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Isomerization of Butenes over Aluminum Phosphate Catalyst

The mechanism of butene isomerization has been extensively studied over various metal oxide catalysts and detailed mechanisms are clarified for certain catalysts such as SiO_2–Al_2O_3 (*1*), ZnO (*2, 3*), and Al_2O_3 (*1, 3*). A unique characteristic of aluminum phosphate catalyst for *cis*-2-butene isomerization is to produce exclusively *trans*-2-butene with negligible occurrence of double bond migration to 1-butene when aluminum phosphate is outgassed above 600°C. One of the authors (H.H.) supposed, on the basis of the result of coisomerization of *cis*-2-butene-d_0/d_8, that the reaction on aluminum phosphate catalyst involves abstraction of an H^- from the olefinic position (*4*). Usage of *cis*-2-butene-d_8, however, is not able to distinguish an olefinic C–H bond breaking from an allylic one. In recent years, Guisnet *et al.* (*5, 6*) found out by use of selectively deuterated *cis*-2-butene as a reactant that selective *cis–trans* isomerization of butenes over Na-exchanged Al_2O_3 involves an allylic C–bond breaking. They proposed a concerted mechanism in which acidic and basic sites participate. Usage of selectively deuterated butene has many advantages in elucidation of the reaction mechanisms. Lombardo *et al.* (*3*) used deuterated butenes to clarify the mechanisms of butene isomerization over ZnO and Al_2O_3, and proposed that a π-allylic carbanion is operating as one of the intermediates on both catalysts. In the present study, we used the selectively deuterated *cis*-2-butene-2,3-d_2 to understand the reaction mechanism of *cis–trans* isomerization over aluminum phosphate.

The aluminum phosphate catalyst was prepared from an aqueous solution containing an equal amount of $Al(NO_3)_3$ and H_3PO_4. To the solution, 10% NH_4OH_{aq} was added as a precipitant until the pH of the supernatant became 7.0. The precipitate was filtered, washed with deionized water, and dried at 120°C for 20 hr in air. Prior to the reaction, aluminum phosphate was calcined at 300°C for 3 hr followed by outgassing at 750°C for 3 hr.

Perdeuterated *cis*-2-butene was prepared by repeated exchange of butenes with D_2 over an MgO catalyst (*7*). *cis*-2-Butene-2,3-d_2 was prepared by deuteration of dimethylacetylene over Pd/Al_2O_3 (*8*).

Coisomerization of *cis*-2-butene-d_0/d_8, *cis*-2-butene-d_0/d_2, and *cis*-2-butene-d_2/d_8 was carried out at 23°C in a microcatalytic pulse reactor with 19 μmol of reactant and 0.1 or 0.2 g of catalyst. Different conversion levels were obtained by varying both the amount of catalyst and the flow rate of helium carrier. Products were separated by a gas chromatographic column and collected in a liquid nitrogen trap. Each collected product was subjected to mass spectrometric analysis.

Selected isotopic distributions are given in Table 1. The isotopic distributions for the products were essentially the same as those for the reactants in all cases. This indicates that the *cis–trans* isomerization involves an intramolecular hydrogen transfer, which coincides with the previous observation for the $AlPO_4$ catalyst activated at 600°C (*4*).

To obtain an isotope effect in the coisomerization of *cis*-2-butene-d_0/d_8, the *trans*-2-butene-d_0/*trans*-2-butene-d_8 ratio was normalized by being divided by the *cis*-2-butene-d_0/*cis*-2-butene-d_8 ratio in the reactant; the ratio was plotted against conversion in Fig. 1. The normalization was also done for the coisomerization of *cis*-2-butene-2,3-d_2/d_8 and of *cis*-2-butene-d_0/2,3-d_2, and the normalized ratios are plotted in Fig. 1.

As seen from the intercepts in Fig. 1, a kinetic isotope effect (about 2.5) was observed in the coisomerization of *cis*-2-

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TABLE 1

Selected Isotopic Distributions in Coisomerizations of *cis*-2-Butene-2,3-d_2/d_8, *cis*-2-Butene-d_0/2,3-d_2, and *cis*-2-Butene-d_0/d_8

Reactant	Product	Percentage each product	Percentage each isotopic species								
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
cis-2-Butene-2,3-d_2/d_8	*cis*-2-Butene[a]		2.0	9.7	32.3	2.9	0.6	0.3	2.1	6.1	44.0
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	6.2	2.9	15.4	46.4	4.0	0.7	0.3	1.5	4.3	24.3
	cis-2-Butene	93.8	1.7	8.9	30.6	2.8	0.6	0.3	2.3	6.3	46.4
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	27.4	3.1	14.3	47.2	4.2	0.7	0.4	1.6	4.4	24.1
	cis-2-Butene	72.6	1.7	8.7	29.7	2.7	0.7	0.4	2.4	6.3	47.4
cis-2-Butene-d_0/2,3-d_2	*cis*-2-Butene[a]		51.3	9.2	36.9	1.8	0.5	0.2	0	0	0
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	19.7	50.5	11.2	35.9	1.7	0.5	0.1	0	0	0
	cis-2-Butene	80.3	50.9	10.1	36.5	1.8	0.5	0.2	0.1	0	0
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	35.8	51.8	9.7	36.3	1.7	0.4	0.1	0	0	0
	cis-2-Butene	64.2	51.2	9.5	36.9	1.8	0.4	0.1	0	0	0
cis-2-Butene-d_0/d_8	*cis*-2-Butene[a]		49.1	0.1	0	0	0	0	0.7	6.1	44.0
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	6.6	69.5	0.8	0	0	0	0	0.5	4.6	24.6
	cis-2-Butene	93.4	50.2	0.2	0	0	0	0	0.6	5.9	43.0
	1-Butene	0	—	—	—	—	—	—	—	—	—
	trans-2-Butene	29.5	68.5	0.6	0	0	0	0	0.4	4.8	25.6
	cis-2-Butene	70.5	41.8	0.3	0	0	0	0	0.8	6.8	50.3

[a] Reactant.

butene-d_0/d_8 and *cis*-2-butene-2,3-d_2/d_8, whereas no isotope effect was appreciable in the coisomerization of *cis*-2-butene-d_0/2,3-d_2. These results strongly suggest that allylic C–H bond breaking is involved in the *cis–trans* isomerization; apparently olefinic C–H bond breaking is not involved in the reaction.

These results on the $AlPO_4$ catalyst are similar to those obtained on Na-Al_2O_3 (*5*, *6*) in the sense that only *cis–trans* isomerization without intermolecular H exchange takes place, and that an isotope effect is observed when the reactant has been exchanged with D at an allylic position. The activity and the selectivity to *trans*-2-butene, however, are much higher for the $AlPO_4$ than for Na-Al_2O_3. Guisnet *et al.* (*6*) proposed that the *cis/trans* isomerization on Na-Al_2O_3 occurs in a concerted way; the removal of an allylic proton by the oxide ion takes place with concomitant formation of a σ-bond between the butene molecule and the aluminum ion. Lombardo *et al.* (*3*) reported that the *cis–trans* isomerization without H exchange occurs even on a pure Al_2O_3, and that, similar to the case of ZnO, a π-allyl intermediate with carbanion character is operating in the reaction.

On the pure Al_2O_3, however, double bond migration also occurs.

Guisnet *et al.* (*6*) and Lombardo *et al.* (*3*) both agree that an H^+ is abstracted from the terminal carbon atom by basic sites. In the case of $AlPO_4$, too, it may be possible that the reaction involves an abstraction of an H^+ from the terminal carbon atom. The surface properties of $AlPO_4$ have been investigated by Peri (*9*). He suggests that $AlPO_4$ has strong acid sites, but the surface oxy-

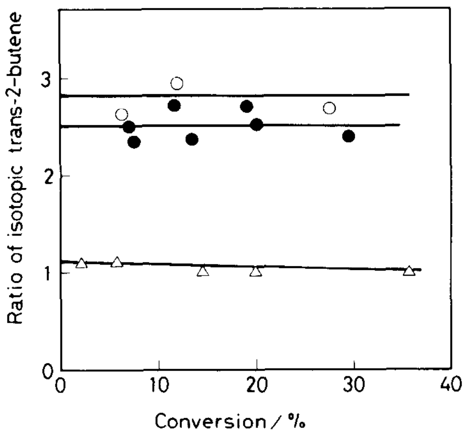
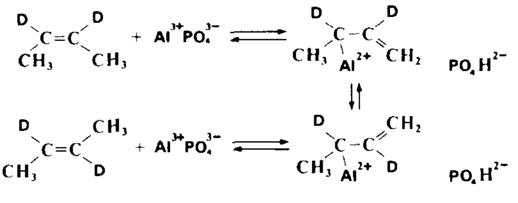


FIG. 1. The normalized ratio of isotopic butenes in coisomerization. ○, (*trans*-2-butene-d_2/*trans*-2-butene-d_8)/(*cis*-2-butene-d_2/*cis*-2-butene-d_8)$_0$ in the coisomerization of *cis*-2-butene-2,3-d_2/d_8. ●, (*trans*-2-butene-d_0/*trans*-2-butene-d_8)/(*cis*-2-butene-d_0/*cis*-2-butene-d_8)$_0$ in the coisomerization of *cis*-2-butene-d_0/d_8. △, (*trans*-2-butene-d_0/*trans*-2-butene-d_2)/(*cis*-2-butene-d_0/*cis*-2-butene-d_2)$_0$ in the coisomerization of *cis*-2-butene-d_0/2,3-d_2.

gen atoms of $AlPO_4$ are not as strong as a Lewis base and weaker than those of Al_2O_3. It could be assumed that a pair of strong acidic and weak basic sites favors *cis*–*trans* isomerization without double bond migration. A weak basic site may be able to abstract an allylic H^+ only with assistance from a strong acidic site to interact with carbon atom 3. As a result, the anion that strongly interacts with the acidic site at carbon atom 3 will be formed. The attack of H^+ at the carbon atom 3 would result in production of 1-butene. However, a strong interaction between the acidic site and carbon atom 3 would not allow an H^+ to attack the carbon atom 3. Therefore, only *cis*–*trans* isomerization occurs. The reaction scheme could be drawn as follows:



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