

## Metathesis of $\alpha,\omega$ -Dienes over a $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ Catalyst in Liquid Phase

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The metathesis of five kinds of  $\alpha,\omega$ -dienes containing from six to ten carbon atoms were investigated over  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst. The reactions were carried out in a continuous-flow system with a fixed catalyst bed at atmospheric pressure in the liquid phase. The  $\alpha,\omega$ -dienes were easily metathesized and all the reaction products were metathesis products. By-products resulting from double-bond isomerization of  $\alpha,\omega$ -diene were not found in the reaction products. Thus, the catalyst appeared to be a very active and selective catalyst for the metathesis of  $\alpha,\omega$ -dienes. 1,7-Octadiene underwent only intramolecular metathesis with quantitative yield of cyclohexene. On the contrary, 1,5-hexadiene and 1,9-decadiene underwent only intermolecular metathesis and both intra- and intermolecular metathesis took place for 1,6-heptadiene and 1,8-nonadiene. The relative reactivities of the  $\alpha,\omega$ -dienes were measured by both conventional and competitive reaction and the reactivity was obtained in decreasing order: 1,7-octadiene > 1,6-heptadiene > 1,8-nonadiene > 1,5-hexadiene > 1,9-decadiene. The reaction behavior and the relative reactivity were discussed and explained on the basis of the metal carbene mechanism.

### INTRODUCTION

Many kinds of catalysts, both homogeneous and heterogeneous, are known to be active for olefin metathesis. Tungsten oxide, molybdenum oxide, including cobalt molybdate and rhenium oxide supported on alumina or silica, are more effective among a number of heterogeneous catalysts. Special attention has been given to rhenium oxide catalysts which are noted for their activity at milder conditions. Heterogeneous rhenium catalysts have been mainly applied for the metathesis in gas phase and relatively little literature can be seen on the metathesis in liquid phase.

The olefin metathesis reaction has been carried out with many olefins of several different types. Little attention has been directed to the metathesis of  $\alpha,\omega$ -dienes except for 1,7-octadiene since the metathesis of light  $\alpha,\omega$ -diene, 1,3-butadiene, over tungsten oxide-silica catalysts was first reported (1, 2). It has been reported that 1,7-

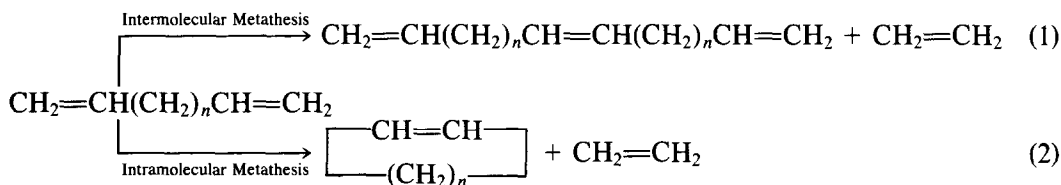
octadiene apparently undergoes intramolecular metathesis to give cyclohexene and ethylene. This has attracted considerable attention because of its interest from a mechanistic point of view. Most of the applied catalysts for the reaction are homogeneous catalyst systems based on compounds of molybdenum (3-6), tungsten (7, 8), and rhenium metal (9, 10) with alkyl aluminum chloride co-catalysts. As to heterogeneous catalyst systems,  $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$  (11, 12) and  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  (13) have been used.

We have reported the metathesis of 1-hexene over rhenium oxide on alumina catalysts in liquid phase with a continuous flow system (14). The selectivity to 5-decene, the primary metathesis product, was about 92% and small amounts of 2-heptene, 4-nonene, and 4-octene were produced over  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst indicating the occurrence of undesirable side reactions such as polymerization, double-bond isomerization, and subsequent metathesis.

However, the selectivity to 5-decene was improved to 97% by addition of a small amount of cesium nitrate to the catalyst. Thus,  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst appeared to be more selective catalyst for olefin metathesis than  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst. This suggests that the reaction behavior of olefins and their reactivities can be revealed

more accurately by the use of such a selective catalyst.

$\alpha,\omega$ -Diene may undergo intramolecular metathesis to form cycloolefin and/or intermolecular metathesis to form opened chain oligomers with terminal double-bonds as represented by



It is of interest to investigate the relation between the structure of  $\alpha,\omega$ -dienes and the reaction behaviors in this connection. The present work deals with the results of metathesis reactions of five kinds of non-conjugated  $\alpha,\omega$ -dienes containing from six to ten carbon atoms. The reactions were carried out in liquid phase with a continuous-flow system at atmospheric pressure using a  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst.

#### EXPERIMENTAL

**Catalyst.** An alumina obtained from alumina sol 200 (Nissan Chemical Industrial Co.) ( $\text{Al}_2\text{O}_3$  content 10–10.5%, pH 4–6, acetic acid as stabilizer 2%) was used as a carrier. The alumina sol was evaporated over a water bath, dried at 120°C, and crushed to 60–100 mesh. After calcination at 250°C for 6 h in a stream of oxygen, it was washed with aqueous solution of 0.1 N  $\text{HNO}_3$  and with ion-exchange grade water thoroughly.  $\gamma$ -Alumina was obtained after dryness and following calcination at 600°C for 6 h in a stream of oxygen.

A  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst was prepared by impregnating the  $\gamma\text{-Al}_2\text{O}_3$  with an aqueous solution of  $\text{Re}_2\text{O}_7$  (Mitsuwa Chemical Co., 99.99%+). After calcination in a stream of oxygen for 2 h at 550°C, the concentration of  $\text{Re}_2\text{O}_7$  on the finished catalyst was found to be 18 wt% by atomic absorption spectrophotometer and also thermal gravity analy-

sis. A  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst also prepared by impregnating the calcined  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst with an aqueous solution of cesium nitrate (99%+), drying at 120°C, and then calcining in a stream of oxygen at 500°C for 2 h. The calculated amount of cesium nitrate was 1 wt% as cesium metal ion and the concentration of  $\text{Re}_2\text{O}_7$  in the finished calcined catalyst was found to be 17.5 wt%.

**Reagents.** 1,7-Octadiene (99%+), monochlorobenzene, or toluene as a solvent and *p*-xylene as an internal standard to estimate percentage of conversion and selectivity were dried over molecular sieve 5A and purified in a stream of dry nitrogen by distillation from the sieves prior to the use. Other  $\alpha,\omega$ -dienes, 1,5-hexadiene, 1,6-heptadiene, 1,8-nonadiene, and 1,9-decadiene were used without any further treatment and their purity were 99%+, respectively.

**Experimental procedure.** The experiments were carried out in a single-pass continuous-flow system with a fixed catalyst bed in a tubular Pyrex glass reactor (8 mm i.d., 80 mm long) at atmospheric pressure in the liquid phase. The catalyst (60–100 mesh, 0.25–2.0 g) was loaded in the lower part of the reactor with the upper portion filled with quartz chips to reduce the dead volume.

The catalyst was activated *in situ* prior to the reaction at 550°C for 1.5 h in a stream of

nitrogen, followed by cooling to reaction temperature in the dry nitrogen flow. The temperature was measured in the center of the catalyst bed with a Chromel–Alumel thermocouple sealed with stainless steel. The feed was pumped at a controlled rate (10 ml/h) into the bottom of the reactor and the liquid effluent from the top was introduced into a receiver at  $-45^{\circ}\text{C}$ . The receiver was changed at regular intervals for analysis. The liquid products from the reactor were analyzed by GLC using a  $5\text{ m} \times 3\text{ mm}$  (i.d.)-column containing a 20 wt% PEG 20M on 60–80 mesh celite 545 and 40-m capillary glass column containing OV-101. Qualitative analyses for volatile gases from the reactor were done using a Porapak Q ( $2\text{ m} \times 3\text{ mm}$ ) column. In some cases GLC–mass spectrometer (ANELVA TE-600S) was also used. The identification of the reaction products were performed by com-

paring retention times and mass spectra with those of authentic samples. The hydrogenation of the reaction products to the corresponding saturated hydrocarbons over 5% Pd/C was also run for the purpose described above at ambient temperature and atmospheric pressure of hydrogen.

The terms “conversion” and “selectivity” used here are defined below:

% Conversion

$$= \% \text{ of starting material reacted} \quad (3)$$

The selectivity was calculated on the basis of a starting material. For example, 1,6,11-dodecatriene and 1,6,11,16-heptadecatetraene are formed as main products in the metathesis of 1,6-heptadiene. In this case, 2 and 3 mol of 1,6-heptadiene as a starting material will be required for their production respectively. Thus;

Selectivity of 1,6,11-dodecatriene (%)

$$= \frac{1,6,11\text{-dodecatriene formed (mol)} \times 2}{1,6\text{-heptadiene reacted (mol)}} \times 100 \quad (4)$$

Selectivity of 1,6,11,16-heptadecatetraene (%)

$$= \frac{1,6,11,16\text{-heptadecatetraene formed (mol)} \times 3}{1,6\text{-heptadiene reacted (mol)}} \times 100 \quad (5)$$

On the other hand, cyclopentene can be produced by intramolecular metathesis of 1,6-heptadiene, then;

$$\text{Selectivity of cyclopentene (\%)} = \frac{\text{cyclopentene formed (mol)}}{1,6\text{-heptadiene reacted (mol)}} \times 100 \quad (6)$$

## RESULTS AND DISCUSSION

### 1. Metathesis of 1,7-Octadiene

There are relatively many reports on the metathesis of 1,7-octadiene and the most have been studied using homogeneous catalyst systems from a mechanistic point of view (3–10). As heterogeneous catalysts, CoO–MoO<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> (11, 12) and Re<sub>2</sub>O<sub>7</sub>–Al<sub>2</sub>O<sub>3</sub> (13) have been used in the reaction. In all cases these were studied in a batch system. Thus, the detailed study on the me-

tathesis of 1,7-octadiene was first investigated in a flow system.

*1.1. Reaction behaviors.* The data on the metathesis reaction of 1,7-octadiene over Re<sub>2</sub>O<sub>7</sub>–Al<sub>2</sub>O<sub>3</sub> and CsNO<sub>3</sub>–Re<sub>2</sub>O<sub>7</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Fig. 1. The rapid deactivation occurred and the selectivity increased gradually with time on stream over Re<sub>2</sub>O<sub>7</sub>–Al<sub>2</sub>O<sub>3</sub> catalyst. These behaviors suggest the existence of some strong acid sites on the catalyst which have activity to polymerization and/or double-bond isomer-

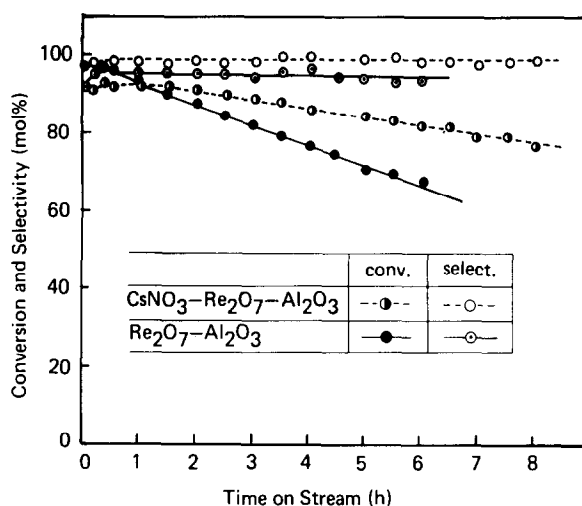


FIG. 1. Changes in conversion and selectivity to cyclohexene in the metathesis of 1,7-octadiene over  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  and  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalysts with time on stream. Reaction temperature:  $30^\circ\text{C}$ ; contact time ( $W/F$ ):  $5.2 \text{ g-cat} \cdot \text{h/mol}$ ; weight of catalyst:  $0.5 \text{ g}$ ; concentration of substrate:  $3.4 \text{ mol}\%$ ; solvent: chlorobenzene.

ization of olefin. There are many papers (2, 15) reporting that the addition of minor amounts of alkali, alkaline earth group, and thallium metal ion to heterogeneous catalysts is effective to poison acid sites on the catalysts, and it results in a decrease in the activities of double-bond isomerization and polymerization and in an increase in the selectivity to metathesis. We applied the addition of cesium ion to the  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst because it seems to be one of the most effective metals. As compared with  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst,  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst showed higher selectivity to cyclohexene and lower deactivation rate by a factor of about one-half.

This shows the addition of cesium to  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst was effective to selective poisoning of acid sites. However, the activity change over  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  was still observed. One of the most possible reasons may be the formation of polymer caused by the acid sites that remained after alkali treatment. The decrease in the number of active sites caused by reduction to inactive sites with time on stream may be another reason. Both deactivated catalysts during metathesis could be

regenerated completely by combustion using a controlled amount of oxygen.

1,7-Octadiene over  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  apparently underwent intramolecular metathesis to give near 100% selectivity to cyclohexene and only trace amounts of 1,7, 13-tetradecatriene were produced by intermolecular metathesis. It was found that cyclohexene produced did not participate in further metathetic process to cyclopolyolefins in the separate experiments.

1.2. *Effects of mass transfer.* As  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst appeared to be very selective catalyst to the metathesis reaction as described above, it was used for further experiments.

The effect of pore diffusion was examined with various mesh size of the catalyst, 40–60, 60–100, 100+ mesh, but the rates were the same for these three sizes, indicating no pore diffusion. The effect of external diffusion was checked by changing the feed rate and the weight of catalyst, but keeping the ratio of  $W/F$  constant. Also the effects of back-diffusion was examined by changing the height of catalyst bed. The same rates were obtained for these experiments. Thus, it was found the mass transfer could

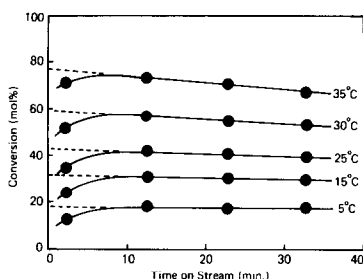


FIG. 2. Effects of reaction temperature on conversion in the metathesis of 1,7-octadiene. Catalyst:  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  (0.25 g); contact time ( $W/F$ ): 2.6 g-cat · h/mol; concentration of reactant: 3.5 mol%; solvent: chlorobenzene.

be ignored at the reaction conditions used in this study.

**1.3. Reaction temperature.** The effect of reaction temperature was examined and the data on the activity changes with time on stream are shown in Fig. 2. The increase in the activity was found at the initial stage of the reaction and then the activity reached a maximum, followed by a gradual deactivation. The initial activity was estimated by the extrapolation of the activity change with time on stream to the intercept, time zero.

The induction period was found to be 10 min for this reaction. The existence of induction period has been found for other metathesis over heterogeneous catalysts. For example, over  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst, about 30 min for propylene (16) and ca. 15 min for 1-hexene (14) has been reported as induction period.

**1.4. Effect of contact time.** The effect of contact time ( $W/F$ ) on the conversion of 1,7-octadiene and the selectivity to cyclohexene was investigated at several reaction temperatures (5–35°C). The data are shown in Fig. 3. The value of  $W/F$  was changed in the range of 0.8–2.5 g-cat · h/mol by keeping the feed rate ( $F$ ) constant and changing the weight of the catalyst ( $W$ ). The conversions increased with increases in  $W/F$  and reaction temperature but the selectivity of 99%+ to cyclohexene was always obtained for the reaction conditions.

**1.5. Activation energy.** Arrhenius plots

were obtained with good linearity. The apparent activation energy obtained by the least-square method was found to be 8.4 kcal/mol. The apparent activation energies for propylene metathesis have been reported to be 4–11 kcal/mol over  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  (16, 17), 5–8 kcal/mol over heterogeneous molybdenum catalysts (18, 19), and 11–59 kcal/mol over heterogeneous tungsten catalysts (18, 20). Other data with homogeneous molybdenum catalysts have been reported to be 6.6 kcal/mol for 2-pentene (21) and 7.0 kcal/mol for 4-nonene (21).

## 2. Metathesis of $\alpha,\omega$ -Dienes

A series of experiments were carried out in order to investigate the reaction behavior of  $\alpha,\omega$ -dienes. The following reaction conditions: temperature, 45°C;  $W/F$ , 5.2 g-cat · h/mol; and concentration of diene, 2.8 mol% were used. Monochlorobenzene or toluene was used as solvent but toluene generally seemed to be more preferable. With toluene higher conversion and slower deactivation were obtained. The main component in the evolved gas was usually ethylene but a small amount of propylene was also found especially during the initial period of the reactions. The concentration of propylene decreased drastically and became negligible after 10–15 min on stream. The selectivity of liquid products also be-

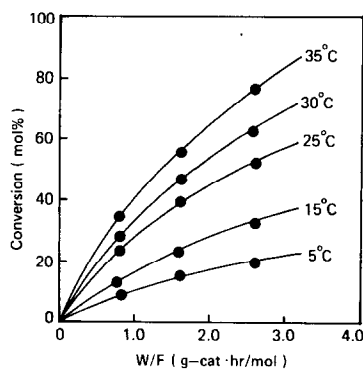

























FIG. 3. Effects of contact time on conversion in the metathesis of 1,7-octadiene. Catalyst:  $\text{CsNO}_3\text{-Re}_2\text{O}_7\text{-Al}_2\text{O}_3$ ; concentration of reactant: 3.5 mol%; solvent: chlorobenzene.

TABLE I  
Reaction Products in the Metathesis of  $\alpha,\omega$ -Diene

| Reactant  | Reaction Products |   |
|---|-------------------|---|
| 1,5-hexadiene<br>  | Intra             |  0%  |
|   | Inter             |  55%,  24%,  11%,  3% |
| 1,6-heptadiene<br> | intra             |  85%   |
|   | inter             |  7%,  1%,  tr.   |
| 1,7-octadiene<br>  | intra             |  99%   |
|   | inter             |  0%  |
| 1,8-nonadiene<br>  | intra             |  30%  1%  |
|   | inter             |  48%,  15%  |
| 1,9-decadiene<br>  | intra             |  tr.   |
|   | inter             |  75%,  14%  |

came constant after 10–15 min. on stream. A gradual deactivation of the catalyst was observed and the rate of decay in the activity was faster than that of 1,7-octadiene shown in Fig. 1. The mass balance was 92–99%. The data obtained for a series of  $\alpha,\omega$ -dienes are summarized in Table 1.

**2.1. Metathesis of 1,5-hexadiene.** 1,5-Hexadiene underwent intermolecular metathesis with 60% conversion. The main reaction products were 1,5,9-decatriene, 1,5,9,13-tetradecatetraene, and 1,5,9,13,17-octadecapentaene. 1,5,9-Cyclododecatriene was detected with only trace amount and was estimated to be formed by the intramolecular metathesis of 1,5,9,13-tetradecatetraene. In the same way the formation of 1,5-cyclooctadiene derived from 1,5,9-decatriene was expected, but it could not be detected in the reaction products. Cyclobutene, an intrametathesis product of 1,5-hexadiene, could not be detected in spite of several trials with bromination and gas chromatography of evolved gas. In the metathesis of 1,5-hexadiene using homogeneous catalysts (4, 6) it has been reported that the main product was linear olefins and cyclobutene could not be detected. The product distribution (mol%) obtained in this study was 1,5,9-decatriene : 1,5,9,13-tetradecatetraene : 1,5,9,13,17-octadecapentaene = 72:21:7, and the value corresponded fairly with the data obtained with

$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Cl}_2(\text{NO})_2\text{Mo}-(\text{CH}_3)_3\text{Al}_2\text{Cl}_3$  catalyst (6).

**2.2. Metathesis of 1,6-heptadiene.** In the metathesis of 1,6-heptadiene, the conversion was 70 or 83% when chlorobenzene or toluene was used as a solvent, respectively, but the product distributions did not differ each other. However, the decay of the catalyst activity was smaller in toluene solvent. The main product was cyclopentene formed by intramolecular metathesis and the selectivity was 85%. On the other hand, 1,6,11-dodecatriene and 1,6,11,16-heptadecatetraene were produced at 7 and 1%, respectively, as intermolecular metathesis products. 1,6-Cyclodecadiene was also produced with a trace amount by intramolecular metathesis of 1,6,11-dodecatriene as it could not be detected in the reaction products of metathesis of cyclopentene. Cyclopentene was stable under the reaction conditions. It seems the behavior of cyclopentene in the metathesis differs largely according to the catalysts used. That is,  $n\text{-Bu}_4\text{N}[\text{Mo}(\text{CO})_5\text{Cl}]-\text{CH}_3\text{AlCl}_2$  catalyst (4) showed high activity such as 90% conversion to produce polycyclopentenes.

**2.3. Metathesis of 1,8-nonadiene.** The metathesis of 1,8-nonadiene took place with 57% conversion. 1,8,15-Hexadecatriene and 1,8,15,22-tricosatetraene were formed by intermolecular metathesis of 1,8-

nonadiene and the selectivities were 48 and 15%, respectively. Cycloheptene formed by intramolecular metathesis was obtained with 30% selectivity. Also a small amount of 1,8-cyclotetradecadiene with three isomers were found. They were estimated to be a mixture of the *cis, cis* (90%), *cis, trans* (7%), and *trans, trans* (3%) isomers. When cycloheptene was metathesized, 1,8-cyclotetradecadiene was formed as a main product. Therefore, one of the formation path of 1,8-cyclotetradecadiene must be the metathesis of the cycloheptene produced. The participation of intramolecular metathesis of 1,8,15-hexadecatriene must be taken into consideration as another possible path in analogy with the formation of 1,5,9-cyclododecatriene and 1,6-cyclodecadiene as described in Sections 2.1 and 2.2.

**2.4. Metathesis of 1,9-decadiene.** The metathesis of 1,9-decadiene underwent with 40% conversion. The principal products were 1,9,17-octadecatriene and 1,9,17,25-hexacosatetraene by intermolecular metathesis and the selectivities were 75 and 14%, respectively. Only small amount of

cyclooctene was formed by intramolecular metathesis. 1,9-Cyclohexadecadiene was also found in the reaction products. When cyclooctene was metathesized, the conversion was about 70% and 1,9-cyclohexadecadiene was formed with ca. 10% selectivity. Turner *et al.* (22) and Wideman (23) have reported that cyclohexadecadiene was produced together with cyclic polymer by the metathesis of cyclooctene. In addition to the products indicated above, the formation of higher polyenes were estimated, but it was impossible to analyze them quantitatively at the analytical conditions.

### 3. The Structures of $\alpha,\omega$ -Dienes and Their Reaction Behaviors

The carbene mechanism has been supported from many studies (7, 8, 9, 25-35) for the olefin metathesis. According to the carbene mechanism the metathesis reaction of  $\alpha,\omega$ -diene will be illustrated as shown in Fig. 4. The factors governing the intra- and/or intermolecular metathesis might be the configuration and the chain length of carbene II in Fig. 4. One of the most important

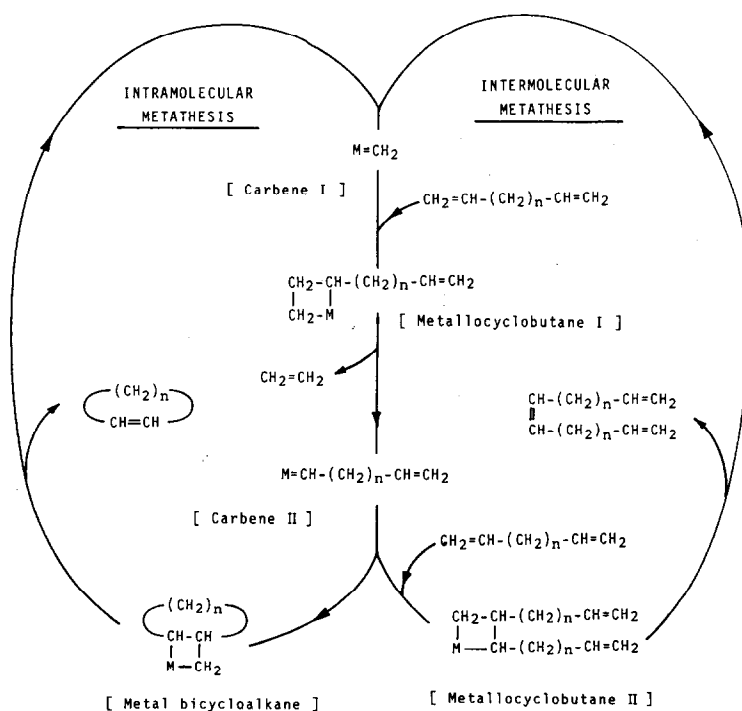


FIG. 4. The mechanism for the metathesis of  $\alpha,\omega$ -diene.

processes for the formation of metal bicycloalkane would be an interaction between the  $\pi$  electrons of the vinyl group and the metal in carbene II. The stability of the configurations of the alkane should be considered in this connection. In the metathesis of 1,7-octadiene, the main reaction product was cyclohexene due to intramolecular metathesis and an intermolecular product was found only in trace amounts. This implies that carbene II formed from 1,7-octadiene will have such a configuration with two double bonds in a chain close enough to each other to form a metal bicycloalkane easily. The configurations of carbene II from 1,7-octadiene were examined using a molecular model and it was found that the interaction would occur easily and steric repulsions in the metal bicycloalkane seemed to be very small. On the contrary, the carbene II from 1,5-hexadiene is too short in the chain length to have the interaction. Angle and torsional strains are required to a certain extent for the carbene II from 1,6-heptadiene, 1,8-nonadiene, and 1,9-decadiene to have an interaction similar to that from 1,7-octadiene.

However, it seems that they are not so big and the interaction occurs sufficiently. The probability of the interaction occurring will decrease as the chain in carbene II becomes longer, and this will result in the decrease of an intramolecular metathesis and the increase of an intermolecular metathesis. In the metathesis of 1,9-decadiene, the formation of intramolecular product was only a trace amount. This might be caused by decreasing the probability of the interaction not due to steric hindrances, but because of the longer chain in the carbene II. Thus, the extent of the intramolecular metathesis will decrease in the order 1,7-octadiene > 1,6-heptadiene > 1,8-nonadiene > 1,9-decadiene > 1,5-hexadiene. At the same time, this order will also indicate the increasing order of the extent of the intermolecular metathesis. The order is in agreement with the data experimentally obtained.

#### 4. The Structures of $\alpha,\omega$ -Dienes and Their Reactivities

The CsNO<sub>3</sub>-Re<sub>2</sub>O<sub>7</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst had an excellent selectivity to metathesis even in high conversion level and negligible activity for double-bond isomerization and polymerization. This means that the catalyst is suitable for getting reliable data about the reactivity of olefins.

The relative reactivity of a series of  $\alpha,\omega$ -dienes was investigated by both conventional and competitive reactions. The equimolar mixture of 1,7-octadiene and  $\alpha,\omega$ -diene was used in competitive reaction. Cross-metathesis products were scarcely formed in all competitive reactions, indicating that 1,7-octadiene is a favorable competitive substrate. As the induction period and the activity change were observed, the initial activity obtained by the extrapolation of the activity change with time on stream to time zero was used. The data on relative reactivity were obtained at low conversion levels less than 25%. Table 2 shows that the data obtained by both methods had fairly good agreement each other. The reactivity of  $\alpha,\omega$ -dienes decreased in the order 1,7-octadiene > 1,6-heptadiene > 1,8-nonadiene > 1,5-hexadiene > 1,9-decadiene.

It is thought that the formation of a metallocyclobutane I by an interaction of a carbene I with  $\alpha,\omega$ -diene becomes easier as the molecular chain becomes shorter but the formation of carbene II from the metallocyclobutane I does not depend on

TABLE 2  
Relative Reactivity and Reaction Behavior of  $\alpha,\omega$ -Diene

|                | Relative reactivity  |                       | Reaction behavior |              |
|----------------|----------------------|-----------------------|-------------------|--------------|
|                | Competitive reaction | Conventional reaction | Inter (mol%)      | Intra (mol%) |
| 1,5-Hexadiene  | 0.26                 | 0.28                  | 100               | 0            |
| 1,6-Heptadiene | 0.53                 | 0.58                  | 9                 | 91           |
| 1,7-Octadiene  | 1.00                 | 1.00                  | 0                 | 100          |
| 1,8-Nonadiene  | 0.30                 | 0.32                  | 68                | 32           |
| 1,9-Decadiene  | 0.15                 | 0.15                  | 100               | 0            |



starting olefins. Both 1,5-hexadiene and 1,9-decadiene underwent exclusively intermolecular metathesis and the reactivity of 1,5-hexadiene was about 1.7 times faster than 1,9-decadiene. The difference in the reactivity might be caused by the following several reasons. The chance of encounter of carbene II and a vinyl group of a different molecule to make metallocyclobutane II decreases with an increase in molecular chain. Therefore, the considerable amounts of molecules adsorbed on the active sites will desorb without undergoing reaction and also the extent of nonproductive metathesis will increase as molecular chain becomes long. These can be understood from steric repulsions between alkenyl chains and also statistic point of view. The available number of active sites decreases as molecule becomes large because the area of catalyst surface covered by a molecule is increased. The relative reactivities of normal 1-alkenes, which undergo only intermolecular metathesis, over a  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst in liquid phase decreased with an increase of molecular chain in the alkenes (24). The result can be interpreted in a similar manner as discussed above. Thus, if the metathesis occurs by only an intermolecular reaction, the reactivity will decrease with the increase in the number of carbon atoms, the length of molecular chain.

It is thought that the difference in the reactivity between intramolecular and intermolecular metathesis depends mainly on the difference in the easiness of formation to metal bicycloalkane and metallocyclobutane II from carbene II. The reactivity of 1,7-octadiene which undergoes intramolecular metathesis was about four times faster than that of 1,5-hexadiene which undergoes intermolecular metathesis. This shows the intramolecular metathesis occurs easier than intermolecular metathesis. The main reasons to make the intermolecular metathesis slower exist in the process to produce metallocyclobutane II as described above. The differences in the number of available active sites should be considered as one of other reasons. The carbene II

formed from 1,7-octadiene has such a configuration as cyclic compound and this makes the area covered by a 1,7-octadiene molecule the smallest among the compounds investigated. These are the reasons why 1,7-octadiene undergoes metathesis with the highest reactivity.

In the metathesis of 1,6-heptadiene, both intra- and intermolecular metathesis took place but the main reaction was intramolecular metathesis. The reactivity of 1,6-heptadiene should be fairly fast if the reasons described for 1,7-octadiene could be applied. However, the reactivity was about one-half of 1,7-octadiene. Angle strains and skew conformation are required to a certain extent in the course to form a metal bicycloalkane from the carbene II. This makes the intramolecular metathesis of 1,6-heptadiene difficult and slower compared with cyclohexene formation from 1,7-octadiene. Some of the carbene II are used consequently for the intermolecular metathesis which proceeds with slower reactivity and uses more active sites as compared with intramolecular metathesis.

In the metathesis of 1,8-nonadiene, the intramolecular metathesis was about 30% and this made the reactivity of 1,8-nonadiene faster than 1,9-decadiene and slower than 1,6-heptadiene.

In the metathesis of 1,9-decadiene, the intermolecular metathesis occurred exclusively and the intramolecular metathesis was negligible because of longer chain in carbene II as discussed above. The main reasons for the smallest reactivity may exist in the decrease in the apparent active sites and the difficulty in the formation of metallocyclobutane II because it has the largest molecule among  $\alpha,\omega$ -dienes investigated.

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