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ON THE REVERSIBILITY OF METAL CARBENE FORMATION PROCESS IN OLEFIN METATHESIS REACTION OVER MoO_x/\beta-TiO<sub>2</sub> CATALYST
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Co-isomerization of d_0^- and d_8^-cis-2 -butene was carried out on a novel catalyst, MoO_x/β -TiO_2(2.9>x>2.3), which is active for olefin metathesis reaction without inter- and intra-molecular hydrogen scrambling of olefins. The ratio, $d_4/(d_0^+d_8)$, in produced trans-2-butene was found to be zero at the initial stage of the reaction, indicating a type of *cis-trans* isomerization by intra-molecular metathesis.

Metal carbene and metallocyclobutane intermediates have been generally accepted for catalytic olefin metathesis reactions.¹⁾ However, detailed behavior of metal carbene intermediates is still unsolved. In order to throw light on this

problem, metathesis reactions of deuterium-labelled olefins were performed on a novel catalyst, MoO_x/β -TiO₂, on which metathesis reaction took place with neither inter-molecular hydrogen scrambling nor isomerization via alkyl or carbonium ion intermediates.²)

To confirm the absence of intra-molecular hydrogen transfer in olefin molecule during its metathesis reaction, $1,1,2-d_3$ -propene (94.1%) was admitted to MoO_x/β -TiO₂ catalyst. If the intra-molecular hydrogen transfer to give $2,3,3-d_3$ -propene would take place, metathesis reaction of these propenes might produce $2-d_1$ - and $1,1,2,3,3-d_5$ -propene by degenerate metathesis and $1,1-d_2$ - and d_0 -ethylene as well as $1,1,2,3-d_4$ - and $1,1,2,3,4,4-d_6$ -2-butene by productive metathesis. The result was not the case as shown in Table 1, which proves that the metathesis reaction proceeds on this catalyst with neither inter-molecular nor intra-molecular hydrogen exchange reaction. The amount of total 2-butene less than that of ethylene in Table 1 gives evidence for the preferential adsorption of 2-butene.

In case of the reaction of a 1:1 mixture of d_0^- and d_8^- *cis*-2-butene on MoO_x/ β -TiO₂, *trans*-2-butene consisting of d_0^- , d_4^- and d_8^- isomers was formed without any induction²,³) showing again the *cis*-*trans* isomerization was exclusively caused by the degenerate metathesis reaction of 2-butene. Taking account of metallocyclo-butane intermediate generally accepted for metathesis reaction, four cases as shown in Scheme can be considered for the formation of *trans*-2-butene.

Table 1 Composition and deuterium distributions of propene, ethylene, cisand trans-2-butene produced in the metathesis reaction of 1,1,2-d₃propene (10.0mmHg) on 6.7wt% MoO_v/ β -TiO₂ (1.0g) at room temperature.

Product	Comp.(%)	d _O	dl	d ₂	dz	d4	d5	d6~
Propene	87.4	0	2.1	4.2	92.2	0	1.6	0
Ethylene	11.3	0	0	4.1	6. I	89.8	-	-
t-2-Butene	1.2	0.5	2.4	91.0	0.6	4.7	0.8	0
c-2-Butene	0.2	2.4	2.8	90.4	1.1	3.3	0	0

Deuterium distributions (%)

Table 2 Relative amounts of deuterio-isomers of *trans*-2-butene expected through metallocyclobutane intermediates formed from respective metal carbenes and *cis*-2-butenes.

Combi. Case	M=C-C + C _{C=C}	M=C-C * + * C * * C C=C	M=Č-Č + C _{\C=C} ,C	M=Č-Č * + * C、* + * C	d4/d ₀₊ d8 of trans-2-Butene
I	3d ₀	2d4+ d8	d ₀ + 2d ₄	3d8	0.5 (4/8)
π−।	2do	d4+ d8	do + d4	2ds	0.33(2/6)
II-2	do	d4	d4	da	1.0 (2/2)
I -3	do	da	do	da	0.0 (0/4)
			* *		

= C-C--- = CH-CH₃, = C-C--- = CD-CD₃

Since Mo=CHCH₃ and Mo=CDCD₃ are produced from d_0^- and d_8^-cis -2-butene, four types of combination of metal carbene with cis-2-butene to form metallocyclobutane intermediates are possible as listed in Table 2. For each type of combination, four cases, as shown in Figure 1, are possible for fission of metallocyclobutane into trans-2-butene and metal carbene and the ratio, $d_4/(d_0^+d_8)$, of trans-2-butene will take steady values of 0.5, 0.3₃, 1.0 and zero for the cases I, II-1, II-2 and II-3, respectively, as equivalent Mo=CHCH₃ and Mo=CDCD₃ are formed from equivalent d_0^- and d_8^-cis -2-butene.

The observed value of the ratio, $d_4/(d_0+d_8)$, of produced trans-2-butene agrees with none of the cases. This ratio is likely to be extraporated to zero at the initial stage of reaction, and rapidly increased to the equilibrium value, 1.0, as the reaction proceeded. This result indicates preferential formation of d_0^- and d_8 -trans-2-butene from d_0^- and d_8 -cis-2-butene, respectively, that is, the preferential intramolecular metathesis at the initial stage of reaction. Furthermore, the time course of the ratio, $d_4/(d_0+d_8)$, of trans-2-butene from zero to 1.0 can not be interpreted by the effects of these cases. It is inconceivable that, instead of case II-1, case II-3 occurs selectively at the initial stage and then shifts to case II-2 with progress of the reaction.

Taking into account that the *cis-trans* isomerization on MoO_x/β -TiO₂ was caused

exclusively by metathesis, the cis-trans isomerization of 2-butene at its initial stage is probably atributed to the recombination of metal carbenes as

$$2Mo + {}^{C}C=C {}^{C} \implies 2Mo=C-C (Mo \leqslant {}^{C-C}_{C-C}) \implies 2Mo + {}^{C}C=C {}_{C}$$

MO: Mo ion.

Scheme







Scheme

- Case I ; Rapid equilibration between C $_2$ alkylidene and adsorbed 2-butene via metallocyclobutane precedes the desorption of trans-2-butene.
- Case II; The reaction between metal carbene olefin complex and metallocyclobutane is irreversible.
 - II-1; Two types of fission of metallocyclobutane into metal carbene and olefin are brought about in equal probability.
 - II-2; C_2 alkylidene of metal carbone is necessarily introduced into $trans\mbox{-}2\mbox{-}butene.$
 - II-3; None of $\rm C_2$ alkylidene of metal carbone is introduced into \$trans-2\$-butene.
- * We neglect in these cases any isotope effect as well as stereo-selectivity attributed to the stability of metallocyclobutane intermediates. $^{4)}$

The time course of the ratio, $d_4/(d_0+d_8)$, of trans-2-butene might be caused by the increase of metallocyclobutane, which accelerates the formation of d_4 - as well as d_0 - and d_8 -trans-2-butene through the chain reaction such as cases I and II-1 shown in the Scheme.



Figure 1 Time course of the ratio, $d_4/(d_0+d_8)$, of *trans*-2-butene produced in the metathesis reaction of a 1:1 mixture of d_0^- and d_8^-cis -2-butene. 6.7 wt% MoO_x/ β -TiO₂ 0.3g

Pressure	(mmHg)	Reaction	Temperature	(^O C)
$56.2 \\ 16.0 \\ 32.5$		2 - -]	23 8 10	

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(Received March 12, 1980)