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NOTE

Tracer Studies of Acid-Catalyzed Reactions

II. The Isomerization of 1-Butene over Silica-Alumina and Alumina Catalysts

Several workers (*1*, *2*) have suggested that the double bond isomerization of olefins occurs via a carbonium ion formed by proton addition to a carbon atom adjacent to the double bond. Supposedly, the proton is furnished by the catalyst; release of a proton from another carbon atom yields the isomer. Turkevich and Smith (*3*) studied the isomerization of 1-butene in tritiated phosphoric acid and concluded that isomerization and exchange with the catalyst occurred in the same step; they proposed a concerted "hydrogen-switch" mechanism. Others have found it necessary to invoke more complicated mechanisms to account for the much higher than equilibrium *cis/trans* butene-2 ratios in the initial products. Haag and Pines (*4*) suggested a secondary butyl carbonium ion as the intermediate, but noted that elimination of the proton must occur after rearrangement to a π complex. Brouwer (*5*) proposed that *cis–trans* isomerization of 2-butene proceeds through a carbonium ion, but that double bond isomerization takes place through the concerted "hydrogen-switch" process (*3*). Most recently, Leftin and Hermana (*6*) presented data favoring a hydride-shift mechanism involving an allylic carbonium ion intermediate.

When an exhaustively deuterated catalyst is contacted with 1-butene, all of the aforementioned mechanisms, except that of Leftin and Hermana (*6*), predict that the initial 2-butene products should contain one deuterium atom per molecule. We have employed the microcatalytic technique to investigate this reaction and have been able to set upper limits for the concentration of active protons on silica-alumina and alumina. In the course of this work, Ozaki and Kimura (*7*) published the results of their investigation of the reaction in a static reactor over catalysts soaked in D_2O and evacuated at various temperatures. When silica-alumina was evacuated below 100°, a large fraction of the product 2-butene was monodeuterated. The larger deuterium concentrations in the 2-butenes decreased with rise in evacuation temperature, falling to a negligible value for evacuation at 500°. Our results confirm and extend their work to a quantitative basis. Ozaki and Kimura concluded that the isomerization over silica-alumina proceeds through a protonic mechanism involving a surface Bronsted acid (at low evacuation temperature) or the surface carbonium ions formed by adsorption of olefins on Lewis acid sites, acting as proton donors (at high evacuation temperature). They noted that this conclusion was open to question over alumina.

Houdry M-46 silica-alumina (SA), 260 m^2/g, 1.29 g, was used; the alumina (A), 150 m^2/g, 1.00 g, was a very pure material prepared from aluminum isopropoxide. The samples were exhaustively deuterated by repeated exchange with deuterium gas before treatment with oxygen and overnight evacuation, all at 525°. In one instance, a sample of alumina was dehydrated at 900° by a special procedure which caused only a 15% loss in surface area. Slugs of 1-butene, ranging from 2.9 to 9.9 cc(NTP), were swept over the catalyst in a stream of helium (31 cc/min). The butenes were separated by gas chromatography, individually collected, and analyzed for deuterium content by mass spectrometry. In all but one experiment the amount of 1-butene in each slug was considerably less than the deuteroxyl content (compare columns 3 and 6 of Table 1); hence, detection of deuterium in the reacted butene would be easy, provided all the deuterium on the catalyst were protonic.

TABLE 1

DEUTERIUM EXCHANGE REACTIONS OF BUTENE ON SILICA-ALUMINA AND ALUMINA

Catalyst and temperature of pretreatment	Reaction temperature (°C)	Slug size, (molecules/cm^2 × 10^{-13})	Number of slugs	Initial conversion, (%)	Initial –OD[b] concentration, (No./cm^2 × 10^{-14})	Maximum –OD exchanged, (No./cm^2 × 10^{-11})	$\frac{2\text{-}C_4H_7D}{2\text{-}C_4H_8}$
SA-525	25	2.5	7	96	1.2	1	0.002
SA-525	22	7.9	3	>96	1.2	3	0.003
A-525	50	14	3	26	2.7	35	0.033
A-900	15	5.2	3	79	<0.1	1	0.002
SA-525[a]	27	3.9	3	94	1.2	—	0.30

[a] Each slug also contained 4.0 × 10^{13} molecules of propylene-d_6/cm^2.

[b] Hall, W. K., Lutinski, F. E., and Gerberich, H. R., *J. Catalysis* **3,** 512 (1964).

The results of several experiments are summarized in Table 1. In the first example, 3.1 cc(NTP) slugs were passed over SA. All the first slug and portions of all succeeding ones were retained by the catalyst. Consequently, the data for this experiment had to be calculated from the second slug. In the other experiments, the slug was of sufficient size that the butene recovered in the first slug could be analyzed accurately. The total olefin retained by the catalyst was substantial, amounting to about 1 × 10^{14} molecules/cm^2 for SA and 5 × 10^{13} molecules/cm^2 for A.

In the experiments with deuterated SA, the initial conversion of 1-butene to 2-butene was 96%. The monodeuterated species appearing in the 2-butene amounted to 0.2–0.3% (last column); this was about the limit of accuracy of the mass spectral analyses. A similar percentage was found in the recovered 1-butene. Using this limit and assuming that the material lost to the catalyst had the same deuterium content as that recovered, one can calculate that the maximum number of deuteroxyl groups exchanged with the initial butene was 1–3 × 10^{11}/cm^2. This almost negligible amount of exchange indicates that 1-butene isomerizes either by a mechanism involving nonprotonic sites or by one involving repeated use of a very small number of Bronsted sites, i.e., 1–3 × 10^{11}/cm^2. This concentration is much less than current estimates of Bronsted (*8*) or Lewis (*9*) acidity and even less than the upper limit of 1 × 10^{12}/cm^2 estimated in a similar tracer study with cyclopropane (*10*). Furthermore, it is only a fraction of the concentration of Lewis sites determined by Leftin (*6*) (9.1 × 10^{12}/cm^2) for the isomerization of 1-butene and of alpha sites measured by Peri (*11*) (5 × 10^{12}/cm^2) for the polymerization of 1-butene.

It may be objected that the catalyst deuterium has been diluted by exchange with the irreversibly adsorbed butene (part of which may be polymer). If the most pessimistic assumption is made, i.e., that the total butene lost from the mass balance has randomized its hydrogen with the catalyst D, then 8 × 1 × 10^{14} H/cm^2 would mix with 1.2 × 10^{14} D/cm^2 to yield an over-all concentration of over 10% D. In this case, the initial butene-2 product should contain at least 10% C_4H_7D, so that this possibility may also be rejected. If only a small portion of the catalyst hydrogen is exchangeable, however, our observations would be satisfied. For example, if the 8 × 10^{14}/cm^2 butene H randomized with 5 × 10^{12}/cm^2 catalyst D, about 0.6% C_4H_7D would be expected in the initial product. Thus, the only possible conclusion is that if a Bronsted acid is present, its concentration cannot exceed that of the Lewis acid (*9*). The data are also consistent with the idea (*7*) that olefin adsorbs on Lewis sites, forming carbonium ions which act as proton donors.

With alumina dehydrated at 525°, the proportion of monodeuterated 2-butene was 3.3% initially, but this rapidly decreased to 1.5% by the third slug. The 1-butene was also exchanged to the extent of 2% in the first slug and 0.5% in the third slug. From these data, it was calculated that the maximum number of initially exchanged deuteroxyl groups was $3.5 \times 10^{12}/\text{cm}^2$. When a sample of alumina was dehydrated at 900° (A-900), its activity increased. Hence, a tracer experiment was conducted at a lower reaction temperature (15° vs. 50°), and yet the conversion was greater (79% vs. 26%). At the same time, the pretreatment brought about a decrease in the deuteroxyl concentration by a factor of 27. The fraction of exchanged butene on A-900 was only 0.2%; this gives a maximum concentration of protonic sites equal to $1 \times 10^{11}/\text{cm}^2$ as with SA. On the same catalyst used here (A-525), we have established (*12*) that there are about 3×10^{12} sites/cm² after dehydration at 525° which can be identified with the alpha sites studied by Peri (*11, 13*). Since the rate of 1-butene isomerization is faster after dehydration at 900° than that at 525°, it can be concluded that there are at least $3 \times 10^{12}/\text{cm}^2$ active sites on A-900. Thus, if this is the lower limit of active sites and no more than 1×10^{11} "protons"/cm² are present, it may be inferred that only a few per cent of the active sites could be protonic. These results confirm some earlier observations by Peri (*13*). Using an infrared absorption technique, he investigated the reaction of 1-butene with deuteroxyl groups on alumina (dehydrated at 800°). After a relatively long reaction time, the number of isomerized butene molecules was found to be 250 times the number of exchanged deuteroxyl groups. From his data, we calculated that the number of exchanged deuteroxyls was $2.5 \times 10^{12}/\text{cm}^2$. This concentration lies between the values of $3.5 \times 10^{12}/\text{cm}^2$ and $1 \times 10^{11}/\text{cm}^2$ for A-525 and A-900, respectively, found in the present study. This evidence suggests that a slow exchange occurs which is not essential to the isomerization mechanism. A forthcoming paper (*14*) provides additional evidence that the sites responsible for butene isomerization on alumina are aprotic. This kinetic evidence suggests that an intramolecular 3–1 hydrogen transfer occurs.

When a 1:1 mixture of 1-butene and propylene-d_6 was passed over unexchanged SA, extensive isotopic mixing occurred; the composition of 2-butenes from the first slug was 66% d_0, 30% d_1, and 4% d_2. This was at least 100 times that which occurs with deuteroxyl groups. In addition to the mixing in 2-butene, 20% of the 1-butene was monodeuterated and 3% dideuterated; 5% of the propylene was C_3D_5H. The extent of mixing decreased with slug number. Since propylene was exchanged to a smaller extent than butene, it is evident that some propylene was not returned to the gas phase. The amount retained by the catalyst was about $4 \times 10^{13}/\text{cm}^2$. These data are consistent with a hydride transfer mechanism involving allylic carbonium ions and with the picture of Ozaki and Kimura.

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REFERENCES

1. THOMAS, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949).
2. OBLAD, A. G., MESSENGER, J. U., AND BROWN, J. N., *Ind. Eng. Chem.* **39,** 1462 (1947).
3. TURKEVICH, J., AND SMITH, R. K., *J. Chem. Phys.* **16,** 466 (1948).
4. HAAG, W. O., AND PINES, H., *J. Am. Chem. Soc.* **82,** 2488 (1960).
5. BROUWER, D. M., *J. Catalysis* **1,** 22 (1962).
6. LEFTIN, H. P., AND HERMANA, E., *Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* Paper No. I-70.
7. OZAKI, A., AND KIMURA, K., *J. Catalysis* **3,** 395 (1964).
8. HIRSCHLER, A. E., *J. Catalysis* **2,** 428 (1963); HIRSCHLER, A. E., AND HUDSON, J. O., *ibid.* 3, 329 (1964).
9. LEFTIN, H. P., AND HALL, W. K., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960* **1,** 1353 (Editions Technip, Paris, 1961).

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

11. Peri, J. B., *Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* Paper No. I-72.

12. Larson, J. G., and Hall, W. K., *Preprints, Petroleum Division, Am. Chem. Soc.* **10**, September 1965.

13. Peri, J. B., *Actes Congr. Intern. Catalyse, 2^e, Paris, 1960* **1**, 1333 (Editions Technip, Paris, 1961).

14. Gerberich, H. R., and Hall, W. K., *J. Catalysis,* to be published.

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