate decreased, however, when 1-butene was added to the *cis*-2-butene. The present work provided an explanation of this inhibition effect and in addition further clarified some of the competitive effects present in this complex reaction system.

Inhibition of the metathesis of internal olefins by terminal olefins has been de-

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scribed previously by Graff and McNelis (*10*) (inhibition of *cis*-2-pentene metathesis by 1-pentene over $W(CO)_5CH_3CN/EtAlCl_2$ catalyst) and by Muetterties and coworkers (*11*) (inhibition of *cis*-2-pentene metathesis by 1-nonene over a WCl_6 + C_2H_5OH + $4C_2H_5AlCl_2$ catalyst). In these cases the inhibition was explained (*12, 13*) by showing that the degenerate metathesis of terminal olefins was so rapid, that their presence effectively inhibited the metathesis of internal olefins by dominating the sites. Since the *cis–trans* isomerization of *cis*-2-butene over inducted molybdena–alumina catalyst was both inhibited by 1-butene and occurred via metathesis, experiments were designed to evaluate the effects of the degenerate metathesis of terminal olefins. These results are reported herein.

EXPERIMENTAL

Catalyst. The same molybdena–alumina catalyst (8% Mo), prepared by impregnation of γ-alumina (Ketjen CK 300) with $(NH_4)_6Mo_7O_{24}$, was used as in previous works (*1–7*). The test sample was calcined before each experiment in flowing dry O_2 overnight at 500°C; this was followed by evacuation for 30 min at the same temperature before cooling to the temperature of the reaction.

Reagents. Ethene, propene, 1-butene, and *cis*-2-butene were Matheson C.P. grade products; they were outgassed before use by the freeze–pump–thaw–freeze technique and then distilled from a trap cooled with dry ice–acetone. The C_2D_4 was prepared by the procedure described by Larson *et al.* (*14*). The C_3D_6 and 1-C_4D_8 were Merck products; the purity of ethene-d_4, propene-d_6, and 1-butene-d_8 were 98, 99, and 97 at.%, respectively.

Procedure. The experiments were carried out in an all-glass recirculation system and in a microcatalytic pulse system. Both were attached to a gas measuring and handling system of the BET type. In the circulation system, the gases were pumped through the Pyrex reactor at 30°C and into a mixing chamber which contained about 87% of the system volume. Pump limitations were negligible (*7*). The exit stream from the mixing chamber could be sampled for gas chromatographic analysis and the separated fractions could be recovered for mass spectrometric analysis.

In the microcatalytic system, pulses containing about 1×10^{19} molecules were injected into a helium stream flowing at 50 cm^3/min and then carried through the reactor at 60°C and 1 atm total pressure. The products emerging from the catalyst were collected in a trap at − 195°C for 30 min and then flushed onto gas chromatographic column. The catalyst weight was 0.5 g.

The samples were separated at 0°C in 4-m-long columns containing Chromosorb P coated with 20% dibenzilamine; thermal conductivity cells were used as detectors. The composition of the gas phase was calculated on the basis of chromatographic peak areas and sensitivity factors determined for each compound. The individual separated compounds were collected for mass spectrometric analysis at the exit of the gas chromatographic columns in traps cooled with liquid nitrogen. Blank tests with known mixtures of isotopic compounds showed this procedure to be satisfactory. Mass spectrometric analysis was carried out using low ionization voltage (11 eV) to minimize fragmentation.

RESULTS

(*a*) *The Effect of 1-Butene on the Metathesis of 2-Butenes*

The results from an experiment in which 50 cm^3 (NTP) *cis*-2-butene was recirculated over the catalyst at 30°C are presented in Fig. 1. It was shown previously (*7*) that the dominant reaction under these circumstances is olefin metathesis. Besides *trans*-2-butene, only the production of an insignificant amount of propene was observed. Most of the *trans*-2-butene was produced via metathesis of 2-butenes; the propene resulted from cross metathesis be-

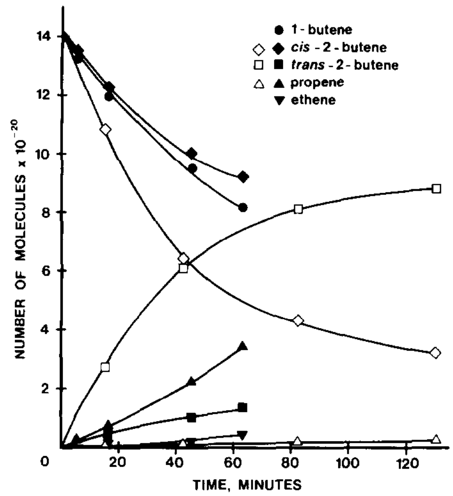


FIG. 1. Inhibiting effect of 1-butene on the metathesis of *cis*-2-butene; open symbols show products from reaction in absence of 1-butene and solid symbols for reaction in its presence over 0.50 g unreduced molybdena–alumina catalyst at 30°C and 150 or 301 Torr pressure, respectively.

tween 2-butenes and 1-butene (*7*). The 1-butene, produced by double-bond shift isomerization, was not itself detectable in the gas phase.

The mixture 50 cm^3 *cis*-2-butene and 50 cm^3 1-butene was reacted under the same conditions; the results of this experiment are also shown in Fig. 1. Although the initial amount of *cis*-2-butene was the same and the system volume was constant, the rate of *trans*-2-butene production was six times lower in the presence of 1-butene than in its absence. The rate of propene production was now higher than that of the *trans*-2-butene. Pentene, the cross-metathesis product of 1-butene with 2-butene, and hexene, the product of 1-butene metathesis, were detected by gas chromatography, but were not determined quantitatively because the amounts recovered were less than those of propene and ethene.

(*b*) *The effect of 1-Butene Concentration on the Rate of trans-2-Butene Formation*

Mixtures of 25 cm^3 (NTP) *cis*-2-butene with different amounts of 1-butene were reacted under the conditions described above. The results are summarized in Fig. 2. The most significant drop in the rate of *trans*-2-butene formation was observed at low 1-butene concentration (5 cm^3 or 17%); the rate decreased more slowly with further increase in the amount of 1-butene added.

(*c*) *Effects of Other Olefins*

The self-metathesis of *cis*-2-butene resulting in the formation of *trans*-2-butene was measured in the presence of equimolar amounts of ethene and propene. Mixtures of 25 cm^3 *cis*-2-butene with the same amount of these olefins were used. From the data summarized in Table 1 it can be seen that the initial rate of isomerization was only slightly inhibited by ethene, and that propene was more effective than 1-butene.

(*d*) *Evaluation of the Degenerative Metathesis*

Mixtures of perdeuterio- and perhydroethene, propene, or 1-butene were reacted as described above. The product distribution for the 1-butene reaction is shown in Fig. 3. In the early stage of the reaction *cis*- and *trans*-2-butene were the chief prod-

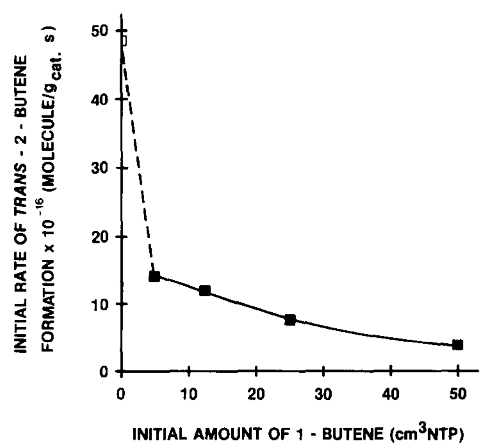


FIG. 2. Effect of the 1-butene concentration on the rate of *trans*-2-butene formation. Initial amount of *cis*-2-butene: 25 cm^3 (NTP); other experimental conditions were as in Fig. 1.

TABLE 1

Initial Rates of *trans*-2-Butene Formation from Mixtures of 25 cm^3 of *cis*-2-Butene and 25 cm^3 of Other Olefins[a]

Hydrocarbon in initial mixture	Initial rate × 10^{-16} (molec/$g_{cat}s$)
None	46.7
Ethene	30.0
Propene	4.0
1-Butene	7.5

[a] 0.50 g of unreduced molybdena-alumina catalyst was used at 30°C reaction temperature in the recirculation system.

uct compounds formed. The initial rate of productive metathesis (calculated from the amount of ethene produced) was more than an order of magnitude lower than the rate of double-bond shift via isomerization. The highest rate, however, was for the formation of 1-butene-d_2 and -d_6 which characterize the degenerative metathesis of 1-butene.

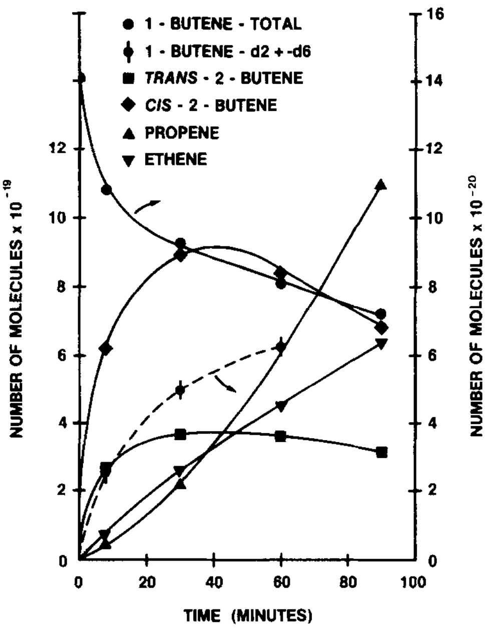


FIG. 3. The degenerative and productive metathesis of 1-butene shown as product distribution from the reaction of 25 cm^3 (NTP) of 1-butene-d_0 and 25 cm^3 (NTP) of 1-butene-d_8 over 0.50 g unreduced molybdena-alumina catalyst at 30°C.

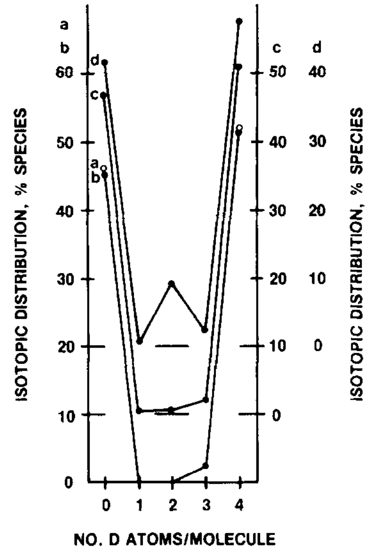


FIG. 4. Deuterium distribution from a C_2H_4 + C_2D_4 mixture: (a) initial; (b) after reaction over freshly oxidized molybdena-alumina catalyst; (c) after reaction over the same catalyst pretreated with C_2H_4; (d) after reaction over the same catalyst pretreated with *cis*-2-C_4H_8. Reaction was studied with the pulse system at 60°C.

The data for propene and 1-butene are summarized in Columns 9–11 of Table 2. When propene was the reactant, the initial rate of degenerative metathesis (propene-d_2 + d_4) was an order of magnitude higher than the rate of productive metathesis (Columns 9–11 of Table 2).

Only degenerative metathesis can occur with ethene; it was observed by the pulse technique, after treatment with *cis*-2-butene (Table 2), using a mixture of ethene-d_0 and -d_4. The isomer distributions obtained from experiments with mixtures of ethene-d_0 + d_4 are shown in Fig. 4. These were carried out in a pulse system at 60°C, after different pretreatments. No degenerate metathesis of ethene was observed over the fresh oxidized catalyst or after the catalyst was soaked in 200 Torr of ethene for 10 min. The metathesis of ethene appeared only when the catalyst was treated with *cis*-2-butene instead of ethene (Curve d).

As with ethene, the degenerative metathesis of propene and 1-butene was not

TABLE 2

Reactions of Olefins over Inducted Molybdena-Alumina Catalysts[a]

Reactant	Olefin used for induction	Olefin adsorbed	Hydrogen atoms exchanged per molecule	Isomerization	Metathesis			Initial rate of		α
					Productive	Degenerative	Σ Metathesis	Productive metathesis	Degenerative metathesis	
1	2[b]	3[c]	4[d]	5[e]	6[f]	7[g]	8	9[h]	10[i]	11[j]
Ethene	None	—	0	—	—	0	0	—	—	—
	C_2H_4	0.06	0	—	—	1.2	1.2	—	0	—
	cis-C_4H_8	0.34	0.004	—	—	12.7	12.7	—	—	—
Propene	None	—	0.37	—	1.3	0	1.3	—	—	—
	C_3H_6	0.23	0.06	—	9.4	53.5	62.9	12.1	103.8	8.6
	cis-C_4H_8	0.36	0.05	—	6.2	47.5	53.7	—	—	—
1-Butene	None	—	1.09	64.6	0	0	0	—	—	—
	1-C_4H_8	0.36	0.34	24.7	4.0 + 15[k]	32.5	51.5	5.4	84.6	15.7
	cis-C_4H_8	0.38	0.32	27.4	1.7 + 9.8[k]	26.0	37.5	—	—	—
cis-2-butene[l]	None	—	0.52	29.8	0	—	—	—	—	—
	cis-C_4H_8	0.36	0.10	1.9	0	81.9	81.9	—	—	—

[a] 0.5 g catalyst; pulse system (Columns 2–8) at 60°C; recirculation system (Columns 9–11) at 30°C.

[b] Catalyst was pretreated with olefins (initial pressure 200 Torr) at 60°C for 10 min and flushed with helium at the same temperature for 1 h.

[c] Total amount of olefins adsorbed on the catalyst in the course of soaking; olefin/atom of Mo.

[d] Number of H/D atoms exchanged per molecule of initial reagent by method of Hightower and Hall (see text).

[e] Percentage concentration of olefins produced by isomerization (see text).

[f] Twice the percentage concentration of ethene.

[g] Twice the percentage concentration of products detectable by mass spectrometer as products of metathesis (see text).

[h] Twice the initial rate of ethene formation × 10^{-16} (molec/g_{cat}s).

[i] Twice the initial rate of propene-d_2 + d_4 or 1-butene-d_2 + d_6 formation corrected to zero hydrogen scrambling × 10^{-16} (molec/g_{cat}s).

[j] Ratio of initial rates for degenerative to productive metathesis.

[k] Twice the percentage concentration of propene produced in the cross metathesis of 1-butene and 2-butenes.

[l] Data from Ref. (*7*) for (internal) metathesis of *cis*-2-butene.

observed in the pulse system over freshly oxidized catalysts (Curves b in Figs. 5 and 6), but hydrogen scrambling was significant in both cases. If the catalyst was inducted with either propene or *cis*-2-butene, the hydrogen scrambling almost completely disappeared with propene and pure degenerative metathesis was observed in the mass spectra (Fig. 5). Hydrogen scrambling also decreased in the 1-butene, but did not disappear completely (Fig. 6).

The results obtained in experiments with perdeuterio- and perhydroethene, propene, and 1-butene are summarized in Table 2. The numbers of hydrogen atoms exchanged per molecule were calculated using the equation given by Hightower and Hall (*15*):

atoms exchanged per molecule

$$= \sum_{i=0}^{k/2} iN_i + \sum_{i=1+k/2}^{k} (k - 1)N_i, \quad (1)$$

where i is the number of deuterium atoms in the molecule and N_i is its mole fraction; k is twice the number of carbon atoms in the olefin studied. In the present application of Eq. (1) where there are contributions to each isotopic isomer from metathesis as well as exchange, the experimental values were corrected for metathesis before the calculation was performed. In the case of propene this calculation gave fairly exact results; over the freshly oxidized catalyst the deuterium distribution was the result of a not too extensive H/D exchange, and after induction the d_1, d_3, and d_5 isomers can be considered to result from stepwise H/D exchange. In the case of 1-butene, however, the calculation gave only approximate values. Over the oxidized catalyst, exchange was very extensive; after induction it was impossible to decide from the mass spectra what fraction of the d_2 and d_6 isomers was formed via metathesis vs exchange.

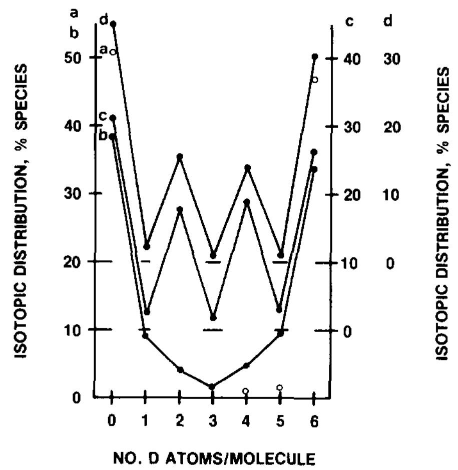


FIG. 5. Deuterium distribution from a C_3H_6 + C_3D_6 mixture: (a) initial; (b) after reaction over freshly oxidized molybdena–alumina catalyst; (c) after reaction over the same catalyst pretreated with C_3H_6; (d) after reaction over the same catalyst pretreated with *cis*-2-C_4H_8. Reaction was carried out in the microcatalytic pulse system at 60°C.

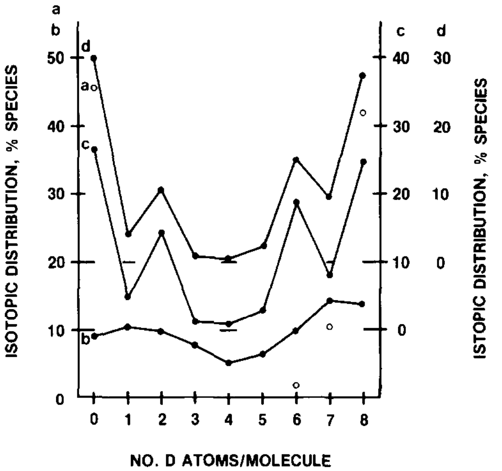


FIG. 6. Deuterium distribution in 1-C_4H_8 + 1-C_4D_8 mixture: (a) initial; (b) after reaction over freshly oxidized molybdena–alumina catalyst; (c) after reaction over the same catalyst pretreated with 1-C_4H_8; (d) after reaction over the same catalyst pretreated with *cis*-2-C_4H_8. Reaction was carried out in the microcatalytic pulse system at 60°C.

The product distributions obtained for the several olefins in the microcatalytic pulse experiments are shown in Table 2 (Columns 4–8). The amount of olefin adsorbed during pretreatment was calculated from the pressure drop in a constant-volume system. The stepwise isotopic exchange (calculated as atoms exchanged per molecule) was decreased by this treatment. Isomerization of 1-butene (Column 5) was calculated from the amount of 2-butenes produced plus the propene that formed by cross metathesis. The data for isomerization of *cis*-2-butene taken from Ref. (*7*) were similarly estimated from the amount of 1-butene formed and that fraction of the *trans*-2-butene that was not produced via metathesis. The values for productive metathesis (Column 6) are twice the amount of ethene produced from propene and 1-butene. The degenerative metathesis of ethene and *cis*-2-butene can likewise be taken as twice the amount of $C_2H_2D_2$ and $C_4H_4D_4$ formed, respectively, because the degenerative metathesis between two perhydro and between two perdeuterio molecules is invisible. For propene and 1-butene, the calculation was analogous.

It was observed that the ratio of the products of degenerative metathesis to those of productive metathesis depended upon the conversion. Therefore, reactions with mixtures of perdeuterio- and perhydroolefins were carried out in a recirculation system at 30°C (Table 2, Columns 9–11). The *initial* rates for the productive and degenerative metathesis were calculated from the chromatographic and mass spectrometric data applying the considerations described above.

(*f*) *Reactions of Mixtures of cis-2-Butene with Perdeuterio- and Perhydro-1-butenes and with Isotopic Propenes*

Reactions were carried out at 30°C in the recirculation system. Thus, the initial rates of productive and degenerative metathesis of terminal olefins, metathesis of *cis*-2-butenes (leading to formation of *trans*-2-butene), and the cross metathesis of 2-butene with terminal olefins could be characterized under competitive conditions. The data are summarized in Table 3. The same value was obtained for the degenerative metathesis of 1-butene and the cross metathesis of 1-butene with 2-butene. The rate of *trans*-butene formation was somewhat lower, but considering that the total *trans*-butene was formed via metathesis, and that there was an equal possibility for the formation of either *cis*- or *trans*-2-butene in the process (*7*), the rate of 2-butene metathesis (internal metathesis) proved to be the highest.

TABLE 3

Initial Rates of Metathesis Reactions in Mixtures of *cis*-2-Butene with 1-Butene and Propene[a,b]

	In molecules produced per gram second × 10^{-16}	
	50 cm^3 *cis*-2-C_4H_8 25 cm^3 1-C_4H_8 25 cm^3 1-C_4D_8	50 cm^3 *cis*-2-C_4H_8 25 cm^3 C_3H_6 25 cm^3 C_3D_6
Productive metathesis	0.8	0.8
Degenerative metathesis	9.5	8.6
Cross metathesis	9.2	Not determined
trans-2-Butene formation	7.5	4.0

[a] 0.50 g inducted molybdena–alumina catalyst at 30°C. Experiments were made in the circulating system.

[b] Productive metathesis was calculated as twice the rate of ethene formation, degenerative metathesis was twice the rate of propene-d_2 + d_4 or 1-butene-d_2 + d_6 formation corrected to zero hydrogen scrambling, cross metathesis as twice the rate of propene formation; the total *trans*-2-butene was regarded to be formed via metathesis; in this process there was an equal possibility for the formation of either *cis*- or *trans*-2-butene (*7*).

DISCUSSION

It was shown previously (*7*) that isomerization of *cis*-2-butene on fresh unreduced molybdena–alumina catalyst proceeds via an acidic mechanism. The acidic character of the catalyst decreased on induction with *cis*-2-butene while the double-bond shift and isotopic mixing decreased significantly; the *cis–trans* transformation increased owing to the increased activity of the catalyst for metathesis.

The reactivity of ethene, propene, and 1-butene in the metathesis reaction was studied and the relative efficiency of these olefins for the production of the active sites and intermediates was characterized. As shown in Table 2, metathesis of ethene and 1-butene was not observed over the freshly oxidized catalyst in the microcatalytic pulse system, and the metathesis of propene was very low. Moreover, no hydrogen scrambling was found in the ethene, but was observed in increasing amounts in the sequence: propene < *cis*-2-butene < 1-butene. The absence of hydrogen scrambling in ethene was possibly due to its inability to form a secondary carbonium ion.

After the catalyst was inducted at 60°C in *cis*-2-butene for 10 min the hydrogen scrambling decreased in each of the olefins, but did not disappear completely (Curves d in Figs. 4–6). This result is in good agreement with the results of Segawa and Hall (*16*), who have found from infrared studies of pyridine adsorption that the Brönsted acidity of unreduced molybdena–alumina catalysts decreased after treatment with *cis*-2-butene.

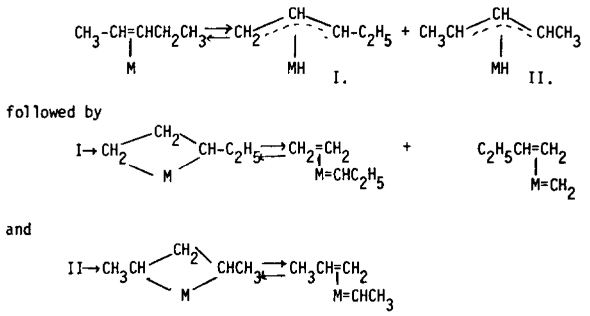
Both productive and degenerative metathesis of olefins occurred after the catalyst was treated with *cis*-2-butene. The reactivity of olefins in metathesis increased in the sequence of ethene < 1-butene < propene < *cis*-2-butene. This sequence of reactivities is different from that observed for the hydrogen scrambling over the oxidized catalyst.

The activity for metathesis of propene and 1-butene was somewhat higher when it was treated with these olefins instead of with *cis*-2-butene (Table 2). Metathesis of ethene, however, was hardly observed after pretreatment with ethene. The amount of ethene adsorbed in the course of pretreatment was lower than with other olefins but a meaningful correlation between the amount of olefin adsorbed during pretreatment and the activity of the catalyst could not be drawn, i.e., the catalyst was more active for propene metathesis after pretreatment with propene than after *cis*-2-butene pretreatment, although less propene was adsorbed than *cis*-2-butene. The availability of an allylic hydrogen may play the key role, vide infra.

Olsthoorn *et al.* also reported (*17*) that metathesis by oxidized rhenia–alumina and molybdena–alumina catalysts was "turned on" by pretreatment with propene, butene, or pentene while remaining inactive after contacting with ethene. Associatively or dissociatively adsorbed water was detected using infrared spectroscopy after pretreatment with olefins. Much less water was formed when the catalyst was contacted with ethene than with the other olefins even when longer times and higher pressures were used. From the water formation they deduced that the catalyst had been reduced by the olefins, and that the reduction was necessary to achieve metathesis activity. The catalysts were only slightly reduced by ethene.

The color change of our catalyst upon pretreatment with propene and butene indicated that reduction had occurred (*7*); the effect was much less pronounced with ethene. This finding was qualitatively confirmed by Wang and Hall (*18*) who found Mo^{5+} spin concentrations per gram of catalyst of 0.09×10^{19}, 1.0×10^{19}, 2.0×10^{19}, and 2.4×10^{19} (out of about 5×10^{20} Mo/g), for the unreduced catalyst after treating with ethene, propene, 1-butene, or *cis*-2-butene, respectively. These results, together with the earlier one (*7, 17*) emphasize the small extent of reduction required to produce metathesis activity.

The possible ways in which carbenes may form initially to carry the reaction have recently been under investigation. Grubbs and Swetnick (*19*) studied the metathesis of mixtures of *cis,cis*-2,8-decadiene and *cis,cis*-2,8-decadiene-1,1,1,10,10,10-d_6. A product distribution was obtained in the early stages of the reaction over a molybdena–alumina catalyst (specifically labeled propenes were formed together with cyclohexene) which was different from that for the "normal" metathesis products (2-butenes, d_6, d_3, and d_0) which *were* formed in the later stages of the reaction. Moreover, an isotope effect was present in the early stages with more butene-d_0 and -d_3 produced than butene-d_6. These results were explained as due to the formation of π-allyl species as an important step in the formation of the metallocycle and hence the carbene intermediate (*20*). Reduction of the catalyst, or products indicating that reduction of the catalyst had occurred were not reported. The work of Farona and Tucker (*21*) supports this view. They compared the initial products from 2-pentene metathesis over $Mo(CO)_6$–alumina with those expected from four possible mechanisms leading to the formation of carbene intermediate. The mechanism advanced by Green and co-workers (*20*) best explained their data. In this, the route to the metallocyclobutane intermediate is via the π-allyl, i.e.,



(2)

(3)

(4)

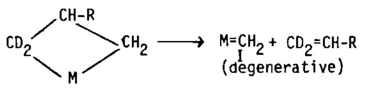
The experimentally determined olefins first formed were propene and 1-butene, as expected from the above mechanism. Thus, Farona and Tucker concluded that the carbene intermediate was formed through π-allyl and metallocyclobutane. They found this hypothesis was confirmed by the observation that metathesis of ethene was not observed over fresh catalyst. According to this picture, carbene formation is possible only with olefins possessing allylic hydrogen. Slow activation of the catalyst by ethene was explained by them by assuming species having allylic hydrogen (e.g., propene and butene) are first produced from ethene (*22, 23*). The recently available data are not sufficient enough to decide whether the reduction of the catalyst or the formation of π-allyl species is the initial step in metathesis.

As pointed out elsewhere (*7, 24*) other pathways to the carbene and metallocycle exist which involve reduction of the catalyst by hydrocarbon. In fact, prereduced molybdena–alumina catalysts are much more active than those "inducted" in hydrocarbon (*7, 25*). In this case an alkyl intermediate may function in the formation of carbenes (*3*). Possibly metathesis is favored by both removal of oxygen (to form CUS) and then allylic hydrogens to provide a route to metallocycle formation.

The difference between the rates of productive and degenerative metathesis of terminal olefins was first recognized in homogeneous systems (*26, 27*). The rate of productive metathesis (leading to ethene and an internal olefin with $2n$-2 carbon atoms, where n is the number of carbon atoms in the olefin reactant) was much slower than the rate of degenerative metathesis (leading to the exchange of methylidene groups between the reacting molecules). The ratio of the rate of degenerative metathesis to the rate of productive metathesis (α) was considerably higher with catalysts based on tungsten (*26*) than with catalysts based on molybdenum. We found that over inducted molybdena–alumina catalysts, the initial α values are 8.6 for propene and 15.7 for 1-butene, far less than the values reported by McGinnis *et al.* (*26*) for the mixture of 1-octene-1, 1-d_2 and 1-hexene with homogeneous molybdenum catalysts. As shown herein, the α value is a sensitive function of the olefin used. This could be partly responsible for these differences. Similar low α values (4.0 to 8.9) were reported by Tanaka *et al.* (*28*) for propene and 1-butene, respectively, over a specially treated supported molybdena catalyst.

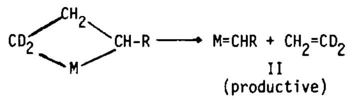
The selectivity for the degenerative metathesis of terminal olefins can be understood in terms of steric interactions (*11, 12, 26*) or in terms of different polarities of intermediates (*13*). The latter may be responsible for the difference in α values for propene and butene-1.

The two pathways (productive vs degenerative) result from the two ways a terminal olefin can add to a surface carbene (e.g., $M{=}CD_2$) to form the metallocyclobutane intermediate. Stepwise addition–elimination of $RCH{=}CH_2$ with this carbene results in either



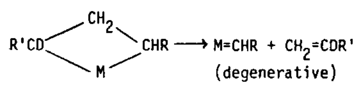
(5)

or



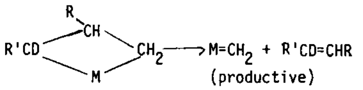
(6)

Similarly, the stepwise addition–elimination of $RCH{=}CH_2$ to the other carbene present in the metathesis, viz., $M{=}CDR'$ (R' is perdeuterio) yields



(7)

or



(8)

The present data do not distinguish the effects of steric factors from those of polarization. The latter have been used recently (*12, 13*) to explain α values greater than unity with homogeneous systems. These arguments can be extended to explain the variation of α with the olefin studied in the present work (*29*). The addition of propene would be favored over 1-butene in Reactions (5), (6), and (8); the opposite would be true for Reaction (7). Thus the productive metathesis [Reactions (6) and (8)] with propene would be favored over 1-butene. The degenerative metathesis is less sensitive to chain length because in Reaction (5) propene is favored while in Reaction (7) it is 1-butene. This leads to the rationalization that the value of α should increase with increasing chain length.

In homogeneous catalytic systems the relative rates of different types of metathesis were found (*12*) to vary in the following sequence: degenerative metathesis of terminal olefins ≫ cross metathesis of terminal and internal olefins > metathesis of internal olefins > productive metathesis of terminal olefins. In a mixture of terminal and internal olefins, competition between the fastest degenerative metathesis of terminal olefins together with the cross metathesis of terminal and internal olefins effectively eliminated the slower metathesis of the internal olefins (*10, 11*). Over the inducted molybdena–alumina catalyst using the same experimental conditions (after pretreatment of the catalysts with *cis*-2-butene) we found that the rate of metathesis of internal olefins, e.g., *cis*-2-butene, was higher than that of degenerative metathesis (1-butene) (Table 2). Even in the mixture of 50% *cis*-2-butene and 50% 1-butene the rate of formation of *trans*-2-butene was almost as high as the rates of cross metathesis and degenerative metathesis (Table 3). However, the present work was with butenes whereas higher (internal) olefins were used in the studies with homogeneous catalysts (*10–12*).

The competition effects are also evident when the metathesis rates of ethene, propene, and 1-butene are compared separately (Table 2, Column 8) with the suppression of *cis*-2-butene metathesis by their presence (Table 1). Both metathesis rates and suppression effects increase in the same sequence: ethene ≪ 1-butene < propene. From this it follows that the olefin with the highest metathesis rate will suppress the metathesis of other olefins most effectively.

Competition between the faster *cis*-2-butene metathesis and the much slower ethene metathesis is also the explanation for the inhibition of ethene metathesis on addition of *cis*-2-butene. This effect was observed over a molybdena–titanium oxide catalyst by Tanaka *et al.* (*28*). The metathesis of ethene was interrupted by the addition of *cis*-2-butene and only reactions of the latter were observed (formation of *trans*-2-butene and propene); no further metathesis of ethene occurred. The inhibition was explained by the authors of postulating that whereas the ethylidene carbene intermediate can react with either ethene or 2-butenes, in the presence of 2-butenes it only reacts with the latter. If the generalization given by Casey *et al.* (*12*) is applied (that in a mixture of two olefins, one of them reacting much faster in metathesis than the other, only the products of cross metathesis and those of the faster metathesis will be observed) to the mixture of ethene and *cis*-2-butene, only *trans*-2-butene and propene formation can be expected.

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