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Isomerization or "Intramolecular Metathesis" of *cis*-2-Butene

Much effort has been expended recently to shed light on the mechanism of olefin metathesis. Studies with nonsupported catalysts provided strong evidence that the reaction is initiated and propagated by coordinated carbene intermediates, but the process leading to the formation of the first carbenes and their behavior are not clear yet. To obtain more valuable information about mechanistic aspects it bears great importance to find catalysts on which metathesis proceeds without side reactions.

Tanaka *et al.* (*1–3*) reported recently a novel catalyst, $MoO_x/\beta\text{-}TiO_2$ ($x = \sim 2.3$–2.9), on which the metathesis reaction takes place without either intermolecular or intramolecular hydrogen transfer, and without isomerization via alkyl or carbonium ion intermediates.

Reaction of a 1 : 1 mixture of *cis*-2-butene-d_0 and *cis*-2-butene-d_8 was studied over the catalyst. The total *trans*-2-butene was regarded as the product of metathesis, and therefore the expected ratio of d_0:d_4:d_8 isotopic species is 1 : 2 : 1. Contrary to this the ratio of $d_4/(d_0 + d_8)$ was found to be close to zero at low conversion and about 0.8 at 30% *cis–trans* conversion. This result indicates that the formation of *trans*-2-butene-d_0 and -d_8 was preferred over the formation of *trans*-2-butene-d_4, especially at the initial stage of the reaction.

A new hypothesis, "intramolecular metathesis," was introduced by Tanaka *et al.* (*2, 3*) for the explanation of the preferential formation of *trans*-2-butene-d_0 and -d_8. According to this hypothesis at the initial stage of the reaction the *cis–trans* isomerization of 2-butenes can be attributed to the formation–decomposition of metal carbenes. The increase in metallocyclobutane intermediates in the course of reaction leads to the formation of normal products of metathesis.

Isomerization of *cis*-2-butene was studied by us over reduced and unreduced molybdena–alumina catalysts (*4–6*). It was found that over the unreduced catalyst isomerization via carbonium ion intermediates was the prevailing reaction in the early stage of the process. Later it was suppressed and the *cis–trans* transformation proceeded almost exclusively via metathesis. Over reduced catalyst the *cis–trans* isomerization proceeded almost exclusively via alkyl intermediates in the early stage of the reaction. Later the participation of metathesis increased in the transformation, but the role of isomerization via an alkyl intermediate remained significant.

Without disputing the reality of such "intramolecular metathesis" proposed by Tanaka *et al.*, we believe that their published experimental results can also be interpreted by *cis–trans* transformation proceeding parallel via metathesis and carbonium ion or alkyl intermediates. The composition of the reaction mixture after 960 min reaction time from Ref. (*1*) can be seen in lines 1–6 of Table 1. The deuterium distribution was recalculated by us as percentages of the initial *cis*-2-butene.

The presence of 1-butene, propene, and pentene in the reaction mixture should be noticed. The latter two olefins can be considered as products of cross-metathesis between 1-butene and 2-butenes. The amount of propene should be equal with the 1-butene consumed. Taking it into account, formation of 3.3% 1-butene was observed experimentally besides 47.1% *trans*-2-butene. In isomerization via carbonium ion intermediate the ratio of *trans*-2-butene/1-butene is approximately 2.5 (*7*). From this

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TABLE 1

Reaction of the Mixture of *cis*-2-butene-d_0 and *cis*-2-Butene-d_8 over MoO_x/β-TiO_2 Catalyst

No.	Product	Percentage composition	Deuterium distribution (% of the initial butene)								
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
1	*cis*-Butene[a]	100	48.4	0	0	0	0	0	0	4.0	47.6
2	*cis*-Butene	49.1	14.8	0.4	0.1	1.7	13.6	0.3	0.3	1.5	16.6
3	*trans*-Butene	47.1	11.8	1.8	0.1	1.3	18.4	0.9	0.1	1.6	10.8
4	1-Butene	0.7									
5	Propene	2.6									
6	Pentene	0.6									
7	*trans*-Butene[b]	100	23.3	0	0	2.0	47.9	0	0.1	2.1	24.7
8	*trans*-Butene[c]	38.5	9.0	0	0	0.8	18.4	0	0	0.8	9.5
9	*trans*-Butene[d]	8.3	2.8	1.8	0.1	0.5	0	0.9	0.1	0.8	1.3

[a] Initial *cis*-2-butene.

[b] Calculated deuterium distribution in *trans*-2-butene if it was produced from *cis*-2-butene with given composition via "pure" metathesis.

[c] Composition of the "metathetic" fraction of *trans*-2-butene.

[d] Composition of the "nonmetathetic" fraction of *trans*-2-butene.

it follows that 8.2% of the initial *cis*-2-butene or 18% of the total *trans*-2-butene can be considered as product of isomerization via carbonium ion intermediate.

The assumption that a certain fraction of *trans*-2-butene was produced via carbonium ion intermediate is supported by deuterium distribution in it. The pure metathesis of *cis*-2-butene with the initial composition given leads to an equilibrium deuterium distribution in the *trans*-2-butene presented in line 7 of the table. The total amount of d_4 species in the experimental mixture can be considered as the product of metathesis. Normalizing it with the calculated equilibrium value the deuterium distribution in the "metathetic" fraction of *trans*-2-butene can be calculated (line 8 of the table). By summarizing the concentration of each species in this fraction we obtain that only 24.7% of the initial *cis*-2-butene or 82% of the total *trans*-2-butene was formed via metathesis.

The deuterium distribution in the "nonmetathetic" fraction of *trans*-2-butene can be calculated as the differences between the experimental concentration of each species and that in the "metathetic" fraction (line 9 of the table). Disregarding the d_3 and d_5 species the deuterium distribution clearly shows that it was the result of a stepwise H/D exchange process. The number of H/D atoms exchanged per molecule can be calculated by using the equation given by Hightower and Hall (*7*);

$$\text{H/D atoms exchanged} = \sum_{i=1}^{4} iN_i + \sum_{i=5}^{8} (8 - i)N_i, \quad (1)$$

where N_i is the mole fraction of each isotopic species containing i deuterium atoms. In this special case d_3 and d_5 species were produced presumably from d_4 species in one exchange step. This assumption is based on the very low concentration of d_2 and d_6 species. Modifying the calculation according to this consideration the number of H/D atoms exchanged per molecule of *trans*-2-butene produced in a "nonmetathetic" way is 0.53, very close to 0.5. This result indicates that the "nonmetathetic" fraction of *trans*-2-butene was produced by a specific hydrogen addition and elimination mechanism characteristic of the isomerization via carbonium ion and alkyl intermediates.

Both the concentration of 1-butene and

the deuterium distribution in *trans*-2-butene strongly suggest that the *cis–trans* isomerization of 2-butene over $MoO_x/\beta\text{-}TiO_2$ catalyst under the given conditions proceeds only partially via "pure" metathesis. The formation of the "nonmetathetic" fraction of *trans*-2-butene can be explained more easily with isomerization via carbonium ion or alkyl intermediate than by metathesis via recombination of metal carbene intermediate.

Bearing this in mind the statement of Tanaka *et al.* that metathesis of *cis*-2-butene over $MoO_x/\beta\text{-}TiO_2$ ($x = 2.3\text{–}2.9$) catalyst under the given conditions takes place without either intermolecular hydrogen scrambling or isomerization via carbonium ion or alkyl intermediate is questionable as well as the hypothesis of "intramolecular metathesis" which served only for the explanation of the experimental product distribution.

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