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HETEROGENEOUS METATHESIS OF UNSATURATED ESTERS USING A RHENIUM-BASED CATALYST

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Summary

The heterogeneous metathesis of unsaturated esters was carried out at room temperature, using the catalyst system Re_2O_7/Al_2O_3 with an organometallic compound as cocatalyst. The influence of several parameters on the activity of the catalyst was studied with methyl oleate (methyl-*Z*-9-octadecenoate) as substrate. The use of a nonpolar solvent and a cocatalyst of general formula SnR_4, in which R is a linear alkyl group, provided optimal reaction conditions. The activity of a deactivated catalyst could be completely restored by recalcination in oxygen, followed by addition of a further amount of cocatalyst.

The reactivities of various unsaturated esters as a function of their molecular structure was studied; these esters undergo metathesis when the double bond and the carboxylic group are separated by at least one methylene group. In general, α-β-unsaturated esters show a reasonable activity for cometathesis with simple alkenes, such as *E*-3-hexene.

Introduction

Alkene metathesis (eq. 1) is a catalytic reaction involving the rupture of double bonds and the recombination of the alkylidene fragments into new unsaturated molecules.

$$2RHC{=}CHR' \rightleftharpoons RHC{=}CHR + R'HC{=}CHR' \quad (1)$$

Both homogeneous and heterogeneous catalysts have been developed for the metathesis of alkenes; the most active are based on tungsten, molybdenum, and rhenium.

One of the most promising applications of the metathesis reaction, both from a synthetic as well as a technological point of view, is to functionalized alkenes, e.g. unsaturated esters, ketones, nitriles etc. [1,2]. The number of active catalysts for these substrates is, however, rather limited because most metathesis catalysts are easily poisoned by polar groups. In 1972 Van Dam et al. [3] reported the succesful homogeneously catalyzed metathesis of methyl oleate (methyl-*Z*-9-octadecenoate), using the catalyst WCl_6-$Sn(CH_3)_4$:

$$2CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + CH_3OOC(CH_2)_7CH{=}CH(CH_2)_7COOCH_3 \quad (2)$$

After this first discovery, reports on the homogeneous metathesis of other unsaturated esters [4] and of other functionalized alkenes such as unsaturated ethers [5], amines [6] and nitriles [7] followed. Homogeneous catalysis, however, suffers from some general drawbacks, such as difficult separation of the products from the reaction mixture and the impossibility of regenerating the catalyst.

Verkuijlen et al. [8] were the first to report the heterogeneously catalyzed metathesis of unsaturated esters; they found that after activation of the solid catalyst Re_2O_7/Al_2O_3 with a small amount of $Sn(CH_3)_4$, 51% of methyl-4-pentenoate was converted into ethene and dimethyl-4-octenedioate with high selectivity. The same catalyst system is also active and highly selective for the metathesis of various other oxygen-containing alkenes, such as unsaturated ethers, ketones and allyl acetate, and for halogeno-alkenes [9], and has recently been shown to be effective in the metathesis of unsaturated nitriles [10]. Furthermore, Fridman et al. [11–13] were able to bring about metathesis of trimethylsilylethene, vinyl and allyl halides, diallyl ether and the allyl ether of allyl carbinol using a Re_2O_7/Al_2O_3 catalyst, activated with SnR_4 (R = alkyl).

In this paper we present a study on the general features of the Re_2O_7/Al_2O_3 catalyst activated with an organometallic cocatalyst. We also describe a systematic study of the metathesis of unsaturated esters, in which both the substitution at the double bond and the number of methylene groups between the double bond and the carboxylic group were varied.

Experimental

Chemicals

The unsaturated esters were either purchased (Fluka, Aldrich) or synthesized from the corresponding acids or alcohols (Aldrich). Before use all esters were first cautiously de-acidified or de-alcoholised and dried. In some cases the esters needed further purification by preparative GLC, because normal work up procedures did not remove all impurities which could either affect the activity of the catalyst or interfere with the GLC analysis. All esters were deoxygenated and stored over molecular sieves 5A under dry argon. *E*-3-hexene (Aldrich, gold label) de-oxygenated and stored over molecular sieves 5A under dry argon was used without further purification.

The solvents were thoroughly dried and de-oxygenated by refluxing over sodium wire (hexane) or phosphorus pentoxide (chlorobenzene, tetrachloromethane) under a constant argon stream. Ethyl acetate was de-acidified and dried over anhydrous sodium sulphate before distillation. After distillation under argon the solvents were stored over molecular sieves 5A under dry argon.

The tin compounds were used as purchased (Fluka, Aldrich). Butyl-lithium (25% in hexane, Merck) and trimethyltrichlorodialuminium (25% in hexane, Alfa Products) were used without further purification.

The Re_2O_7/Al_2O_3-catalyst was prepared by impregnation of γ-Al_2O_3 (Ketjen C.K.-300, surface area 195 m^2/g) with an aqueous solution of ammonium perrhenate (99.999%, Drijfhout) followed by drying in air for 2 h at 383 K.

Procedure

The metathesis reactions were carried out in the liquid phase in a glass batch reactor of about 30 ml capacity. In a typical experiment, the catalyst, 100 mg (18 mass % $Re_2O_7 = 37 \times 10^{-6}$ mol Re_2O_7), was calcined in dry oxygen at 823 K for 2 h, followed by heating in a stream of dry, oxygen-free nitrogen at the same temperature for 2 h. The reaction vessel was equipped with a septum cap and a valve to allow introduction of reagents with hypodermic syringes. During the reaction the valve was closed. Subsequently 1 ml of solvent (hexane) containing 1 μl of $Sn(CH_3)_4$ (7.2×10^{-6} mol) and 37×10^{-5} mol of substrate were introduced into the reaction vessel. In the cometathesis experiments 37×10^{-5} mol of *E*-3-hexene was introduced into the vessel before the ester. All reactions were carried out at room temperature.

Analysis

The metathesis reactions were monitored by GLC analysis of the liquid or gaseous phase. The GLC signals (FID) were real-time processed by a PDP 11/10 computer system, provided with a GC-signal integrating program [14], or a Hewlett-Packard 3370 A integrator. The molecular responses of the substrates were estimated by Ackman's method [15,16]. For the alkane/alkene analysis a β,β'-oxydipropionitrile or a bis-(2(2-methoxyethoxy)ethyl) ether column was used. Reaction mixtures from esters were analysed on carbowax 20 M and UCC-W-982 columns. Reaction products were identified by comparison of the retention times with those of authentic samples.

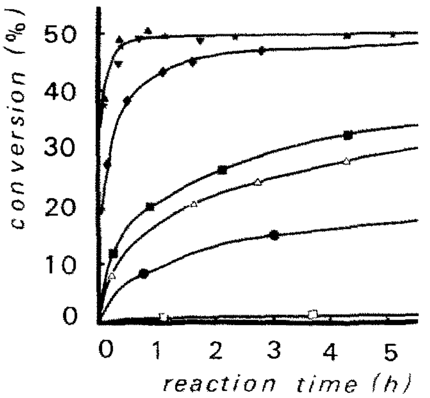
Results

The influence of several parameters on the metathesis of unsaturated esters with the catalyst Re_2O_7/Al_2O_3 in combination with an organometallic cocatalyst

In order to optimize catalyst performance, several reactions were varied and their influence on the reaction investigated. In these experiments methyl oleate was used as a test substrate; unless mentioned otherwise, 126 μl (= 370 μmol) was taken. The reaction was monitored by GLC analysis of the liquid phase. It should be noted, however, that the product di-ester is more strongly adsorbed on the catalyst surface than the substrate mono-ester and so the degree of conversion indicated by analysis of the liquid phase might differ from the actual value.

Effect of different cocatalysts. To optimize the activation of the Re_2O_7/Al_2O_3 catalyst, various organometallic compounds were tried as cocatalyst. In all the experiments 100 mg of Re_2O_7/Al_2O_3 (18 mass % Re_2O_7) was treated with 7.2×10^{-6} mol cocatalyst in 1 ml hexane. After two minutes the methyl oleate was added and the degree of conversion at room temperature was determined at appropriate times.

Figure 1 shows that compounds of general formula SnR_4, where R is a linear alkyl chain, provide the most active catalyst system. When R is a branched alkyl group the activity is markedly lower, and when R is cyclic there is a further decline in activity. $(CH_3)_3Al_2Cl_3$ provides a moderately active catalyst, and butyl-Li shows hardly any activity.



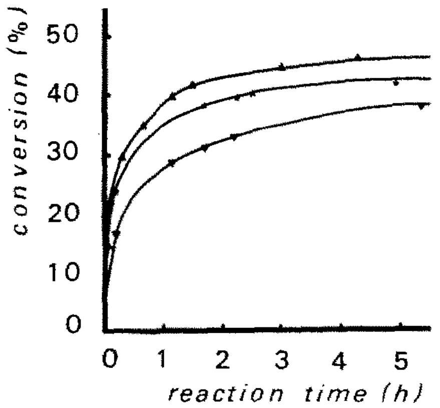


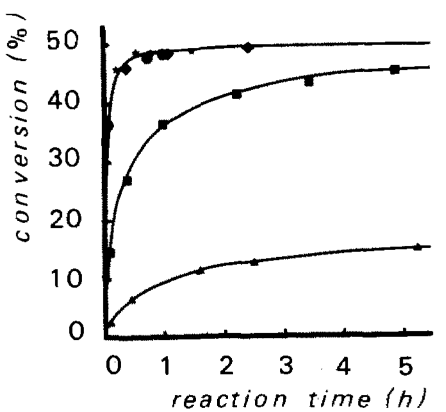
Fig. 1. Effect of different cocatalysts on the metathesis of methyl oleate in the presence of Re_2O_7/Al_2O_3 (126 μl/100 mg Re_2O_7/Al_2O_3) ★ $Sn(CH_3)_4$, ▲ $Sn(C_2H_5)_4$, ▼ $Sn(C_4H_9)_4$, ◆ $Sn(C_8H_{17})_4$, ■ $(CH_3)_3Al_2Cl_3$, △ $Sn(i\text{-}C_3H_7)_4$, ● $Sn(C_6H_{11})_4$, □ $Li(C_4H_9)_4$.

Fig. 2. Effect of several cocatalysts on the metathesis of methyl oleate (252 μl/100 mg Re_2O_7/Al_2O_3). ★ $Sn(CH_3)_4$, ▲ $Sn(C_2H_5)_4$, ▼ $Sn(C_4H_9)_4$.

When the amount of substrate is doubled, the small differences in activity between $Sn(CH_3)_4$, $Sn(C_2H_5)_4$ and $Sn(C_4H_9)_4$ become more pronounced; Fig. 2 clearly indicates that $Sn(C_2H_5)_4$ is the most effective cocatalyst of the three. Since, however, $Sn(CH_3)_4$ is the only one of these cocatalysts which does not interfere with the signals of other compounds in the GLC analysis of the reaction mixtures, this tin compound was used throughout the subsequent work.

Effect of the rhenium content of the catalyst. Kapteijn et al. [17] observed that for the metathesis of propene the activity of Re_2O_7/Al_2O_3 catalysts, without a cocatalyst, increases exponentionally as a function of the Re_2O_7 content, up to the maximum loading of ca 18 mass %. Analogously, the rate of metathesis of methyl oleate in the presence of $Re_2O_7/Al_2O_3\text{-}Sn(CH_3)_4$ increases rapidly when the (calculated) Re_2O_7 content is increased up to ca 12 mass % (Fig. 3). Further increase in activity as a function of the rhenium content could not be observed because the thermodynamic equilibrium conversion is rapidly attained under the conditions used.

Effect of the amount of cocatalyst. To study the relation between the activity of the catalyst and the amount of cocatalyst, some experiments were carried out in which the Re/Sn ratio was varied. The molar ratios Re/Sn were 440/1, 220/1, 110/1, 67/1, 11/1 and 1.1/1, respectively. Figure 4 shows that when the amount of $Sn(CH_3)_4$ is increased to 1.5 mol% of the rhenium present on the catalyst (i.e. Re/Sn > 67/1), the activity of the catalyst system increases. GLC analysis showed that the cocatalyst is completely adsorbed on the catalyst surface. When the amount of cocatalyst is more than 1.5 mol% of the rhenium present, the activity of the system remains constant and part of the cocatalyst is not adsorbed on the catalyst surface. Replacing the solvent (hexane) containing the excess of the cocatalyst by fresh solvent did not influence the activity of the catalyst, and the cocatalyst was not desorbed from the catalyst surface.



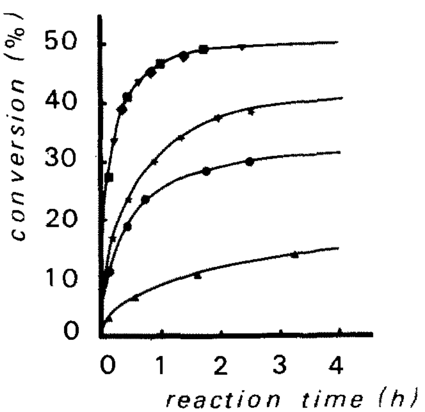


Fig. 3. Effect of the Re_2O_7 content of the Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ catalyst on the metathesis of methyl oleate. ▲ 6 mass% Re_2O_7, ■ 9 mass% Re_2O_7, ◆ 12 mass% Re_2O_7, ★ 15 mass% Re_2O_7, ● 18 mass% Re_2O_7.

Fig. 4. Effect of the molar ratio Re/Sn on the metathesis of methyl oleate in the presence of Re_2O_7/Al_2O_3-$Sn(CH_3)_4$. ▲ Re/Sn = 440/1, ● Re/Sn = 220/1, ★ Re/Sn = 110/1, ▼ Re/Sn = 67/1, ■ Re/Sn = 11/1, ◆ Re/Sn = 1.1/1.

Effect of solvent. Metathesis of methyl oleate in the presence of Re_2O_7/Al_2O_3 activated with $Sn(CH_3)_4$ was carried out in solvents of different polarities (Fig. 5). The highest conversions were obtained with chlorobenzene and hexane. In solvents of high polarity, such as ethyl acetate, diethyl ether and methylisobutyl ketone, hardly any reaction took place. When the catalyst was activated with the cocatalyst in an apolar solvent, its colour changed from white to brown, whereas it remained white when the activation was in a polar solvent. To exclude the possibility that the activation might not have taken place in a polar solvent an additional experiment was carried out. In this experiment the catalyst was activated using hexane as a solvent. The hexane was then evaporated by evacuating the reaction vessel. After the addition of 1 ml of ethyl acetate the progress of reaction was monitored. Figure 5

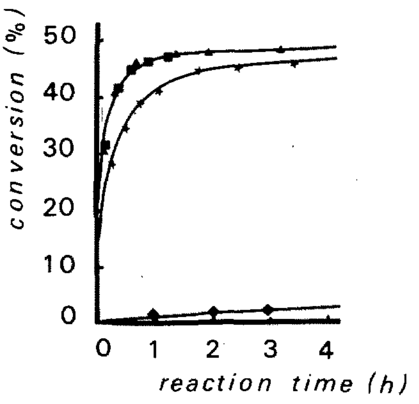


Fig. 5. Effect of the solvent on the metathesis of methyl oleate in the presence of Re_2O_7/Al_2O_3-$Sn(CH_3)_4$. ▲ C_6H_5Cl, ■ C_6H_{14}, ★ CCl_4, ◆ Activation in C_6H_{14}, reaction in ethyl acetate (see text).

shows that the reaction is still much slower than when an apolar solvent is used. However, the results are better than those obtained when both the activation of the catalyst and the reaction of the substrate took place in ethyl acetate. These results suggest that both the activation of the catalyst and the propagation of the metathesis are more effective in an apolar solvent.

Other experiments with an apolar solvent showed that when the substrate is added to the catalyst first, followed by the cocatalyst, the catalyst was much less effective than when the cocatalyst is added first.

Apparently, the activation of the catalyst surface by a cocatalyst is ineffective when polar groups (either from a solvent or from the substrate) are present in the reaction mixture; i.e. adsorption of the polar groups on the catalyst surface prevents the interaction between the cocatalyst and the surface.

Regeneration of the catalyst. The catalyst eventually lost its activity. However, it could be reactivated by the calcination treatment used for the fresh catalyst (see Experimental section). Addition of a further amount of cocatalyst was necessary. The activity of the regenerated catalyst was equal to that of the fresh catalyst, and the same catalyst could be reactivated virtually an unlimited number of times.

Comparison of the activity of the Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ catalyst for the metathesis of unsaturated esters with its activity for the metathesis of nonfunctionalized alkenes

Having optimized several parameters of the catalyst system it seemed of interest to draw a (rough) comparison between the effectiveness of the catalyst for the metathesis of an unsaturated ester and that of a non-functionalized alkene. However, since the thermodynamic equilibrium of the reaction is approximately 50% for most substrates, the reverse reaction slows down the overall reaction rate, even at relatively low conversions. Furthermore, when metathesis of a functionalized alkene is carried out batchwise a considerable number of active sites on the catalyst surface are ineffective for metathesis, because of the interaction with the functional group of the substrate. Both these problems can be at least partly overcome by conducting the reaction in a flow reactor, so that the catalyst is continuously in contact with a small amount of substrate for a short time. Therefore, we studied the performance of the catalyst in a flow reactor, both for a functionalized and a nonfunctionalized alkene.

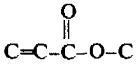
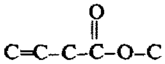
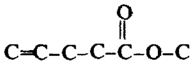
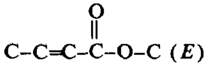
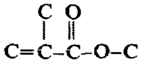
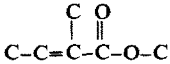
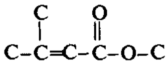
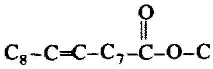
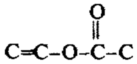
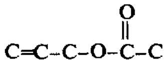
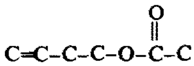
The catalyst (500 mg) was calcined and activated by the standard procedure. 1 ml of hexane containing 100 μl of methyl oleate was passed through the catalyst bed per hour. At first the outflow of the reactor contained only hexane; after about 30 min the product alkene and after 50 min the mono-ester and di-ester appeared in the outflow. The reactor was kept in operation until the conversion measured in the outflow was less than 1%. At that stage 4.5 ml of reactant had passed through the catalyst bed with an average conversion of 27%. In another experiment 75 mg of catalyst was brought into the reactor and then activated. 2-Pentene was passed through the catalyst bed at a flow rate of 1 ml per hour. When the conversion measured in the outflow had decreased to less than 1%, approximately 22 ml of 2-pentene had passed through the reactor, with an average conversion of 35%. These data enabled us to calculate the number of double bonds that had reacted per rhenium atom present on the surface. This figure is ca. 9 for methyl oleate and ca. 2400 for 2-pentene. Since these figures are a measure of the activity of the substrate in metathesis, it can be concluded that the effectiveness of this catalyst system for the metathesis of methyl oleate is about 260 times less than for the metathesis of 2-pentene.

Self-metathesis of unsaturated esters

Several types of unsaturated esters were chosen as starting materials. The esters 1 to 8 in Table 1 are unsaturated carboxylic esters. Substrates 1 to 3 are linear and ω-unsaturated while the number of methylene groups (n) separating the double bond and the ester group, varies from 0 to 2. Esters 4 to 7 are derived from ester 1 by substitution of methyl groups at the double bond. Substrate 8 is a long chain linear unsaturated carboxylic ester (methyl oleate). The double bond and the ester group are separated by seven methylene groups, so that there is no influence of the ester group on the electron density of the double bond (eq. 2). Moreover, none of the self-metathesis products from this substrate is a gas at ambient temperature and pressure (all other substrates would produce ethene or butene-2 in the metathesis reaction; this influences the conversion (vide infra)). Substrates 9 to 11 are ω-

TABLE 1

METATHESIS OF UNSATURATED ESTERS IN THE PRESENCE OF Re_2O_7/Al_2O_3-$Sn(CH_3)_4$ [a]

Substrate	Substr. nr.	Conversion (mol%)	Selectivity (%)
 $C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	1	0	–
 $C{=}C{-}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	2	70	95
 $C{=}C{-}C{-}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	3	70	95
 $C{-}C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$ (E)	4	0	-
 $C{=}\overset{\overset{C}{\mid}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	5	0	–
 $C{-}C{=}\overset{\overset{C}{\mid}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	6	0	-
 $C{-}\overset{\overset{C}{\mid}}{C}{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	7	0	-
 $C_8{-}C{=}C{-}C_7{-}\overset{\overset{O}{\|}}{C}{-}O{-}C$	8	50	95
 $C{=}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C$	9	0	-
 $C{=}C{-}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C$	10	8	95
 $C{=}C{-}C{-}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C$	11	60	95

[a] For reaction conditions: see text. Conversions were determined after ca 24 h reaction time.

unsaturated alkenyl esters; they are linear, with values of n of 0, 1, and 2, respectively.

Table 1 shows that all esters for which $n \geqslant 1$ are active in self-metathesis. In the case of α-β-unsaturated esters ($n = 0$), however, no metathesis products are found. The conversions listed in the Table were determined as follows. After completion of the reaction, first 1 ml of a polar solvent (e.g. acetone) was added to the mixture to desorb the mono-ester and di-ester from the catalyst surface; next the mixture was analyzed by GLC. In general, the equilibrium conversion of the metathesis of linear alkenes is ca. 50%. In the case of ω-unsaturated esters the conversion is often higher than 50% because the ethene produced escapes into the gaseous phase of the reaction vessel. Raising the temperature from room temperature to 323 K enhanced this effect: the conversion increased to values between 80 and 90%.

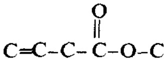
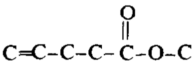
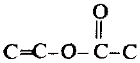
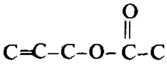
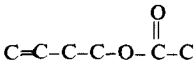
Cometathesis of unsaturated esters with E-3-hexene

All the unsaturated esters which undergo self-metathesis also undergo cometathesis with E-3-hexene. Table 2 shows four examples in which both self-metathesis and cometathesis take place. Theoretically, since the thermodynamic equilibrium of the metathesis corresponds to a random scrambling of alkylidene fragments, the cometathesis conversion should be twice as large as the self-metathesis conversion. Table 2 shows that the cometathesis conversions are indeed higher than the self-metathesis conversions. Here, again, the composition of the reaction mixture is influenced by the fact that ethene disappears into the gas phase. Vinyl acetate (substr. nr. 9), which is inactive in self-metathesis, is very active towards the cometathesis reaction.

Table 3 shows that most of the α-β-unsaturated esters can also undergo cometathesis with E-3-hexene. Both 3-methyl, methyl crotonate (substr. nr. 7) and methyl maleate (substr. nr. 12), however, are inactive.

TABLE 2

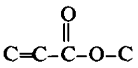
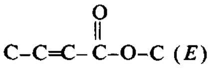
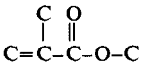
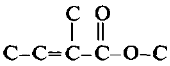
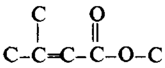
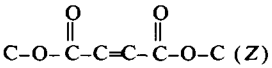
COMETATHESIS OF AN EQUIMOLAR MIXTURE OF UNSATURATED ESTERS AND E-3-HEXENE [a]

Substrate	Substr. nr.	Cometathesis (mol%)	Selfmetathesis (mol%)
 $\mathrm{C{=}C{-}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	2	55	30
 $\mathrm{C{=}C{-}C{-}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	3	53	34
 $\mathrm{C{=}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C}$	9	41	0
 $\mathrm{C{=}C{-}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C}$	10	26	7
 $\mathrm{C{=}C{-}C{-}C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C}$	11	49	41

[a] For reaction conditions: see text. Conversion were determined after ca 24 h reaction time. The selectivity in all these experiments was ca. 95%.

TABLE 3

COMETATHESIS OF α-β-UNSATURATED ESTERS WITH *E*-3-HEXENE (molar ratio ester/*E*-3-hexene, 1/1)[a]

Substrate	Substr. nr.	Cometathesis (mol%)
 $\mathrm{C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	1	20
 $\mathrm{C{-}C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$ (*E*)	4	45
 $\mathrm{C{=}\overset{\overset{C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	5	25
 $\mathrm{C{-}C{=}\overset{\overset{C}{|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	6	30
 $\mathrm{C{-}\overset{\overset{C}{|}}{C}{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$	7	0
 $\mathrm{C{-}O{-}\overset{\overset{O}{\|}}{C}{-}C{=}C{-}\overset{\overset{O}{\|}}{C}{-}O{-}C}$ (*Z*)	12	0

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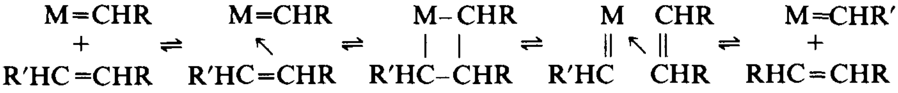
[a] For experimental conditions: see text. Conversions were determined after ca. 120 h reaction time. In all these experiments a double amount of catalyst was used. The selectivity with respect to the ester was 95%; because of the long reaction time the *E*-3-hexene partly isomerized to 2- and 1-hexene. The products of cometathesis reactions of these alkenes with the esters were also found.

Discussion

Currently, it is generally accepted that alkene metathesis proceeds via a chain reaction involving metal-carbene complexes, which react reversibly with the alkene via a metallacyclobutane intermediate:

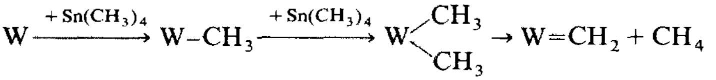


$$\begin{array}{ccccccccc}
\mathrm{M{=}CHR} & & \mathrm{M{=}CHR} & & \mathrm{M{-}CHR} & & \mathrm{M\quad CHR} & & \mathrm{M{=}CHR'} \\
+ & \rightleftharpoons & \nwarrow & \rightleftharpoons & |\quad| & \rightleftharpoons & \|\nwarrow\| & \rightleftharpoons & + \\
\mathrm{R'HC{=}CHR} & & \mathrm{R'HC{=}CHR} & & \mathrm{R'HC{-}CHR} & & \mathrm{R'HC\quad CHR} & & \mathrm{RHC{=}CHR}
\end{array} \tag{3}$$

Since the Re_2O_7/Al_2O_3-catalyst is active for the metathesis of simple alkenes (such as propene, 2-pentene etc.) without a cocatalyst, the initial metal-carbenes on the catalyst surface must be formed in such cases by reaction between the alkene molecule and the catalyst. In contrast, unsaturated esters undergo hardly any metathesis in the presence of this catalyst; apparently the formation of active structures is impeded by complexation of the ester group with the catalyst. When the catalyst is modified by the addition of a small amount of SnR_4 (R = alkyl), its activity for the metathesis of nonfunctionalized alkenes is increased substantially [11] and the catalyst becomes active for the metathesis of unsaturated esters [8].

Role of the cocatalyst

The role of the cocatalyst is still a matter of discussion. For simple alkenes, Grubbs et al. [18] suggested that $Sn(CH_3)_4$ activates the homogeneous catalyst WCl_6 by generating the first carbene ligand on the tungsten, e.g.:



$$W \xrightarrow{+Sn(CH_3)_4} W{-}CH_3 \xrightarrow{+Sn(CH_3)_4} W\begin{matrix}CH_3\\CH_3\end{matrix} \rightarrow W{=}CH_2 + CH_4 \qquad (4)$$

Besides methane, traces of ethene were also observed, which was attributed to the termination reaction:

$$2W{=}CH_2 \rightarrow 2W + CH_2{=}CH_2 \qquad (5)$$

The above model for the activation of the catalyst was corroborated by later experiments of Grubbs et al. [19], using the solid catalyst MoO_3/Al_2O_3, in combination with labeled substrates and labeled $Sn(CH_3)_4$.

We observed that when $Sn(CH_3)_4$ is added to the Re_2O_7/Al_2O_3 catalyst both CH_4 and C_2H_4 are formed. In general, for SnR_4 (R is linear) as cocatalyst, the presence of the corresponding alkane, RH, could always be demonstrated after the reaction between catalyst and cocatalyst. This suggests that the activation of this catalyst takes place by a similar scheme.

Cocatalysts with phenyl ligands, such as $Sn(C_6H_5)_4$, however, can also activate WCl_6 [20–22] for the metathesis of simple alkenes *. The activity of these cocatalysts cannot be explained in terms of the above reaction scheme, but the presence of chlorobenzene and biphenyl in the products indicates that WCl_6 is reduced. In this case the first metal-carbene probably results from the interaction between the reduced WCl_6 and the substrate. Since all the cocatalysts used in this work are reducing agents, activation of the Re_2O_7/Al_2O_3 catalyst may also take place via reduction of the rhenium(VII) to a lower oxidation state.

Reactivity of unsaturated esters

Table 1 shows that methyl butenoate (no. 2) and methyl pentenoate (no. 3) show comparable activities in self-metathesis. Apparently, the reactivity of the double bond is not changed when the number of methylene groups between the double bond and the ester group is increased from one to two. A pronounced difference in activity, however, exists between allyl acetate (no. 10) and 1-butene-4-acetate (no. 11), where the double bond is in the alcohol fragment of the substrate molecule. In this case the presence of two carbons between the double bond and the functional group provides a more active substrate than does one carbon. This behaviour can explained in terms of some delocalisation of the electron density of the double bond in allyl acetate.

Resonance structures do not contribute to the electron density distribution in the case of 1-butene-4-acetate, and so the double bond in this molecule will have a higher electron density and be more localized than in the case of allyl acetate.

The fact that cometathesis of α-β-unsaturated esters with an alkene is possible,

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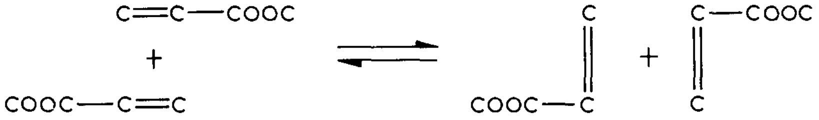
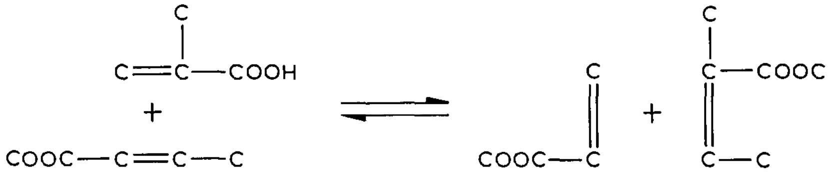
* Treatment of the Re_2O_7/Al_2O_3 catalyst with $Sn(C_6H_5)_4$ or $Sn_2(C_6H_5)_6$ produced no activity for the metathesis of unsaturated esters. WCl_6–$Sn(C_6H_5)_4$, though very active in the metathesis of nonfunctionalized alkenes, is also not active in the metathesis of unsaturated esters.

proves that α-β-unsaturated esters do not quench the reaction, e.g. by reacting with the carbene intermediates to form cyclopropane derivatives as proposed by Gassman et al. [23]. For the same reason the lack of activity in self-metathesis cannot be explained in terms of a lack of active sites. A possible explanation is that the ester molecules do in fact react with each other but only in nonproductive reaction cycles, e.g. in case of methyl acrylate (no. 1):



(6)

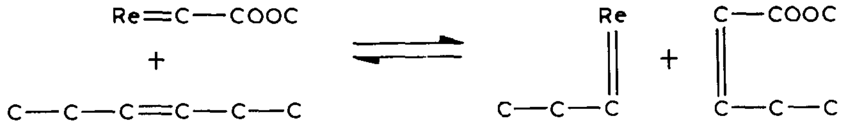
In order to check whether non-productive self-metathesis takes place in the mixture, an experiment was carried out with an equimolar mixture of methyl crotonate and methyl methacrylate. Equation 7 shows that if "non-productive" cometathesis of these compounds had taken place in the mixture, both methyl acrylate and methyl tiglate would have been formed.



(7)

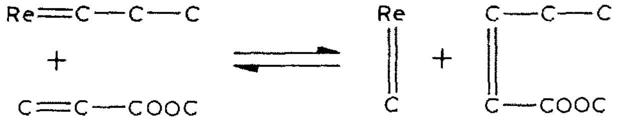
Since the actual presence of active sites has only been established for the cometathesis mixtures (the possibility that α-β-unsaturated esters might not be able to form active sites on the catalyst surface has not been ruled out), the catalyst was first treated with a small amount of a linear alkene after the addition of the cocatalyst. Subsequently, the substrate mixture was added. This experiment was repeated several times but on no occasion could the presence of methyl tiglate or methyl acrylate be detected. Apparently, α-β-unsaturated esters are not active either in productive or in non-productive self-metathesis.

The fact that α-β-unsaturated esters are not active towards self-metathesis, and less reactive in cometathesis than the other unsaturated esters, can be explained in terms of the electron withdrawing effect of the ester group on the double bond. This effect is very pronounced since the carbonyl function of the ester group is conjugated with the double bond. This electron withdrawal lowers the reactivity of the double bond. Possibly the reactivity of the intermediate carbene structure is also lowered by the ester group. In the cometathesis reaction with hexene-3, either the lowered activity of the carbene structure is compensated by the activity of hexene (eq. 8) or the lowered activity of the ester is compensated by the activity of the carbene (eq. 9).



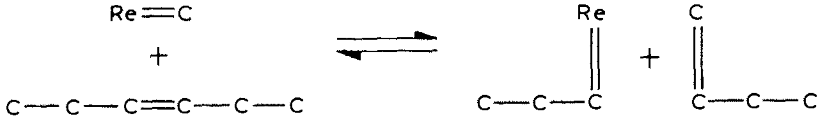
(8)

Another possibility is that α-β-unsaturated esters cannot form carbene structures on the surface of the catalyst, or that carbene structures carrying an ester group are



(9)

totally unreactive. In this case the absence of both productive and non-productive metathesis can be explained by the fact that there are no active sites; cometathesis then takes place according to eq. 9 and 10, without the intermediacy of a carbene structure carrying an ester group,



(10)

The fact that 3-methyl, methyl crotonate (no. 7) is not active in this reaction may be due to steric reasons. The electron density of the double bond in methyl maleate (no. 12) is lowered by the two ester groups in the molecule and this could account for the lack of reactivity in this case.

Acknowledgement

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