Tracer Studies of Acid-Catalyzed Reactions. VI. Deuterium Redistribution and Isotope Effects in *n*-Butene Isomerization over Alumina and Silica–Alumina Catalysts

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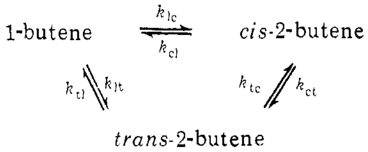
Abstract: The mechanism of *n*-butene isomerization was investigated over alumina and silica–alumina catalysts using deuterium tracers. Microcatalytic experiments showed that only a small fraction of the hydrogen atoms initially present on either catalyst was *directly* involved in the reaction. Strongly adsorbed (polymeric ?) residue formed rapidly on silica–alumina, and this underwent considerable hydrogen exchange with subsequent slugs of butene. Intermolecular exchange when d_0–d_8 mixtures were coisomerized in a static reactor showed that one hydrogen atom was transferred between two molecules during both double-bond and *cis–trans* isomerization, but the relative reactivities of the two species, k_H/k_D, showed no primary isotope effect. These data could be reasonably well explained on the basis of a common *sec*-butyl carbonium ion intermediate formed on "induced" protonic sites in the residue over silica–alumina. Over alumina, very little residue was formed, and most of that which did form was displaced by subsequent slugs in the microcatalytic experiments. The rate-determining step in both double-bond and *cis–trans* isomerization involved carbon–hydrogen bond cleavage, as evidenced by large primary isotope effects ($k_H/k_D \sim 4$). Isotopic scrambling occurred when d_0–d_8 mixtures were coisomerized. However, the mixing was almost as extensive in the reactant as in the product, indicating that isotope exchange may have occurred by a process unrelated to isomerization. The data favor the view that *cis–trans* isomerization occurred by an intramolecular rearrangement, but no decision could be reached concerning double-bond migration. The isomerization reactions over alumina could not be explained on the basis of a single classical concept.

In previous work,[1,2] we employed C^{14} tracers to study the kinetics of *n*-butene interconversion over alumina, silica–alumina, and fluorided alumina catalysts. The reactions followed first-order kinetics in microcatalytic, flow, and static reactors. All six of the relative rate constants in the scheme



were determined under a variety of conditions, and all possible reaction paths interconnecting the three isomers were found to be significant. Some of the selectivities were temperature dependent, and the differences in activation energies between the various paths were quantitatively determined.

The selectivities over silica–alumina were relatively insensitive to poisoning, catalyst source, silica-to-alumina ratio, and temperature; this was consistent with a common intermediate for interconversion among all isomers. The classical *sec*-butyl carbonium ion is the only species considered in the literature which fits this description. Moreover, when treated on a statistical basis, modified by an energetic argument based on the relative ease of secondary *vs.* primary carbon–hydrogen bond cleavage, this intermediate could be used to account for the observed selectivities and their temperature dependencies as well as the relative reactivities of the three isomers.[2]

Over alumina, the selectivities were quite sensitive functions of water content, poisons, method of pretreatment, and temperature. From these observations it appeared that double-bond migration and *cis–trans* isomerization occurred on different sites, each possessing a set of properties unique for that reaction.

In the kinetic experiments, it was possible only to suggest formal reaction schemes, since no *direct* information was obtained regarding the exact nature of the active sites or transition states which might be involved in the various reactions. To investigate these matters, a series of experiments was undertaken employing deuterium tracers, and the results are reported herein. These experiments were designed to provide answers to four questions. (1) Is a significant number of the catalyst protons involved in the isomerization reaction? (2) Can hydrogen associated with residue provide reaction sites? (3) Are there isotope effects? (4) Can some of the reactions be classified as intramolecular rearrangements, or is intermolecular transfer of hydrogen involved?

Partial answers to these questions have provided a clearer picture of the processes which occur over alumina and silica–alumina.

Experimental Section

Reaction Procedures. Two basically different experimental techniques were employed. The first involved a microcatalytic reactor which has been described elsewhere.[1,3,4] Helium carrier gas, purified by passage through a charcoal trap at −195°, flowed over the catalysts at 28 cc (NTP)/min and 2 atm pressure. Measured amounts (4.25 cc (NTP)) of premixed reactants were introduced into the helium stream ahead of the catalyst. Products from each slug were collected for 30 min in a −195° trap before being flash evaporated into a chromatographic column (0.25-in. × 30-ft of 2:1 dimethylsulfolane:hexamethylphosphoramide on firebrick) kept at 0°. Base-line resolution resulted, and the separated isomers were trapped at −195° for mass spectral analysis.

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[1] J. W. Hightower, H. R. Gerberich, and W. K. Hall, *J. Catalysis*, in press.

[2] J. W. Hightower and W. K. Hall, *J. Phys. Chem.*, in press.

[3] R. J. Kokes, H. Tobin, and P. H. Emmett, *J. Am. Chem. Soc.*, 77, 5860 (1955).

[4] W. K. Hall and P. H. Emmett, *ibid.*, 79, 2091 (1957).

The second technique involved use of a static reactor.[2] A 300-cc spherical Pyrex bulb was connected through a stopcock and standard taper to a conventional BET-type gas-handling system. The catalysts were placed in the bottom of a 22-mm o.d. well which extended 4 in. below the bulb. The reactants were first frozen into the reaction vessel which was then rapidly warmed to reaction temperature. Convection currents were relied on to provide mixing, and, since the reactions were quite slow, this was deemed sufficient. Samples (about 3 cc) were removed periodically from the vessel by expansion, separated by glc on the above-mentioned column and subjected to mass spectral analysis.

Mass Spectral Analysis. All mass spectral analyses were carried out using low-energy (10–15 v) electrons in a Nuclide instrument. Fragmentation involving loss of one or two hydrogen atoms amounted to about 10% of the parent peaks for the perprotio molecules, but it was only half that large for loss of deuterium atoms from the perdeuterio molecules. Fragmentation for molecules containing both deuterium and hydrogen was treated in a statistical fashion, the corrections being weighted in favor of loss of hydrogen. Since the fragmentation was relatively small, this approximation should not result in a very large error in the results. In addition to fragmentation corrections, all data were corrected for naturally occurring carbon-13 isotopes. The results were reproducible to within ±0.5%.

Catalysts and Pretreatment. The alumina (GA-48)[5-8] was prepared from the neutral hydrolysis of redistilled aluminum isopropoxide by the MK Research & Development Co., Pittsburgh, Pa. Its total metallic impurity level was less than 50 ppm, and its surface area was 158 m^2/g. X-Ray measurements, made as the catalyst was dehydrated during final stages of preparation, revealed that it was probably a mixture of η- and γ-alumina.

The silica–alumina (M-46) was a commercial Houdry catalyst containing 13% alumina and having a surface area of 270 m^2/g. The major metallic impurity was iron which amounted to between 0.1 and 0.3%. Earlier work[2] has shown that purity has little or no effect on the selectivities over silica–alumina.

For the microcatalytic experiments, the catalysts were pretreated in a stream of dried oxygen at 550° for 2 hr before being evacuated overnight to less than 10^{-5} torr at the same temperature. They were cooled to reaction temperature and exposed to the flowing helium stream. Catalysts used in the static experiments were subjected to two treatments with oxygen at 530° before evacuation overnight at the same temperature. In all cases the catalysts were white after these pretreatments. They were unprotected from mercury vapor present in the vacuum systems.

Reactants. The 1-butene and *cis*-2-butene (Phillips Research Grade) were reportedly 99.8% pure. Just before use, each was distilled from −78 to −195° and outgassed to a sticking vacuum at −195°. No impurities were detected by glc analysis.

The perdeuterio compounds were prepared from 1-butene by repeated treatment with D_2 over a 2-g sample of GA-48 at 180° in a circulation system.[8] The isomers were separated by glc, distilled, and outgassed before use. The isotopic purity of the perdeuterio compounds was about 99%.

Treatment of Data. In all cases the data were expressed in terms of the mole fraction, N_i, of each isotopic species containing i deuterium atoms. By comparing the isotopic distributions in the products with those in the starting mixtures, it was possible to calculate the number of hydrogen atoms which had been exchanged per molecule by the equation

$$\text{atoms exchanged/molecule} = \sum_{i=1}^{4} iN_i + \sum_{i=5}^{8}(8-i)N_i \quad (1)$$

This formulation assumed that all product molecules containing fewer than four D atoms came from the d_0 species; all containing more than four D atoms originated from the d_8 material. Molecules containing four D atoms were assumed to stem equally from both sources; both contributions are lumped in the first summation. The numbers used were corrected for the small amounts of d_6 and d_7 species present in the perdeuterio starting materials. When mixtures of d_0 and d_8 species were used as reactant, it was possible to calculate an isotope effect from the relative reactivities of the two species, as judged from the ratio of "light material" ($^1/_2N_4 + \Sigma^8{}_{i=0}N_i$) to the "heavy material" ($^1/_2N_4 + \Sigma^8{}_{i=5}N_i$) in the products. The isotope effect was simply this ratio in the products divided by (or normalized to) a similar ratio in the starting material. So long as hydrogen–deuterium "scrambling" is not too large and the isotopic distributions are reasonably symmetrical, these assumptions give valid measures of isotope effects since the reactions follow first-order kinetics.

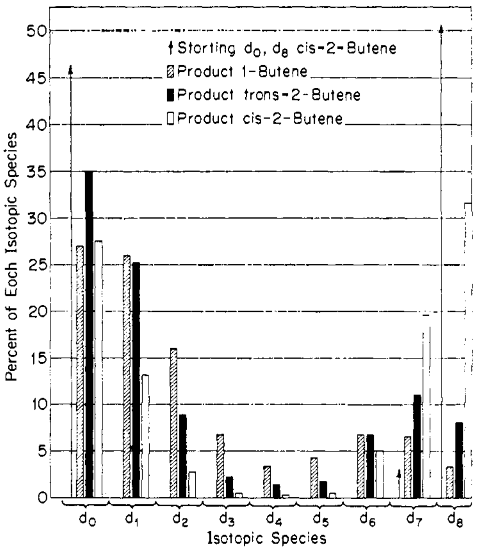

Figure 1. Product distribution from coisomerization of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over alumina.

Results

Microcatalytic Experiments. Results of two microcatalytic experiments are given in Tables I and II. Several 4.25-cc (NTP) slugs of *cis*-2-butene (for alumina, Table I) or 1-butene (for silica–alumina, Table II) having different isotopic compositions were successively passed over the catalysts at 50°. The per cent conversion, the mole fraction of the isomerized product multiplied by 100, can be calculated from these data.

Essentially all the material admitted in each slug was recovered over alumina, and the conversion for a given isotopic species (*e.g.*, d_8 in slugs 1 and 3) did not diminish significantly with time. There were, however, sizeable differences in reactivities of the different isotopic species, d_0 being more than twice that of the d_8 material. When mixtures of the two were used, the conversion was about midway between those for the two pure isotopic species. Also, considerable isotopic scrambling occurred in both the products and the unisomerized reactant when the starting material was a d_0–d_8 mixture (slug 6), as may be seen by the product distribution graph in Figure 1.

Over silica–alumina, most of the first slug and a significant fraction of the second remained on the catalyst as residue (or "coke"), and the catalytic activity for a given isotopic species (compare slugs 2 and 4 for d_0) decreased markedly with slug number. Some isotopic scrambling occurred in the d_0–d_8 mixture (slug 7, Figure 2), but, in contrast with alumina, the redistribution in the products was limited mainly to the d_1 and d_7 positions with little exchange occurring in the unisomerized starting material.

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(5) W. K. Hall and F. E. Lutinski, *J. Catalysis*, **2**, 218 (1963).

(6) W. K. Hall, F. E. Lutinski, and H. R. Gerberich, *ibid.*, **3**, 512 (1964).

(7) W. K. Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *ibid.*, **2**, 508 (1963).

(8) J. G. Larson, J. W. Hightower, and W. K. Hall, *J. Org. Chem.*, **31**, 1225 (1966).

Table I. Microcatalytic Tracer Experiment Showing Intermolecular Hydrogen Exchange during *cis*-2-Butene Isomerization over Alumina[a]

Slug no.	Isotopic compn of reactant	Total recovery, cc (NTP)	Butene product	Amount of each product, cc (NTP)	Isotopic composition of products, %									No. of H or D atoms exchanged (× 10^{-19})	No. of atoms exchanged/ molecule
					d_0	d_1	d_2	d_8	d_4	d_5	d_6	d_7	d_8		
Starting perdeuterio *cis*-2-butene	d_8	...	...	...								5.6	94.4		
Mixture	d_0, d_8	...	...	...	46.3	0.2	0.1					3.1	50.3		
1	d_8	4.08	1-	0.09					0.1	0.1	0.6	10.9	88.3	0.02	0.076
			trans-	0.30					0.1	0.1	0.9	10.9	88.0	0.06	0.072
			cis-	3.69							0.1	6.2	93.7	0.09	0.009
2	d_0	4.31	1-	0.18	94.4	3.9	0.6			0.3	0.3	0.2	0.3	0.02	0.052
			trans-	0.77	91.7	3.9	0.1			0.2	0.6	1.3	2.2	0.09	0.043
			cis-	3.36	96.1	1.9					0.4	0.8	0.8	0.17	0.019
3	d_8	4.15	1-	0.08	1.2	0.9	0.9	0.9	0.7	0.5	1.6	15.4	77.9	0.04	0.174
			trans-	0.28	5.0	3.7	2.0	0.5	0.3	0.2	1.4	12.3	74.6	0.10	0.132
			cis-	3.79	0.6	0.4	0.3	0.1	0.2		0.3	7.4	90.7	0.26	0.026
4	d_0	4.28	1-	0.17	92.2	6.5	0.4			0.2	0.2	0.2	0.3	0.03	0.074
			trans-	0.73	92.5	3.9	0.3			0.2	0.5	1.1	1.5	0.09	0.046
			cis-	3.38	96.1	2.0	0.2				0.4	0.6	0.7	0.22	0.024
5	d_0	4.16	1-	0.17	97.6	2.3	0.1							0.01	0.025
			trans-	0.74	97.6	2.1	0.3							0.05	0.027
			cis-	3.25	98.9	0.9	0.2							0.11	0.013
6	d_0, d_8	4.25	1-	0.12	27.2	25.9	16.1	6.8	3.3	4.3	6.7	6.5	3.2	0.40	1.241
			trans-	0.52	35.1	25.1	8.9	2.2	1.4	1.7	6.7	10.9	8.0	1.18	0.840
			cis-	3.61	27.5	13.2	2.7	0.3	0.2	0.3	5.0	19.3	31.5	4.71	0.486

[a] Catalyst: 0.25 g of GA-48 alumina; 4.25 cc (NTP) of *cis*-2-butene per slug; reaction temperature, 50°; carrier gas flow = 28 cc (NTP)/min at 2 atm absolute pressure.

Table II. Microcatalytic Tracer Experiment Showing Intermolecular Hydrogen Exchange during 1-Butene Isomerization over Silica–Alumina[a]

Slug no.	Isotopic compn of reactant	Total recovery, cc (NTP)	Butene product	Amount of each product, cc (NTP)	Isotopic composition of products, %									No. of H or D atoms exchanged (× 10^{-19})	No. of atoms exchanged/ molecule
					d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
Starting perdeuterio butene-1	d_8	...	...	...							0.2	6.0	93.8		
Mixture	d_0, d_8	...	...	...	47.3	0.3					0.1	3.2	49.1		
1	d_8	0.92	1-	0.10								8.8	91.2	0.008	0.028
			trans-	0.62							0.3	7.9	91.8	0.035	0.021
			cis-	0.20							0.1	8.0	91.9	0.011	0.020
2	d_0	3.73	1-	1.56	93.9	5.3	0.5						0.3	0.264	0.063
			trans-	1.21	74.2	21.9	2.7	0.4	0.1		0.1	0.2	0.4	0.939	0.289
			cis-	0.96	68.1	27.9	2.8	0.4	0.1		0.1	0.2	0.4	0.942	0.351
3	d_0	4.10	1-	2.36	96.9	2.8	0.3							0.215	0.034
			trans-	0.94	81.8	16.4	1.5	0.3						0.513	0.203
			cis-	0.80	76.6	21.7	1.5	0.3						0.543	0.253
4	d_0	4.25	1-	2.82	98.1	1.7	0.2							0.159	0.021
			trans-	0.78	83.0	15.4	1.4	0.2						0.395	0.188
			cis-	0.65	79.0	19.5	1.3	0.2						0.398	0.227
5	d_8	4.12	1-	3.15	0.3	0.1					0.6	6.6	92.4	0.085	0.010
			trans-	0.52	0.6	0.8	0.3	0.2	0.2	0.3	2.6	23.4	71.6	0.352	0.251
			cis-	0.45	0.6	0.7	0.3	0.1	0.2	0.1	2.3	27.6	68.1	0.344	0.285
6	d_0	4.30	1-	2.95	97.6	1.6	0.3					0.1	0.4	0.175	0.022
			trans-	0.71	83.3	14.8	1.0	0.1			0.1	0.4	0.3	0.325	0.171
			cis-	0.64	80.0	18.5	0.9					0.3	0.3	0.320	0.203
7	d_0, d_8	4.23	1-	3.23	43.3	2.7	0.4				0.3	4.6	48.7	0.417	0.048
			trans-	0.53	26.3	20.5	2.5	0.5	0.2	0.5	3.8	25.5	20.2	0.872	0.612
			cis-	0.47	27.2	21.0	2.2	0.4	0.3	0.3	3.4	26.3	18.9	0.788	0.623

[a] Catalyst: 0.50 g of M-46 silica–alumina; 4.25 cc (NTP) of 1-butene per slug; reaction temperature, 50°; carrier gas flow = 28 cc (NTP)/min at 2 atm absolute pressure.

Table III. Static Tracer Experiment Showing Intermolecular Hydrogen Exchange during *cis*-2-Butene Isomerization over Alumina[a]

Reaction time, hr	% conversion	Butene product	% of each product	Isotopic composition of products, % d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	Atoms exchanged/ molecule	Light material/ heavy material
Starting mixture		*cis*-		47.5							2.6	47.9		0.91
1.03	2.6	1-	0.9	42.9	25.2	8.2	1.2	0.6	1.6	4.7	9.2	6.4	0.71	3.50
		trans-	1.7	63.0	13.7	1.1	...	0.1	0.1	0.8	6.5	14.7	0.24	3.52
		cis-	97.4	43.7	2.8	0.3	...	...	...	0.4	5.6	47.2	0.07	0.88
2.25	5.8	1-	1.9	37.7	27.3	10.0	1.9	0.6	2.4	5.7	8.7	5.7	0.82	3.38
		trans-	3.9	61.2	14.1	1.4	0.1	...	0.1	1.1	7.3	14.7	0.26	3.32
		cis-	94.2	42.4	5.8	0.6	0.1	...	...	0.9	8.3	41.9	0.15	0.96
3.50	9.2	1-	2.8	32.1	28.5	12.1	2.6	0.9	3.0	7.0	8.8	5.0	0.96	3.13
		trans-	6.4	58.3	16.6	2.0	0.1	...	0.2	1.3	7.8	13.7	0.31	3.36
		cis-	90.8	37.9	8.5	1.0	0.1	...	0.1	1.5	11.5	39.4	0.23	0.90
4.75	12.9	1-	3.7	27.6	29.7	13.4	3.5	1.3	3.5	7.7	8.9	4.4	1.07	2.97
		trans-	9.2	55.6	19.2	2.5	0.2	...	0.2	1.6	8.1	12.6	0.36	3.46
		cis-	87.1	37.6	10.0	1.4	0.1	...	0.1	2.1	13.6	35.1	0.30	0.96
6.00	16.4	1-	4.6	23.7	28.4	15.9	4.6	1.9	4.2	8.3	8.7	4.3	1.19	0.96
		trans-	11.8	51.4	21.9	3.4	0.3	0.1	0.3	2.0	8.7	11.9	0.43	3.36
		cis-	83.6	30.1	14.2	2.2	0.2	...	0.2	3.1	16.9	33.1	0.41	0.88
7.25	19.4	1-	4.9	20.1	28.7	17.7	5.8	2.3	4.9	9.0	8.9	3.7	1.32	2.65
		trans-	14.5	47.7	24.5	4.3	0.4	0.2	0.4	2.4	9.1	10.9	0.50	3.37
		cis-	80.6	26.4	14.9	3.0	0.2	0.1	0.3	4.2	19.9	31.0	0.51	0.80
9.25	25.9	1-	5.8	15.1	25.3	19.6	7.9	3.5	6.1	10.1	8.8	3.6	1.49	2.29
		trans-	20.1	41.1	27.4	6.4	0.7	0.3	0.6	3.2	10.2	10.1	0.61	3.12
		cis-	74.1	19.7	16.8	4.6	0.7	0.4	0.6	6.8	23.9	26.5	0.67	0.72

[a] Catalyst: 0.030 g of GA-48 alumina; reactants: 35.0 cc (NTP) of an equimolar d_0, d_8 mixture of *cis*-2-butenes; reaction temperature, 25°.

Static Experiments. A mixture of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 (30 cc (NTP)) was isomerized over 0.030 g of GA-48 and over 0.100 g of M-46; the results are tabulated in Tables III and IV. Similar data for the coisomerization of 1-butene over alumina are presented in Table V. Figure 3 shows the progress of the reaction of *cis*-2-butene over the two catalysts, plotted according to the first-order rate equation

$$2.3 \log (x_e - x) = kt + 2.3 \log x_e \qquad (2)$$

where x and x_e represent the conversion at time t and at equilibrium, respectively. This equation holds rigorously for a reversible reaction where one reactant becomes a single product, the reaction being first order in both directions. It is a linear equation (the exact solutions for first-order reactions among three species cannot be linearized) and is useful for plotting the kinetic data. Product distributions calculated using real rate constants in the exact equations were shown to follow this equation through at least 70% conversion.

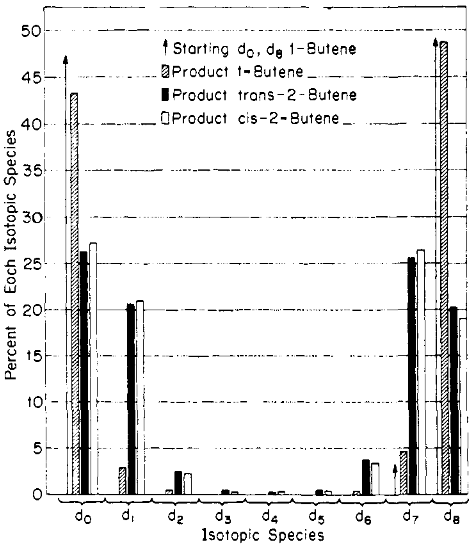

Figure 2. Product distribution from coisomerization of 1-C_4H_8 and 1-C_4D_8 over silica–alumina.

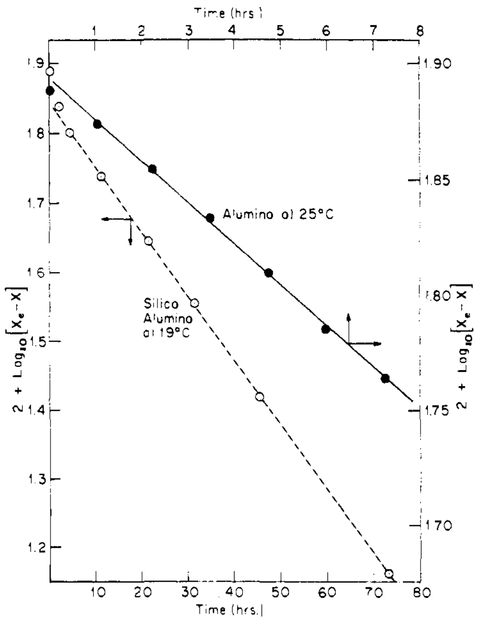

Figure 3. First-order rate plots for coisomerization of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over alumina and silica–alumina in a static reactor.

The ratios of light to heavy molecules in the products from coisomerization of *cis*-C_4H_8 with *cis*-C_4D_8 and 1-C_4H_8 with 1-C_4D_8 over alumina are plotted against conversion in Figures 4 and 5, respectively. Similar

Table IV. Static Tracer Experiment Showing Intermolecular Hydrogen Exchange during *cis*-2-Butene Isomerization over Silica–Alumina[a]

Slug no.	Time, hr	% conversion[b]	Butene product	% of each product	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	Atoms exchanged/molecule	Light material/heavy material
					Isotopic composition of products, %										
Starting mixture	...	...	...	...	45.5	0.3					0.2	3.0	51.0	...	0.839
1	2.3	8.6	1-	1.1	33.7	24.4	2.7	0.1		0.2	3.8	21.3	13.8	0.58	1.557
			trans-	7.5	32.6	18.3	1.4	0.1		0.3	2.7	21.4	23.2	0.47	1.101
			cis-	91.4	43.4	1.9	0.2				0.4	4.7	49.4	0.04	0.835
2	4.5	14.2	1-	2.5	32.0	24.3	3.1	0.2	0.1	0.5	4.2	21.0	14.6	0.61	1.475
			trans-	11.7	32.3	18.0	1.6	0.1	0.1	0.3	2.9	20.9	23.8	0.48	1.083
			cis-	85.8	42.4	2.8	0.2				0.5	5.6	48.5	0.06	0.832
3	11.3	22.6	1-	3.6	28.9	25.2	5.0	0.6	0.2	0.8	5.6	20.8	12.9	0.70	1.488
			trans-	19.0	30.3	19.4	2.4	0.2	0.1	0.5	3.8	22.1	21.2	0.56	1.096
			cis-	77.4	40.1	4.8	0.4				0.7	7.5	46.5	0.11	0.828
4	21.5	33.2	1-	4.1	25.8	24.0	6.6	1.0	0.3	1.2	6.4	19.1	15.6	0.76	1.353
			trans-	29.1	28.4	19.9	3.3	0.4	0.2	0.8	4.8	22.2	20.0	0.61	1.088
			cis-	66.8	36.0	7.6	1.0	0.2	0.1	0.2	1.4	10.1	43.4	0.20	0.815
5	31.5	41.6	1-	3.3	21.9	25.2	9.2	1.8	0.5	1.7	8.1	19.9	11.7	0.91	1.398
			trans-	38.3	26.3	20.6	4.1	0.5	0.2	1.0	5.7	22.5	19.1	0.67	1.066
			cis-	58.4	32.6	10.0	1.6	0.2	0.2	0.3	2.2	12.4	40.5	0.29	0.802
6	45.5	51.2	1-	3.8	19.6	24.7	11.4	2.8	0.9	2.5	9.0	18.2	10.9	1.02	1.433
			trans-	47.4	23.9	21.1	5.2	0.8	0.3	1.3	6.9	22.5	17.9	0.74	1.049
			cis-	48.8	27.7	13.0	2.7	0.4	0.2	0.6	3.8	15.5	36.1	0.42	0.783
7	73.1	62.9	1-	3.9	13.3	22.4	15.6	5.6	2.0	4.2	11.4	17.0	8.5	1.30	1.375
			trans-	59.1	19.1	20.7	7.4	1.5	0.6	2.0	8.9	24.7	15.1	0.90	0.961
			cis-	37.0	19.2	16.9	6.0	1.4	0.6	1.7	7.5	20.0	26.7	0.74	0.779

[a] Catalyst: 0.100 g of M-46 silica–alumina; reactants: 30.0 cc of d_0, d_8 mixture of *cis*-2-butenes; reaction temperature, 19°. [b] (1-Butene + *trans*-2-butene)/Σ(butenes).

data for silica–alumina are given in Figure 6. In Figures 7–9 the atoms exchanged/molecule (or the "exchange concentration") are also plotted against conversion for the same three systems.

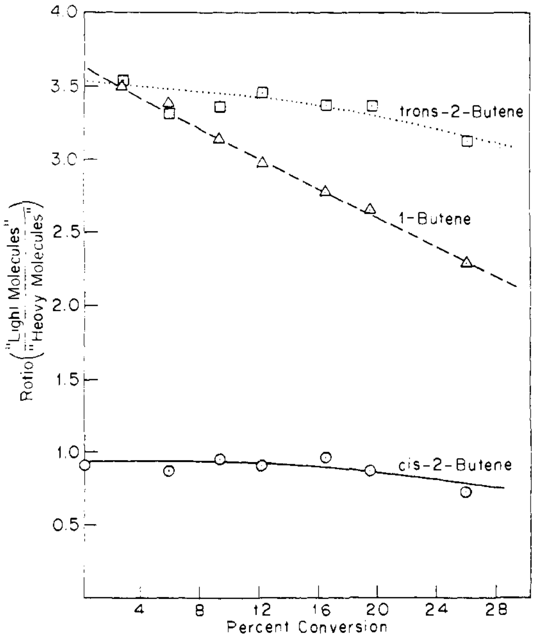

Figure 4. Relative reactivities of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over alumina at 25°.

Discussion

Catalyst Hydrogen Atoms as Sites for *n*-Butene Isomerization. If hydrogen atoms on the catalyst surface (probably in lattice terminating hydroxyl groups) are directly involved in the isomerization mechanism, they should undergo exchange with the butenes and appear in the reaction products. It is apparent from the results of the microcatalytic experiments that exchange did not occur to an appreciable extent over either catalyst. Products from the first d_8 slug passed

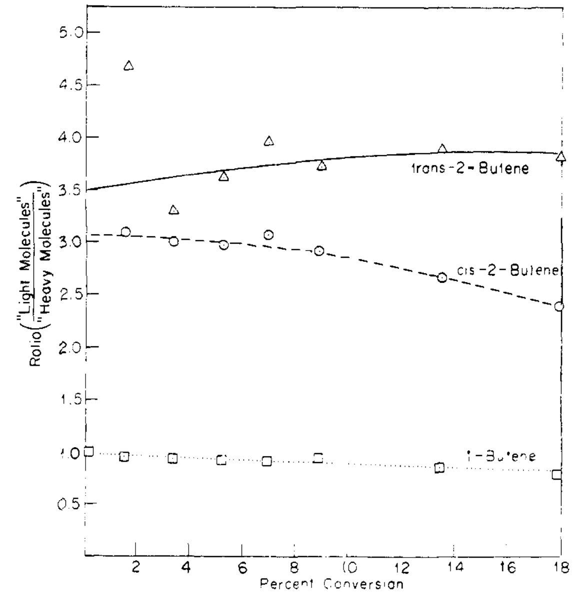

Figure 5. Relative reactivities of 1-C_4H_8 and 1-C_4D_8 over alumina at 25°.

over alumina (Table I) contained less than 2% (or an amount equivalent to $3 \times 10^{12}/cm^2$) of the original 1×20^{20} H atoms[5] on the catalyst. This amount was, however, about equal to that which is involved in the exchange of CH_4 with CD_4 over the same catalyst at about the same temperature;[9] it is also close to the

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[9] J. G. Larson and W. K. Hall, *J. Phys. Chem.*, **69**, 3080 (1965).

Table V. Static Tracer Experiment Showing Intermolecular Hydrogen Exchange during 1-Butene Isomerization over Alumina[a]

Reaction time, hr	% conversion	Butene product	% of each product	Isotopic composition of products, %									Atoms exchanged/ molecule	Light material/ heavy material
				d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8		
Starting mixture	...	1-	...	50.0					0.1	0.5	2.6	46.8	...	1.00
1.00	1.5	1-	98.5	43.9	4.4	0.5			0.1	1.0	6.7	43.4	0.12	0.96
		trans-	0.2	63.7	16.8	2.9				2.4	6.1	9.1	0.32	4.67
		cis-	1.3	58.2	14.3	3.1	0.1	0.2	0.3	2.4	7.5	13.9	0.34	3.10
2.00	3.4	1-	96.6	39.3	7.8	1.2	0.1	0.1	0.2	1.7	10.0	39.6	0.23	0.94
		trans-	0.6	54.9	17.4	3.3	0.1		0.3	2.0	8.3	12.7	0.37	3.30
		cis-	2.8	53.2	18.5	3.1	0.1	0.1	0.4	2.5	9.9	12.2	0.41	3.00
3.00	5.2	1-	94.8	36.0	10.5	1.8	0.2		0.3	2.5	12.6	36.1	0.31	0.94
		trans-	1.0	55.0	18.3	3.8	0.3	0.2	0.3	2.6	8.3	10.2	0.42	3.44
		cis-	4.2	50.9	19.8	3.7	0.4	0.2	0.4	2.8	10.1	11.8	0.46	2.97
4.00	6.9	1-	93.1	32.0	12.9	2.5	0.2	...	0.5	3.3	15.2	33.4	0.40	0.91
		trans-	1.2	53.3	21.6	4.4	0.4	0.1	0.5	2.7	8.4	8.6	0.47	3.96
		cis-	5.7	49.1	21.6	4.4	0.4	0.1	0.5	3.2	10.1	10.7	0.50	3.08
5.00	8.9	1-	91.1	29.8	15.2	3.4	0.3	0.1	0.5	4.1	17.0	29.6	0.49	0.95
		trans-	1.7	51.2	22.4	4.7	0.5	0.2	0.5	2.8	8.8	8.9	0.50	3.73
		cis-	7.2	46.2	22.8	4.8	0.6	0.2	0.6	3.6	10.5	10.7	0.54	2.92
7.00	13.3	1-	86.7	22.2	18.1	5.2	0.5	0.1	0.9	6.2	20.7	26.1	0.65	0.85
		trans-	2.8	47.4	25.0	6.3	0.7	0.2	0.7	3.6	8.5	7.6	0.58	3.88
		cis-	10.5	39.3	25.4	7.0	0.9	0.2	1.0	4.6	11.3	10.3	0.66	2.66
9.00	18.0	1-	82.0	17.1	18.8	7.3	1.1	0.2	1.4	9.1	23.7	21.3	0.83	0.80
		trans-	4.0	43.1	27.1	7.8	1.0	0.3	1.1	4.2	8.7	6.7	0.67	3.81
		cis-	14.0	33.4	26.7	9.0	1.3	0.4	1.4	6.1	12.1	9.6	0.78	2.39

[a] Catalyst: 0.020 g of GA-48 alumina; reactants: 50.0 cc of d_0, d_8 mixture of 1-butene; reaction temperature, 25°.

value given by Peri[10] for the density of α sites, which he suggests are responsible for butene isomerization. Over silica–alumina (Table II), the products had exchanged with only about 1% (1.4 × 10^{12}/cm^2) of the initial 2 × 10^{20} H atoms.[7] This value is in reasonable agreement with results reported by Gerberich, Larson, and Hall[11] and by Ozaki and Kimura[12] for perprotio-*n*-butene exchange at room temperature with deuterated catalysts which had been evacuated at 550°. Isomerization of cyclopropane[13,14] over a similar catalyst indicated that less than 1 × 10^{12} catalyst H atoms/cm^2 were exchangeable at 150°. As all these authors con-

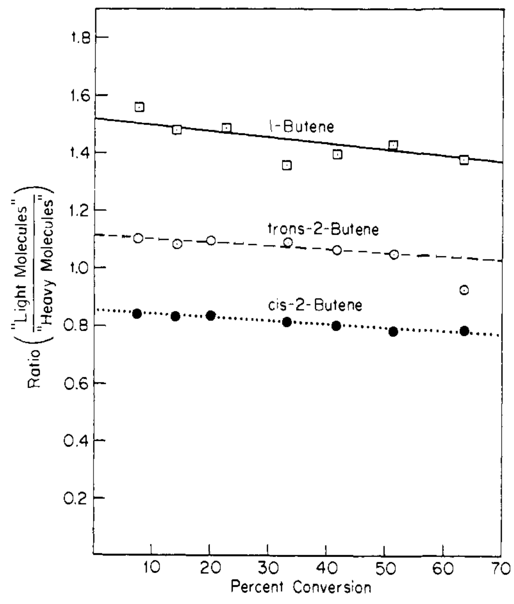

Figure 6. Relative reactivities of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over silica–alumina at 19°.

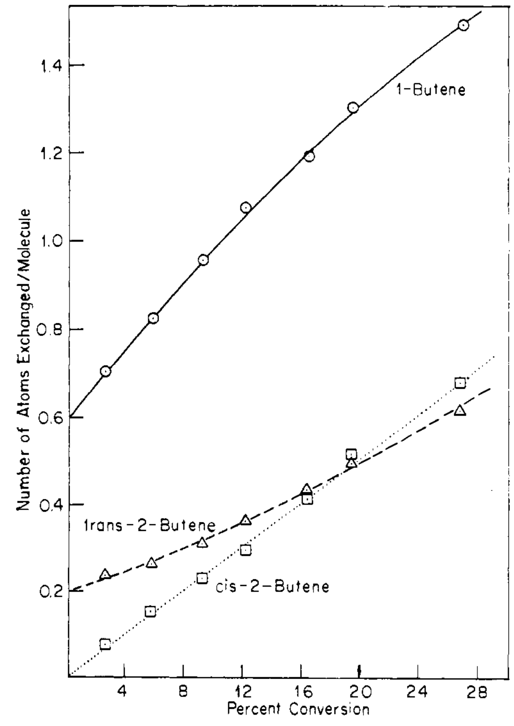

Figure 7. "Exchange concentration" in products of coisomerization of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over alumina.

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(10) J. B. Peri, *J. Phys. Chem.*, **70**, 1482 (1966); *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960*, **1**, 1333 (1961); *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **2**, 1100 (1965).

(11) H. R. Gerberich, J. G. Larson, and W. K. Hall, *J. Catalysis*, 4, 523 (1965).

(12) A. Ozaki and K. Kimura, *ibid.*, **3**, 395 (1964).

(13) W. K. Hall, J. G. Larson, and H. R. Gerberich, *J. Am. Chem. Soc.*, **85**, 3711 (1963).

(14) J. G. Larson, H. R. Gerberich, and W. K. Hall, *ibid.*, 87, 1880 (1965).

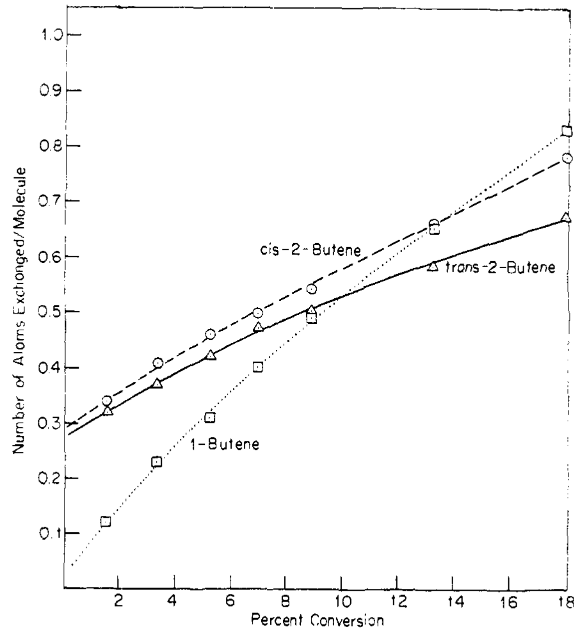

Figure 8. "Exchange concentration" in products of coisomerization of 1-C_4H_8 and 1-C_4D_8 over alumina.

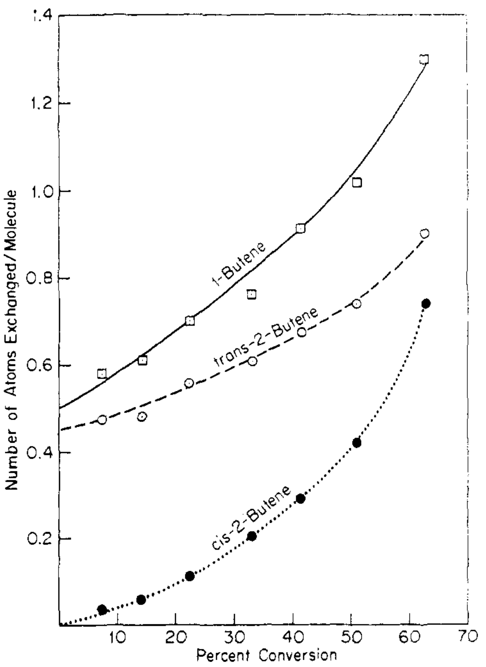

Figure 9. "Exchange concentration" in products of coisomerization of *cis*-2-C_4H_8 and *cis*-2-C_4D_8 over silica–alumina.

cluded, at most only a very small fraction (less than 2%) of the catalyst's hydrogen atoms can be *directly* involved as sites for the isomerization reactions over alumina and silica–alumina.

Residue as Sites for *n*-Butene Isomerization. It is, however, entirely possible that hydroxyl groups may be *indirectly* involved in the isomerization mechanism by participating in the formation of coke which could subsequently furnish protonic sites for the reaction. This does not appear to be the case with alumina where only a small amount of residue was formed from the first d_8 slug and little additional exchange was observed in the second (d_0) slug (compare with silica–alumina). Furthermore, most of the residue deposited from one slug over alumina was displaced by the next slug, as seen by the appearance of "heavy material" among the products of the second slug. These results accord with the radioactive tracer data reported earlier[1] where about the same amount of radioactive material deposited in one slug was displaced into the following nonradioactive slug. As the rate of isomerization was found to correlate inversely with the hydrogen content of alumina,[15] neither catalyst hydroxyl groups nor residue molecules appeared to act as sites for *n*-butene isomerization. It is possible, however, that a small number of active sites has associated OH groups and that these are responsible for intermolecular mixing or exchange with D_2.

The situation was quite different over silica–alumina. Most of the first slug and significant portions of slugs 2 and 3 of Table II were irreversibly lost to the catalyst as residue; the total amount chemisorbed, calculated as butene molecules, was about 2×10^{20}/g (7×10^{13}/cm^2). The second slug (d_0) underwent over an order of magnitude more exchange with the residue than did the first slug (d_8) with the catalyst hydrogen atoms. Only a very small amount of the residue was displaced into subsequent slugs, again in accordance with the earlier C^{14} tracer work.[1] Presumably this residue is a type of polymer, as has been suggested by Peri,[10] and this material may provide reaction sites capable of furnishing protons for carbonium ion formation.[1,2] Others[12–14] have made similar findings using propylene-d_6 as a source of deuterated residue.

The true nature of the silica–alumina surface is evidently masked by this residue, which could be formed on Brønsted sites or on aprotic sites. Since the rate of butene isomerization correlated directly with catalyst hydrogen content,[15] it is possible that the residue is a polymeric carbonium ion formed by reaction of the olefin with a small number of Brønsted sites. On this basis, the Brønsted acidity may be estimated as 7×10^{13}/cm^2 divided by the number of butene molecules per residue. Since it seems likely that there are at least two per residue,[10] this would indicate a value less than 3.5×10^{13}/cm^3. This does not prove that this much Brønsted acid is present, however, because the residue could be formed on aprotic sites as suggested by Ozaki and Kimura[12] or by Basila, Kantner, and Rhee.[16]

It seems likely that the residue formation in our experiments corresponds to the "polymerization" studied spectroscopically by Peri[10] and to the 310-mμ species which Leftin and Hermana[17] attributed to the butenyl carbonium ion. These authors supposed their observations were made on molecules or ions adsorbed on aprotic sites. Peri noted that his "polymerization" was severely inhibited by the adsorption of 3×10^{13}/cm^2 H_2O molecules, whereas Gerberich and Hall[15] showed that this much water increased the rate of butene isomerization. These observations are compatible if H_2O can occupy sites which initiate residue formation, but act as cocatalyst for butene isomerization.

Isotope Effects. A large primary kinetic isotope effect was observed for all isomerization reactions over

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[15] H. R. Gerberich and W. K. Hall, *J. Catalysis*, **5**, 99 (1966).

[16] M. R. Basila, T. R. Kantner, and K. H. Rhee, *J. Phys. Chem.*, **68**, 3197 (1964).

[17] H. P. Leftin and E. Hermana, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, **2**, 1064 (1965).

alumina. Initial ratios of light to heavy material in the isomerized products (Figures 4 and 5) indicated isotope effects, k_H/k_D, of between 3 and 4 when normalized to a similar ratio in the starting isomer. These were not far from the value expected (6.9) for bond cleavage at 25° if the difference in zero-point energy for C–H and C–D is 1.5 kcal/mole.[18] Evidently, carbon–hydrogen bond rupture occurred in the transition state during both double-bond and *cis–trans* interconversions over alumina.

Isotope effects were also found for silica–alumina, but were much less pronounced than those obtained for alumina. From Figure 6 the ratio of light to heavy product molecules at low conversion (intercepts) gave k_H/k_D ratios of 1.3 for *cis–trans* isomerization and 1.8 for double-bond migration when normalized to the starting mixture. Neither of these values was sufficiently high to demonstrate a primary kinetic isotope effect, although they were somewhat larger than those normally observed for secondary effects. There have been some cases, however, where secondary isotope effects "of the first kind"[19] have been reported as large as 1.4[20] and 2.1.[21] Over silica–alumina, therefore, the nature of the effect was indeterminate. It was too small to indicate bond cleavage was rate determining, as with alumina, and yet a little too large to classify confidently as a secondary effect.

Intermolecular Hydrogen Exchange during Isomerization. Considerable intermolecular hydrogen exchange occurred when d_0–d_8 mixtures were coisomerized over both alumina and silica–alumina, but the hydrogen redistribution patterns were different over the two catalysts. Over silica–alumina the exchange into product molecules at low conversions was limited mainly to the d_1 and d_7 positions (Tables II and IV, and Figure 2), and the absolute amounts of d_0, d_1, d_7, and d_8 were comparable. This would result if one hydrogen atom were exchanged each time a molecule underwent isomerization. Extrapolation of the exchange concentration curves to zero conversion (intercepts near 0.5, Figure 9) also indicated that one atom had exchanged per molecule isomerized for *both* double-bond migration (product 1-butene) and *cis–trans* isomerization (product *trans*-2-butene). The small amount of exchange into the unisomerized *cis*-2-butene at low conversions indicated that the intermolecular exchange occurred mainly during isomerization.

The situation was considerably more complex over alumina. Firstly, extensive intermolecular hydrogen exchange occurred independently of isomerization, as may be seen in the isotopic distribution for the unisomerized starting isomer (Figure 1) and in the exchange concentration curves in Figures 7 and 8. Moreover, the "exchangeability" (lability) of hydrogen atoms differed markedly among the three isomers, the order being 1-butene >> *cis*-2-butene > *trans*-2-butene. Large isotope effects further complicated the situation. It is therefore impossible to say categorically that either double-bond or *cis–trans* isomerization occurred by an intermolecular rather than an intramolecular mechanism, or conversely. With an isotope effect $k_H/k_D = 4$, one would expect an exchange concentration intercept of 0.32 (rather than 0.50 for no isotope effect) for a pure intermolecular mechanism. Also, the initial isotopic distribution would be 64:16:16:4 = $d_0:d_1:d_7:d_8$ (all other isotopic species = 0), for products of such a reaction, since both the light and heavy molecules would have a 4:1 probability of picking up an H atom during the exchange.

Such an intercept (*ca.* 0.3) was in fact observed for both 2-butenes formed by double-bond migration from 1-butene in Figure 8, but the isotopic distributions (Figure 1, Tables I and III) were not limited to the d_0, d_1, d_7, and d_8 species, nor did d_7 ever equal d_1. The binomial-like isotope distribution could have resulted from exchange reactions which were not a necessary consequence of the isomerization process, *i.e.*, molecules might have been adsorbed, undergone exchange, and desorbed without isomerizing. This would be consistent with the significant exchange into the unisomerized starting isomers.

The intercepts in Figure 7 (0.6 for 1-butene and 0.2 for *trans*-2-butene) suggest considerable differences between the double-bond and *cis–trans* reaction mechanisms, but again these differences may only reflect the relative exchangeabilities of the two product isomers in secondary reactions. Since the intercept for the *trans* isomer is well below the 0.32 value predicted for an intermolecular mechanism with isotope effect of 4, it appears that the *cis–trans* interconversion probably occurred intramolecularly.

Reaction Mechanism over Silica–Alumina. The pertinent experimental observations are summarized as follows.

1. All reactions are first order in reactant, both on a conversion and on a time basis[1,2,22] (see Figure 3).
2. Each reactant can be converted directly into either of the other two *n*-butenes; the selectivity is always near unity.[1,2]
3. The over-all reactivities follow the order 1-butene ~ *cis*-2-butene > *trans*-2-butene.[1,2]
4. Activation energies for the reaction fall between 12 and 18 kcal/mole,[2,15] and the top of the energy barrier for 1-butene reaction to *cis*-2-butene coincides with that for reaction to *trans*-2-butene, but it is higher than the barrier between *cis*- and *trans*-2-butene by about 0.8 kcal/mole.[2]
5. The reaction rate correlates directly with the surface density of OH groups,[15] but only a small fraction of these appears to be involved directly in the isomerization reaction (slug 1, Table II; also see ref 11).
6. About 0.5 butene molecule/catalyst OH group is lost to the catalyst as irreversibly adsorbed (polymerized?) residue,[1] and hydrogen atoms from this material may act as reaction sites (Table II).
7. Intermolecular hydrogen transfer occurs during both double-bond and *cis–trans* isomerization reactions (Figure 9).
8. Only a small isotope effect is involved in all reactions (Figure 6).

Recent kinetic studies[1,2] revealed that several mechanisms suggested in the literature probably cannot be solely responsible for the *n*-butene isomerization reac-

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(18) R. P. Bell, *Discussions Faraday Soc.*, **39**, 18 (1965).

(19) E. A. Helevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(20) S. Borcic, M. Nikoletic, and D. E. Sunko, *J. Am. Chem. Soc.*, **84**, 1615 (1962).

(21) R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

(22) (a) J. Wei and C. D. Prater, *Advan. Catalysis*, 13, 203 (1962); (b) R. G. Hay, J. Coull, and P. H. Emmett, *Ind. Eng. Chem.*, **41**, 2809 (1949).

tions over silica–alumina because they do not allow interconversion between two of the three isomers. These included the suggestions advanced by Lucchesi, *et al.*[23] (fixed configuration nonclassical carbonium ions, implies $k_{1t} = k_{t1} = 0$), by Leftin and Hermana[17] (butenyl carbonium ions, implies $k_{ct} = k_{tc} = 0$), and by Turkevich and Smith[24] ("hydrogen switch" mechanism, implies $k_{ct} = k_{tc} = 0$). Carbanion complexes are not likely to occur on acidic surfaces such as silica–alumina, and they too would not allow for direct *cis–trans* interconversion.[25]

The gross aspects of the mechanism can be explained by assuming the reaction goes through the *sec*-butyl carbonium ion intermediate formed from protons supplied by chemisorbed residue, rather than by the Brønsted acid (hydroxyl groups) of the catalyst as often postulated.[26] This is the only intermediate which has been considered in the literature which allows for the direct transformation of each butene into both of the other two. The carbonium ion is not, however, identical with the transition state. The latter is at the top of the energy barrier between reactant and product. This may be between one of these and the carbonium ion, which therefore may be a metastable state.[2] Thus, the top of the energy barrier is not the same for isomerization of *cis*-2-butene into *trans*-2-butene (loss of one secondary hydrogen) as into 1-butene (loss of one of three primary hydrogens). This mechanism[2] also accounts for the intermolecular exchange of one hydrogen (or deuterium) atom per molecule isomerized when equimolar mixtures of C_4H_8 and C_4D_8 are coisomerized, with the exchange being limited mainly to the d_1 and d_7 positions. The picture suggests that the selectivities should be fairly insensitive to catalyst preparation and poisoning, as observed.[1,15,27]

Although a proton-transfer mechanism can be used to explain most of the observations, it also has its inadequacies. If the activation energy involved in the rate-determining step of the isomerization corresponded to proton transfer, as implied by the energetic argument used to justify the selectivities, a fairly sizeable primary kinetic isotope effect might be expected; such was not observed. It may be that for some reason the full expected isotope effect on breaking a C–H or C–D bond cannot be developed in the transfer of a proton (deuteron). According to Ausloos and Gordon,[28] proton transfer occurs without activation energy in ion–molecule reactions. Perhaps the same phenomenon, occurring on a catalyst surface, also need not require an isotope effect. Despite this inconsistency, the 2-butyl carbonium ion intermediate theory provides the most plausible scheme of all those advanced in the literature for *n*-butene isomerization over silica–alumina.

Reaction Mechanism over Alumina. The mechanism of *n*-butene isomerization over alumina appears to be much more complicated than that over silica–alumina. The sensitive dependence of selectivity on poisoning, method of catalyst preparation, pretreatment, water content, and temperature indicates that different types of sites and/or reaction complexes are involved in each of the reaction paths. This dual complication, having no common intermediate for all reaction paths and the unlimited possibilities for alteration of the surface sites distribution with changing environment,[29] makes it difficult to draw generalities from the data. The experimental observations, which should be considered in any future attempt to formulate a mechanism, are summarized below.

1. All reactions are first order in reactant.[1,2,22,30]
2. Each reactant can be converted directly into each of the other two *n*-butenes, but the selectivity is usually far from unity; high *cis*/*trans*, *trans*/butene-1, and *cis*/butene-1 ratios are typical for the isomerization of 1-butene, *cis*-2-butene, and *trans*-2-butene, respectively.[1,2,15]
3. The activation energies fall between 10 and 15 kcal/mole,[2] with the most energetically favored path lying between 1-butene and *cis*-2-butene. The top of the energy barrier between *cis*-2-butene and *trans*-2-butene is higher than between 1-butene and *cis*-2-butene by about 1.7 kcal, and its top coincides with that between 1-butene and *trans*-2-butene. It is evident, therefore, that the high selectivities found for isomerization of *cis*-2-butene and *trans*-2-butene are *not* controlled by energetic factors; they must reflect statistical factors, parameters of the catalyst, or olefin geometry.
4. The order of reactivities is 1-butene ≈ *cis*-2-butene > *trans*-2-butene. Again the disproportionately high activity for *cis–trans* isomerization is a salient feature.
5. The reaction rate is inversely related to the surface density of hydroxyl groups,[15] suggesting that the active sites are formed as the alumina is dehydroxylated.
6. Residues do not appear to be a factor; therefore, the active sites may be sought among the possibilities suggested by the model of Peri.[29]
7. There is a large primary isotope effect associated with each reaction, indicating that a C–H or C–D bond is ruptured in the transition state.
8. *cis–trans* isomerization reactions appear to take place intramolecularly, but secondary exchange reactions make it impossible to classify the double-bond migration as either intramolecular or intermolecular.

No model so far advanced will satisfactorily rationalize all these requirements. Moreover, the picture which is developing suggests that different sites and transition states may be operating on the same surface. The classical *sec*-butyl carbonium ion is probably not effecting any of the processes over alumina. The very different behavior from that of silica–alumina, as well as the inverse correlation with catalyst hydrogen content, favors this view.

Gerberich and Hall (see Figure 8d of ref 15) invoked a cyclic intermediate, frozen in the *cis* configuration, to explain the high *cis–trans* ratios found in the isomerization of 1-butene over alumina. It now appears that this was unnecessary. The high selectivity is predicted by the lower activation energy for the formation of *cis*-2-butene. There remains, nevertheless, some merit in these ideas. The model[15] envisioned a butene molecule draped over (or between) surface oxygens, with substrate atoms interacting with the field emanating from aluminum ions imbedded in the surface. Hy-

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[23] P. J. Lucchesi, D. L. Baeder, and P. J. Longwell, *J. Am. Chem. Soc.*, **81**, 3235 (1959).

[24] J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 466 (1948).

[25] S. Bank, A. Schriesheim, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, 87, 3244 (1965).

[26] A. E. Hirschler, *J. Catalysis*, **2**, 428 (1963).

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drogen-atom transfer was envisioned to occur intramolecularly through "solvolysis" in the surface oxide ion. Recently, Pines[31] summarized evidence that alumina acts as an effective solvent in the catalysis of hydrocarbons.

Whereas *n*-butene isomerization over silica–alumina seems to be relatively well understood, the mechanism over alumina continues to be elusive. The true picture probably is a composite of several mechanisms acting on different sites. Whatever mechanisms are considered, however, they must include C–H (or C–D) bond cleavage in the transition state.

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X-Ray-Induced Hydrogen-Atom Addition and Removal in Diethyl Glutaconate–Urea Crystals

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Abstract: X-Ray-produced free radicals in single crystals of the diethyl glutaconate–urea inclusion compound were investigated by esr at room temperature. The two long-lived free radicals are $CH_3CH_2OOC\dot{C}HCH{=}CH\text{-}COOCH_2CH_3$ (I) and $CH_3CH_2OOC\dot{C}HCH_2CH_2COOCH_2CH_3$ (II). Spectra taken shortly after X-irradiation exhibit a remarkably low relative concentration of the allyl-type radical I. Heating experiments demonstrate that radical I is thermally more stable than radical II and that the two radicals decay independently. The relative concentration of radical I at 23° observed after X-irradiation at 77, 273, or 298°K is 20 ± 10%. A table of proton coupling constants is given.

A large number of stable, oriented free radicals have been observed and studied in X- or γ-irradiated organic single crystals.[1–7] Among the chief goals of such studies are the understanding of the interaction of high-energy radiation with organic crystals and the prediction of the structures and stabilities of the resulting free radicals. Molecules containing carboxyl groups are frequently chosen for study because relatively intense and simple esr hyperfine patterns are observed. In many carboxylic acids or esters only one free radical is observed at room temperature. In some compounds this radical is related to its parent molecule simply by the removal of one α-hydrogen atom, and in other compounds it is obtained by the addition of one hydrogen to a position β to the carboxyl group. The purpose of this paper is to report a carboxylic ester in which long-lived radicals of both types are observed simultaneously. From a study of this compound, diethyl glutaconate ($EtOOCCH_2CH{=}CHCOOEt$), the relative concentrations and stabilities of the two general types of free radicals are determined *in the same crystalline lattice*.

Experimental Section

Diethyl glutaconate (Aldrich) was vacuum distilled before use. (However, using the unpurified compound did not result in observable differences in the spectra.) Crystals were grown by adding diethyl glutaconate to a mixture of three parts saturated solution of urea in methanol to one part methanol. This solution was cooled from room temperature to 7° over a period of 1 or 2 days in a 600-ml dewar containing 200 ml of water.

The crystals obtained were rinsed several times in cold methanol. The *z* axis was defined to lie along the needle axis of the hexagonal crystals, and the *xy* plane was perpendicular to the needle axis.

Crystals were irradiated at 77°K or at 0° using a tungsten target X-ray tube operating at 44 kv and 35 ma. The irradiation time was 2 hr. Spectra were taken at room temperature on a standard Varian V4502 9.5 kMc/sec esr spectrometer. The scan rate was calibrated with peroxylamine disulfonate (Aldrich), assuming an over-all splitting of 26.0 gauss. A dual cavity, with the Varian strong pitch sample as a reference, was utilized for intensity measurements.[8]

Results and Discussion

Typical esr spectra of a diethyl glutaconate–urea crystal after X-irradiation at 77°K are shown in Figure 1. Spectrum 1a in the upper left-hand corner of Figure 1 was recorded with the magnetic field parallel to the *xy* plane immediately after the crystal was warmed to room temperature. Spectra obtained several hours later at room temperature were very nearly the same as the 1a spectrum. After heat treatment, however, a

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