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A Reply to the Comment by Engelhardt

We reported that reaction of a 1 : 1 mixture of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8 on $MoO_x/\beta\text{-}TiO_2$ ($x = \sim 2.3\text{–}2.9$) yielded selectively *trans*-but-2-ene-d_0, -d_4, and -d_8 (*1*), and that the ratio of $d_4/(d_0 + d_8)$ in *trans*-but-2-ene was found to be close to zero at low conversion (*2*).

This fact indicates preferential formation of *trans*-but-2-ene-d_0 and *trans*-but-2-ene-d_8 in the initial stage of reaction by some mechanism. As we reported (*3*), a reduced catalyst having a constitution of $MoO_{\sim 2.3\text{–}2.0}/\beta\text{-}TiO_2$ is active for isomerization via alkyl intermediates. In conformity with these facts, we had carefully examined the possibility of isomerization via alkyl or alkyl cation intermediates on $MoO_x/\beta\text{-}TiO_2$ ($x = \sim 2.3\text{–}2.9$) in the early stage of reaction and arrived at the conclusion that the contribution of the isomerization via alkyl or alkyl cation should be ruled out from plausible mechanisms to explain the low ratio of $d_4/(d_0 + d_8)$.

We wish to report in this paper some unpublished data that will dispel Engelhardt's misgivings.

Table 1 shows deuterium distribution in the earlier stage of the reaction which was reported in Ref. (*1*) in which the deuterium distributions at 300 and 960 min were reported. By using the deuterium distribution at 960 min (the highest conversion), Engelhardt speculated that the isomerization of *cis*-but-2-ene to *trans*-but-2-ene via carbonium cation intermediates in the early stages of the reaction over $MoO_x/\beta\text{-}TiO_2$ (and he conjectured) yields but-1-ene and *trans*-but-2-ene in a ratio of *trans*-/1- = 2.5.

It is a reasonable assumption that the isomerization via a carbonium cation intermediate necessarily exchanges one hydrogen atom as Engelhardt assumed in his calculation. If his conclusion were correct, that is, 18% of the total *trans*-but-2-ene could be considered to be the product of isomerization via carbonium cation intermediates, the sum of the fractions of *trans*-but-2-ene-d_1 and *trans*-but-2-ene-d_7 should

TABLE 1

Metathesis Reaction of a 1 : 1 Mixture of *cis*-2-Butene-d_0 and *cis*-2-Butene-d_8 at Room Temperature

Product	Time (min)	Composition (%)	Deuterium distribution (%)								
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8
cis-2-Butene	0	100.0	48.4	0	0	0	0	0	0	4.0	47.6
	15	96.9	49.4	0	0	0	1.3	0	0	3.8	45.5
	60	92.9	47.9	0	0	0.2	2.3	0	0	3.9	45.6
	300	82.3	44.2	0	0	0.9	9.5	0	0	3.5	41.9
	960[a]	49.1	30.2	0.8	0.2	3.4	27.6	0.6	0.6	3.1	33.9
trans-2-Butene	0	0.0	—	—	—	—	—	—	—	—	—
	15	3.1	32.1	0.3	0	1.5	33.7	0	0	3.2	34.2
	60	7.1	29.1	0.4	0.2	1.6	35.9	0	0	2.8	30.1
	300	17.7	28.2	1.4	0.1	1.8	37.9	0	0	3.0	27.6
	960[a]	47.1	25.0	3.9	0.3	2.7	39.0	2.0	0.3	3.5	22.9

[a] After 960 min, 0.7% of 1-butene, 2.6% of propene, and 0.6% of pentene were obtained.

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be nearly 9% in the total *trans*-but-2-ene in the early stage of reaction because *cis* to *trans* rotation accompanies necessarily one hydrogen atom exchange. It is obviously not the case as shown in Table 1, i.e., the sum of d_1 and d_7 species is about 1% of the total *trans*-but-2-ene. This fact clearly indicates that the Engelhardt's calculation assuming carbonium cation intermediates and the data at 960 min (highest conversion) led to an unsound conclusion for the early stage of reaction on MoO_x/β-TiO_2.

In fact, if a mixture of propene-d_0 and propene-d_6 was contacted with MoO_x/β-TiO_2 catalyst, ethylene-d_0, -d_2, -d_4, and but-2-ene-d_0, -d_4, -d_8 were preferentially formed, but the fractions of ethylene-d_1, -d_3, propene-d_1, -d_3, -d_5, and but-2-ene-d_1, -d_2, -d_3, -d_5, -d_6, -d_7 were gradually increased.

The sum of these hydrogen-exchanged species is a measure of hydrogen scrambling taking place concurrently with metathesis reaction. As shown in Fig. 1, the sum of the fractions proves negligible contribution of hydrogen exchange in the early stage of metathesis. Accordingly, we can conclude safely that the isomerization via alkyl and/or alkyl cation intermediates should be ruled out as possible mechanisms to explain the characteristic low ratios of $d_4/(d_0 + d_8)$ in *trans*-but-2-ene formed in the reaction of a 1 : 1 mixture of *cis*-but-2-ene-d_0 and *cis*-but-2-ene-d_8 in the early stages of reaction on MoO_x/β-TiO_2.

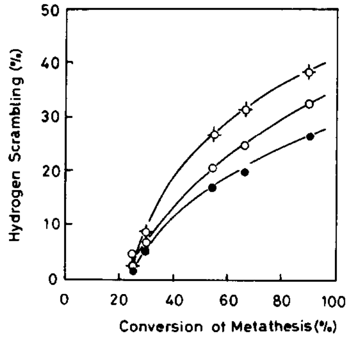
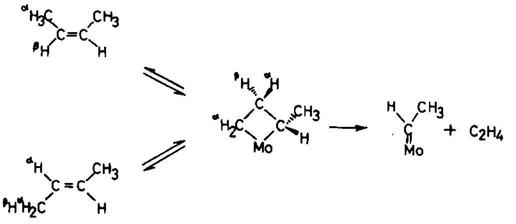


FIG. 1. Fraction of hydrogen-scrambled products concurrently formed in metathesis of a 1 : 1 mixture of propene-d_0 and -d_6 on MoO_x/β-TiO_2 ($x = \sim 2.3$–2.9) at room temperature (○) Ethylene; (○) but-2-ene; (●) propene.

Engelhardt referred to the isomerization of olefins on unreduced molybdena–alumina catalyst to explain the low ratios of $d_4/(d_0 + d_8)$ in the initial stage of reaction on MoO_x/β-TiO_2 (x = 2.3–2.9), but he should note the facts that the fraction of hydrogen-scrambled products formed in metathesis depends strongly on supporting materials of molybdena and that alumina is one of the worst supports to prohibit the hydrogen-scrambling processes taking place concurrently with metathesis reaction, as reported in Ref. (*3*).

To explain the characteristic low ratio of $d_4/(d_0 + d_8)$ of *trans*-but-2-ene, the intramolecular metathesis process was proposed by us (*2*), but another probable mechanism has been proposed recently as follows (submitted for publication):



where an initiation process of metathesis reaction, formation of metallocyclobutane from olefin, is assumed to be reversible, and which results in the preferential formation of *trans*-but-2-ene-d_0 and *trans*-but-2-ene-d_8 in the early stages of the reaction over MoO_x/β-TiO_2 (x = 2.3–2.9). Direct formation of alkylidene complex by α, β-hydrogen transfer is also a probable mechanism. In spite of this speculation, the initiation process is still an unsolved problem, because the initiation of metathesis by ethylene could not be attributed to a metallocyclobutane.

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