

69. Morton, J.F., *Econ. Bot.* 24:217 (1970).  
 70. Morton, J.F., Q.J. *Crude Drug Res.* 12:1829 (1972).  
 71. Morton, J.F., *Econ. Bot.* 32:111 (1978).  
 72. Das, N.P., *Biochem. Pharmacol.* 20:3435 (1971).  
 73. Eggum, B.O., in *Vicia faba* Feeding Value: Processing and Viruses, D.A. Bond, ed., Brussels-Luxembourg, U.K., p. 107 (1980).  
 74. Sathe, S.K., and D.K. Salunkhe, *J. Food Sci.* 46:1389 (1981).  
 75. Butler, L.G., M.L. Price and J.E. Brotherton, *J. Agric. Food Chem.* 30:1087 (1980).  
 76. deLumen, B.O., and L.A. Salamat, *Ibid.* 28:533 (1980).  
 77. Rao, P.U., and Y.G. Deosthale, *J. Sci. Food Agric.* 33:1013 (1982).  
 78. Bond, D.A., *J. Agric. Sci. (Cambridge)* 86:561 (1976).  
 79. Armstrong, W.D., W.R. Featherston and J.C. Rogler, *Poultry Sci.* 52:592 (1973).  
 80. Ford, J.E., and D. Hewitt, *Brit. J. Nutr.* 42:325 (1979).  
 81. Fuller, H.L., S.I. Chang and D.K. Potter, *J. Nutr.* 91:477 (1967).  
 82. Wah, C.S., K. Sharma and M.G. Jackson, *Indian J. Anim. Sci.* 47:8 (1977).  
 83. Price, M.L., L.G. Butler, W.R. Featherston and J.C. Rogler, *Nutr. Rep. Intern.* 17:229 (1978).  
 84. Price, M.L., L.G. Butler, J.C. Rogler and W.R. Featherston, *J. Agric. Food Chem.* 27:441 (1979).  
 85. Swain, T., in *Plant Biochemistry*, J. Bonner and E.V. Varner, eds., Academic Press, Inc., New York, NY, p. 552 (1965).  
 86. Sarwadhari, P.N., S.S. Kadam and D.K. Salunkhe, *Qual. Plant.—Plant Foods Hum. Nutr.* 31:71 (1981).  
 87. Ologhobo, A.D., and B.L. Fetuga, *Nutr. Rep. Intern.* 26:605 (1982).  
 88. Tan, N.H., Z.H.A. Rahim, H.T. Khor and K.C. Wong, *J. Agric. Food Chem.* 31:916 (1983).  
 89. Singh, U., *Nutr. Rep. Intern.* 29:745 (1984).  
 90. Stickland, R.G., *Plant Sci. Letters* 34:403 (1984).  
 91. Thompson, L.U., and J.H. Yoon, *J. Food Sci.* 49:1228 (1984).

[Received June 6, 1984]

## Metathesis of Methyl Oleate with a Homogeneous and a Heterogeneous Catalyst

HITOSHI KOHASHI<sup>1</sup> and THOMAS A. FOGLIA,\* Eastern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Philadelphia, PA 19118

### ABSTRACT

The cometathesis reaction of methyl oleate (MO) with unsaturated dicarboxylic acid esters has been studied using either a homogeneous catalyst system ( $WCl_6$ - $Me_4Sn$ ) or a heterogeneous catalyst system ( $Re_2O_7$ - $Al_2O_3$ - $Me_4Sn$ ). In the presence of the homogeneous catalyst, dimethyl-3-hexenedioate (DMHD) reacted with MO to give cometathesis products in 47% yield with a distribution of products that agreed with the theoretical equilibrium composition. When dipropyl-4-octenedioate (DPOD) was used, however, the yield of cometathesis products was less than 1%. The lower reactivity of DPOD might be due to the formation of a stable complex of DPOD with the catalyst. The cometathesis reaction of MO and DMHD was also catalyzed by the heterogeneous catalyst. However, the reaction rate decreased significantly and the distribution of products did not attain the theoretical. Similar results were obtained in the cometathesis reaction of MO and DPOD catalyzed by the heterogeneous catalyst. These results suggest that MO and DMHD are preferentially adsorbed onto the surface of this catalyst according to their polarity, and that the molar ratio of MO and DMHD at the catalytic site was different from that in the reaction medium.

### INTRODUCTION

The first study of the metathesis reaction of functionally substituted alkenes catalyzed by a homogeneous catalyst was reported by Van Dam et al. (1). The self-metathesis reaction of esters having a double bond in the  $\omega$  position catalyzed by a homogeneous catalyst subsequently were reported by Nakamura et al. (4) and Baker et al. (5). The self-metathesis reaction of methyl oleate catalyzed by a homogeneous catalyst ( $WCl_6$ -cocatalyst) was studied in detail by Ichikawa and Fukuzumi (6). The latter authors reported the optimum conditions for the self-metathesis reaction as well as the cometathesis reaction of methyl oleate with 1-decene.

On the other hand, the first study concerning the metathesis reaction of alkenes bearing a functional group catalyzed by a heterogeneous catalyst was reported by Verkuijlen et al. (7). This author studied the self-metathesis reaction of methyl-4-pentenoate using a  $Re_2O_7$ - $Al_2O_3$ - $Me_4Sn$  system. Mol et al. reported the self-metathesis

reaction of various oxygen-containing alkenes (8) and the cometathesis reaction of methyl oleate with ethylene (9), all catalyzed by the  $Re_2O_7$ - $Al_2O_3$ - $Me_4Sn$  catalyst system. In this latter report, the catalytic activity of the homogeneous catalyst ( $WCl_6$ - $Me_4Sn$ ) and the heterogeneous catalyst were compared.

Only a limited number of studies have been reported on the metathesis reaction of alkenes bearing functional groups. Accordingly, little is known about the scope of the cometathesis reaction of functionally substituted alkenes. Moreover, alkenes which were studied in the cometathesis reaction of methyl oleate were alkenes having no other functional group; e.g., ethylene, 3-hexene, 1-decene and cyclododecene (10). The present study was undertaken to investigate the cometathesis reaction of methyl oleate with unsaturated dicarboxylic acid esters catalyzed by both a homogeneous and a heterogeneous catalyst system.

### EXPERIMENTAL

#### Materials

Methyl oleate was obtained from Applied Science Laboratories (State College, Pennsylvania). Its purity was <99.5% as determined by GLC.  $WCl_6$  was purchased from Strem Chemicals, Inc. (Newburyport, Massachusetts). Tetramethyl tin ( $Me_4Sn$ ), 4-pentenoic acid, and  $Re_2O_7$  were obtained from Alfa Products (Danvers, Massachusetts).  $\gamma$ - $Al_2O_3$  (surface area 200  $m^2/g$ ) was obtained from Nikki Kagaku, Nippon Oil and Fats Company (Tokyo, Japan). 3-Hexenedioic acid and 10-undecenoic acid were purchased from Fluka Chemical Corporation (Hauppauge, New York) and Eastman Organic Chemicals (New York, New York), respectively. All solvents used were distilled and dried over 4A molecular sieve prior to use.

#### Methods

Gas liquid chromatography (GLC) was conducted with a Perkin-Elmer model Sigma 3 chromatograph equipped with dual flame ionization detectors. Separations were obtained on a 15 m methyl silicone fluid capillary column (OV-101, Hewlett Packard). A Perkin-Elmer model 720B infrared spectrophotometer was used for IR analysis. Mass spectral

<sup>1</sup> Visiting Scientist, Nippon Oil and Fats Company, Japan.

\*To whom correspondence should be addressed.

confirmation of all reaction products was obtained on a Hewlett Packard model 5995 GC-MS mass spectrometer. Column chromatography was carried out on Silica gel 60A (75-150 micron) using hexane:methylene chloride:ether gradients as the eluant. Fractions (50 ml) from the column were monitored by GLC. Major products from the self-metathesis reaction of MO and the cometathesis reaction of MO and DMHD were isolated by means of column chromatography, and then the GLC response (GLC area/mg) of each compound determined. These results were used for calculating the composition (mole %) of reaction products.

#### Preparation of Esters

Methyl esters were prepared using  $\text{CH}_2\text{N}_2$ , and other esters (ethyl, isopropyl and butyl) were prepared using  $\text{BF}_3 \cdot (\text{C}_2\text{H}_5\text{OC}_2\text{H}_5)$  reagent. All esters were purified on chromatographic columns packed with basic  $\text{Al}_2\text{O}_3$  to remove unreacted acids. Results from the metathesis reaction of esters catalyzed by the heterogeneous catalyst showed that no homologous compounds of expected products were formed, indicating that no migration of the double bond of acids occurred during esterification and metathesis reactions. Diisopropyl-4-octenedioate (DPOD) was prepared by the self-metathesis reaction of isopropyl-4-pentenoate catalyzed by  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3\text{-Me}_4\text{Sn}$ . It was purified by column chromatography.

#### Preparation of $\text{WCl}_6$

$\text{WCl}_6$  was purified by sublimation of the more volatile impurities under a dry nitrogen stream at about 200 C, leaving a residue of pure  $\text{WCl}_6$  (11). Purified  $\text{WCl}_6$  was dissolved in chlorobenzene to give a 0.1 M solution. A freshly prepared  $\text{WCl}_6$  solution was used for each reaction.  $\text{Me}_4\text{Sn}$  also was dissolved in chlorobenzene to give a 0.1 M solution.  $\text{WCl}_6$  is very sensitive to air and moisture, so all procedures must be performed under dry nitrogen.

#### Preparation of $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$

$\text{Re}_2\text{O}_7$  (0.12 g, 0.25 mM) was dissolved in dry methyl alcohol (5 ml), then added to precalcined  $\gamma\text{-Al}_2\text{O}_3$  (0.26 g). The precalcination (500 C, 2 hr) of  $\gamma\text{-Al}_2\text{O}_3$  is necessary to prepare an active catalyst. Methyl alcohol was evaporated using a rotary evaporator at 40 C under vacuum (10 mm Hg). The  $\gamma\text{-Al}_2\text{O}_3$  impregnated with  $\text{Re}_2\text{O}_7$  was dried for 18 hr at 120 C, then packed in a glass tube (inside diameter, 4 mm). The glass tube was mounted vertically in an electric tube furnace and calcined at 550 C for 2 hr in dry air stream (1 ml/min) from the bottom of the glass tube. About half the amount of  $\text{Re}_2\text{O}_7$  sublimed during calcination and recrystallized on the inside wall of the glass tube. The recrystallized  $\text{Re}_2\text{O}_7$  was collected and used in the next catalyst preparation. After the calcination, the catalyst was cooled to room temperature in a dry air stream and used for the metathesis reactions. The loading amount of

$\text{Re}_2\text{O}_7$  on  $\gamma\text{-Al}_2\text{O}_3$  was calculated by weight gain. The range of loading amount was 14 ~ 18 wt %. The reaction is not sensitive to air, and no rigorous precautions are necessary to exclude air (10). A freshly prepared  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  catalyst was used for each reaction.  $\text{Me}_4\text{Sn}$  was dissolved in chlorobenzene to prepare a 2% solution.

#### Reaction Procedure

*Method A (homogeneous catalyst).* The cometathesis of methyl oleate (MO) and dimethyl-3-hexenedioate (DMHD) is a typical example. A screw-cap vial (1 ml) equipped with rubber septum stopper was dried carefully to exclude moisture, and air was exchanged with dry nitrogen. Fresh  $\text{WCl}_6$  solution (100  $\mu\text{l}$ , 10  $\mu\text{M}$ ) and  $\text{Me}_4\text{Sn}$  solution (100  $\mu\text{l}$ , 10  $\mu\text{M}$ ) was introduced into the reaction vial by means of hypodermic syringe through the rubber septum. Then a mixture of MO (51  $\mu\text{l}$ , 150  $\mu\text{M}$ ), DMHD (24  $\mu\text{l}$ , 150  $\mu\text{M}$ ), and chlorobenzene (20  $\mu\text{l}$ ) were injected. The reaction vial was placed in an oil bath, heated to 100 C, and sampled and analyzed periodically by GLC.

*Method B (heterogeneous catalyst).* The cometathesis of MO and DMHD is a typical example. The reaction vial equipped with a small stirring bar was dried carefully, and air was exchanged with dry nitrogen. Freshly prepared  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  (17.4%  $\text{Re}_2\text{O}_7$  by weight; 0.0653 g,  $\text{Re}_2\text{O}_7$  23.5  $\mu\text{M}$ ) was introduced and then a mixture of  $\text{Me}_4\text{Sn}$  solution (72  $\mu\text{l}$ , 11.7  $\mu\text{M}$ ) and chlorobenzene (80  $\mu\text{l}$ ) was injected into the reaction vial with a hypodermic syringe. The catalyst slurry was stirred and a mixture of MO (24  $\mu\text{l}$ , 70.5  $\mu\text{M}$ ), DMHD (11.3  $\mu\text{l}$ , 70.5  $\mu\text{M}$ ) and chlorobenzene (40  $\mu\text{l}$ ) were injected. The reaction vial was heated to 70 C. The liquid phase was sampled and analyzed periodically by GLC. When the amounts of adsorbed MO and DMHD on the catalyst surface were determined, the reaction mixture supernatant was analyzed after standing for 1 hr at room temperature.

## RESULTS AND DISCUSSION

### Metathesis By Homogeneous Catalyst

The self-metathesis reaction of MO was studied as a standard reaction. When MO **1** was reacted with the  $\text{WCl}_6\text{-Me}_4\text{Sn}$  catalyst, 9-octadecene **2**, dimethyl-9-octadecenedioate **3**, and methylmonochlorostearate **4** were isolated as the major products (Fig. 1). The composition of the reaction mixture became constant after 4 hr, after which no further conversion of MO to products was noted. When the molar ratio of  $\text{WCl}_6$  to MO was 1 to 30, the conversion of MO was 51% and the selectivity (% metathesis products to MO reacted) of the metathesis reaction was 89%. The addition of HCl to MO to form methyl monochlorostearate also was observed. The composition of the reaction mixture is shown in Table I. Homologous compounds (heptadecene, nonadecene, heptadecenoate, nonadecenoate, heptadecenedioate and nonadecenedioate) of the expected metathesis

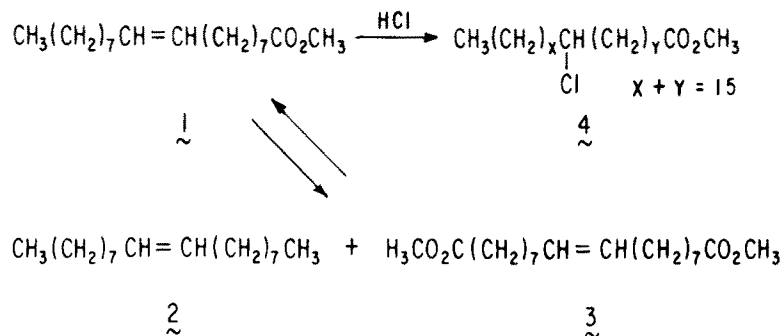


FIG. 1. Self-metathesis of methyl oleate.

## COMETATHESIS OF METHYL OLEATE

TABLE I

## Self-metathesis of Methyl Oleate

Reaction products		WCl <sub>6</sub> -Me <sub>4</sub> Sn <sup>a</sup>	Re <sub>2</sub> O <sub>7</sub> -Al <sub>2</sub> O <sub>3</sub> -Me <sub>4</sub> Sn <sup>b</sup>
Methyl oleate	1 <sup>d</sup>	48.5	50.0
9-Octadecene	2	23.4	25.5
Dimethyl-9-octadecenedioate	3	22.2	24.0
Methyl monochlorostearate	4	2.8	0
Others		3.0	0.5
Selectivity <sup>c</sup>		89	99

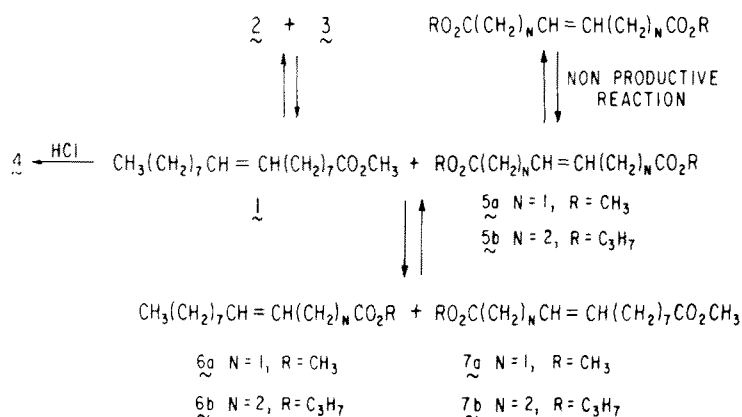
<sup>a</sup>Molar ratio WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO = 1/1/30, 100 C, 4 hr.<sup>b</sup>Molar ratio Re<sub>2</sub>O<sub>7</sub>/Me<sub>4</sub>Sn/MO = 1/0.5/6, 70 C, 4 hr.<sup>c</sup>% Metathesis products to methyl oleate reacted.<sup>d</sup>Structures given in Figure 1.FIG. 2. Co-metathesis of methyl oleate **1** with dimethyl-3-hexenedioate **5a** or diisopropyl-4-octenedioate **5b**.

TABLE II

Cometathesis Yield<sup>a</sup> (M %) of MO<sup>b</sup> and DMHD Catalyzed by WCl<sub>6</sub>/Me<sub>4</sub>Sn

Molar ratio of alkenoates	Reaction time (hr)		
	1	4	21
WCl <sub>6</sub> /Me <sub>4</sub> Sn/MO/DMHD <sup>c</sup>			
10/10	32	42	46
15/15	29	40	42
20/20	29	39	45
30/30	17	26	34

<sup>a</sup>Methyl-3-dodecenoate **6a** + dimethyl-3-dodecenedioate **7a**.<sup>b</sup>MO = methyl oleate; DMHD = dimethyl-3-hexenedioate.<sup>c</sup>Molar ratio of WCl<sub>6</sub>/Me<sub>4</sub>Sn constant at 1:1.

products were found as minor co-products. This suggested that a small amount of migration of the double bond of MO occurred during the metathesis reaction, which probably was due to HCl formation from WCl<sub>6</sub>. Evidence for the latter was obtained by oxidative cleavage of the residual methyl oleate (13). GLC analysis of the methyl esters of the diacids formed showed the presence of C<sub>8</sub> and C<sub>10</sub> diacids in addition to the expected C<sub>9</sub> diacid.

When DMHD was co-reacted with MO using the WCl<sub>6</sub>-Me<sub>4</sub>Sn catalyst system, methyl-3-dodecenoate **6a**, dimethyl-3-dodecenedioate **7a**, and self-metathesis products of MO were formed (Fig. 2). The position of the double bond of methyl-3-dodecenoate and dimethyl-3-dodecenedioate was determined after conversion to acids by means

of a RuO<sub>4</sub> oxidation procedure (13). The only dicarboxylic acid detected from methyl-3-dodecenoate **6a** by oxidation was nonanedioic acid. This result showed that the position of the double bond was at the Δ<sub>3</sub> position and that no migration of the double bond occurred in the metathesis reaction. The cometathesis yield (**6a** + **7a**) is a function of the molar ratio of WCl<sub>6</sub> to reactants and a function of reaction time (Table II). When the molar ratio was 1/1/30/30, the reaction rate decreased. The self-metathesis reaction of MO (molar ratio WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO = 1/1/30) came to equilibrium after 4 hr reaction, whereas, the cometathesis reaction of MO and DMHD (molar ratio WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO/DMHD = 1/1/15/15) required a longer reaction time to attain equilibrium. The composition of the reaction mixture of MO and DMHD agreed with the theoretical composition (Table III) after 21 hr reaction. The cometathesis reaction at various molar ratios of MO to DMHD was studied keeping the molar ratio of WCl<sub>6</sub> to esters at a 1 to 30 ratio (Fig. 3). The best yield of cometathesis products was obtained when the molar ratio of MO to DMHD was 1 to 1. The yield of cometathesis products of MO and DMHD at the various molar ratios approached theoretical.

Different esters of 3-hexenedioic acid were prepared using ethyl, isopropyl and n-butyl alcohol to give diethyl-3-hexenedioate (DEHD), dipropyl-3-hexenedioate (DPHD), and dibutyl-3-hexenedioate (DBHD), respectively. The cometathesis reactions of DMHD and these esters with MO were studied keeping the molar ratio of WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO/hexenedioate at 1/1/15/15. The results obtained showed that the alcohol residue of the esters has little effect on either reaction rate or yield of cometathesis products. On

TABLE III  
The Composition of Cometathesis Reaction of MO and DMHD<sup>a</sup>

Reaction products		Theoretical composition	WCl <sub>6</sub> -Me <sub>4</sub> Sn <sup>b</sup>	Re <sub>2</sub> O <sub>7</sub> -Al <sub>2</sub> O <sub>3</sub> -Me <sub>4</sub> Sn <sup>c</sup>
DMHD	5 <sub>a</sub> <sup>d</sup>	25.0	26.0	42.9
Methyl-3-dodecenoate	6 <sub>a</sub>	25.0	23.3	3.6
Dimethyl-3-dodecenedioate	7 <sub>a</sub>	25.0	21.4	4.0
MO	1	12.5	18.5	35.9
9-Octadecene	2	6.25	3.6	6.9
Dimethyl-9-octadecenedioate	3	6.25	3.0	6.7
Others		0	4.2	0

<sup>a</sup>MO = methyl oleate; DMHD = dimethyl-3-hexenedioate.

<sup>b</sup>Molar ratio WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO/DMHD = 1/1/15/15, 100 C, 21 hr.

<sup>c</sup>Molar ratio Re<sub>2</sub>O<sub>7</sub>/Me<sub>4</sub>Sn/MO/DMHD = 1/0.5/3/3, 70 C, 24 hr.

<sup>d</sup>Structures given in Figure 2.

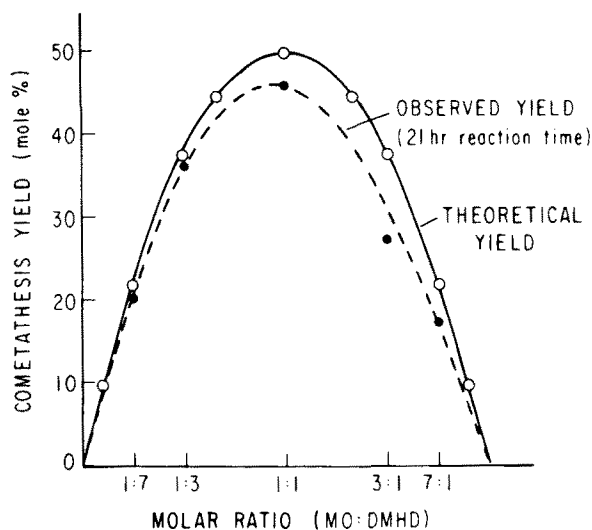


FIG. 3. Theoretical vs actual yields of cometathesis reaction of methyl oleate and dimethyl-3-hexenedioate.

the other hand, when dipropyl-4-octenedioate (DPOD) was reacted with MO using the WCl<sub>6</sub>-Me<sub>4</sub>Sn catalyst, the reaction rate decreased markedly. Only a trace amount of cometathesis products was found, and less than 2% of 9-octadecene **2** and dimethyl-9-octadecenedioate **3** were formed. Accordingly, in the cometathesis reaction of MO with ROCC<sub>n</sub> = C<sub>n</sub>COOR, the reaction proceeds theoretically when n is 2, but proceeds poorly when n is 3.

TABLE IV  
Composition of Cometathesis Reactions (Area % by GC Analysis)

Reaction composition	MO and C = C <sub>3</sub> COOC <sub>3</sub>		MO and C = C <sub>9</sub> COOC	
	WCl <sub>6</sub> <sup>a</sup>	Re <sub>2</sub> O <sub>7</sub> <sup>b</sup>	WCl <sub>6</sub> <sup>a</sup>	Re <sub>2</sub> O <sub>7</sub> <sup>b</sup>
Starting materials <sup>c</sup>	87.7	21.5	34.4	28.0
Cometathesis yield <sup>d</sup>	5.7	57.5	42.4	48.4
MO self-metathesis yield	trace	13.7	11.4	16.9
C = C <sub>n</sub> COOR self-metathesis yield <sup>e</sup>	2.3	7.3	4.4	5.6
Others	4.3	0	7.4	1.1

<sup>a</sup>Molar ratio WCl<sub>6</sub>/Me<sub>4</sub>Sn/MO/C = C<sub>n</sub>COOR = 1/1/15/15, 100 C, 24 hr.

<sup>b</sup>Molar ratio Re<sub>2</sub>O<sub>7</sub>/Me<sub>4</sub>Sn/MO/C = C<sub>n</sub>COOR = 1/0.5/3/3, 70 C, 4 hr.

<sup>c</sup>MO + C = C<sub>n</sub>COOR.

<sup>d</sup>C<sub>9</sub> = C<sub>n</sub>COOR + ROCC<sub>n</sub> = C<sub>n</sub>COOR.

<sup>e</sup>ROCC<sub>n</sub> = C<sub>n</sub>COOR (C = C is not detected).

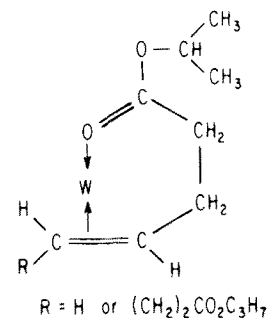


FIG. 4. Complex of WCl<sub>6</sub> and isopropyl-4-pentenoate.

The cometathesis reactions of MO with terminal alkeneoates of structure C = C<sub>n</sub>COOR (n = 3 and 9) also were studied (Table IV). Isopropyl-4-pentenoate is very inactive in metathesis reactions catalyzed by the WCl<sub>6</sub>-Me<sub>4</sub>Sn system, whereas when n = 9 the reaction proceeds as expected.

Bosma et al. (4) reported that the reactivity of unsaturated nitriles of general formula CH<sub>2</sub> = CH[CH<sub>2</sub>]<sub>m</sub>CN, in metathesis reactions catalyzed by WCl<sub>6</sub>-Me<sub>4</sub>Sn system, is dependent on their alkyl chain length; a significant decrease in reactivity was found when m is 3 and 4 (14). Ichikawa and Fukuzume (6) confirmed by IR analysis that methyl oleate coordinates by its carbonyl group to the WCl<sub>6</sub> catalyst to form a stable complex.

Accordingly, the lower reactivity of both of C = C<sub>3</sub>-COOC<sub>3</sub> and C<sub>3</sub>COCC<sub>3</sub> = C<sub>3</sub>COOC<sub>3</sub> may be due to the formation of stable complexes (Fig. 4). If such a complex is formed, the coordination of the second alkene, which is

TABLE V

Effect of Molar Ratio of  $\text{Re}_2\text{O}_7$  to MO<sup>a</sup> in Self-metathesis Reaction of MO

$\text{Re}_2\text{O}_7/\text{Me}_4\text{Sn}/\text{MO}^b$	Reaction time (hr) (70 C)		
	1	4	24
1/0.5/6	42	50	50
1/0.5/9	39	50	50
1/0.5/20	18	26	40

<sup>a</sup>MO = methyl oleate.

<sup>b</sup>Molar ratio.

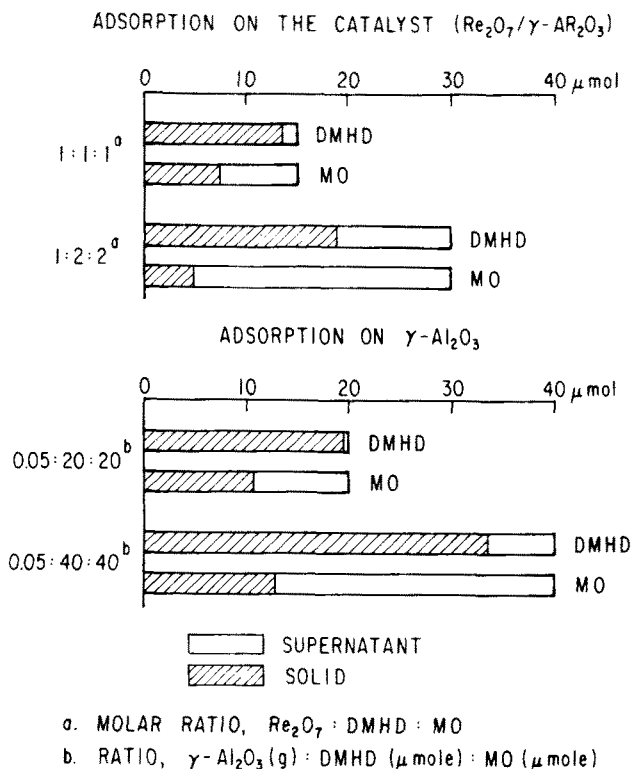


FIG. 5. Adsorption of methyl oleate and dimethyl-3-hexenedioate onto  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$  catalyst.

essential for a metathesis reaction, is blocked. Consequently, the reaction rate should decrease significantly.

#### Metathesis By Heterogeneous Catalyst

Cometathesis reactions of MO with DMHD and other esters was also studied using a heterogeneous catalyst ( $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3\text{-Me}_4\text{Sn}$ ). Recently, Van Den Aardweg et al. reported the catalytic activities of both catalyst systems in the self-metathesis of unsaturated nitriles (15).

The self-metathesis reaction of MO was studied as a standard reaction. In the self-metathesis reaction of MO, an extremely high reaction selectivity (99%) was observed (Table I). The reaction rate as a function of the molar ratio of  $\text{Re}_2\text{O}_7$  to MO and a function of time is given in Table V. In comparison with the homogeneous catalyst, the heterogeneous catalyst has the advantage of high selectivity; however, a disadvantage is that it requires a higher ratio of  $\text{Re}_2\text{O}_7$  to MO to obtain good conversion.

In the cometathesis reaction of MO and DMHD, not only was a significant decrease of reaction rate observed, but also the composition of the reaction mixture did not agree with the theoretical distribution. The self-metathesis reaction of MO dominated over the cometathesis reaction

of MO with DMHD (Table III). This result suggested that the molar ratio of MO and DMHD at the active site of the catalyst was not the same as it was in the reaction medium. In order to clarify this point, the molar ratios of MO and DMHD in the supernatant were estimated by GC analysis, and then the amounts of adsorbed MO and DMHD on the catalyst, or  $\gamma\text{-Al}_2\text{O}_3$  were calculated (Fig. 5). The results show that the amount of adsorbed DMHD on the catalyst is greater than that of MO. The amount of adsorption may be dependent on the polarity of the ester. Alkeneoate compounds should adsorb competitively according to their polarity on the surface of  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3$  (and  $\text{Al}_2\text{O}_3$ ), which is made very polar by previous calcination. Consequently, the amount of MO in the supernatant is greater than that of DMHD. This may be the reason why the self-metathesis reaction of MO dominates in the cometathesis reaction of MO with DMHD catalyzed by  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3\text{-Me}_4\text{Sn}$ . The significant decrease in reaction rate of the cometathesis reaction may be that DMHD is more strongly adsorbed onto the catalyst surface, since the sites where DMHD and MO adsorb are not only on  $\text{Re}_2\text{O}_7$ , but also on  $\gamma\text{-Al}_2\text{O}_3$ . A similar phenomenon of preferential adsorption of DMHD onto calcined  $\gamma\text{-Al}_2\text{O}_3$  alone also was observed. Accordingly, the main sites where DMHD adsorb are onto the surface of  $\gamma\text{-Al}_2\text{O}_3$  support, and this accounts for the decrease in cometathesis yield.

The cometathesis reaction of MO and DPOD, a reaction that did not proceed with the  $\text{WCl}_6\text{-Me}_4\text{Sn}$  catalyst, was catalyzed by the  $\text{Re}_2\text{O}_7\text{-Al}_2\text{O}_3\text{-Me}_4\text{Sn}$  catalyst. However, the reaction rate was slow and the composition of products did not agree with the theoretical distribution. The cometathesis yield (isopropyl-4-tridecenoate **6b** + diisopropyl-4-tridecenedioate **7b**) was only 3%, and the self-metathesis yield of MO was 4%. These results are similar to those observed in the cometathesis reaction of MO and DMHD.

The cometathesis reactions of MO with terminal alkeneoates of general structure  $\text{C} = \text{C}_n\text{COOR}$  ( $n = 3$  and 9) also were studied using the heterogeneous catalyst (Table IV). The rates of these cometathesis reactions were as fast as that of the self-metathesis reaction of MO, and the yields of products reached equilibrium after 4 hr reaction. The heterogeneous catalyst rapidly catalyzed the cometathesis of MO and isopropyl-4-pentenoate ( $\text{C} = \text{C}_3\text{COOC}_3$ ), which is very slow using the homogeneous catalyst. The reason why the cometathesis reaction of MO and  $\text{C} = \text{C}_3\text{COOC}_3$  proceeds rapidly and the cometathesis reaction of MO and DPOD ( $\text{C}_3\text{OCC}_3 = \text{C}_3\text{COOC}_3$ ) proceeds slowly with the heterogeneous catalyst may be due to the polarity of these esters. Because isopropyl-4-pentenoate is not as polar as DPOD, it does not adsorb as strongly onto the  $\text{Al}_2\text{O}_3$  to inhibit the cometathesis reaction. The self-metathesis of isopropyl-4-pentenoate to form DPOD is catalyzed by both the homogeneous and the heterogeneous catalysts. The yield of DPOD was 45% with the heterogeneous catalyst (molar ratio  $\text{Re}_2\text{O}_7/\text{Me}_4\text{Sn}/\text{pentenoate} = 1/0.5/6$ , 4 hr), and 1% with the homogeneous catalyst (molar ratio  $\text{WCl}_6/\text{Me}_4\text{Sn}/\text{pentenoate} = 1/1/30$ , 24 hr). These results also suggest that isopropyl-4-pentenoate is not strongly enough adsorbed onto the catalyst surface to inhibit its cometathesis.

#### ACKNOWLEDGMENT

Ray H. Liu operated the MS.

#### REFERENCES

1. Van Dam, P.B.; M.C. Mittlemeijer and C. Boelhouwer, J.C.S. Chem. Comm. 1221 (1972).

