

Tracer Studies of Acid-Base Catalyzed Reactions

XIII. The Isomerization of the *n*-Butenes over Zinc Oxide and Alumina¹E. A. LOMBARDO,* W. C. CONNER, JR.,* R. J. MADON,* W. KEITH HALL,*²

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The isomerization of *n*-butenes was studied over zinc oxide in a glass recirculation system. Experiments were made with each of the pure isomers at temperatures between 0 and 90°C. At low temperatures and conversions the reactions were all zero order in olefin. Below 50°C the Arrhenius plots were linear so that the reaction coordinates of the system could be mapped. At 90°C, the reaction was no longer zero order. These results indicated that the reaction occurred in the nonlinear part of the adsorption isotherm. Tracer experiments using *cis*-2-butene-2,3-*d*₂ showed that *cis*-2-butene can be converted directly into the *trans*- isomer (without going through 1-butene as an intermediate). At higher temperatures both the kinetic data and the tracer results were complicated by secondary processes. The tracer studies of these reactions were also carried out over a γ -alumina catalyst. Experiments were made using *cis*-2-butene-2,3-*d*₂ and *cis*-2-butene-*d*₃ as well as binary mixtures of these compounds. In contrast with ZnO, intermolecular exchange was important over alumina, particularly in the 1-butene product. CO₂, which is a good poison for olefin-D₂ exchange, was not nearly as effective for intermolecular exchange. Moreover, the alumina OH groups contributed to the intermolecular exchange under the reaction conditions. ZnO behaved as an "ideal system" in which the kinetic and tracer data were entirely consistent with the previous ir studies (Dent, A. L., and Kokes, R. J., *J. Phys. Chem.* **75**, 487, 1971; Chang, C. C., Conner, W. C., Jr., and Kokes, R. J., *J. Phys. Chem.* **77**, 1957, 1973) of the intermediate species. Although on alumina the picture was obscured by simultaneous exchange processes, comparison of the present results with other published data led to the conclusion that the mechanisms for *n*-butene isomerization over ZnO and alumina are the same or very similar at temperatures below 100°C.

INTRODUCTION

The mechanism of *n*-butene isomerization over ZnO has been studied by Dent and Kokes (1) and Chang *et al.* (2) using a combination of ir and kinetic techniques. Five different surface species were charac-

terized, i.e., π -complexes of 1-butene, *cis*-2-butene, and *trans*-2-butene and *syn*- and *anti*- π -allyls. Their ir and kinetic data were consistent with a mechanism involving these species and so a qualitative picture of the reaction mechanism was derived. To make the picture more quantitative additional information is needed, viz., establishment of the heights of the energy barriers connecting the different reaction inter-

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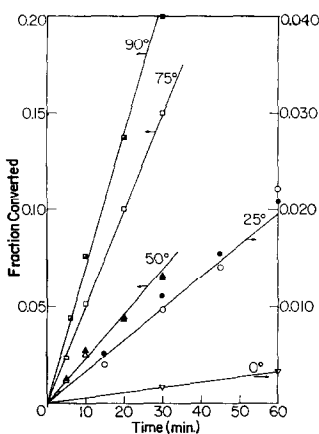


FIG. 1. Conversion vs time plots for *cis*-2-butene \rightarrow *trans*-2-butene isomerization over ZnO (2.0 g) at various temperatures. Empty and full symbols at a given temperature represent duplicate runs. Data for 60°C are not shown to avoid overcrowding.

mediates and determination of whether or not direct *syn*- to *anti*- π -allyl interconversion occurs. The present study was made to clarify these two questions by defining the reaction kinetics at different temperatures (Dent and Kokes and Chang *et al.* only used one) and by using deuterium-labeled butenes to determine the extent of direct *cis*-*trans* interconversion without going through the 1-butene isomer. Another objective was to investigate further the mechanism of *n*-butene isomerization over alumina. Despite numerous studies of this system, the mechanism remains uncertain. Comparison of our data (3) with those of Chang *et al.* (2) showed that, under certain pretreatment conditions, the behavior of alumina and ZnO was strikingly similar. Therefore, it was thought worthwhile to extend the tracer experiments to alumina in order to clarify further the common characteristics or differences between the two catalysts.

Recently Maurel and co-workers (4, 5) reported experiments with alumina catalysts using selectively deuterated butenes. With relatively inactive catalysts the tracer data (at 250°C) for alumina resembled those for silica-alumina. With a

more active preparation (at 85°C), however, the data looked more like those of Hightower and Hall (3, 6, 7). In another recent paper Amenomiya (8) studied a more active alumina (at 19°C) and concluded that his results could be explained, like silica-alumina, by a Brønsted mechanism. The characteristics of the acid-catalyzed reactions are well understood; in fact, they are diagnostic for the proton-catalyzed reaction. If the same simple mechanism operates over alumina and zinc oxide, it may likewise become diagnostic when it is fully understood. The present work contributes a step in this direction.

EXPERIMENTAL

Catalyst and pretreatment. The ZnO (Kadox-25) was obtained from the New Jersey Zinc Co. and the γ -alumina (GA-48) was prepared by the neutral hydrolysis of redistilled aluminum isopropoxide (3, 6). Both were extremely pure and each was given a standard pretreatment. ZnO was degassed by raising the temperature to 480°C at which point O₂ (170 Torr) was admitted and circulated for 1 hr; a cold trap (78°K) was used downstream from the reactor to remove any condensables produced (1, 2). Following the O₂ treatment the sample was evacuated for another hour before quenching to the reaction temperature. The alumina was treated with oxygen (200 Torr) at 530°C for 1 hr, followed by overnight evacuation at the same temperature (6).

Reactants. 1-Butene and *cis*-2-butene were research-grade 99.8% pure; the *trans*-2-butene (research grade) contained 0.4% 1-butene. Before use they were repeatedly outgassed by freezing and pumping in a conventional high-vacuum system. The perdeutero-*cis*-2-butene was prepared as before (9), by repeatedly exchanging the olefin with D₂ over high-purity alumina. The *cis*-2-butene-2,3-*d*₂ was made by selective deuteration of dimethylacetylene over a Pd/Al₂O₃ catalyst (10).

Reaction system. The reactor was similar to that used previously (6); it was a static reactor (a 250-cm³ spherical Pyrex flask with the catalyst contained in a finger which extended below the bulb). This reactor was stirred by convection due to the temperature gradient between the catalyst (finger) and the bulb (room temperature) and by making it part of an all-glass circulation system. The reacting gases were recycled over the catalyst with a glass pump at a rate which was fast compared with the conversion rate. The latter was very slow (less than 1% conversion per minute) and the data are therefore free of diffusion effects. This is confirmed by the results. The very high initial *cis*-/*trans*-2-butene ratios produced in the isomerization of 1-butene, which were similar to those of others (2, 3, 12a), demonstrate this point. Pore diffusion effects should not be important with ZnO in any case, as it is crystalline and essentially nonporous.

The products of the reaction were analyzed using a 12-ft \times 0.25-in. dimethyl-sulfolane column at 0°C. A 0.355-cm³ sampling volume in the circulation loop was used to remove aliquots of gas from the reactor and transfer them into the He stream to the glc column. The separated isomers were recovered as they emerged from the glc for mass spectral analysis. The mass spectral data were always recorded at low voltage (13–15 eV) to minimize cracking. An IR-12 Beckman spectrometer was used to determine the position of the isotope when necessary.

RESULTS

Zinc Oxide: Kinetic Studies

Experiments were made at temperatures ranging from 0 to 90°C. A 2.0-g sample of catalyst was used and the reactant pressure was 100 Torr unless otherwise stated. Three series were done starting with each pure isomer. Dent and Kokes (1) and Chang *et al.* (2) showed that the reaction was zero order

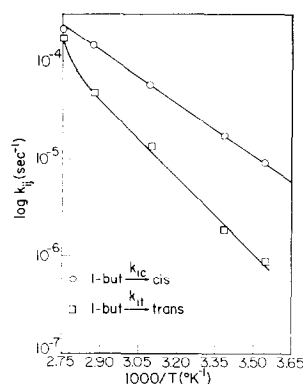


FIG. 2. Arrhenius plots for 1-butene isomerization over ZnO. Rate constants obtained from conversion vs time plots. (To calculate rate constants into molecules per square centimeter per second, multiply by 8.6×10^{15} .)

at room temperature. During the present work it was verified that the reaction was also zero order at 50°C. Data for the isomerization of *cis*-2-butene at 100, 160, 290, and 500 Torr all fell on the same straight line (for conversions up to 20% at 100 Torr) when the number of molecules converted was plotted versus time. The rate constants at each temperature were calculated from zero-order plots; they are indeed the actual experimental rates of formation of the individual isomers. (The reaction was not, however, zero order at higher temperatures, *vide infra*.) One typical set of data (for *cis* \rightarrow *trans* isomerization) is given in Fig. 1.

Arrhenius plots for 1-butene isomerization to both *cis*- and *trans*-2-butene are shown in Fig. 2. The 1-butene to *cis*-2-butene curve (top) was linear throughout the temperature range studied with an apparent activation energy, E_{1c} , of 7.8 kcal/mole. The 1-butene \rightarrow *trans*-2-butene plot, however, deviated from linearity at the high-temperature end. The activation energy for the linear low-temperature range ($E_{1t} = 12.3$ kcal/mole) was calculated from data obtained by both increasing and decreasing the reaction temperature with one aliquot of catalyst. Similar data for the

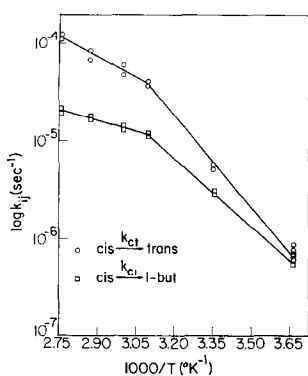


Fig. 3. Arrhenius plots for *cis*-2-butene isomerization over ZnO. See legend for Fig. 2. An extra point was determined at 60°C (not shown on Fig. 1) to define sharp intersection of curves.

isomerization of *cis*-2-butene are given in Fig. 3. The apparent activation energies calculated for temperatures between 0 and 50°C are $E_{c1} = 11.2$ kcal/mole and $E_{ct} = 15.3$ kcal/mole. Note the sharp break at about 50°C.

The isomerization of *trans*-2-butene gave good Arrhenius plots for both 1-butene and *cis*-2-butene formation over the full temperature range. The activation energies calculated from the data of Fig. 4 are $E_{tc} = 7.4$ kcal/mole and $E_{t1} = 10.8$ kcal/mole. At room temperature the two points correspond to the first and last runs in this series. The good agreement between these two points is indicative of the reproducibility of the data. Interestingly, the differences between activation energies for the forward and reverse directions did not give reasonable values for the enthalpy changes of the reactions, e.g., note that $E_{ct} - E_{tc} = +7.9$ kcal/mole (the activation energy for *trans* \rightarrow *cis* is lower than for *cis* \rightarrow *trans*). This experimental fact is in apparent violation of simple kinetic principles and of the principle of microscopic reversibility. It must be remembered, however, that the kinetics are not simple; they are coupled and the system is far removed from equilibrium, *vide infra*.

The changes observed in some of the

Arrhenius plots at temperatures above 50°C are evidence for some important change in a kinetic variable. Particularly striking were the breaks in the plots obtained from *cis*-2-butene. This was traced to a change in the reaction order with *cis*-2-butene. At 90°C the reaction rate was found to increase with pressure and the data at each pressure could be fitted to a first-order rate equation of the kind used by Gerberich and Hall (11). The slopes of the straight lines so obtained, decreased with increasing pressure. As shown earlier (12b), this behavior is symptomatic of a Langmuir-Hinshelwood mechanism in the non-linear region of the adsorption isotherm. For this reason, only the data for the low-temperature (zero order) regime are treated herein.

ZnO: Tracer Studies

Experiments were designed to provide information concerning the interconversion between the *syn*- and *anti*- π -allyls and to check for a possible change in mechanism at higher temperatures; also, it was hoped to gain insight into the rate-limiting step through the possible discovery of isotope effects.

cis-2-Butene-2,3 d_2 was used to study the *syn* to *anti* interconversion. Figure 5 shows

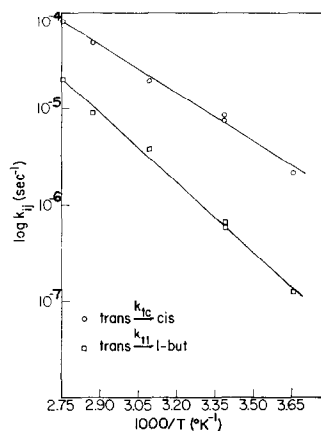


Fig. 4. Arrhenius plots for *trans*-2-butene isomerization over ZnO. See legend for Fig. 2.

the rationale. Five intermediates have been detected by ir (1, 2). If direct interconversion between the two π -allyls occurs, then the deuterium atoms will not move around in the molecule. On the other hand, if the mechanism requires the formation of π -1-butene as an intermediate, either migration of D (if the process is intramolecular) or loss of deuterium plus some degree of scrambling will occur (if the process is intermolecular).

Experiments were made at 25 and 90°C with *cis*-2-butene-2,3*d*₂. The results for ZnO are shown in Table 1. Intermolecular exchange was minimal at 25°C in the isomerized products. Moreover, the ir spectrum of *trans*-2-butene indicated that the deuterium atoms had both remained in the vinyl positions. Evidently, *cis*-*trans* isomerization occurred without movement of these tracer atoms.

At 90°C evidence for intermolecular ex-

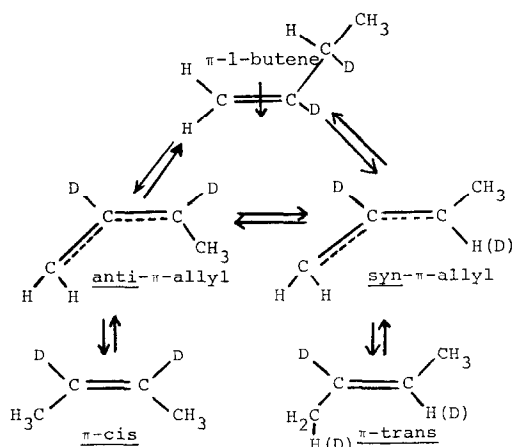


FIG. 5. *cis*-2-Butene-2,3*d*₂ as a probe for the isomerization mechanism.

change was unmistakable, but was still a secondary process. It could have been due to the onset of a second mechanism involving intermolecular hydrogen transfer or to unrelated exchange reactions between

TABLE 1
Tracer Experiments Showing Deuterium Distribution in Products of Labeled *cis*-2-Butene Isomerization over ZnO^a

Starting material	Con- version (%)	Temper- ature (°C)	Reaction time (min)	Product	Isotope distribution (%)					
					<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₇	<i>d</i> ₈
1. Reactant <i>cis</i> -2-Butene-2,3 <i>d</i> ₂	7.8	25	105	1-Butene	3.0	97.0				
				<i>trans</i> -Butene	2.3	5.6	92.1			
				<i>cis</i> -Butene	2.2	5.4	92.4			
2. Reactant <i>cis</i> -2-Butene-2,3 <i>d</i> ₂	12.3	90	10	1-Butene	3.0	97.0				
				<i>trans</i> -Butene	13.8	72.6	13.6			
				<i>cis</i> -Butene	21.2	59.2	19.6			
3. Reactant mixture <i>cis</i> - <i>d</i> ₀ : <i>cis</i> -2,3 <i>d</i> ₂ (1:1)	5.8	25	105	1-Butene	50.0	2.0	48.0			
				<i>trans</i> -Butene	51.8	2.5	45.7			
				<i>cis</i> -Butene	48.3	4.8	46.9			
4. Reactant mixture <i>cis</i> -2,3 <i>d</i> ₂ : <i>cis</i> - <i>d</i> ₈ (1:1)	4.0	25	105	1-Butene	48.9	4.0	47.1			
				<i>trans</i> -Butene	50.0	2.0	48.0	3.0	47.0	
				<i>cis</i> -Butene	2.5	8.3	69.0	2.7	3.0	14.5
				<i>cis</i> -Butene	1.4	7.8	66.0	2.0	2.8	20.0
					0.4	4.1	45.2	3.2	47.1	

^a Recirculation system volume: 300 cm³. Reactant pressure: 100 Torr. Catalyst weight: 2.00 g.

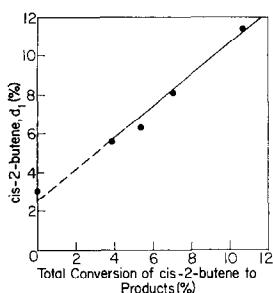


FIG. 6. Increase in concentration of the d_1 species in cis -2-butene with total conversion of cis -2-butene-2,3 d_2 over alumina at 25°C.

molecules or between molecules and surface OH groups.

When an equimolar mixture of cis -2-butene- d_0 and cis -2-butene- d_2 was used, again intermolecular exchange was minimal. These results are given as the third experiment in Table 1. No isotope effects were found for the formation of either isomerization product. This result was consistent with the finding above that the vinyl hydrogens do not move when cis -2-butene is isomerized.

When the reactant was an equimolar mixture of cis -2-butene- d_2 and cis -2-butene- d_3 , again no intermolecular exchange was detected in the products. However, large isotope effects of 4.7 for 1-butene and 3.4 for $trans$ -2-butene were recorded (Table 1, Expt 4). Presumably these correspond to the formation of the *syn*- or *anti*- π -allyl by removal of H or D from the methyl group.

Alumina: Tracer Studies

In previous studies by Hightower and Hall (3, 6, 12a) and Gerberich and Hall (11) kinetic and tracer experiments were made with aliquots of the same catalyst used in the present work (GA-48). It was a highly pure sample made by the neutral hydrolysis of redistilled aluminum isopropoxide. In contrast with ZnO, the reaction on alumina was first order in the temperature range studied (0–100°C) and the activation energies were constant. The apparent ac-

tivation energy for 1-butene \rightarrow $trans$ -2-butene was 12.0 kcal/mole (3).

Tracer experiments similar to those given above for ZnO were carried out with alumina at 25°C. The first row of Table 2 was obtained when cis -2-butene-2,3 d_2 was the reactant. The 1-butene product had a wide distribution of deuterated species ranging from d_0 to d_5 with a maximum at d_3 . On the other hand, $trans$ -2-butene contained mainly d_1 and d_2 species. The ir spectrum of $trans$ -2-butene showed that the deuterium atoms remained in the vinyl positions. The data indicate a flux of deuterium from cis -2-butene (90%) to 1-butene (3%). In fact, Fig. 6 shows that the percentage of cis -2-butene- d_1 increased steadily with conversion during this experiment. The ir spectra of 1-butene taken at the end showed that the ethylenic position was almost completely deuterated. These results are consistent with our previous work (13) which demonstrated that the terminal vinyl hydrogens of 1-butene were the ones most easily exchanged among the isomers.

When the reactant was an equimolar mixture of cis -2-butene-2,3 d_2 with cis -2-butene- d_0 or - d_3 , the intermolecular exchange was very important and the 1-butene was more extensively exchanged than the $trans$ -isomer. As with ZnO, significant isotope effects were detected: 3.6 for formation of 1-butene and 2.5 for the $trans$ isomer (Table 2, Expts 2 and 3).

Experiments were made with alumina selectively poisoned with CO₂. It had been shown that the exchange reaction between D₂ and *n*-butenes over alumina was effectively poisoned by CO₂ while the isomerization activity, which took place concurrently, was not (3, 14, 15). The lethal dose was about 0.8 cm³/g. Based on these observations, it was thought that exchange reactions not related to the isomerization mechanism might be eliminated by CO₂. Thus, the tracer results would then resemble those given in Table 1 for ZnO.

TABLE 2
Tracer Experiments Showing Intermolecular Hydrogen Exchange during *cis*-Butene Isomerization over γ -Alumina at 25°C^a

Starting material	Conversion (%)	Reaction time (min)	Product	Product (%)	Isotope distribution (%)												
					<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅	<i>d</i> ₆	<i>d</i> ₇	<i>d</i> ₈				
1. Reactant <i>cis</i> -2-Butene-2,3 <i>d</i> ₂	10.7	60	1-Butene <i>trans</i> -Butene <i>cis</i> -Butene	(3.0) (7.7) (89.3)	0.6 2.0 2.3	3.0 5.6 18.2 11.4	97.0 29.8 79.8 86.3	33.3	24.6	6.1							
2. Reactant mixture <i>cis</i> - <i>d</i> ₀ : <i>cis</i> -2,3 <i>d</i> ₂ (1:1)	7.6	60	1-Butene <i>trans</i> -Butene <i>cis</i> -Butene	(2.5) (5.1) (92.4)	50.0 28.2 36.4 40.7	2.0 26.8 31.9 22.3	48.0 34.3 31.7 37.0	10.7									
3. Reactant mixture <i>cis</i> -2,3 <i>d</i> ₂ : <i>cis</i> - <i>d</i> ₈ (1:1)	8.5	60	1-Butene <i>trans</i> -Butene <i>cis</i> -Butene	(2.3) (6.2) (91.5)	0.3 1.4 0.9	2.0 2.1 10.4 5.9	48.0 11.2 53.6 42.5	22.9 2.8 0.9	28.6 1.9 0.4	13.0 0.8	3.6 1.4 0.9	3.0 7.7 6.3 6.2	47.0 10.5 21.4 42.3				
4. Reactant <i>cis</i> -2-Butene-2,3 <i>d</i> ₂ (0.8cc CO ₂ /g added)	3.4	60	1-Butene <i>trans</i> -Butene <i>cis</i> -Butene	(0.6) (2.8) (96.6)	1.4 2.2 1.0	4.0 10.0 10.7 9.0	96.0 58.4 86.3 89.5	24.6 0.8 0.5	5.6								
5. Reactant mixture <i>cis</i> -2,3 <i>d</i> ₂ : <i>cis</i> - <i>d</i> ₈ (1:1) ^b	12.0	120	1-Butene <i>trans</i> -Butene <i>cis</i> -Butene	(3.1) (8.9) (88.0)	1.0	2.0 3.4 10.2 5.8	48.0 19.7 61.0 50.0	26.5 1.7	24.2 0.8	9.5 0.2	2.9 0.2	3.0 6.2 4.2 5.2	47.0 7.6 20.9 39.0				

^a Recirculation system volume: 300 cm³. Reactant pressure: 100 Torr. Catalyst weight: 0.5 g.
^b CO₂ added: 0.8 cm³/g.

Comparison of the results of Expts 1 and 4 in Table 2 show that CO₂ is not an effective poison for the intermolecular exchange. Whereas the scrambling was somewhat reduced, so was the activity for isomerization. Essentially the same conclusions hold when the results of Expts 3 and 5 are compared.

The role of alumina hydroxyls in exchange and/or isomerization was assessed in a series of special experiments. A fresh sample of alumina was contacted with *cis*-2-butene-*d*₈ following the standard pretreatment. After reacting for 30 min the mixture of butenes was removed from the reactor and analyzed. The conversion was 2.4%. Then the reactor was evacuated for another 30 min at 25°C and a charge of *cis*-2-butene-*d*₀ was admitted to the system. After 30 min the product mixture was removed from the reactor and analyzed. The conversion was 9.9%. In the first part of the experiment the labeled isomer reacted to form 1-butene containing as many as four H atoms in the C₄D₂H₈₋₂. The *trans* isomer, like the unreacted *cis* isomer, was much less affected. The data suggested, however, that the catalyst OH groups might function in the exchange process (intermolecular mixing) reported above. The number of such OH groups was calculated (as those transferred from the alumina into products). The result (1.3 × 10¹⁸/sample or 1 × 10¹²/cm²) was comparable with the site concentrations for exchange reactions over alumina reported for poisoning experiments (3, 15).

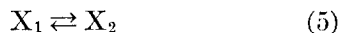
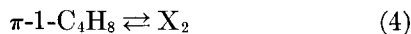
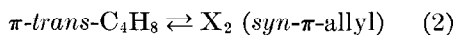
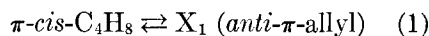
In the second part of the experiment, the 1-butene product again was more extensively exchanged than the *trans* product. Moreover, about 2% of the product stemmed from *cis*-2-butene-*d*₈ which had remained adsorbed, in spite of the evacuation, from the first part of the experiment; this was displaced by the new reactant. The isotope effect determined by the ratio of the percentage conversions for the two parts of the experiment was about 4.0. This value was in good agreement with

those calculated for the *d*₂:*d*₈ mixtures (Table 2).

DISCUSSION

Zinc Oxide

Before discussing our results, it will be useful to review the chief conclusions reached by Dent and Kokes (1) and Chang *et al.* (2) for ZnO.³ They adopted the following kinetic model.



The ir spectra revealed that the butenes were rapidly adsorbed to form π -complexes; hence, this step was not considered in the reaction scheme since it was not rate controlling. The kinetic and ir data, which had been obtained at 25°C and below, indicated that the rate of reaction was zero order in π -complex. In fact, the 1572 cm⁻¹ band assigned to the *anti*- π -allyl species remained constant during the isomerization of either *cis*- or 1-butene.

The kinetic studies reported herein also showed that the isomerization reactions are zero order at temperatures below 50°C. Figures 2 and 3 demonstrate that a change in activation energy occurred at higher temperatures for certain rate constants. Probably this corresponded to a change in the order of the catalytic reaction, if not its mechanism. Consequently, the Discussion will be limited to the 0–50°C temperature range.

The activation energies and values of rate constants at 25°C are collected in

³ Kokes *et al.* (1, 2) derived kinetic equations which (to conserve space) are not reproduced here. For readers interested in the unusual aspects of the kinetics reported herein, it is important to refer to these papers.

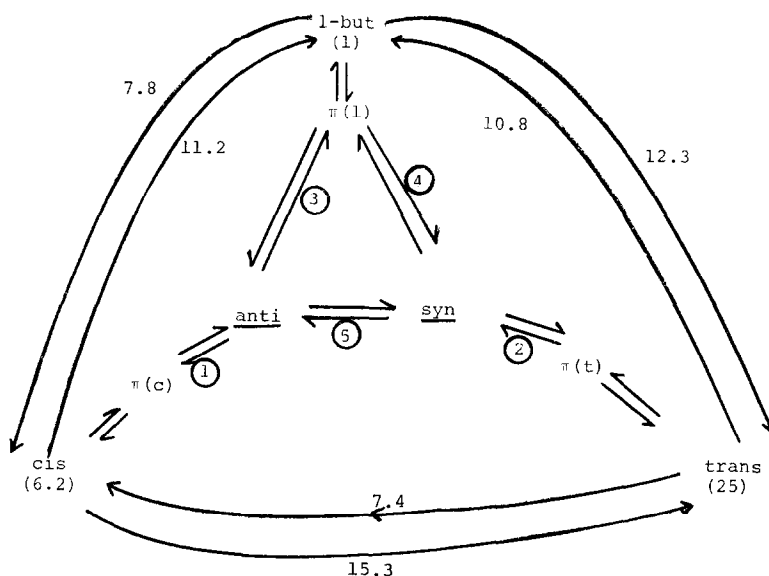


FIG. 7. Flow diagram for the reaction. The inner network represented by steps numbered in circles is the reaction model suggested by Dent and Kokes (1) and Chang *et al.* (2), while the outer circular arrows indicate the rate vectors actually measured; the numbers on these arrows are the corresponding activation energies taken from Table 3. The numbers in parentheses after the indicated isomer are the thermodynamic equilibrium ratios, 1-butene:*cis*-2-butene:*trans*-2-butene = 1:6.2:25.

Table 3. Note that $E_{c1} \approx E_{t1}$ (11.2 vs 10.8 kcal/mole) and that $E_{1c} \approx E_{1t}$ (7.8 vs 7.4 kcal/mole). Figure 7 presents the flow pattern of the reaction in the measured homomorphic representation (outer sphere) and as it was conceived to occur by Chang *et al.* (2) (inner network). The numbers on the outer arrows are the experimentally determined activation energies. It is seen that the activation energy for formation of *cis*-2-butene is almost the same, regardless of whether it is formed from *trans*- or from 1-butene. A similar result is present for the formation of 1-butene, but not for *trans*-2-butene. Each step in the inner network labeled with a number within a circle may be rate limiting and have the experimental activation energy associated with it. These facts, together with previous evidence from both ir and kinetic work, allow one to construct the reaction coordinates shown in Fig. 8.

Since the reactions are of zero order, the

Arrhenius plots yield the true activation energies of the rate-controlling surface reactions. Starting with 1-butene, the $\pi - 1$ complex may form either the *syn*- or *anti*- π -allyl.⁴ The formation of *syn*- π -allyl requires a much higher activation energy (barrier 4) than the formation of *anti*- π -allyl (barrier 3). Since $E_{1c} = E_{1t}$, the same barrier limits the formation of *cis*-2-butene from either of the other isomers; this can only be barrier 1. Moreover, since $E_{c1} = E_{t1}$, barrier 4 must be much higher than either 2 or 5. In other words, both *cis*-2-butene and 1-butene are formed mainly via the *anti*- π -allyl, in agreement with findings (1, 2) that, upon admission of 1-butene, a

⁴ These species were observed spectroscopically by Kokes *et al.* (1, 2), who did not specify whether or not they were charged or radical, although it was implied that they were complexed with CUS zinc ions. Thus, they may be considered as neutral or as having carbanion character until further evidence is produced.

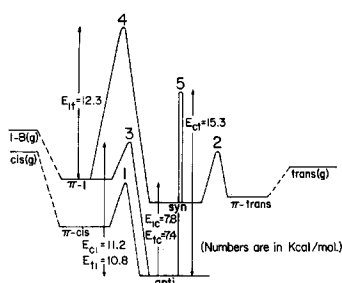


FIG. 8. Activation energy profile for isomerization of the *n*-butenes over ZnO at temperatures between 0 and 50°C. The barrier numbers correspond to the same steps in Fig. 7.

strong ir band corresponding to the *anti*- π -allyl was detected while no *syn* band appeared even though both *trans*- and *cis*-2-butene were produced from the beginning. Evidently, barrier 2 is quite low and the *syn*- π -allyl is unstable with respect to the *trans*- π complex at low concentrations of the latter. This may be the reason that $k_{ct} > k_{cl}$ even though the activation energy of the former is higher than that of the latter by 4 kcal/mole.

Starting with *cis*-2-butene the *anti*- π -allyl can be formed very readily and it rapidly reaches its steady-state concentration on the surface. The *anti*- π -allyl species can react either by surmounting barrier 3 to $\pi - 1$ or by passing over barrier 5 to the *syn* configuration and then being converted very rapidly into *trans*-2-butene. Again the ir results (1) are consistent and, in addition, the tracer experiments (Table 1) clearly demonstrate that *cis*-2-butene is directly converted into *trans*-2-butene without going through 1-butene as an intermediate. Chang *et al.* (2) speculated about the quite reasonable possibility that Reaction (5) occurs through a σ -allyl complex.

An apparent discrepancy with the ir data appears when the isomerization of *trans*-2-butene is considered. The *syn* band appeared rapidly, but *cis*-2-butene was detected before the appearance of the *anti*- π -allyl band (1). This would seem to indicate that barrier 5 is limiting the rate of reaction.

Probably the unknown height of this barrier above the *syn*-allyl is not very different from E_{lc} and the possibility remains open that barrier 5 is limiting the production of π -*cis*.

An interesting feature becomes evident when the isomerization of 1-butene is considered. The pathway to *cis*-2-butene is through the *anti*- π -allyl, as expected, i.e., via barriers 3 and 1. However, the pathway to *trans*-2-butene through the *syn*- π -allyl may be achieved by two pathways, i.e., via barrier 4 directly, or indirectly via the *anti*-to *syn*- π -allyl conversion (barrier 5). Since the latter is the higher, the former is preferred. Thus, the easiest pathway for the flow between *trans*-2-butene and 1-butene may not correspond to that for the reverse reaction. Note also that the ratios of rate constants listed in Table 3 do not correspond to the equilibrium ratios of the gas-phase isomers. In fact, they correspond much better to the ratios of stabilities of the π complexes (last column). As noted by Chang *et al.* (2), these kinetics cannot hold over the entire range. If they did, the system would be unable to come to thermodynamic equilibrium. In fact, we have tested this point and find that it can and does (*vide infra*).

It was suggested by a referee that this description of our experimental results may contradict the principle of microscopic reversibility. We are quite sure that it does not. The system is far removed from equilibrium and the kinetics must change as equilibrium is approached. The situation arises because, under the experimental conditions, the concentrations of the surface intermediates are temperature independent (reaction is zero order), and the flow of molecules from 1-butene to *trans*-2-butene can occur via two concurrent pathways. The ratio of flows by the two pathways, however, may be temperature dependent and this may be the reason for the increase in activation energy for this reaction at higher temperatures, as shown in Fig. 2.

TABLE 3
Summary of Kinetic Parameters for *n*-Butene Isomerization over ZnO

Activation energy ^a (kcal/mole)	Rate constant at 25°C ^b ($\times 10^6$ /sec)	Selectivity at 25°C ^c	Equilibrium constant from rate data ^d	Equilibrium constant for adsorbed π -butenes ^e
$E_{1t} = 12.3$	$k_{1t} = 1.8$	$k_{1c}/k_{1t} = 10.0$ (0.26)	$k_{1c}/k_{1t} = 0.34$ (0.04)	$[\pi - l]_e/[\pi - t]_e = 0.33$
$E_{1c} = 7.8$	$k_{1c} = 18.0$			
$E_{c1} = 11.2$	$k_{c1} = 3.2$	$k_{c1}/k_{ct} = 0.6$ (0.04)	$k_{1c}/k_{ct} = 1.48$ (0.26)	$[\pi - c]_e/[\pi - t]_e = 3.3$
$E_{ct} = 15.3$	$k_{ct} = 5.4$			
$E_{tc} = 7.4$	$k_{tc} = 8.0$	$k_{t1}/k_{tc} = 0.076$ (0.15)	$k_{1c}/k_{c1} = 5.62$ (0.15)	$[\pi - c]_e/[\pi - t]_e = 10.0$
$E_{t1} = 10.8$	$k_{t1} = 0.6$			

^a Calculated from Arrhenius plots between 0 and 50°C.

^b Calculated from conversion vs time plot. To convert to molecules per square centimeter per second, multiply by 8.6×10^{15} molecules/cm² = number of reacting gas molecules per square centimeter-second.

^c The equilibrium ratios are given in parentheses.

^d The true equilibrium constants (in parentheses) are completely different from those calculated from initial rates (as expected for zero-order reactions).

^e Calculated from ir data (Fig. 5) of Chang *et al.* (2).

Thus, depending upon whether the reactant is 1-butene or *trans*-2-butene, the pathway of least resistance will not be the same. However, at all times both pathways are populated with molecules reacting in both directions.

The rates reported in Table 3 and Figs. 2-4, are very much slower (by about 10^{-9}) than rates for zero-order unimolecular surface reactions estimated by absolute reaction rate theory. Whereas it does not seem worthwhile to go into all of the ramifications of this result here, it does point out the critical importance of the frequency factors in limiting the rates and perhaps in controlling the selectivities in these reactions. The chief lesson is that an interesting and unusual kinetic problem has been uncovered which deserves further study.

The comparisons shown in columns 4 and 5 of Table 3 suggest that starting with each pure isomer, the reaction paths should converge to the composition corresponding to the relative π complex stabilities. Chang *et al.* (2) noted in experiments in which the reaction was carried to equilibrium that the rate (which was initially pressure independent) became exceedingly slow. It was

of interest, therefore, to evaluate the rates of formation of the isomers as the system moves toward equilibrium from an initial composition near that of the surface at π -complex equilibrium. Such an experiment was attempted and it was found that the system moved toward thermodynamic equilibrium more slowly than with any of the pure isomers. Furthermore, the time evolution of the system could not be modeled using the set of zero-order rate constants listed in Table 3. This is a necessary consequence of the fact that, if the system is to reach thermodynamic equilibrium, it must become pressure dependent at some point along the way.

The significant isotope effects found for both 1-butene and *trans*-2-butene formation when a *cis*-2-butene- d_8 :*cis*-2-butene- d_0 mixture was isomerized at 25°C were also consistent with the overall picture (Table 1). Note that no isotope effects appeared when a d_0 : d_2 mixture was isomerized. These results indicate the involvement of methyl hydrogens in the reaction mechanism. In terms of the model one can envisage the surface saturated by π -allyl intermediates coming from either d_2 or d_8 *cis*-2-butenes,

the d_2 to d_7 allyl ratio being controlled by barrier 1, i.e., the relative strength of a CH versus a CD bond in the methyl group.

It was found that the reaction was no longer zero order at 90°C. This change in reaction order became evident only at temperatures above 50°C and therefore apparent, rather than true activation energies are determined in Figs. 2-4 at the higher temperatures. The kinetic equations derived by Chang *et al.* (2) based on Reactions (1 to 5) have two limiting forms: zero order or first order in reactant. At low temperatures the active sites are saturated with the π -allyl intermediates and the reaction is zero order. Presumably, the surface concentration of intermediates decreases as the temperature increases above about 50°C and the reaction kinetics now should be described by a Langmuir-Hinshelwood formalism in the nonlinear region of the adsorption isotherm. In fact, Dent (23) observed a substantial decrease in intensity of the ir bands corresponding to the π -allyl intermediates when the spectra were taken at 90°C.

Alumina

It is very interesting to compare the data for ZnO with those for alumina. The former behaved as an ideal system where the kinetic and tracer results fit together with ir studies into a self-consistent model. On the other hand, alumina departed from ideal behavior because of the coexistence of exchange reactions and the extreme sensitivity of the alumina surface to small changes in impurity concentration, pretreatment conditions, and even to the previous history of the sample. Moreover, to date the surface reaction intermediates found with ZnO using spectroscopy have not been detected on alumina, possibly due to their much lower concentration. This would be consistent with zero-order kinetics for ZnO and first order for alumina near room temperature. This intrinsic complication of the system has led workers to differ-

ent views concerning the nature of active sites on alumina and its reaction mechanisms. Nevertheless, the present data strongly suggest that the reaction over alumina proceeds by the same basic mechanism as for ZnO over our catalyst under our pretreatment and reaction conditions.

Among the numerous aluminas which have been studied, two types can be distinguished: (a) those active enough to isomerize butenes below 100°C and (b) the more inactive ones which require higher reaction temperatures. The alumina reported here (after activation at 530°C) belonged to the first class. The results from this alumina showed several important details concerning the reacting system.

(a) *Cis* \rightarrow *trans* isomerization occurred without deuterium movement within the molecule as shown in Expt 1 of Table 2 and the ir spectra of the products. Furthermore, when the results contained in Table 1 (ZnO) are compared with those in Table 2 (Al_2O_3) it is seen that the deuterium distributions and isotope effects for *trans*-2-butene are quite similar, except for more intermolecular exchange in the latter case ($\sim 15\%$ d_1). This supports the assignment of a π -allyl intermediate with carbanion character as an intermediate over both oxides.

(b) The data for the double bond isomerization are not so clear, because the extensive deuterium scrambling in the 1-butene product has obscured the picture. It is probable, as the isotope effect seems to suggest, that the same reaction mechanism as over ZnO is operative, while a simultaneous faster exchange produces the wide deuterium distribution. The terminal vinyl positions of 1-butene are known to exchange much faster than those of 2-butenes (13) and this would explain the different deuterium distributions found in the reaction products.

(c) CO_2 , which is an excellent poison for olefin- D_2 exchange over alumina, only re-

duced the intermolecular exchange to roughly the same extent as it reduced the isomerization activity. (Compare Expts 1 and 3 with 4 and 5 in Table 2).

(d) A small number of alumina hydroxyls ($\sim 1 \times 10^{12}$ OH/cm²) reacted with C₄D₈. As before, the 1-butene tended to pick up more deuterium than the 2-butenes. It was also found that C₄H₈ exchanged with preadsorbed C₄D₈.

The present results are of value in interpreting the available related literature. Peri (16, 17) was among the first to correlate the activity for butene isomerization with exposed aluminum ions. He also suggested that the isomerization should result in formation of a transient carbanion. Hightower and Hall (3, 6) and Gerberich and Hall (11) ascertained a few years later that, while the mechanism of butene isomerization over silica-alumina was entirely consistent with carbonium ion chemistry (sec-butyl carbonium ion), the mechanism over alumina was completely different. The activity over alumina increased with decreasing concentration of surface hydroxyls while with silica-alumina the opposite was true (11). A concerted mechanism was proposed by Gerberich and Hall (11) to explain the intramolecular double-bond isomerization. The importance of the surface oxygen anions as catalytic sites was emphasized. In more recent years, evidence has accumulated concerning the nature of active sites on alumina. Dent and Kokes (1) and Chang *et al.* (2) elucidated the mechanism over ZnO and showed that the reaction probably passed through the π -allyl intermediates. Product distributions, etc., were remarkably similar to those reported for alumina (3, 12). Others listed below have suggested the formation of an allyl carbanion or a concerted mechanism with carbanion character.

(i) Gati and Knözinger (18) and Corado *et al.* (19) studied the isomerization of 14 terminal olefins; tracer data were obtained

using 2,3-dimethyl-1-butene-3d. A carbanion-like intermediate was proposed for the double-bond isomerization based on large changes in reactivity with different substituents and on deuterium loss and isotope effects in the tracer experiments. Two adjacent exposed aluminum ions were suggested as the active sites.

(ii) Lunsford *et al.* (20) and Rosynek and Strey (21) studied this problem using a combination of EPR and poisoning techniques. They demonstrated (20) the interaction of NO with exposed aluminum on the alumina surface. They also showed how the concentration of exposed aluminum ions increased with activation temperature, reaching a maximum at 700°C. Using H₂S they gradually poisoned the isomerization activity and at the same time observed a parallel decrease in the EPR signal. Following Gerberich and Hall (11) they suggested that the isomerization sites have only one aluminum ion with adjacent oxide ions.

(iii) Perot *et al.* (4) and Guisnet *et al.* (5) studied the isomerization of *cis*-2-butene-2,3d₂ and *cis*-2-butene-1,4d₆ on both silica-alumina and alumina. In the first article (4) the alumina was pretreated at 500°C and the reaction was run at 250°C. Under these conditions the tracer data looked very similar to those for silica-alumina and this led to the proposal that a carbonium ion mechanism was operative in the reaction. However, in the second article (5), with higher pretreatment temperature (580°C), a more active catalyst was obtained (reaction temperature 85°C and higher). Under these conditions, the tracer data resembled those reported herein for ZnO; hence, the reaction proceeded through the mechanism discussed above (π -allyl and σ -allyl carbanion intermediates). Moreover, the isotope effects reported (at 85°C) were similar to ours. In those experiments (4, 5) the secondary exchange processes were reduced to negligible proportions by the nature of the catalyst or by the way the experiments were carried out. Whatever

TABLE 4
Comparison of Tracer Data for ZnO and Two Different Aluminas

		ZnO ^a Kadox-25 (25°C) ^c	γ -Al ₂ O ₃ ^a GA-48 (25°C)	Al ₂ O ₃ ^b (85°C)	
<i>cis</i> -2-Butene	1-Butene	Isotope distribution	100% d_2	d_0-d_3	100% d_2
		Isotope effect	1.0	1.0	1.0
<i>cis</i> -2-Butene-2,3- d_2	1-Butene	Isotope distribution	100% d_2	85% d_2	100% d_2
	<i>trans</i> -Butene	Isotope effect	1.0	1.0	1.0
<i>cis</i> -2-Butene-1,4- d_6	1-Butene	Isotope distribution			100% d_6
		Isotope effect			3.0
<i>cis</i> -2-Butene	1-Butene	Isotope distribution			100% d_6
	<i>trans</i> -Butene	Isotope effect			3.0
<i>cis</i> -2,3- d_2 : <i>cis</i> - d_6	1-Butene	Isotope distribution	d_2 and d_6	~Binomial	
		Isotope effect	4.7	3.6 (3.7) ^d	
<i>cis</i> -2,3- d_2 : <i>cis</i> - d_6	1-Butene	Isotope distribution	d_2 and d_6	~Binomial	
	<i>trans</i> -Butene	Isotope effect	3.4	3.5 (3.7) ^d	

^a Static reactor (recirculating), pressure = 100 Torr.

^b Alumina pretreated at 580°C, pulse reactor. Slug made of labeled butene:propene = 1.10. Data from Guisnet *et al.* (5).

^c Reaction temperature.

^d Numbers in parentheses are values obtained by Hightower and Hall (6) from coisomerization of *cis*- d_0 :*cis*- d_6 .

the cause, their results resembled those obtained for ZnO (see Table 4).

(iv) Amenomiya (8) recently studied 1-butene isomerization over η -alumina poisoned with ammonia at different temperatures. As previously reported (16, 17) ammonia was found to be an effective poison when adsorbed at high temperatures. Two forms of chemisorbed butene (Types I and II) were characterized by temperature-programmed desorption. The author associated Site I with isomerization activity and suggested that this corresponded to multiply exposed Al ions. He associated Site II with isolated aluminum ions with adjacent hydroxyl groups. He also reported results of coisomerization of 1-butene- d_0 and 2-butene- d_6 . Only single exchange of hydrogens occurred for both reactants, even at 40% conversion. His

tracer data were in general agreement with the results presented herein. Amenomiya explained his results by adopting the mechanism postulated by Ozaki and Kimura (22) in which Brønsted acidity is supposed to be somehow generated from the butene molecules or polymeric residues chemisorbed on Lewis acid centers. It is difficult, however, to explain with this mechanism the large isotope effects reported in several investigations (3, 4, 6) and the vastly different product selectivities found for alumina and silica-alumina as well as the absence of polymeric material on the alumina (99.5% of the reactant was recovered as such) in his experiments.

When the present results are compared with the results of these other research groups it is seen that the mechanisms for *n*-butene isomerization over alumina and

ZnO are the same or very similar. This is supported by the kinetic results, the kinds of active sites available in both catalysts, and the tracer patterns and isotope effects reported.

Table 4 summarizes and compares the present results with those obtained by other workers. Also for comparison the results on ZnO are shown. The tracer results for alumina, particularly for double-bond migration, are obscured by a simultaneous intermolecular exchange. Note, however, that this is not a problem for the *cis-trans* isomerization. Also note that, for the alumina pretreated at 580°C, used by Guisnet *et al.* (5) (last column), this intermolecular exchange was not present and the results are in all ways similar to those obtained on ZnO. Moreover, note the similarity of isotope effects found for ZnO, for the alumina used by Guisnet *et al.*, and for the alumina used in the present studies.

The mode of preparation, history, and particularly the pretreatment temperature (extent of dehydroxylation) have dramatic effects on the catalytic properties of alumina. For aluminas which are active only at higher temperatures (above 200°C) it is conceivable that different sites become active. It could be, for example, that, with the less active aluminas, the surface hydroxyls are forced to act as Brønsted acids and at higher temperatures catalyze the isomerization of *n*-butenes as suggested by the recent tracer experiments of Perot *et al.* (4) and Guisnet *et al.* (5).

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