Mechanism of Skeletal Isomerization of *n*-Butane Using 1, 4-$^{13}C_2$-*n*-Butane on Solid Strong Acids

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Mechanism of skeletal isomerization of *n*-butane over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as well as sulfated ZrO_2 was revealed at a temperature range 393 - 523 K by using 1,4-$^{13}C_2$-*n*-butane. ^{13}C-Distributions of isobutane at 393 K were close to binomial distribution, indicating a bimolecular pathway. On the other hand, an intramolecular (monomolecular) rearrangement became significant over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ at 523 K.

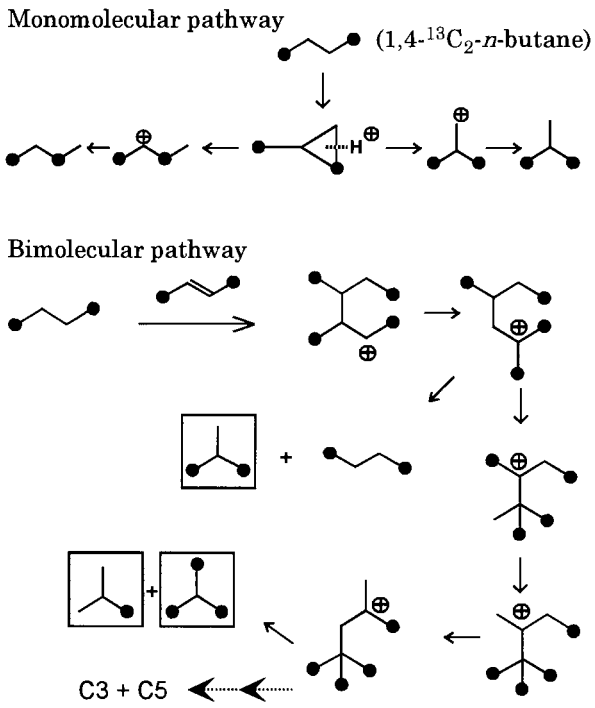
Skeletal isomerization of *n*-butane is practically important, because the product isobutane is a raw material for alkylation with butenes to form clean gasoline (C8 branched alkanes), and the dehydrogenation product, isobutylene can be transformed into methyl *tert*-butyl ether (MTBE). There are many reports about the catalysts active and selective for this reaction. Liquid acids like HF are effective,[1] but these have problems of environmental protection, etc. As solid acids, sulfated ZrO_2,[2-4] a Cs hydrogen salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$,[5-7] and their Pt-promoted catalysts[8,9] have been demonstrated to be promising catalysts.

Since the selectivity to isobutane is closely related to the reaction mechanism, elucidation of mechanism is required for development of prominent catalysts. Matsuhashi et al.[10] proposed that monomolecular and bimolecular mechanisms operated on sulfated ZrO_2 at the initial and latter stage of the reaction, respectively. Recently, isotopic studies have intently been performed on sulfated ZrO_2,[11,12] but there is a controversy on the mechanism. Garin et al.[11] claimed that this reaction occurred through monomolecular mechanism at 523 K and Adeeva et al.[12] inferred that it proceeded through bimolecular mechanism at 353 K, while these discussions are qualitative because of strong influence of fragmentation in mass analysis.

In the present study, we chose $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as well as sulfated ZrO_2 as solid acids, since the former possesses pure and very strong protonic acids available for this reaction,[5] and the latter is exceptionally active at low temperatures for this reaction.[2,4] Zeolites are active, but are non-selective.[6]

The isotopic composition was analyzed by Field-Ionization Mass Spectrometry. By this, we obtained the parent peak pattern which makes possible to discuss quantitatively. Here we report first the reaction mechanism of *n*-butane isomerization over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ as well as sulfated ZrO_2.

In the monomolecular mechanism, the isomerization would involve a protonated cyclopropane and a sequent primary carbenium ion as intermediates to form isobutane with 100%-selectivity.[13] Reaction paths via the monomolecular mechanism are shown in Scheme 1, when 1,4-$^{13}C_2$-*n*-butane was used as a reactant. $^{13}C_2$-Isobutane would be produced exclusively (intramolecular rearrangement), together with 1,3-$^{13}C_2$-*n*-butane as an isotopomer by self-isomerization. On the other hand, the bimolecular mechanism (Scheme 1) is possible if butenes and *sec*-butyl carbenium ion are formed on the catalyst surface to form octyl cation.[13] The β-scission of octyl cation would give C_4 moieties, together with C_3 and C_5 hydrocarbons as byproducts. In this case, the intermolecular isotopic scrambling in isobutane is expected. Thus we can distinguish two mechanisms by the ^{13}C isotopic distribution, intramolecular or intermolecular pattern.



Scheme 1. Reaction pathways for skeletal isomerization of 1,4-$^{13}C_2$-*n*-butane.

The reaction was performed in a closed circulation system (300 cm^3) equipped with an on-line GC at 393—523 K. After $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (110 m^2 g^{-1}, abbreviated as Cs2.5) and sulfated ZrO_2 (90 m^2 g^{-1}, abbreviated as SZ) were pretreated in a vacuum at 573 and 673 K, respectively, 40 torr of 1,4-$^{13}C_2$-*n*-butane (Isotec Inc., ^{13}C: 99%) was introduced. The product isobutane and reactant *n*-butane were separated to be analyzed by Field Ionization Mass Spectrometry (FI-MASS, JEOL JMS-SX102A) for ^{13}C-distribution.

The selectivity to isobutane for Cs2.5 was changed from 91% to 87% when the reaction temperature was raised from 393 K to 523 K, while it decreased from 92% to 78% over SZ. Figure 1 shows the isotopic distributions of isobutane over Cs2.5, where the binomial patterns were optimized to fit the

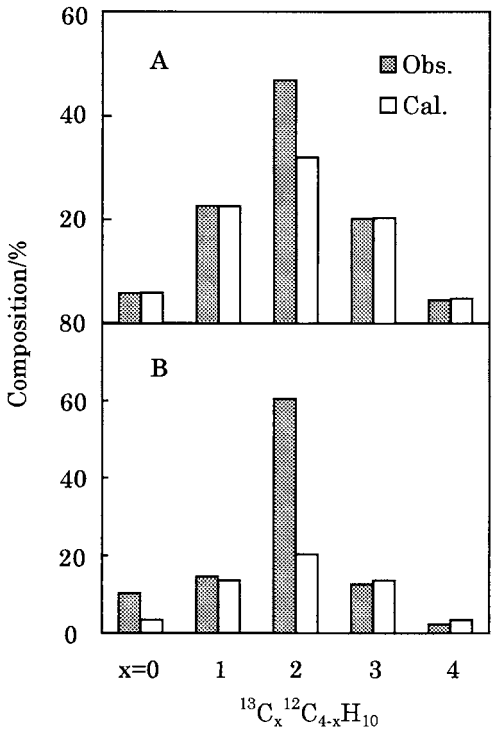


Figure 1. ^{13}C-Distributions of isobutane in the isomerization of 1,4-$^{13}C_2$-*n*-butane over $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. A: 393 K (Conv. =10%) and B: 523 K (Conv. =11%).

observed values of x = 0, 1, 3, and 4 in $^{13}C_x\,^{12}C_{4-x}H_{10}$. As was not shown here, *n*-butane consisted mainly of $^{13}C_2$-*n*-butane. It was observed that the isotopic distribution in isobutane at 393 K was close to a binomial distribution, while the fraction of $^{13}C_2$-isobutane was slightly higher than that of the binomial distribution (Figure 1A). This indicates that at the low temperature, the isomerization on Cs2.5 is the intermolecular process (bimolecular pathway), which is in accordance with the results with SZ.[12] On the other hand, as shown in Figure 1B, the fraction of $^{13}C_2$-isobutane was much greater than that of the binomial one at 523 K. The ^{13}C-distributions in isobutane over SZ were essentially the same as those over Cs2.5, while the patterns of ^{13}C-distribution were more close to the corresponding binomial distributions.

In Figure 2, the ratios (R) of contribution of monomolecular pathway to that of bimolecular pathway are plotted against the reaction temperature, where the ratio was estimated from the fraction of $^{13}C_2$-isobutane which exceeded from that of the binomial distribution. The ratios were 0.13 and 0.04 for Cs2.5 and SZ at 393 K, respectively, demonstrating that the reaction at 393 K occurred exclusively via bimolecular mechanism. The ratio increased greatly as the reaction temperature increased and reached about 0.8 and 0.4 at 523 K over Cs2.5 and SZ, respectively, indicating that the contribution of the monomolecular mechanism became significant on Cs2.5 at the high temperature. This temperature dependence explains the controversy of the previous results for SZ.[11,12] It should be noted that the contribution of monomolecular mechanism was always higher over Cs2.5 than over SZ. This is accordance with the presence of

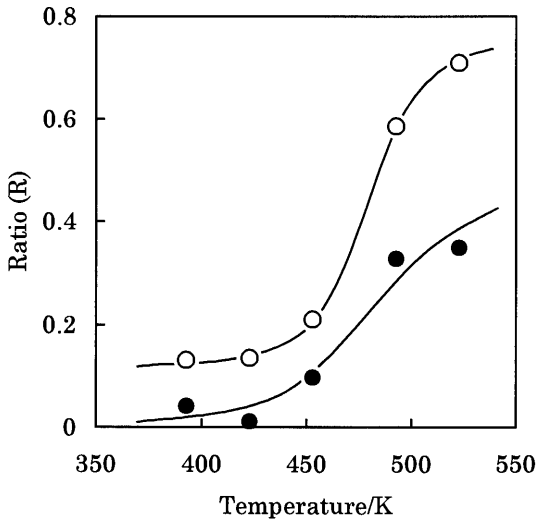


Figure 2. Ratio (R) of contribution of monomolecular pathway to that of bimolecular pathway. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (○) and SO_4^{2-}/ZrO_2 (●). The conversions were around 10%.

the larger amount of strong acid sites on Cs2.5 than on SZ.[14] The trend that SZ preferred bimolecular mechanism is probably due to the oxidative dehydrogenation ability of SZ,[3] by which *n*-butane is dehydrogenated to butenes over SZ to change readily to butyl carbenium ion, and then it forms octyl cation intermediate of bimolecular mechanism.

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