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NOTES

Catalytic Isomerization of Ethylenic Hydrocarbons

XI. Isotope Effects in the Isomerization of Butenes Labeled in the Allylic and Vinylic Positions Over Alumina and Silica–Alumina

Various mechanisms have been put forward to account for the isomerization of ethylenic hydrocarbons over acid catalysts (*1–4*). After a number of investigations, the carbonium ion theory proposed by Whitmore (*1*), i.e., the addition of a proton to the olefin followed by the abstraction of another one from the carbonium ion to get an isomeric olefin seems to be the least questionable (*11, 12, 14, 15*).

Haag and Pines (*5*) have introduced π-complexes to explain the stereo-selectivity obtained in 1-butene isomerization. This kinetic scheme accounts for the structural effects we noted in the isomerization of a series of olefins over γ-alumina (*13*).

However, the changes in selectivity of acid catalysts according to pretreatment, water content, poisoning and temperature (*6–10, 16*) led a number of workers to postulate different mechanisms for *cis–trans* isomerization and double-bond migration. According to Brouwer (*6*) the double-bond shift occurs mainly through a concerted reaction while *cis–trans* isomerization takes place through a classical carbonium ion process.

An important and exhaustive study of isomerization of olefins over alumina and silica–alumina (*8–12*) has been reported by Gerberich, Larson and Hall (*8, 9*) and Hightower and Hall (*10–12*). From their kinetic data and carbon-14 and deuterium labeling experiments, they finally came to the conclusion that over silica–alumina all reactions occur on induced protonic sites in a residue as suggested by Ozaki and Kimura (*7*). On the other hand, over alumina, the carbonium ion mechanism cannot account for the data obtained and it seems that different intermediates are likely to be involved in the course of *cis–trans* isomerization and double-bond shift.

This assumption, which does not agree with our own results, led us to undertake a new investigation of acid catalysts with a view to clarifying the role of each kind of hydrogen in a molecule of *cis*-butene. To this end we prepared the *cis*-butenes selectivity labeled with deuterium in the vinylic(II) and allylic(III) positions. We will report here the isotope effects observed in double-bond shift and *cis–trans* isomerization of those hydrocarbons over alumina and silica–alumina.

2,3-d_2-*cis*-2-butene(II) was prepared with an isotopic purity of up to 99% by the following procedure:

$$\mathrm{CH_3{-}CO{-}CO{-}CH_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiAlD_4}} \mathrm{CH_3{-}CDOH{-}CDOH{-}CH_3} \xrightarrow[\mathrm{H^+(17)}]{\mathrm{HC(OC_2H_5)_3}} \mathrm{CH_3{-}CD{=}CD{-}CH_3}\ \mathrm{(II)}.$$

1,4-d_6-*cis*-2-butene (5.4 D/mole) was obtained in a similar way from previously exchanged butanedione:

$$\mathrm{CD_3{-}CO{-}CO{-}CD_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{LiAlH_4}} \mathrm{CD_3{-}CHOH{-}CHOH{-}CD_3} \xrightarrow[\mathrm{H^+(17)}]{\mathrm{HC(OC_2H_5)_3}} \mathrm{CD_3{-}CH{=}CH{-}CD_3}\ \mathrm{(III)}.$$

The allylic or vinylic positions of the deuterium atoms in the molecules prepared were assessed from the NMR spectra of the corresponding dibromides.

The isomerization of the light (I), d_2(II) and d_6(III) *cis*-2-butenes was carried out in a microcatalytic pulse reactor in the presence of 3-methyl-1-butene over the previously studied alumina (*13*) at 250°C and over Ketjen silica–alumina (13% Al_2O_3) at 85°C. The alumina was preheated at 500°C in a hydrogen flow for 12 hr, then in a nitrogen flow overnight just before use. The silica–alumina was preheated at 400°C in a nitrogen flow overnight before use. The isomerization conditions for the three *cis*-butenes were exactly identical; the carrier gas flow was 3 to 12 liters/hr, the quantity of butene in the mixture of *cis*-2-butene and 3-methyl-1-butene was 1/4 over alumina and 2/1 over silica–alumina, and the quantity of reactant admitted in each slug was 1 cc.

The percentages of the produced 1-butene (Figs. 1 and 2) and *trans*-2-butene (Figs. 3 and 4) are plotted against the converted 3-methyl-1-butene. The ratio of the slopes of the curves near zero conversion leads directly to the values of the isotope effects reported in Table 1.

a. Double-Bond Migration

It may be seen from Figs. 1 and 2 that deuterium atoms initially in the vinylic position do not introduce any isotope effect for double-bond shift. However, the presence of deuterium in the allylic position in the reacting *cis*-butene leads to a marked lowering of 1-butene yield.

The isotope effect shows clearly that over alumina and silica–alumina double-bond migration involves an allylic carbon–hydrogen bond cleavage in a rate-determining step. This agrees with most of the mechanisms proposed until now and especially with the classical carbonium ion mechanism.

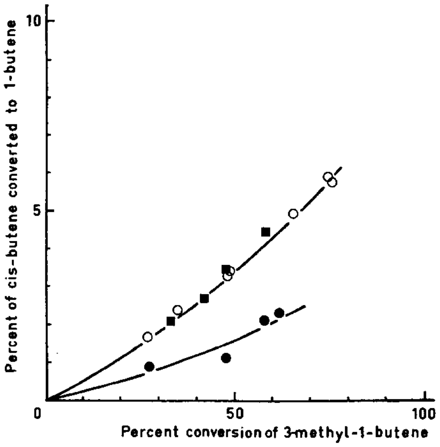

Fig. 2. 1-Butene yield in the isomerization of *cis*-butenes in the presence of 3-methyl-1-butene over silica–alumina (10 mg) at 85°C; (○) d_0-*cis*-2-butene(I); (■) 2,3-d_2-*cis*-2-butene(II); (●) 1,4-d_6-*cis*-2-butene(III).

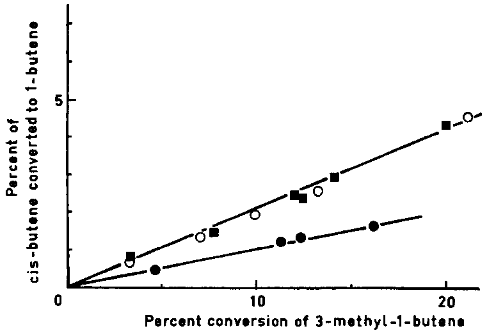

Fig. 1. 1-Butene yield in the isomerization of *cis*-butenes in the presence of 3-methyl-1-butene over alumina (300 mg) at 250°C; (○) d_0-*cis*-2-butene(I); (■) 2,3-d_2-*cis*-2-butene(II); (●) 1,4-d_6-*cis*-2-butene(III).

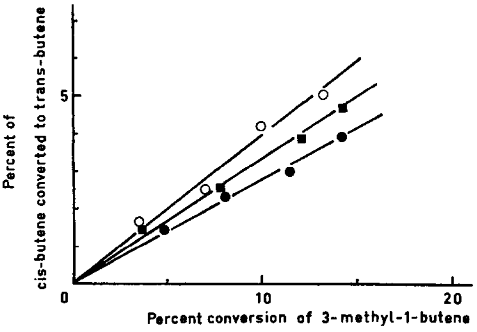

Fig. 3. *Trans*-Butene yield in the isomerization of *cis*-butenes in the presence of 3-methyl-1-butene over alumina (300 mg) at 250°C; (○) d_0-*cis*-2-butene(I); (■) 2,3-d_2-*cis*-2-butene(II); (●) 1,4-d_6-*cis*-2-butene(III).

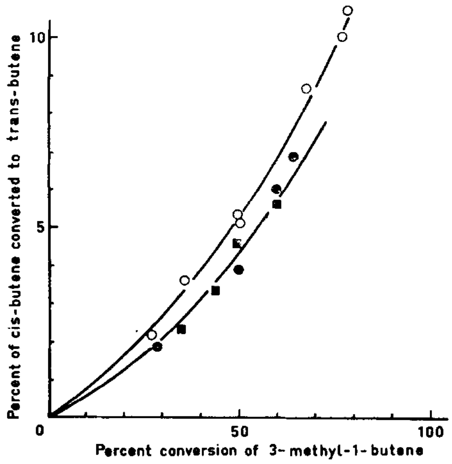

FIG. 4. *Trans*-Butene yield in the isomerization of *cis*-butenes in the presence of 3-methyl-1-butene over silica–alumina (10 mg) at 85°C; (○) d_0-*cis*-2-butene(I); (■) 2,3-d_2-*cis*-2-butene(II); (●) 1,4-d_6-*cis*-2-butene(III).

b. *cis–trans* ISOMERIZATION

The observed isotope effects are much smaller than for the double-bond shift. Nevertheless, the presence of deuterium in either of the two positions lowers the *trans*-butene yield (Figs. 3 and 4).

The carbonium ion mechanism does not account correctly for this observation since, according to it, allylic hydrogen atoms do not play any part in *cis–trans* reaction. Moreover, the relative weakness of the effects noted here seems to show that C–H bond breaking does not have the same importance in that reaction as in the double-bond shift. A similar conclusion was drawn by Shannon, Lake and Kemball over titanium oxide (*18*).

TABLE 1
ISOTOPE EFFECTS IN *cis*-2-BUTENE ISOMERIZATION

Isotope effects in:	Double-bond shift		*cis–trans* isomerization	
cis-2-Butene:	d_2(II)	d_6(III)	d_2(II)	d_6(III)
SiO_2–Al_2O_3 85°C	1.0	2.9	1.3	1.3
Al_2O_3 250°C	1.0	2.0	1.2	1.4

In conclusion, the isotope effects observed in the isomerization of deuterated butenes are qualitatively the same over alumina as they are over silica–alumina. As for the reacting molecule, the mechanisms should therefore be basically similar with both catalysts. Unless it could be demonstrated that various intermediates could lead to identical isotope effects, our results tend to favor the assumption that reaction intermediates are the same on alumina and silica–alumina. For the latter catalysts, the following intermediates have been proposed up to now: carbonium ions with or without π-complexes (*1*, *5*), the butenyl carbonium ion proposed by Leftin and Hermana (*4*), allylic carbanions (*19*) and various intermediates which allow intramolecular or concerted hydrogen transfer (*2*, *6*, *9*). A carbonium ion mechanism is very likely to occur over silica–alumina (*7*, *12*) where olefins are generally supposed to react on protonic sites. As mentioned above, the isotope effects observed for double-bond migration are in agreement with this hypothesis not only as far as silica–alumina is concerned but also for alumina. Thus it may be supposed that over the latter catalyst isomerization also goes through carbonium ions. This might seem abnormal because of the low Brønsted acidity of alumina. However, it should be stressed that the activity of the alumina studied here is approximately 10^3 times lower than that of the silica–alumina: our experiments were carried out at 250°C for alumina and 85°C for silica–alumina. It is therefore possible to explain both the large difference in activity and the equality of isotope effects by assuming that in both cases the isomerization of the butenes takes place on Brønsted sites.

However, the carbonium ion mechanism does not account for the fact that allylic deuterium brings about an isotope effect in *cis–trans* isomerization. We are of the opinion that the intervention of any of the above species cannot explain this result unless it arises from secondary isotope effects that could be particularly important due to the six deuterium atoms in the molecule. Nevertheless, it seems difficult to assume that these should be of the same magnitude as the primary isotope effects due to vinylic deuterium.

The problem of the mechanism of double-bond shift and of *cis–trans* isomerization still remains open to question. Mass spectral analysis of the products is in progress and we hope it will cast more light on the subject.

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