Studies of the Mechanism of the Isomerization of *n*-Butene over *p*-Toluene Sulfonic Acid by Means of Microwave Spectroscopy

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Recently the microwave spectra of 1-butene, *cis*-2-butene and their deuterated species were successfully assigned. This presented a new powerful tool for studying the isomerization of butene, both *cis-trans* and double-bond migration over solid acids.

The monodeuterated species of 1-butene are designated as 1-d_1 ($CHD{=}CHCH_2CH_3$), 2-d_1 ($CH_2{=}CDCH_2CH_3$), 3-d_1 ($CH_2{=}CHCHDCH_3$), and 4-d_1 ($CH_2{=}CHCH_2CH_2D$), each of them giving different rotational spectra. As for *cis*-2-butene, however, there exist only two different monodeuterated species: 1-d_1 ($CH_2DCH{=}CHCH_3$) and 2-d_1 ($CH_3CD{=}CHCH_3$). The amounts and distribution of deuterium among each of the 1-butenes could be determined by measuring the relative intensities of the neighboring peaks of the species. In the case of *cis*-2-butene mass spectroscopy was also employed to determine the deuterium concentration, but the deuterium distribution or the relative amounts of 1-d_1 and 2-d_1 species could be determined only by means of microwave spectroscopy.

The isomerization of butene was carried out over *p*-toluene sulfonic acid (PTS) deposited on an equal amount of silica gel to get a greater surface area. The *p*-toluene sulfonic acid was pretreated with an amount of pure D_2O (99.8% or above) sufficient to deuterate its proton, and then it was evacuated at 50°C for 5 hr. This procedure was repeated three times to assure the complete deuteration of the PTS.

trans-2-Butene was isomerized over the deuterated PTS at room temperature for the purpose of studying both *cis-trans* isomerization and double-bond migration simultaneously.

The gas-chromatographic technique was employed to analyze the reaction mixture, and 1-butene and *cis*-2-butene were separated for microwave spectroscopic measurements in order to study the deuterium content and distribution. The results are summarized in the following tables.

The striking features of these results are as follows:

1) The amounts of the d_0 and 2-d_1 species of the *cis*-2-butene isomerized from *trans*-2-butene were approximately equal at the initial stage of the reaction. As the reaction proceeded, however, the 2-d_1 species predominated over the d_0 species, and the d_2 species, which was not detected at the initial stage, became appreciable, though its amount was not considerable at any time during the reaction.

2) The only 1-butene produced by the double-bond migration from *trans*-2-butene was the 3-d_1 species at the initial stage of the reaction; thereafter the relative concentration of the 3-d_1 species decreased continuously with the isomerization. The d_0 and 2-d_1 species, which could not be detected at the initial stage, appeared increasingly with the progress of the reaction.

Conversion to *cis*-2-butene from *trans*-2-butene	d_0	2-d_1	d_2
1.0%	51.3%	47.2%	1.5%
3.2	35.9	60.3	3.8
6.4	29.8	66.8	3.4
7.0	28.7	68.6	2.7
8.5	31.5	63.9	4.6
13.6	27.2	68.5	4.3
17.4	34.2	61.8	4.0
Conversion to 1-butene from *trans*-2-butene	3-d_1	2-d_1	d_0
0.20%	92.0%	6.0%	2.0%
0.58	85.5	7.5	7.0
0.75	78.4	13.1	8.5
1.00	75.3	14.7	10.0
2.86	67.1	20.9	12.0

The results thus obtained lead to the following reaction mechanism: the PTS behaves as a typical Brönsted acid, and the *cis-trans* isomerization of 2-butene over the PTS proceeds *via* the *s*-butyl carbonium ion, producing approximately equal amounts of the d_0 and 2-d_1 species of 2-butene, while the double-bond migration of 2-butene to 1-butene also takes place, taking a proton from the PTS at =CH– and giving it back to the PTS from the methyl group on the opposite side. The deuterated PTS acts as the reaction site, and the deuterium is replaced with a hydrogen on the reaction. These nondeuterated 1-butenes accordingly increase with the progress of the reaction; this is in accordance with the results obtained. Similarly, the 2-d_1 species of 1-butene produced may be interpreted to have been formed by the double-bond migration of the 2-d_1 of the *cis*-2-butene on the nondeuterated PTS.

The microwave spectroscopic measurements have thus been demonstrated to be capable of being use dsuccessfully in elucidating the reaction mechanism of the isomerization of *n*-butene.