

COMETATHESIS OF METHYL OLEATE WITH α -OLEFINS

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Cometathesis of methyl oleate with 1-hexene or with other α -olefins affords two new esters and two new olefins. In the case of 1-hexene these products are methyl 9-decenoate, methyl 9-tetradecenoate, 1-decene and 5-tetradecene. At the same time, the formation of the esters and olefins with shorter chains (i.e. decene and decenoate) is distinctly preferred. Obviously, the transfer of methylene group from the alkene to the ester molecule is much easier than that of the alkylidene moiety. The non-stoichiometric course of cometathesis is associated with the carbene mechanism of the reaction.

Cometathesis of esters of unsaturated fatty acids with olefins, consisting in a mutual exchange of alkylidene groups between both reactants, represents a simple method for shortening or extension of the carbon chains of the esters. For instance, in this way esters obtained from vegetable oils can be transformed to homologous compounds not easily accessible by other methods and useful in various special syntheses. Of particular importance in practical applications may be also the ethene cleavage of higher fatty acid esters to the homologues with shorter chains and ω -unsaturation¹. The direct ethenolysis of fatty oils allows the transformation of long chain triglycerides into glycerides of lower molecular weight which play an important role in some diets².

Nearly all authors who have studied metathesis of unsaturated esters refer also to the importance and prospects of their cometathesis with olefins. Likewise, examples of these reactions can be found in various review articles³⁻⁵. In most cases, however, the published data are only illustrative and they do not provide information sufficiently complex so that many aspects of these reactions remain still to be clarified. Since their closer investigation could contribute to a better knowledge of the reaction mechanism and it might also provide a basis for the control and optimization of the yields, it seemed to be worthwhile to undertake a more extensive study of the cometathesis on a model system methyl oleate — 1-hexene, and illustratively also with some other olefins in place of hexene.

EXPERIMENTAL

Chemicals. Starting samples of methyl esters were prepared by transesterification of triglycerides from olive oil and by distillation. In addition to the main component — methyl oleate — they contained also 18% (molar) of methyl palmitate, 7% of methyl linolate and 3% of methyl stearate. After distillation, the mixture of methyl esters was degassed and stored over molecular sieves. Both methyl palmitate and methyl stearate are inert in metathesis; methyl linolate was not differentiated from methyl oleate as both esters could not be distinguished chromatographically under conditions used in this work. 1-Hexene and 1-heptene (Fluka, purum) were distilled and dried by 48 h-refluxing over NaH. Ethylene and 1-butene were charged into the reactor directly from the pressure bottles through a column containing activated molecular sieves. Purification and drying of other chemicals has been described in detail elsewhere^{6,7}.

Procedure. Cometathetic reactions were carried out in an all glass reactor free of ground joints preevacuated to 10^{-2} Pa. Preparation, purification and dosing of all reaction components was accomplished using vacuum technique. Solutions of individual compounds were prepared and stored in preevacuated phials equipped with breakable seals. The phials were attached to the reactor and after evacuation of the whole system and dosing of the reactants by breaking the seals the reactor was sealed off and placed into the bath. The catalyst system $WCl_6/(CH_3)_4Sn$ in benzene was used throughout the work. The molar ratio $WCl_6/(CH_3)_4Sn$ /methyl oleate was kept constant at 1/4/50. Analyses of the reaction products were carried out chromatographically using a $2\text{ m} \times 0.4\text{ cm}$ column with Dexsil 400 on Chromosorb W within the temperature range 100–290°C. Methyl palmitate present in the starting mixture of the esters was used as the inner standard. Under these conditions the peaks of 1-decene and 5-decene (the products of cometathesis and selfmetathesis of 1-hexene, respectively) were not separated.

RESULTS AND DISCUSSION

The S-shaped conversion curves of the cometathesis of methyl oleate with 1-hexene show that the reaction has three different stages (Fig. 1). The induction period is evidently associated with the formation of active centres during the reaction of tungsten hexachloride with tetramethyltin⁸. In the second stage the reaction rate reaches maximum and thereafter it declines practically to zero. The retardation or even cessation of the reaction in the third stage is due to the destruction of the majority of active sites. The raise of the reaction temperature results in shortening of the induction period together with the increase of both the reaction rate and maximum conversion. On the other hand, at higher temperatures the catalyst activity drops sooner. It seems, however, that a minor part of the catalyst remains in some sort of active form even in the stage of the zero rate of cometathesis. This conclusion is supported by the observation that the addition of a further amount (the same as that at the start) of 1-hexene to the reaction mixture in which the cometathesis has already stopped leads to an increase of the yield by about 10 per cent. The same effect has also the raise of the temperature from 60 to 100°C in a quiescent mixture.

Conversion curves shown in Fig. 1 illustrate also the contribution of selfmetathesis to the total conversion of methyl oleate. Its extent increases gradually with time and temperature. The increase of the molar ratio methyl oleate/1-hexene at

a constant concentration of the ester (i.e. when lowering the concentration of 1-hexene) results in a moderate drop of its total conversion (Fig. 2). Because the consumption of the ester in selfmetathesis increases in the same direction, the yield of cometathesis diminishes rather steeply. Analogical plots of the conversions of 1-hexene are seen in Fig. 3. In this case, the dependence of the conversion in selfmetathesis has a somewhat unusual course with a maximum.

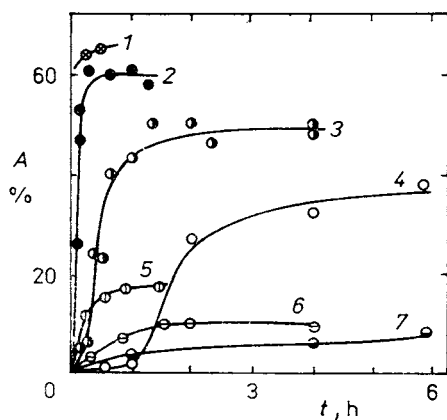


FIG. 1

Conversions (A , mole %) of methyl oleate in cometathesis with 1-hexene. Benzene, $[\text{WCl}_6]_0 = 13 \text{ mmol l}^{-1}$, molar ratio oleate/1-hexene = 1, curves 1–4 cometathesis, 5–7 selfmetathesis, reaction temperature ($^{\circ}\text{C}$): 1 100; 2, 5 80; 3, 6 60; 4, 7 40

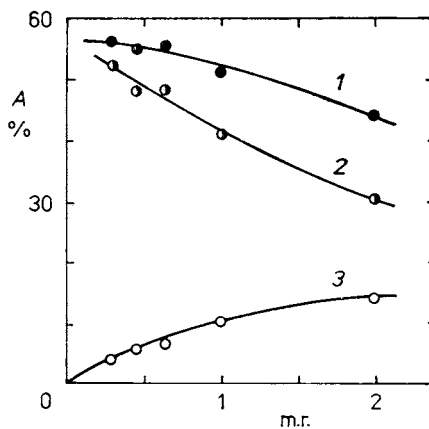


FIG. 2

Dependence of the conversion of methyl oleate in cometathesis with 1-hexene on the molar ratio (m.r.) oleate/1-hexene. Benzene, 60°C , $t = 4 \text{ h}$, $[\text{WCl}_6]_0 = 10 \text{ mmol l}^{-1}$, conversion (A , mole %): 1 total, 2 in cometathesis, 3 in selfmetathesis

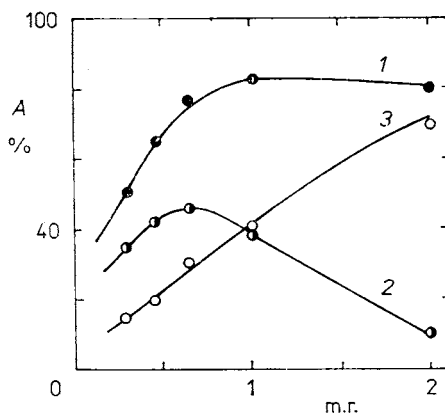


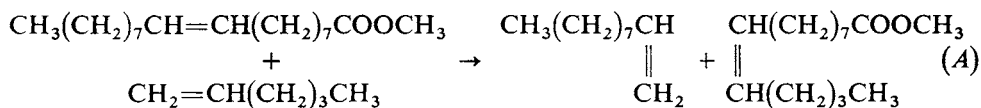
FIG. 3

Dependence of the conversion of 1-hexene in cometathesis with methyl oleate on the molar ratio (m.r.) oleate/hexene. Conditions cf. Fig. 2, conversion (A , mole %): 1 total, 2 in cometathesis, 3 in selfmetathesis

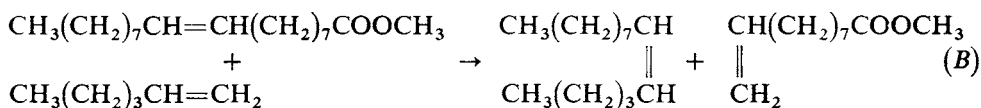
of the conversion of 1-hexene with diminution of its concentration has not been explained unambiguously. Presumably, this effect should be related to an increasing number of active sites as a result of the interaction of methyl oleate with tungsten species. Figs 2 and 3 demonstrate also that the selfmetathesis of each component can be suppressed by the use of an excess of the other one, selfmetathesis of which, however, is enhanced.

In cometathesis of methyl oleate with 1-hexene, the following reactions take place:

- selfmetathesis of methyl oleate yielding 9-octadecene and dimethyl 9-octadecene-1,18-dioate,
- selfmetathesis of 1-hexene leading to the formation of ethylene and 5-decene,
- cometathesis of both reaction partners involving the following reactions: formation of methyl 9-tetradecenoate and 1-decene:



formation of methyl 9-decenoate and 5-tetradecene:



If the stoichiometry expressed by the Eqs. (A) and (B) was valid, then both products of each cometathetic reaction would be formed in equal amounts. For example, in the case described by the Eq. (B) the amounts of tetradecene and methyl decenoate in the final reaction mixture should be the same. Table I contains the results of analyses of the products resulting from the cometathesis of methyl oleate with 1-hexene at different temperatures and Table II shows similar data for the cometathesis of methyl oleate with 1-heptene at different times of the reaction. It appears that in cometathesis of methyl oleate with 1-hexene, the yield of decenoate always exceeds that of tetradecene or in cometathesis oleate-heptene that of pentadecene (in both cases at variance with the Eq. (B)). At the same time, in the latter case also the yield of 1-decene is much higher than that of pentadecenoate, again in disaccord with the Eq. (A). In spite of a rather appreciable scattering of the analytical data (cf. standard deviations given in Table I), it is beyond doubt that the Eqs (A) and (B) do not account for the observed stoichiometry. In principle, the figures given in Tables I–III could be influenced by the isomerization of the initial compounds (above all of 1-olefins) followed by the cometathesis of the products. However, according to the GC analysis, the content of these byproducts was quite negligible and therefore it was not taken into account.

TABLE I

Relative yields of the products in cometathesis of methyl oleate(MOI) with 1-hexene after cessation of the reaction. Benzene, $[WCl_6]_0 = 10 \text{ mmol l}^{-1}$, molar ratio $WCl_6/(CH_3)_4Sn/oleate/hexene = 1/4/50/50$; symbols: $C_{10}oate$ methyl 9-decenoate, $C_{14}oate$ methyl 9-tetradecenoate, 1- $C_{10}ene$ 1-decene, 5- $C_{14}ene$ 5-tetradecene

Temp. °C	Conversion of MOI(%)	$C_{10}oate$	5- $C_{14}ene$	5- $C_{14}ene$	Number of experiments
		$C_{14}oate$	$C_{10}oate$	$C_{14}oate$	
20	29 ^a	1.4	0.95	1.3	1
40	39	1.35	0.88	1.2	3
60	53	1.47 ^b	0.77 ^c	1.1	28
80	65	1.4	0.75	1.1	9
100	66	1.35	0.7	0.8	2

^a Reaction not completed after 24 h; ^b standard deviation $s = 0.11$; ^c standard deviation $s = 0.076$.

TABLE II

Relative yields of the products in cometathesis of methyl oleate with 1-heptene. Conditions and symbols cf. Table I, 6- $C_{15}ene$ 6-pentadecene, $C_{15}oate$ 6-pentadecenoate, molar ratio oleate/heptene = 0.93

Reaction time, min	Conversion of MOI(%)	$C_{10}oate$	$C_{10}oate$	1- $C_{10}ene$	1- $C_{10}ene$
		$C_{15}oate$	6- $C_{15}ene$	6- $C_{15}ene$	$C_{15}oate$
60°C					
15	5	—	—	—	—
30	12.5	1.25	1.25	1.45	1.45
45	22.5	1.34	1.4	1.6	1.5
60	48	1.4	1.4	1.45	1.5
110	51	1.3	1.44	1.44	1.3
80°C					
10	48	1.3	1.5	1.5	1.5
25	61	1.35	1.4	1.4	1.34
40	65	1.3	1.4	1.35	1.25
60	64	1.35	1.4	1.35	1.4
120	64	1.35	1.45	1.4	1.3

From the values of the ratios decenoate/tetradecene and decenoate/tetradecenoate or decenoate/pentadecenoate it follows that the formation of the esters with shorter carbon chains is always preferred, independently from the temperature and duration of the cometathesis. The same holds also for the formation of the shorter chain alkenes. Similar effects, i.e. preferential formation of esters and olefins with shorter chains, have been observed also in cometathesis of methyl oleate with 1-butene. It seems that the difference in the yields between the shorter and longer chain products is smaller with lower olefins (Table III).

The explanation of the non-stoichiometric course of the cometathesis of methyl oleate with 1-alkenes follows directly from the carbene–metallacyclobutane mechanism. Active carbenes in the system methyl oleate–1-hexene are derived from both reaction partners: $-\text{W}=\text{CH}_2$ (I), $-\text{W}=\text{CH}(\text{CH}_2)_3\text{CH}_3$ (II), $-\text{W}=\text{CH}(\text{CH}_2)_7\text{CH}_3$, (III), $-\text{W}=\text{CH}(\text{CH}_2)_7\text{COOCH}_3$ (IV). Therefore, the reactions which can take place simultaneously (when neglecting all degenerate metatheses not leading to new compounds) are described by the equations:

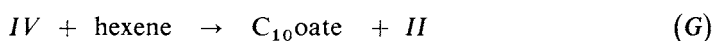
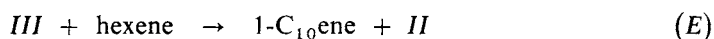
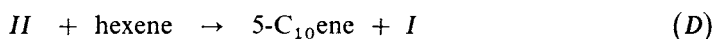
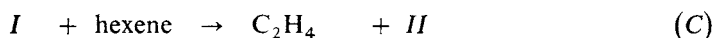
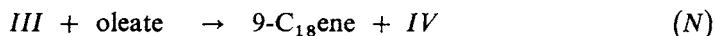
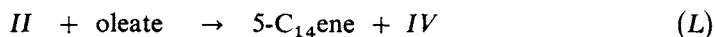
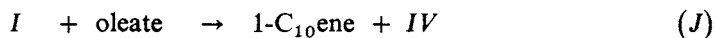


TABLE III

Cometathesis of methyl oleate with α -olefins. $[\text{WCl}_6]_0 = 13 \text{ mmol l}^{-1}$, benzene, 60°C , reaction time 4 h, symbols cf. Table I

Olefin	Mol. ratio oleate/olefin	Conversion of MOI(%)	C_{10}oate	C_{10}oate	$1\text{-C}_{10}\text{ene}$
			$\text{C}_{10+n}\text{oate}$	$\text{C}_{10+n}\text{ene}$	$\text{C}_{10+n}\text{ene}$
Ethene	1.4	67	—	—	—
1-Butene	0.84	68	1.15 ^a	1.3	1.2
1-Hexene	0.98	53	1.4 ^b	1.4	—
1-Heptene	0.93	58	1.4 ^c	1.5	1.5

^a $n = 2$; ^b $n = 4$; ^c $n = 5$.



Symbols: cf. Table I.

Reactions of carbenes *I* and *II* with 1-hexene and of carbenes *III* and *IV* with methyl oleate represent selfmetathesis of both compounds. When neglecting all self- and cometatheses of the products we can see that the reactions (*A*) and (*B*) in reality involve eight reactions of carbenes. Because each of the starting compounds takes part in at least six different reactions it is clear that the relations between the concentrations of the products are complicated. Among the factors governing the formation of individual compounds an important role is played by the stability of the particular carbenes and by the rates of their reactions with parent compounds. The predominance of the shorter chain compounds (i.e. decene and decenoate) reveals that the transfer of methylene group from the olefin to the ester molecule is much easier than that of alkylidene. It means that carbene *I* reacts with methyl oleate faster than carbene *II* and/or carbenes *III* and *IV* react with 1-hexene preferentially under the formation of the carbene *II*. This conclusion is in accordance with the nucleophilicity of the tungsten atom in both carbenes *III* and *IV* (ref.⁹).

REFERENCES

1. Boelhouwer C., Mol J. C.: J. Am. Oil Chem. Soc. *61*, 425 (1984).
2. Rosenburg D. W. (A. E. Staley Manufact. Co.): Eur. Pat. Appl. 130039 (1984); Chem. Abstr. *102*, 1315440 (1985).
3. Mol J. C.: J. Mol. Catal. *15*, 35 (1982).
4. Verkuijlen E., Boelhouwer C.: Chem. Phys. Lipids *24*, 305 (1979).
5. Streck R.: CHEMTECH *13*, 758 (1983).
6. Balcar H., Dosedlová A., Hanuš V., Petrusová L., Matyska B.: Collect. Czech. Chem. Commun. *49*, 1736 (1984).
7. Balcar H., Dosedlová A., Matyska B.: J. Mol. Catal. *41*, 367 (1987).
8. Balcar H., Dybal J.: React. Kinet. Catal. Lett. *30*, 17 (1986).
9. Casey Ch. P., Tuinistra H. E.: J. Am. Chem. Soc. *100*, 2270 (1978).

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