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The Isomerization and Metathesis of *n*-Butenes

II. Acid Catalysis on the Fully Oxidized Catalyst

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The mechanism of *n*-butene isomerization was studied over a freshly oxidized molybdena–alumina catalyst using the microcatalytic pulse technique. A 2-butyl carbonium ion common intermediate was invoked to interpret the results. A model was derived which was built upon statistical and energetic arguments and based on the experimental energy profile; it accounted for the selectivities and their temperature dependencies. In particular it was shown that temperature-dependent *cis/trans* ratios very different than unity are possible and sometimes found for acid-catalyzed reactions. The model also correctly described the relative reactivities and equilibrium constants for the three isomers.

INTRODUCTION

In the previous paper (*1*) it was shown that butene isomerization over oxidized molybdena–alumina exhibited most of the characteristics of acid catalysis. One intermolecular transfer of H or D occurred with each reaction step in the co-isomerization of equimolar mixtures of C_4H_8 and C_4D_8. Isotope effects were small and pyridinium ions formed when pyridine was adsorbed, etc. The *cis/trans*-2-butene ratios were, however, much higher (~2.5) than expected (~1.0) based on the *sec.*-butyl carbonium ion model of Hightower and Hall (*2*) [see Table 1, Ref. (*1*)] and they were temperature dependent, in contradiction with expectation. It has been remarkable that this grossly oversimplified model has worked as well as it has; yet, on the other hand, it has simply afforded a reasonable explanation for the observed experimental facts for almost all known cases of proton-catalyzed reactions (*2–6*) [data previous to 1965 are collected in Ref. (*3*)]. Distinction has also been made between these characteristics of carbonium ion chemistry and the intramolecular H-transfer (allylic) mechanisms found for more basic oxides such as zinc oxide and alumina (*7*), the latter sometimes being called an "acid catalyst." Because of the widespread use of the magnitude of the *cis/trans* ratio as diagnostic of mechanism and the apparent exceptions (such as the present one) which sometimes occur, we have reinvestigated this problem.

The model of Hightower and Hall (*2*) rests on the assumption that the product distribution is controlled by the relative heights of the activation energy barriers between the metastable intermediate and the three isomers. For reasons given by the authors, this feature has been observed with most (if not all) Brønsted acid catalysts. Because the formation of *cis*- or *trans*-2-butene depends on the loss of one or the other of the two methylene hydrogen atoms from the three-carbon atom of the carbonium ion (equally probable processes), the expected (and observed) ratios were shown to be temperature independent and close to unity. Similarly, temperature-dependent but nearly equal, initial 1-

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butene/*cis* and 1-butene/*trans* ratios less than 3.0 (and usually less than 1.0) were predicted and observed. In the present work we have investigated the constraints which need be relaxed, to what extent, and what new assumptions need be made to explain the "abnormal behavior" reported herein.

Some other examples of supposedly acid catalysis which show high *cis*/*trans* ratios include: (a) SnO_2 (*8*), where the ratio reported by Kemball *et al.* was close to 1.5; (b) WO_3–TiO_2 with an initial ratio of 1.8 shown by Yamaguchi *et al.* (*9*); (c) TiO_2–SnO_2 with an initial ratio of 2.5 as reported by Tanabe and co-workers (*10*), and (d) WO_3–Al_2O_3 (*11*) where the initial ratio was 2.1.

TABLE 1

Activation Energies for Butene Isomerization over Oxidized Molybdena–Alumina Catalyst

Step	E_a[a] (kcal/mole)	ΔE_a[b] (kcal/mole)
1 → *trans*	5.5	$\delta_1 = 0.7$
1 → *cis*	4.8	
cis → 1-butene	6.8	$\delta_3 = 1.1$
cis → *trans*	5.7	
trans → 1-butene	8.0	$\delta_2 = 1.8$
trans → *cis*	6.2	

[a] Obtained from the Arrhenius plots in Fig. 1.

[b] Difference in activation energy for two isomer products from each reactant isomer.

EXPERIMENTAL

The catalyst pretreatment, purification of reactants, and procedures were described in the previous paper. As noted previously (*1*), metathesis was not detectable with the fully oxidized catalyst, but developed with slight reduction in butene gas at room temperature on prolonged contact. Therefore, a microcatalytic pulse technique was used with a carrying gas stream of ultrapure helium. Selectivity ratios were obtained at low conversion (always less than 10%) for each of the isomers at different temperatures. Because a very slight reduction occurred in each experiment, the catalyst was reoxidized after passage of each pulse [see the previous paper (*1*)].

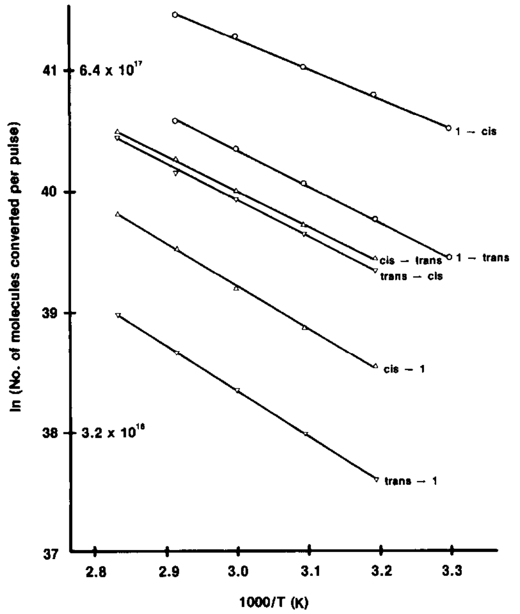


FIG. 1. Arrhenius activation energy plots for *n*-butene isomerization over freshly oxidized molybdena–alumina catalyst (pulse method). Units of conversion are number of molecules × 10^{17} produced per pulse containing 1.04 × 10^{19} molecules. The values for the activation energies are listed in Table 1.

RESULTS AND TREATMENT OF DATA

Experiments were carried out in the temperature range 30–80°C. The data are presented as Arrhenius plots for each of the individual reactions in Fig. 1; Table 1 summarizes the experimental activation energies (column 2) and the differences in activation energy for the two isomer products from each reaction. These ΔE_a values (δ_1, δ_2, and δ_3) correspond to differences in the tops of the energy barriers for the two pathways (*2*) because the pairs each start with the same ground-state energy (the same reactant molecule). To compare different reactants, enthalpy differences must also be taken into account; these are obtained from the literature (*12*), as before.

Before proceeding, it is essential to obtain an estimate of the simple reaction order, n; the equation,

$$\log \frac{P}{P^0} = \frac{1}{n-1} \log \frac{(dx/dt)}{(dx/dt)^0} \simeq \frac{-1}{n-1} \log \frac{x^0}{x} \quad (1)$$

taken from (*13*) was used for this purpose, where x is the percentage reactant converted per pass, P^0 is the initial pressure in the doser which yielded the highest initial rate, $(dx/dt)^0$ or conversion x^0 (the latter approximation holding for small x). The straight line of Fig. 2 yields $n = 0.41$ for 1-butene. This fractional value of n suggests that the intermediate complex is fairly strongly held, i.e., that the coverage is not sparse, but *is* pressure dependent. That the reaction is not first order is confirmed by Fig. 3 where the results have been plotted according to the first-order equation of Bassett and Habgood (*14*):

$$Kk = (-F/273RW) \ln(1 - x). \quad (2)$$

Here F is the carrying gas flow rate, k the reaction rate constant, K the adsorption equilibrium constant, R the gas constant, and W the weight of catalyst. The curve deviated from linearity at long contact time (low F) in a direction which is consistent with the reaction being less than first order. Because $n \gg 0$, back reaction may be neglected at low conversion.

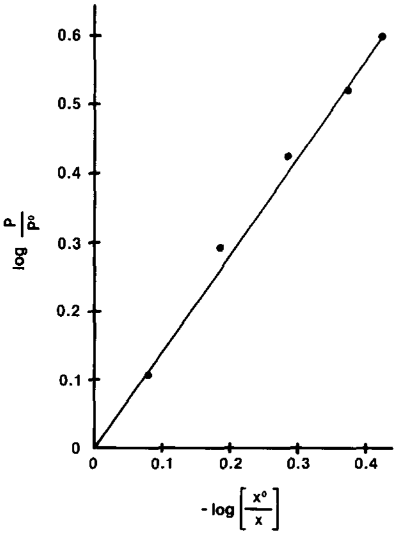


FIG. 2. Reaction order ($n = 0.41$) plot for microcatalytic pulse data for the isomerization of 1-butene over freshly oxidized molybdena–alumina catalyst. For the calculation details see Ref. (*13*).

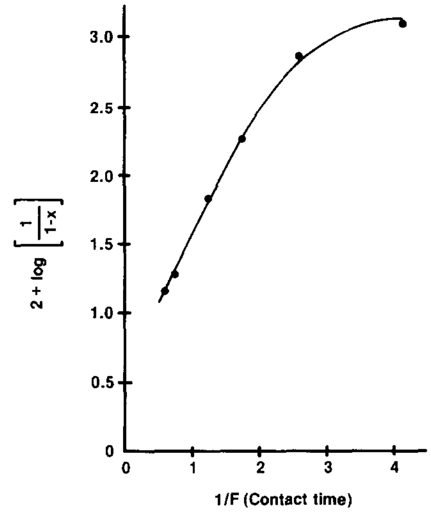
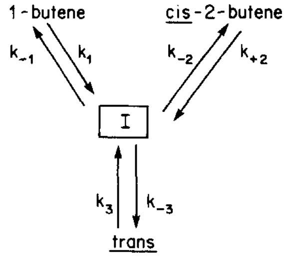


FIG. 3. Negative test for first-order kinetics [method of Ref. (*14*)].

In order to calculate reaction parameters such as selectivities, relative reactivities, and equilibrium constants the following kinetic scheme was adopted:



(3)

where I is a common surface intermediate, e.g., the *sec*.-butyl carbonium ion. Making the steady-state approximation for I and neglecting back-reaction of product molecules, the kinetic expressions shown in Table 2 were obtained. Figure 4 was constructed from the difference in thermodynamic heats of formation (*12*) and the differences in activation energy for each pair

TABLE 2

Rate Expressions[a] for Butene Isomerization over Fresh Oxidized Molybdena–Alumina Catalyst

$-\frac{d(\text{1-but})}{dt} = \frac{k_1k_{-2}P^n}{k_{-1}+k_{-2}+k_{-3}} + \frac{k_1k_{-3}P^n}{k_{-1}+k_{-2}+k_{-3}} = \frac{d(cis)}{dt} + \frac{d(trans)}{dt}$	(1)
$-\frac{d(cis)}{dt} = \frac{k_2k_{-1}P^n}{k_{-1}+k_{-2}+k_{-3}} + \frac{k_2k_{-3}P^n}{k_{-1}+k_{-2}+k_{-3}} = \frac{d(\text{1-but})}{dt} + \frac{d(trans)}{dt}$	(2)
$-\frac{d(trans)}{dt} = \frac{k_3k_{-1}P^n}{k_{-1}+k_{-2}+k_{-3}} + \frac{k_3k_{-2}P^n}{k_{-1}+k_{-2}+k_{-3}} = \frac{d(\text{1-but})}{dt} + \frac{d(cis)}{dt}$	(3)

[a] Derived from the steady-state treatment shown in the text.

of isomers formed from each of the three isomers (Table 1). These reaction coordinates were used with the kinetic expressions of Table 2 to calculate the various reaction parameters. Note that the activation energy, E, may be determined experimentally but that the depth of the well, ε, cannot. However, the parameters δ_1, δ_2, and δ_3, have been measured; see Table 1. For calculating the selectivities for each of the reacting isomers, the rate of formation of one product isomer was divided by the rate of formation of the other using the kinetic expressions given by Table 2. The rate constants of the resulting equations were then written in terms of their corresponding Arrhenius expressions using the reaction coordinates of Fig. 4. As before (*2*), the preexperimental factors were assumed to cancel except for a statistical factor of 3 or 1. (Loss of any one of three hydrogens will produce 1-butene whereas loss of a single specific H is required to produce either *cis*- or *trans*-2-butene.) Thus, the ratio 1-butene/*trans* when *cis*-2-butene was the reactant may be estimated as follows:

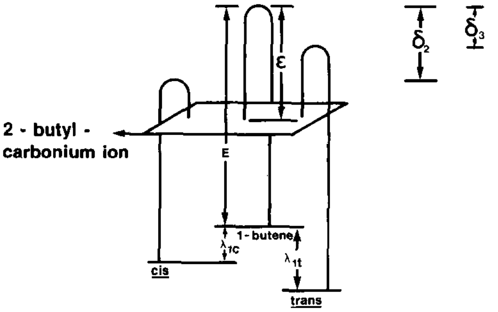


FIG. 4. Energy profile (with reaction coordinates) showing common intermediate in the isomerization of *n*-butenes over freshly oxidized molybdena–alumina catalyst.

$$\frac{\text{1-but}}{trans} = \frac{k_{-1}}{k_{-3}} = \frac{3Ae^{-\varepsilon/RT}}{Ae^{-(\varepsilon-\delta_3)/RT}} = 3e^{-\delta_3/RT}, \quad (4)$$

where $\delta_3 = 1.1$ kcal/mole (Table 1). The experimental and calculated selectivities at different temperatures are listed in Table 3. The theory provides fair agreement with the experimental values and correctly predicts the variation with temperature.

In order to calculate the relative reactivities a similar procedure was followed, e.g., the relative rate of disappearance of 1-butene with respect to *cis*-2-butene was estimated as follows:

$$\frac{-d(\text{1-but})/dt}{-d(cis)/dt} = \frac{k_1k_{-2}P^n + k_1k_{-3}P^n}{k_2k_{-1}P^n + k_2k_{-3}P^n} = \frac{e^{\delta_2/RT} + e^{\delta_3/RT}}{[e^{-(\lambda_2-\delta_2)/RT}]\,(3 + e^{\delta_3/RT})}, \quad (5)$$

where δ_2 and δ_3 are given in Table 1 and $\lambda_2 = \lambda_{1\to c} = 1.8$ kcal/mole and $\lambda_3 = \lambda_{1\to t} = 2.6$ kcal/mole (*12*). The relative rates of disappearance at 60°C are listed in Table 4.

For the calculation of the equilibrium constants the same procedure was employed, i.e., the ratio of rate constants for

TABLE 3

Experimental and Calculated Selectivities at Different Temperatures for *n*-Butene Isomerization over Oxidized Molybdena–Alumina

Product ratio	Experimental ratios	Calculated ratios[a]	Temp. (°C)
	cis-2-butene		
trans/1-butene	2.46	1.93	40
	2.35	1.82	50
	2.30	1.73	60
	2.14	1.65	70
	2.00	1.60	80
	trans-2-butene		
cis/1-butene	5.68	5.91	40
	5.31	5.40	50
	4.90	4.97	60
	4.60	4.60	70
	4.00	4.26	80
	1-butene		
cis/*trans*	2.84	3.17	30
	2.77	3.05	40
	2.67	2.95	50
	2.60	2.86	60
	2.47	2.77	70

[a] Calculated from theory; only experimental parameter is the difference in activation energy, δ_i; see text.

each pair was estimated with the aid of the data of Table 1 and the model of Fig. 4. The results are listed in Table 5 where the calculated equilibrium constants at 23°C are compared with the theoretical values taken from Ref. (*12*); see Table 5.

TABLE 4

Relative Rates at 60°C for Butene Isomerization over Unreduced Molybdena–Alumina Catalyst

	Experimental	Calculated[a]
$\dfrac{-d(\text{1-but})/dt}{-d(cis)/dt}$	4.0	3.3
$\dfrac{-d(\text{1-but})/dt}{-d(trans)/dt}$	8.8	9.2
$\dfrac{-d(cis)/dt}{-d(trans)/dt}$	2.2	2.8
	Ratios of rates	
	Experimental	Theoretical
trans : *cis* : 1-butene	1 : 2.2 : 8.8	1 : 2.8 : 9.2

[a] Calculated from equations of Table 2.

DISCUSSION

When the isomerization of *n*-butenes was studied over oxidized molybdena–alumina catalyst in the microcatalytic pulse system, the isomerization exhibited some of the characteristics of acid catalysis (*1*). After the catalyst was inducted with *cis*-2-butene, however, the acidic characteristics decreased substantially and the *cis* → *trans* isomerization was found to proceed almost exclusively via metathesis. The "pure" isomerization found for the freshly oxidized catalyst produced exchange patterns, isotope effects, and exchange effects with "residues" similar to those reported by Hightower and Hall (*2*) for SiO_2–Al_2O_3. However, the *cis*/*trans* ratios, which have been widely used as a diagnostic tool for the acid mechanism, were not close to unity as predicted by the Hightower and Hall (*2*) model. As pointed out in the Introduction there are several other examples in the literature where supposedly acid systems also show high *cis*/*trans* ratios (*8–11*). Noteworthy is the work of Tanabe and coworkers (*10*) who reported that compositions between about 10 and 90% SnO_2 coprecipitated with TiO_2 were acidic and yet produced *cis*/*trans* ratios near 2.0 when

TABLE 5

Equilibrium Constants for Butene Isomerization over Fresh Oxidized Molybdena–Alumina Catalyst

Equilibrium constants	Experimental value[a]	Calculated[b]
$k_{1c}/k_{c1} = \dfrac{k_1k_{-2}}{k_{-1}k_2}$	0.15	0.21
$k_{tc}/k_{ct} = \dfrac{k_3k_{-2}}{k_{-3}k_2}$	0.26	0.13
$k_{1t}/k_{t1} = \dfrac{k_1k_{-3}}{k_{-1}k_3}$	0.04	0.03

[a] Taken from Ref. (*12*).
[b] See text.

1-butene was isomerized at 200°C. It was presumed that the acid sites (identified by *n*-butylamine titration) were responsible for the isomerization of 1-butene. In a more recent paper (*9*), ratios of around 1.8 were reported for the isomerization of 1-butene over tungsta–titania preparations. Again, the catalytic activity for butene isomerization at 100°C correlated well with the acidic properties estimated using the *n*-butylamine titration technique. The question which obviously arises is: how can these systems with initial *cis*/*trans* ratios different than unity be accounted for, if not in terms of a *sec.*-butyl carbonium ion? Seeking an answer we have reinvestigated the Hightower and Hall (*2*) model. Their equations reveal that the rate of formation of *cis*- and *trans*-2-butene were equal because they were both limited by the same highest barrier along the reaction coordinate, viz., that between 1-butene and the carbonium ion. In the present model these rates were unequal because they were limited by the different barriers between the steady-state population of carbonium ions and the product molecules, i.e.,

$$\frac{d(cis)}{dt} = k_{-2}(I) \neq k_{-3}(I) = \frac{d(trans)}{dt}, \quad (6)$$

where (I) is the concentration of the intermediate species, and

$$(I) = \frac{k_1P_1{}^n + k_2P_2{}^n + k_3P_3{}^n}{k_{-1} + k_{-2} + k_{-3}} \simeq \frac{k_1P_1{}^n}{(k_{-1} + k_{-2} + k_{-3})}, \quad (7)$$

where P_1, P_2, and P_3 are the partial pressures of 1-butene, *cis*-2-butene, and *trans*-2-butene, respectively; at low conversion the approximation made above is justified for 1-butene as the reactant. The present model is the more general of the two. The data of Hightower and Hall will fit either model, but the present data will not fit the Hightower and Hall model.

In essence, the difference between the two models is that the earlier one (*2*) treated the kinetics for the initial stages of the reaction (back-reaction neglected) as a set of consecutive reactions. Thus, given sufficient energy to surmount the barrier E (Fig. 4), a 1-butene molecule could not discriminate between the pathways to *cis*- vs *trans*-2-butene. Similarly, starting with one of the other isomers, a higher barrier had to be passed to form 1-butene than the remaining isomer. In the present model the stabilization energies (ε, $\varepsilon - \delta_2$, and $\varepsilon - \delta_3$) all must be large enough to provide a lifetime of the intermediate long enough so that Eq. (3) can apply. When this is not true, the reactions become concerted.

Reference to Fig. 4 shows that a given intermediate, e.g., the 2-butyl carbonium ion, is not the same species on all surfaces. Both the energy of the ion ($E - \varepsilon$) and its stabilization energies may vary depending upon the local environment at the reaction site, i.e., ϵ, δ_2, and δ_3 are all variables which define the nature of the intermediate. In solution these variations might be called solvation effects. Apparently, the lesson to be learned is that when the carbonium ion is free on a surface of high acidity, the barriers between the intermediate and the product 2-butene molecules are about equal for the reasons suggested earlier. If the intermediate is something less than a free ion, this may not be true. Special interactions may exist which affect the energetic factors. This being so, it follows that the *cis*/1-butene and the *trans*/1-butene ratios cannot be equal as they were in other strong acid systems (*2, 5, 6, 15*); this is also as shown by the data in Table 3. Evidently, H_a and H_b (see Fig. 5) are not equivalent toward abstraction to yield the *cis*- or the *trans*-2-butene products, possibly for steric reasons. Alternatively, the charge on the carbonium ion may be less positive and the ion less than planar. Whatever the cause, the inequivalence operates through a difference in activation energy. This (and the model) was confirmed experimentally by the observation (from Fig. 1) that $\delta_1 = \delta_2 - \delta_3$ (see Table 1).

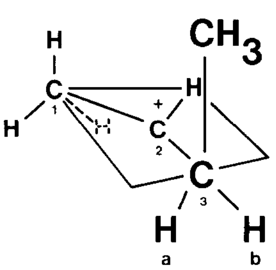


FIG. 5. Model of classical 2-butyl carbonium ion intermediate (on surface) for the isomerization of *n*-butenes [taken from Ref. (*1*)].

Lombardo *et al.* (*15*) working with modified Na–Y zeolites (modified by substituting small amounts of Ca^{2+} for $2Na^+$), showed that as the Ca^{2+} content (acidity) was increased, *cis–trans* isomerization of the 2-butenes was enhanced relative to double-bond migration. The variations in the selectivities with increasing Ca^{2+} substitution were similar to those reported by Misono *et al.* (*12*) for the same reactions over supported metal sulfates (and H_2SO_4). The activities increased and the 1-butene/2-butene ratios decreased with the catalyst acidity, although the *cis/trans* ratios (from 1-butene isomerization) remained practically unchanged. From these results it is apparent that more is involved with molybdena–alumina and tungsta–titania catalysts than simple changes in acidity of the catalyst protons.

The simple model presented herein was able to account for practically all of our experimental observations, viz., selectivities (Table 3), temperature dependence of the *cis/trans* ratios (Fig. 1, Table 1), relative reactivities (Table 4), and equilibrium constants (Table 5). It also accounted for the observed intermolecular exchange of one hydrogen atom per molecule isomerized [see Ref. (*1*)]. Moreover, Fig. 4 answers in an affirmative way the question concerning *cis/trans* ratios different than unity in a reaction mechanism involving a common intermediate. Until reason to think otherwise develops, it will be presumed that this intermediate is a carbonium ion with some kind of special interaction with the surface. Possibly, this may be related to the non-first-order dependence on the reactant pressure exhibited in Figs. 2 and 3. In any case the salient feature of this work is that all the important reaction characteristics could be accounted for on the basis of a single common intermediate on the basis of energetic factors alone. This is not true in other cases, e.g., the allylic mechanisms (*7*, *16*), where as many as five intermediates may be required to describe the reaction.

A legitimate question is why are the known equilibrium constants in such reasonable agreement with those deduced from the present model in view of the low value of the pressure dependence, $n = 0.41$, determined in this work. Two possibilities suggest themselves: (a) that the order of the reaction is actually unity in all three isomers *when the system is at equilibrium* and that the rate constants determined at low conversion still apply or (b) that the true dependence is really much higher. The microcatalytic method is never a good method for studying kinetics. A number of factors could contribute to an apparent low order, including pulse broadening by adsorption or diffusion, mass loss by reaction with the oxidized surface, etc. Regrettably, the pulse technique was the only way we could study the fully oxidized catalyst.

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