Catalyst Isotope Effect in *n*-Butene Isomerization Catalyzed by Metal Sulfates

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We have reported that rate and selectivity increase monotonously with the acid strength of catalyst in the isomerization of *n*-butene catalyzed by metal sulfates.[1] The results were explained on the basis of the relative rate of proton transfer between catalyst and butene. If the proton transfer is involved in the reaction, it would be expected that (i) over deuterated catalysts, deuterium atoms are incorporated preferentially into the isomerized butenes, and (ii) isomerization proceeds more slowly over deuterated catalysts than normal catalysts (catalyst isotope effect). Preferential deuteration (i) was reported by Ozaki and Kimura for some solid acids.[2] However, catalyst isotope effect (ii) does not seem to have been reported in solid-acid catalysis so far, although it was reported that perdeuterobutene reacted 1.3—1.8 times more slowly than normal butene over silica-alumina.[3]

We observed catalyst isotope effect (ii), in addition to preferential deuterium incorporation (i), in the case of butene isomerization catalyzed by aluminum and magnesium sulfates supported on silica gel (Al-S and Mg-S). The extent of consumption of catalytically active deuteron on the catalyst surface could be examined by the measurement of the deuterium content of butenes.

Reaction apparatus was a closed circulating system (124 cc) connected to a conventional vacuum-line. Catalysts were first evacuated for 1 hr at 100°C in the system and then equilibrated three times with H_2O or D_2O vapor at 70°C. Further equilibration had no effect on the reaction. A catalyst pre-equilibrated with H_2O is denoted by H-catalyst and that with D_2O by D-catalyst. They were evacuated for 1 hr at 70°C, prior to reaction. Reaction temperature was 60 ± 0.5°C. Butene pressure was 10—15 cmHg. Repeated runs on the same catalyst after the same treatment gave sufficiently reproducible results for Mg-S ($\pm 3\%$) and for Al-S ($\pm 10\%$). The rate obviously decreased upon deuteration of Mg-S and the original activity was recovered by re-equilibration with H_2O. The change was much smaller for Al-S. The ratio of the conversion of *cis*-2-butene over H-Mg-S to that over D-Mg-S at the same reaction time is plotted against the latter in Fig. 1. Extrapolation of this ratio to zero conversion gives an isotope effect of 1.7 ± 0.2. A similar effect was also observed for 1-butene isomerization. The rapid decrease in ratio during the course of the reaction may be due to the substitution of deuteron by a more active proton. A slower decrease observed in an experiment with low butene pressure is in accord with this view. The ratio of two isomerized products from *cis*-2-butene (*trans*/1) was 10% lower over D-catalyst (D-Mg-S and D-Al-S), probably reflecting a secondary isotope effect. There was little change in *cis*/*trans* ratio from 1-butene upon deuteration of the catalyst.

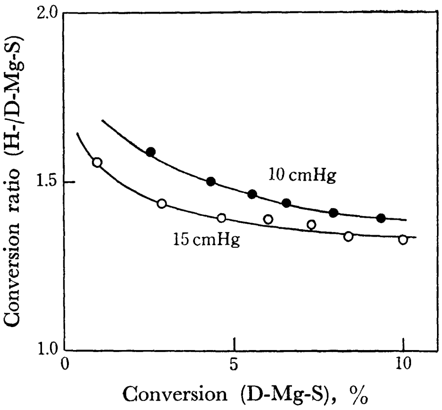

Fig. 1. The ratio of conversion of *cis*-2-butene over normal magnesium sulfate supported on silica gel (H-Mg-S) to that over deuterated magnesium sulfate (D-Mg-S) at 60°C. Butene pressure: 10 cmHg (●), 15 cmHg (○)

Table 1. Composition of products in the isomerization of *cis*-2-butene over deuterated Mg-S and Al-S at 60°C

		Composition (%)	Isotopic composition (%)[a] d_0	Isotopic composition (%)[a] d_1
Mg-S	1-	0.9	38	62
	trans-	0.6	44	56
	cis-	98.5	99.5	0.5
Al-S	1-	3.6	39	61
	trans-	11.9	46	54
	cis-	84.5	91	9

a) Multi-deuterated species observed in small amounts were neglected.

The results of mass spectrometric analysis of the products are given in Table 1. Preferential incorporation of deuterium atoms into isomerized products was obvious. The results show that proton transfer was involved in the reaction and that it was the origin of the observed isotope effect. The fractions of the deuterated products are shown to be only 50—60% and should be compared with the rapid decrease of the conversion ratio in Fig. 1. If the energy profile of the reaction is considered,[4] the observed isotope effect may be regarded as that in the step of proton addition to butene. The reason for the weak effect with a strong acid such as Al-S is now under investigation.

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[1] M. Misono, Y. Saito, and Y Yoneda, *J. Catal.*, **9**, 135 (1967); **10**, 88 (1968); M. Misono and Y. Yoneda, This Bulletin, **44**, 3236 (1971).

[2] A. Ozaki and K. Kimura, *J. Catal.*, **3**, 395 (1964).

[3] J. W. Hightower and W. K. Hall, *J. Amer. Chem. Soc.*, **89**, 778 (1967).

[4] M. Misono and Y. Yoneda, *Shokubai*, **13**, 22P (1971); *J. Phys. Chem.*, in press.