# METATHESIS OF METHYL 10-UNDECENOATE

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The metathesis of methyl 10-undecenoate was studied using the $WCl_6 + (CH_3)_4Sn$ catalyst system. The rate of metathesis and the maximum degree of conversion are affected markedly by the reactions of the ester, and of other oxygen compounds if present, with tungsten hexachloride. Introduction of an oxygen ligand to the central tungsten atom of the active centre increases the reactivity and stability of the latter, thus affecting positively the initial rate of the metathesis reaction. At the same time, however, the rate of the catalyst deactivation increases with increasing concentration of the ester, whereupon the degree of conversion decreases. As a result of competition of the two effects, a maximum appears in the dependence of the amount of the ester reacted on the ester-to-tungsten hexachloride ratio.

Representing a novel versatile route to many valuable products, often hardly available in other ways, metathesis of alkenes and their derivatives, consisting in the exchange of alkylidene groups between their molecules, is attracting ever-increasing interest[1,2]. A specific group of metathesis reactions is metathesis of functionalized olefins. The first to report on metathesis of esters of some higher unsaturated acids were Van Dam and coworkers[3]. Since then, an ever-increasing number of papers have been published dealing with metathesis of esters of unsaturated acids of various structures, cross-metathesis with acyclic or cyclic olefins, reaction mechanisms, *etc.* (see the surveys[4-6]). Practical applications of these reactions are hampered by the fact that satisfactory degrees of conversion can only be attained if the catalyst is present in a high concentration with respect to substrate, presumably due to the inhibiting effect of the interaction of the polar group with the active centre or its precursor[4].

Most frequently used catalyst in metathesis of esters of unsaturated acids is tungsten hexachloride combined with tetramethyl tin, although other systems have proved active as well[7,8]. A wealth of data is available in the literature concerning the activity of various catalyst systems under various conditions, but no systematic study has been so far undertaken to examine the effect of the reaction conditions on the rate and yield of the reaction. Some data can be found in the paper by Otton and coworkers[9].

The present work is devoted to the study of the metathesis of methyl 10-undecenoate using $WCl_6 + (CH_3)_4Sn$ as catalyst. The reaction was investigated in dependence on the concentration ratios of the components, temperature, and presence of some oxygen compounds as potential promotors or inhibitors. The aim of the work was to seek for conditions in which the activity of the system is at its optimum, and to gain insight into the inhibiting or promoting effects of some components of the reaction mixture.

## EXPERIMENTAL

*Chemicals.* Tungsten hexachloride *purum* (Fluka) was multiply fractionally sublimed in vacuum. and the final fraction was used. Tetramethyl tin *purum* (Fluka) was used with no pretreatment Methyl 10-undecenoate was prepared by conventional acid catalyzed esterification of 10-undecenoic acid *p.a.* (Merck), which, depending on the acid number of the product, was either repeated or carried out by reaction with oxalyl chloride and methanol. The product was dried by means of a 4A molecular sieve. Benzene *p.a.* (Lachema) was agitated successively with concentrated $H_2SO_4$ (up to 6 times), distilled water, 5% sodium carbonate solution, water (3 times), then predried by refluxing over $CaH_2$ and fractionated on a column with 30 theoretical plates, and the medium fraction was dried for 48 h by boiling with NaH in a circulation apparatus previously evacuated perfectly and filled with argon. From this apparatus the benzene was fed directly into the reactor. The remaining chemicals were commercial products used with no pretreatment except distillation and drying over $CaH_2$ or molecular sieves.

*Apparatus and procedure.* The benzene solutions of all the components concerned were prepared by vacuum techniques in ampoules fitted with breakable seals. The apparatus was all-glass, free of ground joints and equipped with metallic vacuum valves. The reactor was sealed by its side arm, over a reflux condenser, to the vacuum or argon feed, and over a valve, to the volumetric section. Ampoules with the solutions of the reactants were sealed to the side arm. Prior to the experiment, the apparatus was dried by long-run evacuation to $10^{-2}$ Pa using occasional annealing with open flame. After delivering the components by breaking magnetically the seals in ampoules (tetramethyl tin was delivered last), argon freed from oxygen by means of BTS catalyst (Fluka) and dried with molecular sieves was admitted. The experiment was finished by adding water or several ml of methanol.

*Analysis.* The course of the metathesis was monitored by measuring the volume of ethylene evolved. The resulting degree of conversion was determined chromatographically based on the takeup of the starting monoester relative to internal standard (Chrom 4 instrument, FID, column 3·7 m × 3 mm i.d., 10% neopentyl glycol succinate on Chromaton, 200°C, standard: *o*-dichlorobenzene). The components of the reaction mixture were identified by GC-MS (Jeol D100) and IR spectroscopy. The quantitative determination of the monoesters and diesters was carried out chromatographically. The concentrations of the products were determined from the ratios of the corresponding peak area to the total area of all peaks (Perkin Elmer F21, column 2 m × 3 mm i.d., Dexsil 300 GC on Chromosorb W, exponential temperature rise 190–290°C, 60 ml $N_2$/min). The peaks were identified by using the method of standard additions of the components separated on a silica gel column and analyzed by MS.

## RESULTS AND DISCUSSION

The metathesis of methyl 10-undecenoate involves the formation of ethylene and dimethyl 10-eicosendioate ("$C_{22}$ diester"):

$$2\,CH_3OOC{-}(CH_2)_8{-}CH{=}CH_2 \rightarrow$$
$$\rightarrow CH_3OOC{-}(CH_2)_8{-}CH{=}CH{-}(CH_2)_8{-}COOCH_3 + CH_2{=}CH_2 \quad (A)$$

Provided that no impurities are present, the reaction proceeds with a high selectivity (85–100%) to $C_{22}$ diester. No marked dependence of the selectivity on the reactants ratio or temperature has been observed; the quality of solvent and the purity of argon, however, have a substantial effect. Although benzene had been purified always by the same procedure and no impurities were found in it chromatographically, with some batches a poor selectivity (as low as 30%) and degree of conversion were attained. These results were rejected. The major cause of this drop consists probably in the presence of traces of polar substances in the reaction system, which could not be eliminated even by a thorough purification.

In these cases the starting monoester isomerizes to a high extent so that the double bond is displaced to position 9, 8, or 7, and the isomers co-metathetize with the methyl 10-undecenoate according to schemes (*B*) and (*C*) ($n = 0, 1, 2$):

$$\begin{aligned}&CH_3OOC—(CH_2)_{7-n}—CH{=}CH—(CH_2)_n—CH_3 + \\ &+ CH_3OOC—(CH_2)_8—CH{=}CH_2 \rightarrow CH_3OOC—(CH_2)_{7-n}—CH{=}CH_2 + \\ &+ CH_3OOC(CH_2)_8—CH{=}CH—(CH_2)_n—CH_3 \qquad (B)\end{aligned}$$

$$\begin{aligned}&CH_3OOC—(CH_2)_{7-n}—CH{=}CH—(CH_2)_n—CH_3 + \\ &+ CH_3OOC—(CH_2)_8—CH{=}CH_2 \rightarrow \\ &\rightarrow CH_3OOC—(CH_2)_{7-n}—CH{=}CH—(CH_2)_8—COOCH_3 + \\ &+ CH_2{=}CH—(CH_2)_n—CH_3 \qquad (C)\end{aligned}$$

The chromatogram of such a reaction mixture, where the selectivity to $C_{22}$ diester was as low as 35%, is shown in Fig. 1. The positional isomers of the starting ester are not discriminated. In the experiment in question, predrying with $CaH_2$ was omitted from the purification of benzene, and an insufficiently active BTS catalyst was employed.

The activity of the systems was evaluated in terms of the degree of conversion of the starting ester attained in 6 h of reaction. As the course of evolution of gases (ethylene and gaseous products of reaction of $WCl_6$ with $(CH_3)_4Sn$) reveals, the metathesis reaction comprises two kinetically different stages (Fig. 2). After a short induction period whose duration, being determined by the way of delivery of the components, is of no consequence, a rapid metathesis takes place giving rise to 60–80% products. After approximately 2–3 h the reaction slows down substantially or even ceases to proceed. The slowing down appears the sooner the higher excess of tetramethyl tin or the esters with respect to tungsten hexachloride, which points to deactivation of the catalytic centres by interaction with these components. However, since in 6 h the reaction is rather slow anyway, the difference between the actual degree of conversion in 6 h and the maximum attainable value is low and could be neglected.

Despite the care taken to avoid any contact of the reactants with air, beginning from the preparation of the components and ending with the metathesis proper, the reproducibility of the conversion in 6 h of reaction was not very good, which is typical of metatheses of functionalized olefins in general. Responsible is probably the very low concentration of the active carbene centres, constituting a minute fraction with respect to the $WCl_6$ added, which are highly reactive with respect to polar impurities. For experiments repeated under identical conditions using ester, benzene, or $WCl_6$ and $(CH_3)_4Sn$ solutions of different origin, the mean square error, at the 0·7 probability level, was 7%. In contrast to benzene the replacement

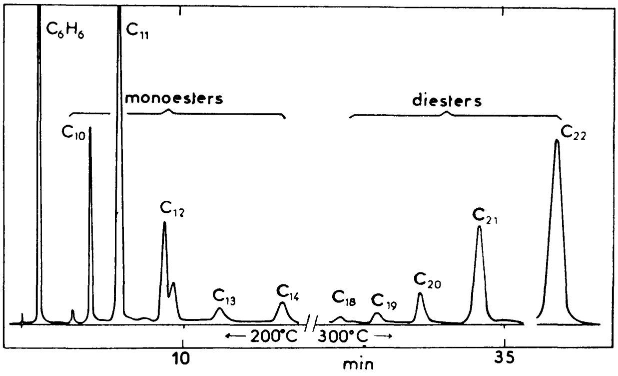

FIG. 1

Chromatogram of the products of metathesis of methyl 10-undecenoate. Reaction conditions: molar ratio W : Sn : EtOH : ester = 1 : 3 : 2 : 45, $c_W^0$ = 13·3 mmol l$^{-1}$, 60°C, benzene, reaction time 6 h

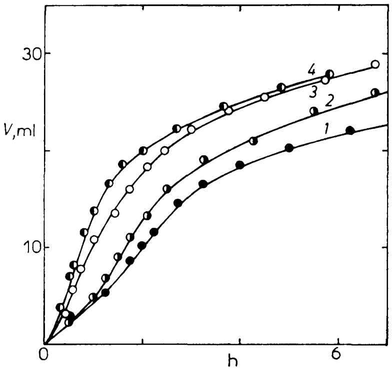

FIG. 2

Dependence of the volume of the gas evolved on time for various $(CH_3)_4Sn/WCl_6$ ratios. Reaction conditions: molar ratio W : EtOH : : ester = 1 : 2 : 45, $c_W^0$ = 13·3 mmol l$^{-1}$, 60°C, benzene, reaction mixture volume 10 ml; Sn/W: curve *1* 1, *2* 2, *3* 3, *4* 4 of $WCl_6$, $(CH_3)_4Sn$, or ester solution had but a minor effect on the degree of conversion. In the individual experiment series, benzene from one batch was employed, whereupon the error diminished considerably.

The activity of catalysts for metathesis of olefins is known[4-6,10-12] to be affected appreciably by oxygen and oxygen-containing substances, in particular, by alcohols, ethers, water, *etc.* No oxygen-containing co-catalysts are commonly employed for metathesis of esters of unsaturated acids. However, as the data of Table I demonstrate, addition of ethanol, up to the ethanol-to-tungsten hexachloride ratio of 3 for the ester-to-tungsten ratio of 45, affects the conversion in the positive way. The activity and selectivity are also increased slightly if 10-undecenoic acid is added to $WCl_6$ (before the remaining components) in a molar ratio of 1 with respect to $WCl_6$; if the ratio, however, is raised up to the value of 2, the maximum degree of conversion becomes markedly poorer, although the system is not deactivated completely. This observation is of importance in view of the fact that esters of higher unsaturated acids always contain some free acid, which is commonly thought a catalyst poison. Some authors claim[13,14] that for a successful metathesis, particularly of esters of acids from vegetable oils, the acid number must be very low indeed (below 0·05). It seems, however, that this requirement is not critical: for instance, in the metathesis of methyl 10-undecenoate with acid number 1, the free acid-to-tungsten ratio 1 is only attained with a 300 fold excess of ester over $WCl_6$, which is 3 to 10 times

TABLE I

Effect of oxygen substances on the activity of the $WCl_6 + (CH_3)_4Sn$ catalytic system. Ester-to-$WCl_6$ molar ratio 45, $[WCl_6]_0 = 13·3 \text{ mmol l}^{-1}$, benzene, 60°C

| Oxygen substance (O) | Molar ratio O/W | Molar ratio Sn/W | Degree of conversion[a] % | Selectivity[b] |
|---|---|---|---|---|
| — | — | 1 | 22 | 0·3 |
| $C_2H_5OH$ | 1 | 1 | 35 | 0·3 |
| $C_2H_5OH$ | 2 | 1 | 41 | 0·5 |
| $C_2H_5OH$ | 3 | 1 | 42 | 0·4 |
| — | — | 4 | 44 | 0·9 |
| $C_2H_5OH$ | 2 | 4 | 50 | 0·9 |
| $(C_4H_9)_2O$ | 2 | 4 | 24 | 0·7 |
| Epichlorohydrin | 2 | 4 | 37 | 0·9 |
| Undecenoic acid | 1 | 4 | 50 | 0·9 |
| Undecenoic acid | 2 | 4 | 20 | — |

[a] In 6 h; [b] Number of mol of $C_{22}$ diester/(number of mol of methyl 10-undecenoate consumed) × 2.

more than as commonly used. As to water, however, no positive effect was established; on the contrary, even small amounts of water, at the water-to-tungsten ratio 0·25, added to the $WCl_6$ + ester mixture cause a nearly complete deactivation of catalyst. The major product then is methyl 9-chloroundecanoate. Of other co-catalysts frequently employed in metathesis of olefins, epichlorohydrin and dibutyl ether were tested; both exerted a negative effect.

The dependence of the degree of conversion on temperature, over the region of 40–70°C, appeared to be insignificant. On the other hand, the conversion is definitely affected positively by a slight excess of tetramethyl tin with respect to tungsten hexachloride; the optimum is reached at molar ratios of 3–4 (Fig. 3). The same effect has been observed by Otton and coworkers[9] for the cross-metathesis of methyl oleate with 2-hexene. The selectivity of the reaction to $C_{22}$ diester has an analogous course. As the shape of the curves of the gas evolution during the metathesis shows (Fig. 2), increase in the tin-to-tungsten ratio is accompanied by increase in the reaction rate particularly in the initial stage, due to the increase in the actual concentration of the active centres resulting from the accelerated reduction of W(VI). At higher excess of tetramethyl tin this effect is compensated by the increased rate of decay of the centres.

In metathesis of esters of unsaturated acids, the ester-to-tungsten ratio is decisive to the degree of conversion. Most frequently ratios of 10 to 50 are used. The coordination sites necessary for the coordination of the ester double bond are assumed to be blocked by the carbonyls of the ester groups coordinated to the central atoms of the active centres. Otton and coworkers[9] observed infrared spectral bands at 1 610 and 1 655 $cm^{-1}$ appearing on the addition of ethyl 3-pentenoate to a suspension of $WCl_6$ in chlorobenzene; the former band is attributed to the vibration of the C=C bond coordinated to tungsten, the latter, to the vibration of the C=O group

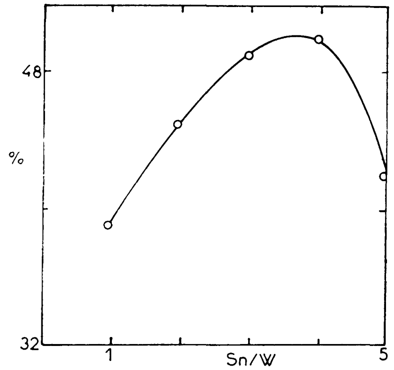

FIG. 3

Dependence of the degree of conversion attained in 6 h of reaction on the $(CH_3)_4Sn/$ $/WCl_6$ molar ratio. Reaction conditions: molar ratio W : EtOH : ester = 1 : 2 : 45, $c_W^0$ = 13·3 mmol $l^{-1}$, benzene, 60°C of the ester coordinated in the same manner. Van Roosmalen and coworkers[15] suggest that $WCl_6$ reacts with the ester to form $WOCl_4$, which in turn reacts with other molecules of the ester to give less active coordination compounds. Experiments performed using different ester-to-tungsten ratios in the presence or absence of ethanol as co-catalyst (Fig. 4) indicate that the degrees of conversion in 6 h for the ester-to-tungsten molar ratios 90 and 45 are identical. If the excess of ester over $WCl_6$ is raised to more than a hundredfold, the degree of conversion drops considerably both in the presence and in the absence of ethanol, although the degree of conversion is higher than 5% even for ester-to-$WCl_6$ ratios as high as 360. The data plotted in Fig. 4 also indicate that at the low ester-to-tungsten ratio 45, a small portion of ethanol has a positive effect on the conversion, whereas the reverse is true for ratios in excess of 100. The changes in the catalyst activity in dependence on the ester-to-tungsten ratio are better illustrated by Fig. 5, showing that the number of moles of the diester formed per mol of $WCl_6$ added ($Y$) increases with increasing ester-to-tungsten molar ratio up to a maximum at about the value of 100 in the presence of ethanol and much higher in its absence. Moreover, in the presence of ethanol the value of $Y$ at the ester-to-tungsten ratio as high as 225 is the same as at the ratio 45, and in the absence of ethanol, even about three times as high. The dependence of the maximum rate of metathesis (measured as the rate of the gas evolution at the inflexion point of the plot of volume of the evolved gas *versus* time) on the ester-to-tungsten ratio displays a monotonic increase over this region (Fig. 6).

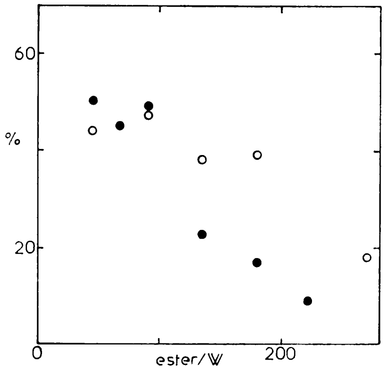

FIG. 4

Dependence of the maximum degree of conversion (%) on the ester/$WCl_6$ molar ratio. Reaction conditions: $c_W^0 = 10 \text{ mmol l}^{-1}$, 60°C; ○ W : Sn molar ratio 1 : 4, ● W : Sn : : EtOH molar ratio 1 : 4 : 2

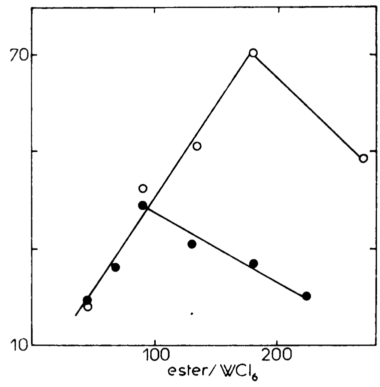

FIG. 5

Dependence of the reaction yield on the ester/$WCl_6$ molar ratio. Reaction conditions: $c_W^0 = 10 \text{ mmol l}^{-1}$, 60°C, benzene; ○ W : Sn molar ratio 1 : 4, ● W : Sn : EtOH molar ratio 1 : 4 : 2; $A$ is the $C_{22}$ diester-to-$WCl_6$ molar ratio

These dependences can be discussed assuming that the concentration of the active carbene complexes and the metathesis rates within the given time interval of the reaction are governed by the kinetics of the partial reactions in the system, in particular, the rates of formation and decay of the active centres, rather than by the coordination of the ester group to the carbene complex or to its precursor. The effect of the ester concentration on the metathesis yield and rate can be ascribed to several types of its interaction with $WCl_6$ or its reduction products.

In addition to the reaction of $(CH_3)_4Sn$ with $WCl_6$ itself, reactions in which oxygen ligands are attached to the central W atom are also significant for the formation of the active centres, their concentration, lifetime, and reactivity, the stability of the centres and their donor properties being thereby increased. This has been proved, theoretically as well as experimentally, by Rappé and Goddard[16] and by Schrock and coworkers[17].

In our case the oxygen ligand is attached to the initial $WCl_6$ in reactions of the latter with the free acid present in the ester (for the system free of oxygen and water), and in reaction with the ester and also with the alcohol if present. All those reactions were monitored spectroscopically, based on the intensity of the absorption by $WCl_6$ at 326 nm. The reactions of $WCl_6$ with the acid or ethanol at the concentrations used ($\sim 10^{-4}$ mol $l^{-1}$) are considerably faster than the reaction with $(CH_3)_4Sn$. The reaction of $WCl_6$ with ester, on the other hand, is very slow under these conditions, even if the ester-to-tungsten ratio is as high as 50.

Since the esters used by us contained free acid in concentrations of 0·1 – 0·2 mol%, only 3 – 6% $WCl_6$ transformed into the corresponding monocarboxylate, pentachloro(10-undecenoato)tungsten, on mixing the components in the ester-to-tungsten ratio 45. Under these conditions also the reaction of $WCl_6$ with the ester can be neglected. Thus, few centres sufficiently stabilized by the oxygen ligand could form in the reaction with $(CH_3)_4Sn$. However, if the tungsten hexachloride is allowed

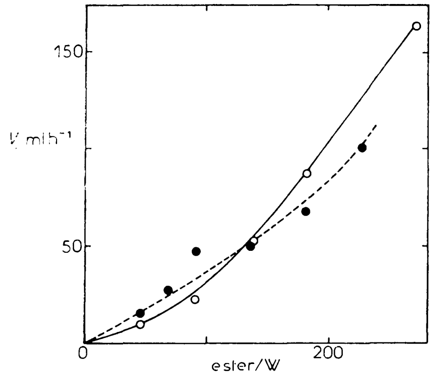

FIG. 6

Dependence of the metathesis rate on the ester/$WCl_6$ molar ratio. Reaction conditions: $c^0_W = 10$ mmol $l^{-1}$, 60°C, benzene, reaction mixture volume 10 ml, atmospheric pressure; ○ W : Sn molar ratio 1 : 4, ● W : : Sn : EtOH molar ratio 1 : 4 : 2

to react for some time with the ester at elevated temperature before adding tetramethyl tin, this reaction begins to play a role and the metathesis yield increases slightly (Table II). Extension of the period of this reaction conducted at 60°C to 6 h, however, results in a lowering of the activity. A similar conclusion has been arrived at by Otton and coworkers[9] in their study of cross-metathesis of methyl oleate with 2-hexene.

The increase of the ester concentration results in the increase of the fraction of the carboxylated tungsten due to increasing concentration of free acid with respect to $WCl_6$ and also to the accelerated reaction of the latter with the ester. Thus, both the concentration of the active centres (which, however, may be far from identical with the total concentration of carboxytungsten chlorides) and the rate of the metathesis increase. For instance, if the concentration of ester was increased so that the ester-to-tungsten molar ratio was raised from 45 to 90, the degree of conversion remained virtually constant; this is to say, the absolute amount of ester that transformed into the products in 6 h was double as high, and the maximum rate in the initial stage increased as well. On the other hand, the increase in the ester concentration leads also to a faster deactivation of the centres so that the metathesis ceases in a shorter time. In the absence of ethanol, this effect starts to prevail at ester-to-tungsten ratios 150–200. As it follows from a comparison of the curves in Figs 4 and 6, the conversion in such conditions decreases although the rate of metathesis in the inflexion point of the plots of amount of ethylene evolved *versus* time continues

TABLE II

Dependence of the catalyst activity on the time of the reaction of $WCl_6$ with ester before the start of the metathesis. Sn/W molar ratio 4, conditions as in Table I

| Molar ratio | | Time h | Degree of conversion % | Selectivity | Colour of the reaction mixture[a] |
|---|---|---|---|---|---|
| ester/W | $C_2H_5OH/W$ | | | | |
| 45 | 0 | 0 | 44 | 0·9 | dark violet |
| 45 | 0 | 1 | 47 | — | red |
| 45 | 0 | 3 | 52 | 0·65 | red |
| 45 | 0 | 6 | 40 | 0·7 | dark green |
| 45 | 2 | 0 | 50 | 0·85 | dark brown |
| 45 | 2 | 3 | 61 | — | red |
| 180[b] | 0 | 0 | 39 | 1 | dark brown |
| 180[b] | 0 | 0·5[c] | 59 | 1 | red |

[a] Before adding $(CH_3)_4Sn$, hence, before starting the metathesis; [b] $[WCl_6]_0 = 3{\cdot}3$ mmol l$^{-1}$ [c] reaction temperature 20°C.

to grow. It can be inferred that the reaction of ester or acid with the starting $WCl_6$ has a positive effect on the metathetic activity up to a high excess of ester, whereas the effect of the interaction with the active centres already formed is negative.

The positive effect of ethanol on the degree of conversion and the reaction rate, at ester-to tungsten ratios 45 – 90, can be similarly ascribed to the stabilizing effect of the alkoxy group on the active centre. With higher ester-to-tungsten ratios (above 100), however, additional reactions of alkoxy tungsten chlorides with acid and ester lead to an increased number of oxygen ligands at a tungsten above the optimum and thereby to a decrease in the fraction of tungsten atoms capable of formation of active centres. The results indicate that the activity of the $WCl_6$-based catalyst for metathesis of esters of unsaturated acids is affected by the reactions of $WCl_6$ and its reduction products with the oxygen components of the reaction mixture to a considetably greater extent than by the coordination of the carbonyl group of the ester to the central atom of the active centre; which, however is not excluded by the conclusion given above.

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