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Studies of Acid–Base-Catalyzed Reactions

XIV. Isomerization of Butene over La_2O_3 and ZnO

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The hydrogenation and isomerization of *n*-butenes have been studied over ZnO and La_2O_3. The kinetic data for ZnO showed that 1-butene was the only isomer which hydrogenated at 28°C and that the rate of isomerization of 1-butene in the absence of H_2 was about equal to the rate of isomerization in the presence of H_2 plus the rate of hydrogenation. Moreover, the H_2–D_2 equilibration reaction was strongly inhibited in the presence of butene. In the absence of hydrocarbon, the time for half-reaction was less than 2 min, whereas in the presence of about 150 Torr of *cis*-2-butene or 1-butene the half-life times were 59 and 61 min, respectively. For La_2O_3, hydrogenation of butene did not occur at 60°C although C_2H_4 reacted at room temperature. In isomerization, the initial selectivity of *cis*-2-butene towards formation of *trans*-2-butene increased (from nearly zero) with temperature and tracer experiments indicated that, as with ZnO, the mechanism of isomerization was intramolecular with a substantial primary isotope effect associated with the removal of a H or D in the formation of the π-allyl intermediate. The mechanism was the same for these two catalysts; the chief difference is in the higher activation energy (20 kcal/mol) for the *anti*- to *syn*-π-allyl conversion over La_2O_3 than for ZnO (15 kcal/mol).

INTRODUCTION

Since the isomerization of *n*-butenes has been the subject of many detailed investigations, these reactions should, in principle, provide useful tools for the characterization of reaction intermediates in heterogeneous catalysis. Three mechanisms have been proposed for different catalytic systems:

(a) A hydride addition mechanism for metals and organometallic systems (*1, 2*);

(b) a carbonium ion mechanism for acid catalysts (*3*); and,

(c) an allylic (carbanion) mechanism which is operative over basic catalysts, e.g., ZnO.

The latter has received much attention in the past few years (*4–8*). Each of these mechanisms has certain characteristic features which may be termed diagnostic. For example, the rate-limiting step of the carbonium ion mechanism is the formation of the metastable intermediate while the product distribution is dependent upon the relative heights of the barriers between the intermediate and three isomers. For reasons summarized elsewhere (*3*), these features lead to relative initial rates of isomerization: 1-butene $\gg$ *cis*-2-butene $\gg$ *trans*-2-butene. Moreover, temperature-independent initial *cis/trans* ratios close to unity result, together with temperature-dependent but similar initial 1-butene/*cis* and 1-butene/*trans* ratios less than 3.0 and usually less than 1.0.

The hydride insertion mechanism is also an "add-on" mechanism, although the diagnostic features have not been well characterized. Hydrogen is required as a cocatalyst for formation of the half-hydrogenated state (*1, 2*). The reaction with 1-butene can be either degenerative or productive, with the former favored because isomerization can only occur when the less favored secondary alkyl is formed. The latter is the only possibility with the 2-

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butenes so that initial rates of isomerization higher than that for 1-butene are conceivable. Again initial isomer distributions similar to those for acid catalysis may be anticipated, but convincing data are lacking.

Over basic oxides, proton transfer from the butene to a surface oxygen ion may occur leading to the formation of an allylic carbanion associated with the (paired) cation exposed at an anion vacancy. Two allylic species are possible: the *syn-* and *anti*-π-allyl which may interconvert via the σ-allyl (*5*). Because the *anti* configuration is more stable than the *syn* configuration and since either may be formed from 1-butene while only the former can commute with *cis*-2-butene and only the latter with *trans*-2-butene, high *cis*/*trans* ratios result. Moreover, the initial 1-butene/*cis* and 1-butene/*trans* ratios are no longer equal, the latter usually being larger than the former. The relative initial rates of isomerization are rather similar to those for the acid-catalyzed reactions, i.e., the rate of isomerization of 1-butene > that of *cis*- > *trans*-2-butene. However, because the reactions are frequently zero order, the rate-determining step is not controlled by an activation energy for formation of the allylic species and hence, not on the enthalpy differences between the isomers, but it is dangerous to generalize, because of the sparsity of data given in sufficient detail. (Frequently only one of the isomers has been studied.)

Additional criteria can be generated from tracer experiments. With the carbonium ion and hydride insertion mechanisms, one intermolecular transfer of H or D must occur with each molecule reacted during the coisomerization of equimolar mixtures of C_4H_8 and C_4D_8; extra exchange would be expected with 1-butene, however, because of the degenerate formation of the primary alkyl, but in all cases isotope effects are minimal (*3*). With the allylic mechanism, the isomerization takes place by intramolecular transfer of H or D and the isotope effect is large (*8*).

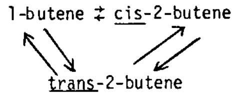
Studies by Kokes and co-workers (*6, 7*) provided convincing infrared evidence for these π-allylic species over ZnO. Isolated pair sites, on which H_2 was heterolytically dissociated, functioned in an analogous way in the formation of allylic carbanions and surface OH groups, the former functioning as intermediates for olefin isomerization. A qualitative energy diagram was proposed (*6, 7*) which was quantified by Lombardo *et al.* (*8*). One of the basic conclusions of both Kokes and co-workers (*6, 7*) and Lombardo *et al.* (*8*) was that all six initial rate vectors had measurable finite values at room temperature. Rosynek and Fox (*9*), working with the La_2O_3 system, observed no direct interconversion of *cis*- to *trans*-2-butene in the range 0–50°C, and suggested the following reaction scheme:

$$\textit{cis}\text{-}2\text{-}C_4H_8 \rightleftarrows 1\text{-}C_4H_8 \rightleftarrows \textit{trans}\text{-}2\text{-}C_4H_8, \quad (1)$$

whereas Minachev and co-workers (*10*), had previously suggested that the scheme was

$$1\text{-butene} \rightarrow \textit{cis}\text{-}2\text{-butene} \rightarrow \textit{trans}\text{-}2\text{-butene}. \quad (2)$$

Recently, Goldwasser and Hall (*11*) showed that the interpretations reached by the two groups mentioned above were dependent on the way the experiments were made, not on differences in the catalysts used. In the present paper we will show that the actual scheme probably is



(3)

Thus, the mechanism for the isomerization reactions over La_2O_3 is the same as that over ZnO, the principal difference being a larger activation energy for the *anti*- to *syn*-π-allyl interconversion. Although the above mechanistic classification for the isomerization of *n*-butenes now appears adequate, some additional insight has been obtained by testing the role of hydrogen in the isomerizations represented by Eq. (3). Note that according to Kokes and coworkers (*6, 7*), H_2 adsorbs on the same sites on which the allylic species are presumed to form. We have tested the effect of H_2 on the isomerization rate to determine whether hydrogenation will compete with isomerization in an important way.

EXPERIMENTAL

Catalyst and pretreatment. The ZnO (Kadox-25) was obtained from the New Jersey Zinc Company, and the La_2O_3 was prepared by the method described by Rosynek and Magnuson (*12, 13*). The surface area of the former was about 10 and the latter 8.6 m^2/g. The ZnO (2.0 g) was degassed by raising the temperature to 500°C at which point O_2 (160 Torr) was admitted and circulated through a liquid nitrogen trap for 1 h. Following the O_2 treatment the sample was evacuated for an hour before quenching to the reaction temperature. The La_2O_3 was evacuated overnight at 680°C (temperature of maximum activity (*9, 10*)). Because of the high activity of this material the sample weight used was 5–20 mg. A fresh sample of catalyst was used in each experiment, including each point on Arrhenius plots.

Reactants. The three *n*-butene isomers were research-grade 99.8% pure. Before use they were repeatedly outgassed by freezing and pumping in a conventional high-vacuum system. For the La_2O_3 experiments, a double distillation was necessary to provide stable reproducible activities because of the small amount of catalyst required and its high sensitivity to poisons such as CO_2 and H_2O (*9, 12*). The perdeutero-isomers were prepared as described by Larson *et al.* (*14*). The H_2 and D_2 (Matheson) were passed through charcoal traps cooled to 78°K.

Reaction system. A conventional all-glass recirculation system was used. It has been described elsewhere (*15*). Check experiments were made with the fastest reactions and at the highest reaction temperatures employed (82°C) to confirm that the rates were not limited by the pumping speed. The products of the reaction were separated with a 15 ft × 0.25-in dimethylsulfolane column at 0°C. Aliquots amounting to about 1% of the total gas volume were removed for analysis and the separated isomers were recovered for mass spectral analysis as they emerged from the glc. The mass spectral data were always recorded at low voltage (11 eV) to minimize cracking. The H_2–D_2 analysis was performed in a system copied from Burwell and Stec (*16*).

RESULTS

Zinc Oxide Kinetic Studies

Experiments were made at 28°C using 2.0 g of catalyst. Figure 1 shows the concentration of the several products vs time for 1-butene isomerization in the presence and absence of hydrogen. The rate of isomerization (measured as the appearance of *cis*-

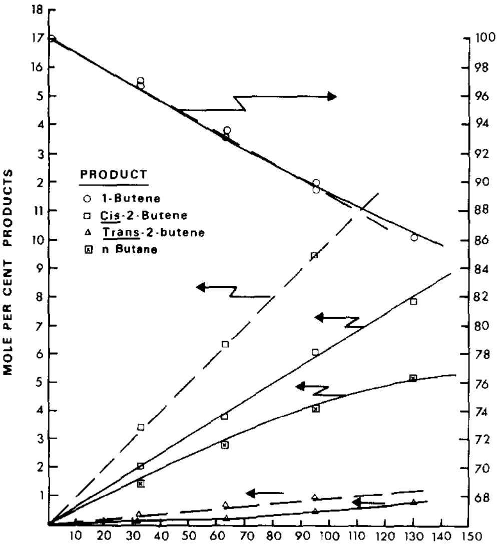


FIG. 1. The isomerization of 1-butene over ZnO in the presence and absence of H_2 at 28°C, P°_{1-b} = 150 Torr and $P^\circ_{H_2}$ = 252 Torr; the right scale is for 1-butene and the left scale is for the rest of the products; broken lines = absence of H_2, solid lines = presence of H_2.

TABLE 1

Rate of Isomerization and Hydrogenation of *n*-Butenes on ZnO

Initial hydrocarbon	Product	Rate of isomerization[a] (molec/sec × cm^2 × 10^{-9})	Rate of isomerization[b] (molec/sec × cm^2 × 10^{-9})	Rate of hydrogenation[c] (molec/sec × cm^2 × 10^{-9})	P_{H_2} (Torr)
cis-2-Butene	*trans*-	48.9	46.1	—	150
	1-Butene	34.7	33.0	—	207
				—	252
trans-2-Butene	*cis*-	81.5	80.0	—	150
	1-Butene	5.9	4.9	—	207
				—	252
1-Butene	*trans*-	12.4	6.5	47.0	150
				55.3	207
	cis-	144.	89.1	62.3	252
				68.3	300

[a] Rate of isomerization in the absence of hydrogen, calculated from the appearance of product; T = 28°C; initial amount of gas = 150 cm^3(NTP); recirculation system, total volume = 301 cm^3.

[b] Rate of isomerization in the presence of hydrogen; initial amounts hydrocarbon = 50 cm^3(NTP), H_2 = 84 cm^3(NTP); reaction conditions same as in *a*.

[c] Rate of hydrogenation; initial amount of hydrocarbon = 150 Torr (constant), variable amounts of hydrogen indicated in last column, other reaction conditions same as in *a* and *b*. Butane was not formed from *cis*- or *trans*-2-butene.

2-butene and *trans*-2-butene) was larger than the rate of hydrogenation, and the rate of isomerization in the absence of hydrogen was larger than in its presence.

Similar experiments were carried out using *cis*-2-butene and *trans*-2-butene as reactants. The results are collected in Table 1. The rate of isomerization in the absence and in the presence of hydrogen was nearly the same for the 2-butenes, neither of which hydrogenated at 28°C, but with 1-butene which did hydrogenate, the isomerization rate was strongly suppressed.

Dent and Kokes (*6*) showed that for the hydrogenation of C_2H_4 over ZnO, the order of the reaction with respect to hydrogen was 0.5. The data of Table 1 include measurements carried out with the pressure of hydrocarbon held constant while the hydrogen pressure was varied. When these and similar additional data were plotted (log rate vs log P_{H_2}) it was determined that the order of the reaction in hydrogen was 0.51.

TABLE 2

Half-life Time[a] for the H_2–D_2 Equilibration in the Presence and Absence of *n*-Butenes

Hydrocarbon	Half-life time (min)
None[b]	<2
cis-2-Butene[c]	59
1-Butene[d]	61

[a] Half-life time calculated as $0.69/k$, where k is the slope for the ln $(x_e - x_t)$ vs time plot, x_e is the equilibrium fraction of HD.

[b] Initial mixture: 49.1% H_2, 50.9% D_2; total amount = 100 cm^3(NTP); T = 28°C; recirculation system, total volume = 280 cm^3.

[c] Initial mixture: 32% H_2, 33.5% D_2, 34.5% *cis*-2-butene; total amount = 150 cm^3(NTP); other conditions same as *b*.

[d] Same as *c* but using 1-butene instead of *cis*-2-butene.

Effect of Butene Isomerization on H_2–D_2 Equilibration Rate

To more definitely identify the active sites for the hydrogenation with those responsible for isomerization, a set of H_2–D_2 equilibration experiments were made in the absence and in the presence of butenes. The data of Table 2 show that the time for half-reaction was greatly increased by the presence of olefin (over the value in its absence). The half-life times were about the same for 1-butene (which isomerizes as well as hydrogenates) as for *cis*-2-butene (which only isomerizes). The experimental conditions for these experiments are given in Table 2. Earlier work (*8*) with labeled butenes was in all ways consistent with the allylic carbanion mechanism.

Kinetic Results over La_2O_3

Since the main difference between the scheme proposed by Rosynek and Fox (*9*) and that suggested by Kokes and coworkers (*6, 7*) and confirmed by Lombardo *et al.* (*8*) for ZnO is the apparent absence of a direct pathway for *cis*- to *trans*-2-butene interconversion at low temperatures, we have studied the isomerization of *cis*-2-butene over La_2O_3 at several increasing temperatures in the range 25–70°C. Figure 2 shows the variation of product composition vs time at 30 and 42.5°C. The salient feature is that at 30°C there was apparently no initial formation of *trans*-2-butene while at 42.5°C it was a primary product. Interestingly, the reverse reaction, *trans*- to *cis*-2-butene (Fig. 3) did occur at 30°C and indeed was about 10 times faster than the conversions of *trans*-2-butene to 1-butene (Table 3).

Arrhenius plots for 1-butene, *cis*-2-butene, and *trans*-2-butene are shown in Fig. 4. For 1-butene and *trans*-2-butene the curves expressing the individual reaction rates to the other two isomers were linear and the corresponding activation energies were $E_{1\to c} = 4.0$ and $E_{1\to t} = 9.0$, $E_{t\to c} = 13.0$ and $E_{t\to 1} = 18.2$ kcal/mol. The plot for *cis*- to *trans*-2-butene was also linear with $E_{c\to t} = 20.0$ kcal/mol, being the highest of all;

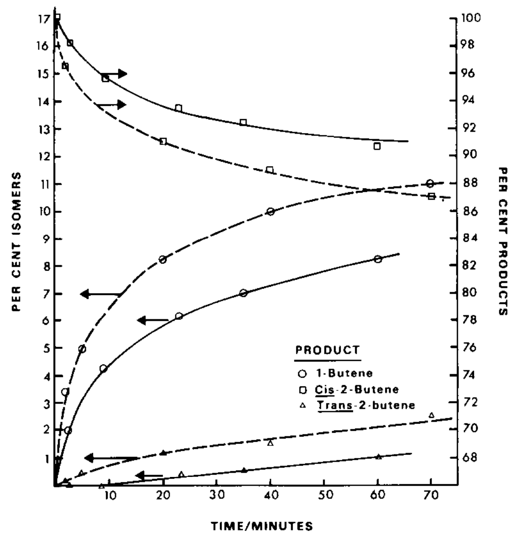


FIG. 2. Conversion vs time plot for *cis*-2-butene isomerization over La_2O_3 at 30°C (solid lines) and at 42.5°C (broken lines); $P^{\circ}_{cis} = 150$ Torr. Right scale is for *cis*-2-butene and left scale is for the rest of the isomers.

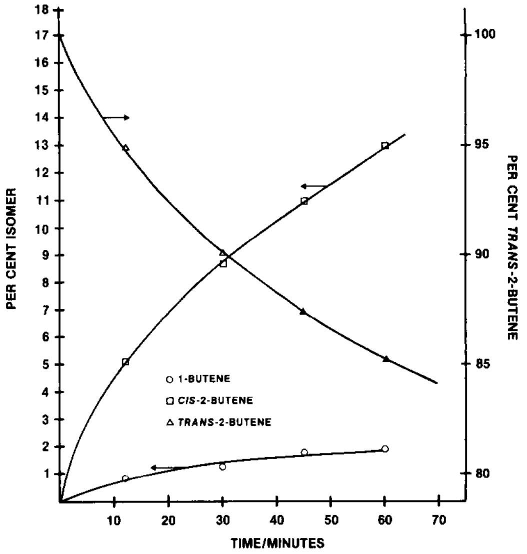


FIG. 3. Conversion vs time plot for *trans*-2-butene isomerization over La_2O_3 at 49°C; $P^{\circ}_{trans} = 150$ Torr. Right scale is for *trans*-2-butene and the left scale is for the rest of the isomers.

the plot for *cis*-2-butene conversion to 1-butene deviated from linearity at the high-temperature end; the activation energy was 8.0 kcal/mol at lower temperatures.

Interestingly, the differences between activation energies for the forward and reverse directions did not generally give reasonable values for the enthalpy changes of the reactions, e.g., $E_{t\to c} - E_{c\to t} = -7.0$ kcal/mol or $E_{c\to t} > E_{t\to c}$ rather than the reverse as expected. This situation was also observed by Lombardo *et al.* (*8*), for ZnO; it is not completely understood, but as they mentioned, the kinetics are coupled, the reactions are close to zero order (*9*), and the system is far from equilibrium. Table 3 gives a summary of initial rates and activation energies for the isomerization of the *n*-

TABLE 3

Initial Rates and Activation Energies for *n*-Butene Isomerization on La_2O_3 (T = 30°C)

Step	Initial rate[a] (molec/sec × cm² × 10^{-10})	Activation energy[b] (kcal/mol)
trans → 1-Butene	3.5 (0.5)[c]	18.2 (10.8)[d]
trans → *cis*	36.3 (6.9)	13.0 (7.4)
cis → 1-Butene	2500. (2.8)	8.0 (11.2)
cis → *trans*	*trans* was not produced initially (4.6)	20.0 (15.3)
1-Butene → *trans*	2300. (1.6)	9.0 (12.3)
1-Butene → *cis*	21000. (15.6)	4.0 (7.8)

[a] Calculated from conversion vs time plot.

[b] Calculated from Arrhenius plots (see Fig. 4).

[c] The numbers in parentheses correspond to the rates on ZnO at 25°C; they were obtained from Ref. (*8*).

[d] The numbers in parentheses correspond to the activation energies on ZnO; they were obtained from Ref. (*8*).

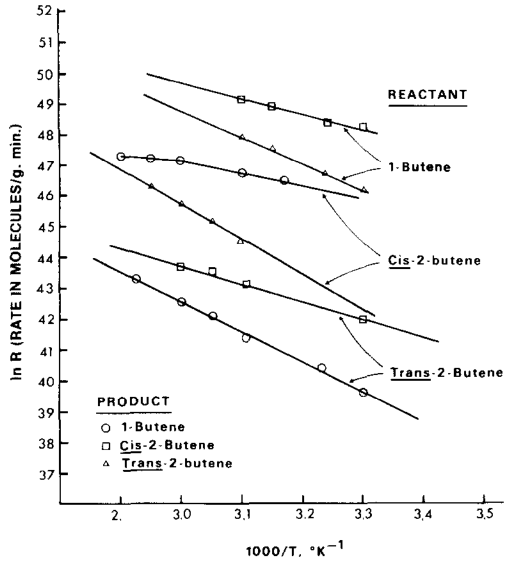


FIG. 4. Activation energy plots for *n*-butene isomerization over La_2O_3. Rates obtained from conversion vs time plots (surface area of the catalyst = 8.6 m^2/g).

butenes on La_2O_3; these are compared with similar data (*8*) for ZnO (in parentheses).

La_2O_3; Tracer Studies

Experiments were designed to provide information concerning: (a) the nature of hydrogen transfer during isomerization (intermolecular or intramolecular), by determining the isotopic distribution in the product molecules and (b) the isotope effects (if any) for the several reactions. Equimolar mixtures of *cis*-2-butene-d_8 + *cis*-2-butene-d_0 and *trans*-2-butene-d_8 + *trans*-2-butene-d_0 were reacted at 45 and 35°C, respectively. Table 4 shows a lack of isotopic intermolecular mixing in either case, but always primary isotope effects (see last column).

DISCUSSION

ZnO

The mechanism of butene isomerization over ZnO has been well studied by Kokes and co-workers (*6*, *7*), and Lombardo *et al.* (*8*). The data are in agreement with a π-allylic mechanism where the intermediate *syn* and *anti* conformers have carbanion character. In the present paper the role of hydrogen in this type of mechanism has been investigated and some additional insight obtained. The only isomer which hydrogenated at 28°C was 1-butene (Table 1). This was not unexpected since terminal olefins usually do hydrogenate faster than internal olefins, possibly because of the higher coordinating ability of terminal olefins (*17*). Another reason may be related

TABLE 4

Tracer Experiments Showing Deuterium Distribution during *cis*-2-Butene and *trans*-2-Butene Isomerization over La_2O_3[a]

Starting material	Conversion (%)	Product (%)	Isotope distribution (%)									k_H/k_D[b]
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
1. Reactant mixture			46.4	0.7						4.0	48.9	
cis-d_8 + *cis*-d_0												
(1 : 1)	12.0	1-Butene (6.6)	65.4	0.8	2.7					3.8	27.3	2.5
		trans-Butene (5.4)	83.6	1.0						3.4	12.0	6.2
		cis-Butene (88.0)	39.0	0.7						5.1	54.4	—
2. Reactant mixture			46.5	0.2						3.0	50.3	
trans-d_8 + *trans*-d_0												
(1 : 1)	3.3	1-Butene (0.3)	63.0	0.6						4.0	32.4	2.0
		trans-Butene (36.7)	45.7	0.3						3.3	50.6	—
		cis-Butene (3.0)	68.8	0.7						3.2	27.3	2.6

[a] Recirculation system volume: 310 cm^3. Reactant pressure: 90 Torr. Reaction temperature: *cis*-2-butene, 45°C; *trans*-2-butene, 35°C.

[b] $\left(\sum_{0}^{3} N_i + \frac{1}{2}N_4\right) \Big/ \left(\sum_{5}^{8} N_i + \frac{1}{2}N_4\right)$ = Light molecules in product/Heavy molecules in product.

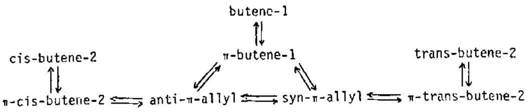
to the smaller steric hinderance associated with the formation of a primary alkyl intermediate required for hydrogenation of terminal olefins as compared with the secondary alkyl species formed from internal olefins. This notion is supported by the results of Wilkinson and co-workers using selective homogeneous catalysts for hydrogenation of 1-alkenes, e.g., $RuH(Cl)(PPh_3)_3$ (*18*) and $RhH(CO)(PPh_3)_3$ (*19*); primary olefins hydrogenated readily whereas internal olefins did not.

In the present work, the rate of isomerization of 1-butene (measured by appearance of *cis*-2-butene + *trans*-2-butene) in the absence of H_2 was larger than in its presence. Moreover, as shown in Fig. 1 and Table 1, the sum of the rates of hydrogenation and isomerization in the presence of hydrogen was very close to the rate of isomerization in the absence of H_2. This immediately led to the idea of competition for sites in these reactions. The studies done by Kokes and co-workers (*6, 7*) support this point. The hydrogenation of ethylene and the isomerization of *n*-butenes over ZnO were shown to occur on the same sites which chemisorb hydrogen. These Zn–O CUS pairs appear to act in an analogous way in the heterolytic dissociation of H_2 and in the formation of the allylic species required for isomerization.

Dent and Kokes (*6*) reported that the rate of hydrogenation was about half-order in hydrogen pressure. This was also confirmed in the present work for hydrogenation of 1-butene, the order derived being 0.51. The agreement of this result with that of Kokes and co-workers (*6, 7*) for hydrogenation of ethylene and 1-butene further linked hydrogenation and isomerization to the same set of sites, viz., those where the π-allylic species are formed by heterolytic dissociation (*6, 7*). Finally, the poisoning of the H_2–D_2 equilibration by *cis*- and by 1-butene provided direct evidence in support of this picture. Interestingly, the half-life times for the H_2–D_2 equilibration in the presence of 1-butene and *cis*-2-butene are very similar (Table 2). This fact also indicated that hydrogenation and isomerization occur on the same sites since *cis*-2-butene isomerized but did not hydrogenate, while 1-butene isomerized as well as hydrogenated and since both isomers caused the same retardation effect on the H_2–D_2 equilibration reaction. Evidently hydrogenation occurred on sites on which H_2 (or D_2) is already chemisorbed; isomerization occurred on the same (empty) sites.

La_2O_3

Like ZnO, butene isomerization had all of the characteristics of a π-allylic carbanion mechanism, viz., double-bond isomerization occurred by an intramolecular transfer of H (D) from one carbon to another; intermolecular exchange was absent; high *cis/trans* ratios were observed (a characteristic of base catalysis); large isotope effects were exhibited indicating that the removal of H or D occurred either before or during the rate-determining step; the activity of the catalyst was developed and increased as the surface was dehydroxylated [up to a maximum at about 650°C (*9, 23*)], and the reactions were zero order or Langmuir dependent. It is by now fairly well established (*7, 8*) that the π-allyl scheme



(4)

for which the homomorphic representation is Eq. (3), is operative over ZnO and Al_2O_3.

It is reasonable therefore to expect another basic oxide, viz., La_2O_3, to follow similar chemistry. Reference to Table 3 shows that whereas *trans*-2-butene was apparently not formed initially from the *cis* isomer at 30°C, the reverse reaction was about 10 times faster than conversion to 1-butene. Because of the high rate of conversion of 1-butene to *cis*-2-butene, however, these data alone are insufficient to prove that direct *trans*- to *cis*-2-butene interconversion occurred. Therefore, the isomerization of *cis*-2-butene was studied over La_2O_3 over the temperature range 25–75°C. The picture obtained above 42.5°C was significantly different from that suggested by the data at 30°C. Figure 2 reveals that at 30°C the only initial product was the 1-butene, but at 42.5°C *trans*-2-butene is clearly observable as one of the initial products. Under our experimental conditions, the *cis*-2-butene transformation was slow enough that points at very low conversion (2 to 4%) could be obtained. These should be free of major contributions due to secondary reactions.

The Arrhenius plots of Fig. 4 provided additional insight into the problem. At 75°C, the *trans*/1-butene ratio produced from *cis*-2-butene was about unity; this change was evidently brought about by the high activation energy for the *cis* → *trans*-2-butene reaction (Table 3). The 12 kcal/mol higher value for this reaction over that for the conversion of *cis*-2-butene to 1-butene is thus the cause of the observed differences between the results for ZnO and La_2O_3. The forbidding activation energy for *cis* → *trans*-2-butenes conversion over La_2O_3 effectively eliminated the direct *anti*- to *syn*-π-allyl transformation at low temperatures. When the temperature was raised to 42.5°C, however, the product from the reaction with high activation energy started to appear.

Rosynek and co-workers (*9*, *12*, *13*, *23*) have argued that sites capable of effecting the direct *anti*- to *syn*-π-allyl interconversion are absent in the La_2O_3 surface, i.e., that the homomorphic scheme is given by Eq. (1), rather than Eq. (3). In view of the foregoing discussion this seems to be a moot point, but the conceptual difference of the root cause is important. Therefore, a few comments are in order concerning the relationship between the present work and that contained in the accompanying paper of Rosynek *et al.* (*23*), which did not become available to us until recently. Their work was centered around work at 0°C, whereas ours was carried out mainly at 30°C; in both cases temperature dependencies and supporting experiments were investigated up to 50°C (*23*) or 75°C (present work). Careful comparison of the data shows the agreement is generally very good. Both sets indicate that at low temperature direct *cis*- to *trans*-2-butene conversion is not a significant pathway, i.e., most of the *trans* product is formed by way of 1-butene. We have attributed this finding to the high activation energy for the *anti*- to *syn*-π-allyl conversion and suggest that the direct *cis*–*trans* conversion may become important at higher temperatures. For the reverse reaction, both sets of data show that down to 1% conversion, at least, more *cis*-2-butene is formed from *trans*- than 1-butene. Rosynek *et al.* (*23*) show, however, that the ratio of *cis*- to 1-butene falls at low conversion and contend that 1-butene becomes the sole product at very low conversions. At 0°C, this may indeed be true, but we think that the higher-activation-energy process must become dominant at higher temperatures. The data of Fig. 4 illustrate this point; the activation energy for the formation of 1-butene (18.2 kcal/mol)[2] is higher than that for *cis*-2-butene (13.0 kcal/mol); this could not be true if the latter were formed in a successive step from 1-butene. Interestingly, these data show that whereas *cis* converts to 1-butene faster

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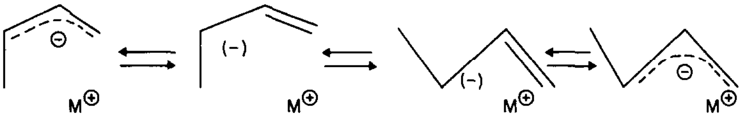
[2] Unfortunately here is the sole important discrepancy between our work and that of Rosynek *et al.*; they quote 8.2 kcal/mol for this step, but show no data. Our experiment was repeated three times.

than into *trans*-2-butene, the latter transforms to *cis* faster than back to 1-butene. A similar phenomenon was observed over ZnO (*18*) where it was noted that products were formed in ratios approximating the expected surface concentrations of the π-complexes and that whereas the preferred route from *cis*- to *trans*-2-butene was via 1-butene, the reverse pathway appeared to be the direct conversion of the *syn*- to the *anti*-π-allyl.

The question of why with some catalysts such as La_2O_3 (*9*) and CdO (*21*) the *cis* $\leftrightarrows$ *trans*-2-butene interconversion is difficult when compared with other catalysts such as Al_2O_3 (*8*) and ZnO (*8*) is an interesting one. Thompson and Ford (*22*) have shown that the rotational barrier for allyl–alkali metal complexes increases with softness (electropositivity) of the countercation. (The value estimated for a free allyl carbanion was 18 kcal/mol.) Kokes and coworkers (*7*), and Lombardo *et al.* (*8*), speculated that the *anti*-π-allyl $\leftrightarrows$ *syn*-π-allyl interconversion occurred through a σ-allyl complex. In metallo-organic chemistry (*17*), a σ-allyl complex is usually thought of as a covalent species. The results of Thompson and Ford (*22*) cannot be understood as readily on this basis as with the ionic, nondelocalized intermediate, which they pictured for reactions in solution, viz.,



(5)

Thompson and Ford found that the activation energy for the *anti*- to *syn*-allylic carbanions increased in the order of the size of the paired cation, i.e.,

$$Cs^+ > Rb^+ > K^+ > Na^+.$$

Foster and Cvetanovic (*24*), studying the isomerization reaction over alkali metal hydroxides, showed that the initial value of the 1-butene/*trans* ratio for the isomerization of *cis*-2-butene decreased as the size of the cation decreased. This result can also be explained in terms of the above scheme. The rather different behavior of ZnO and CdO is also consistent with this picture. ZnO catalyzed the *cis*- to *trans*-2-butene interconversion at room temperature (*7*, *8*), while CdO showed a strong selectivity towards the 1-butene (*21*). Again, with Zn^{2+} and Cd^{2+} in the same group in the periodic table one would expect the smaller cation to be more effective for the *anti* to *syn* interconversion. The experimental value for the *cis* to *trans* conversion over La_2O_3 was 20 kcal/mol; according to Thompson and Ford (*22*) the estimated barrier for rotation for the 1-methyl-allyl system is 18–22 kcal/mol. Since these numbers are very similar one might expect the rotation from *anti* to *syn* to be the slow step in the *cis* to *trans* transformation. This agrees with the findings of Lombardo *et al.* (*8*) who drew the same conclusion working with deuterated compounds on ZnO. It offers an interpretation of the similarities and differences between ZnO and La_2O_3, viz., ZnO promotes the *cis* to *trans* isomerization at room temperature, while La_2O_3 is incapable of the *anti* to *syn* conversion at a competitive rate until higher temperatures are used.

Systematic data for many more oxide catalyst systems are needed to isolate the factors controlling the reaction coordinates. We are, however, just approaching the stage of eliminating mythology concerning mechanisms of butene isomerization from the literature. It is suggested that future studies of this kind include tests made with all three isomers at several temperatures and that a sufficient number of tracer experiments be made. Hopefully, it will soon be possible to establish diagnostic criteria for the kind of mechanism which is operative and thus use these reactions as tools for studies of surface chemistry.

Finally, a couple of discrepancies between the present results and earlier literature should be noted. Naito *et al.* (*25*) reported that whereas the deuteration and isomerization proceeded simultaneously over ZnO at room temperature, the absolute rate of isomerization was unaffected by D_2; we found it was lowered significantly (Table 1). Moreover, they reported that the order in D_2 for deuteration was unity whereas we determined it to be close to 0.5.

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