INTERACTIONS OF TUNGSTEN HEXACHLORIDE WITH ESTERS OF CARBOXYLIC ACIDS

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The interactions of tungsten chlorides and oxychlorides with methyl 10-undecenoate, methyl palmitate and methyl acetate, respectively, have been investigated by UV-VIS, IR and EPR spectroscopic methods. The primary complex formed by coordination of the carbonyl group to WCl_6 is converted successively to an analogical, very stable complex $WOCl_4$.ester under the simultaneous formation of acyl chloride and methyl chloride. In the case of methyl undecenoate, the coordination reaction is accompanied by a partial reduction of WCl_6 to WCl_5. The latter reacts with the ester in excess to give a complex characterized by a broad EPR single line at $g = 1\cdot767$ ($\Delta H = 7\cdot8$ mT). At higher ester-to-tungsten molar ratios, this complex undergoes deeper reduction to products containing tungsten in a lower oxidation state, and competitively, a parallel oxygen abstraction reaction yielding $WOCl_3$, acyl chloride and methyl chloride. The participation of these reactions in the formation of active WCl_6-based catalysts for methathesis of unsaturated esters is discussed.

It seems generally accepted that the metathesis of esters of unsaturated acids catalyzed by the WCl_6-based catalysts is hampered by the formation of complexes between the ester group and WCl_6 or other tungsten species formed subsequently. An IR spectroscopic evidence of such complexes of ethyl acetate with a variety of Lewis acids has been brought by Lappert[1]. The formation of analogical complexes of WCl_6 with several saturated and unsaturated esters has been reported by Ichikawa and coworkers[2], Verkuijlen[3], and Otton and coworkers[4]. The poisoning effect of the complexes has been explained by blocking free coordination sites by carbonyl groups, and thus reducing their number accessible to the interaction with the double bond[3]. The coordination reaction of the ester group to WCl_6 is rather slow (*e.g.* compared with the reduction of WCl_6 by tetramethyltin[5]).

However, some experimental facts can be hardly explained solely by the complexation of WCl_6. Thus Otton and coworkers[4] observed the dependence of the metathesis activity of the $WCl_6/(CH_3)_4Sn$ system on the way of mixing of the reaction components. Best results were obtained if WCl_6 was allowed to react with the substrate at elevated temperature prior to the addition of the cocatalyst. Recently, it has been shown[6] that the catalyst activity exhibits a maximum depending on the duration of this forerunning reaction ($20°C$, molar ratio ester/$WCl_6 = 50$). The interaction of WCl_6 with unsaturated esters is also accompanied by substantial

changes of the color of the reaction mixture, *i.e.* from dark violet through various shades of red to orange, and finally to gray-green. Optimum yields of metathesis are obtained when the cocatalyst is added at the stage "deep red". Obviously, the formation of the complex is followed by several subsequent reactions which may influence the resulting activity of the catalyst.

The aim of the present study is to identify the main types of the reactions following the formation of the complexes between WCl_6 and methyl 10-undecenoate, methyl palmitate and methyl acetate, respectively. Saturated esters have been chosen in order to separate the effect of the ester group from that one of the double bond. A combination of the UV-VIS, IR and EPR spectroscopy was used to elucidate the changes in the composition of the reaction mixtures.

EXPERIMENTAL

Chemicals. WCl_6 (Fluka) was purified by sublimation *in vacuo*. Methyl esters of acetic, palmitic and 10-undecenoic acids were prepared by the conventional esterification procedure. The residual traces of free acids were esterified using the oxalyl chloride method. The final acid number varied from zero to 0·03. WCl_5 and $WOCl_4$ were synthesized and purified according to the known methods[7,8]. The purification and drying of benzene was described elsewhere[6].

Apparatus and procedure. All preparations of the reaction components were carried out using the vacuum technique. Benzene solutions of the reactants were stored in preevacuated phials equipped with breakable seals. The glass reactor with attached phials and cuvettes was preevacuated to 10^{-2} Pa and before mixing the reaction components it was sealed off from the vacuum manifold. The cuvettes for IR spectra were filled under argon.

IR *spectra* were recorded on the Specord 75 instrument (Zeiss, Jena, GDR) and in several cases on the FFT Nicolet MX 1 spectrometer. UV-VIS spectra were taken with a Varian Cary 17 D spectrometer and EPR spectra were measured on the ERS-200 spectrometer (ZWG, Berlin, GDR).

Semiquantitative analysis of the reaction mixtures by means of the IR spectroscopy was carried out using the base-line method.

RESULTS

Electronic spectra. Fig. 1 illustrates the changes occuring in the electronic spectra of the reaction mixture WCl_6–methyl palmitate in benzene medium at several time intervals after the mixing. An analogical picture affords also the reaction between WCl_6 and methyl 10-undecenoate. These changes, however, do not provide much information on the structure of the reaction products. It is possible to determine the rate of the primary reaction between WCl_6 and the ester (from diminution of the strongest band of free WCl_6 at 326 nm), and under suitable conditions even the corresponding rate constants can be evaluated[5]. However, the newly growing band of the products in the region $350-357$ nm is of limited analytical value as it does not characterize a single compound. The positions of this band $(CT(Cl) \rightarrow metal)$

in the spectra of the mixtures of WCl_6 with some oxygen-containing compounds (registered to the point when no bands of free WCl_6 could be detected) and in the spectra of the model mixtures of $WOCl_4$ and WCl_5 with methyl undecenoate, are collected in Table I. It is seen that this band is common for a number of reaction products. Under the conditions used throughout this work, the reactions of WCl_6 with esters are relatively slow (the bands of WCl_6 disappear completely after several days), whereas the reactions with acids, alcohols or water are rather fast (WCl_6 is consumed in a few minutes). After prolonged reaction time at elevated temperature, free WCl_6 is no more detected even for the molar ratio WCl_6/methyl palmitate $= 2$.

The product of the reaction of methyl palmitate with WCl_6 is relatively stable, whereas that one obtained with methyl undecenoate undergoes further changes. The rate of these changes goes up when raising the reaction temperature and/or the molar ratio ester/WCl_6. In the case of methyl palmitate, the position of the band at 356 nm remained constant over several days, while the same band of the product of the reaction between WCl_6 and methyl undecenoate shifted gradually to shorter wavelengths, and simultaneously its intensity diminished. At the same time, a new band arose at 295 − 305 nm. In later stages of the reaction, two additional weak bands appeared also at 600 and 900 nm. The same bands were observed in the reaction mixture of WCl_5 with methyl undecenoate but not with methyl palmitate.

TABLE I

Characteristic absorption bands of the products of the reactions of WCl_6 with some oxygen-containing compounds, and of the model mixtures of $WOCl_4$ and WCl_5 with methyl 10-undecenoate. Benzene, 20°C, $c^0_{WCl_6} \sim 0.5$ mmol l^{-1}

Reaction mixture[a]	Substrate/W mol/mol	λ_{max}, nm[b]		
		A	B	C
WCl_6–MU	100	300 vw	356 s	contin.
WCl_6–MP	114	300 vw	356 s	decrease
WCl_6–UAc	2	305 vw	352 s	of A at
WCl_6–C$_2$H$_5$OH	2	300 vw	353 s	$\lambda > 400$
WCl_6–H$_2$O	2	not obs.	352	480 br, w
WCl_5	—	295 vw	345 s	480 br, w
WCl_5–MU	50	300 w	352 s	480 br, vw
$WOCl_4$	—	not obs.	352 s	480 br, vw
$WOCl_4$–MU	10	300 vw	356 s	460 − 480 w

[a] MU methyl 10-undecenoate, MP methyl palmitate, UAc 10-undecenoic acid; [b] A absorbance, br broad, s strong, vw very weak; A not identified, B CT(Cl) → metal, C CT (benzene) → metal.

TABLE II

Characteristic IR bands of some carboxylic acids and of their methyl esters coordinated to tungsten chlorides (cm^{-1}). Benzene, 20°C

Complex[a]	$\nu_{C=O}$[b]	ν_{W-O}	Complex[a]	$\nu_{C=O}$[b]	ν_{W-O}
WCl_6.MP	1 643	1 008	WCl_6.AcAc	1 665	1 008
WCl_6.MU	1 640				
	1 612 w	1 010	WCl_5.MP	1 650	1 002
				1 630 w	
WCl_6.UAc	1 656	1 003	$WOCl_4$.MU	1 640	1 007
WCl_6.LAc	1 660	1 010	$WOCl_4$.MP	1 640	1 003
WCl_6.LCl	1 658	1 007	$WOCl_4$.LAc	1 656	1 007

[a] MP methyl palmitate, MU methyl 10-undecenoate, UAc 10-undecenoic acid, LAc lauric acid, AcAc acetic acid, LCl lauroyl chloride; [b] w weak.
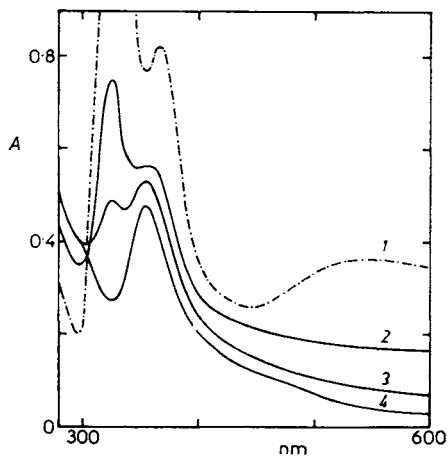

FIG. 1

Changes of the UV-VIS spectra during the reaction between WCl_6 and methyl palmitate (MP). $c^0_{WCl_6} = 0.48$ mmol l^{-1}, molar ratio ester/W = 83, $l = 1$ mm, benzene, 20°C; *1* WCl_6, *2* reaction mixture after 7.5 h, *3* 21 h, *4* 48 h
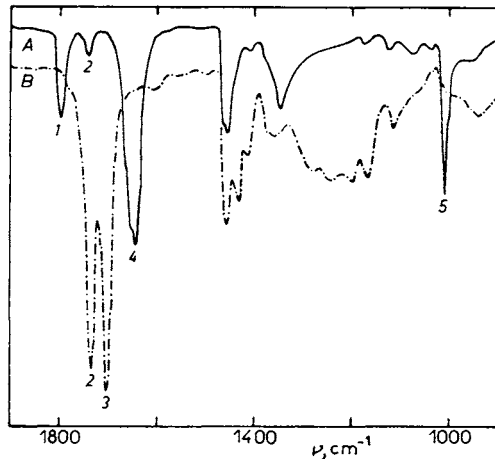
FIG. 2

IR spectrum of the reaction mixture WCl_6–methyl palmitate. $c^0_{WCl_6} = 34$ mmol l^{-1}, molar ratio ester/W = 2; *A* after 120 h at 20°C; *B* after 10 min passing wet air; assignment of the peaks: *1* palmitoyl chloride, *2* free ester, *3* free acid, *4* and *5* complexes WCl_6.ester + $WOCl_4$.ester

Therefore, their assignment to some kind of low-valent tungsten compound seems to be justifiable.

Infrared spectra. The interactions of WCl_6 or other tungsten chlorides with esters of carboxylic acids can be followed readily at low ester-to-tungsten ratios only. Under these conditions the reaction rates are rather low. Therefore, in most cases, the spectra were recorded after the originally violet solution had changed the colour to red or orange. This stage was achieved after several days or after prolonged heating at $50-60°C$.

The chlorides WCl_6 and WCl_5 do not exhibit any vibrational transition within $400-4\,000\ cm^{-1}$. Saturated benzene solutions of $WOCl_4$ showed two very weak IR adsorption bands (at $895\ cm^{-1}$ of the v_{W-O-W} and at $380\ cm^{-1}$ of the v_{W-Cl}), which could be observed under special conditions only (FFT spectrometer, two hundred scans). Therefore, their analytical value is limited. The interaction of WCl_6 with esters of carboxylic acids manifests itself, above all, by the shift of the $v_{C=O}$ band of the free ester by $80-100\ cm^{-1}$ to lower frequencies due to the coordination of the carbonyl to WCl_6^{2-4}. In the case of methyl palmitate or methyl undecenoate, this new band appears at $1\,642\ cm^{-1}$. In most cases, however, it is broad and bears two or three shoulders indicating the coincidence of several bands belonging to slightly different products. For instance, in the same region occur the bands of the complexes of acids and acyl chlorides with WCl_6 or $WOCl_4$, as well as the band of the $C=C$ stretching of free methyl undecenoate (Table II). Another characteristic band of the complexes of tungsten chlorides with acids and esters is a sharp band of medium intensity at $1\,000-1\,010\ cm^{-1}$ which is usually assigned to the vibration of the W—O bond of a higher order than one[9]. Both bands of the complexes increase with time to a limiting value with the rate depending on concentration and temperature. Molecules of the esters are displaced from the complexes by water, alcohols, oxygen, and acids, resp. Diminution of both bands of the complex is accompanied by a simultaneous increase of the band of the free ester at $1\,735\ cm^{-1}$ (Fig. 2). Furthermore, in the spectrum of the mixture of WCl_6 with ethyl 3-pentenoate, Otton and coworkers[4] mention another band at $1\,610-1\,620\ cm^{-1}$ which they have assigned to the stretching vibration of the double bond coordinated to tungsten. Identification of this band in the spectra of the reaction mixtures under investigation was difficult due to its overlap with the band at $1\,620-1\,630\ cm^{-1}$ which, however, in some cases appeared also with methyl palmitate. This band probably originates from the reaction of WCl_6 with adventitious traces of moisture or oxygen adsorbed on the windows of the cell.

In addition to the bands of the complexes mentioned above, the spectra of the reaction mixtures of WCl_6 with esters show further bands, the strongest of them appearing at $1\,790-1\,800\ cm^{-1}$. This range is typical for the $v_{C=O}$ in acyl chlorides. Upon addition of water this band disappears. Simultaneously free acid is liberated as follows

from the increase of the band of its dimer at $1\,712\,\mathrm{cm}^{-1}$ (Fig. 2). Under the same conditions no hydrolysis of the free ester takes place. Among the products of the reaction of WCl_6 with methyl esters, GLC-MS analysis showed also the presence of methyl chloride and in some cases a little amount of acylated benzenes.

The formation of acyl chlorides and methyl chloride accounts for the existence of a further reaction between the components of the complex WCl_6.ester, which is connected with the oxygen abstraction from the ester group yielding $WOCl_4$. Although $WOCl_4$ has not been identified directly by chemical analysis, its formation is favored by the fact that sublimation of the solid residue, after distilling off the liquid compounds from the reaction mixture WCl_6–CH_3COOCH_3, affords red-orange crystals typical of $WOCl_4$.

The formation of complexes and their transformations to acyl chlorides and $WOCl_4$ are illustrated by the analysis of palmitoyl chloride and of the consumed ester in some reaction mixtures of WCl_6 with methyl palmitate (Table III). The accuracy of the analysis was not high $(\pm 10\%)$ because the intensities of the absorption bands were evaluated by using the simple base-line method without band separation. Moreover, an unknown amount of the palmitoyl chloride was bound in the complex with WCl_6. Nevertheless, some conclusions resulting from these analyses are unambiguous. Firstly, it is beyond doubt that the amount of the palmitoyl chloride increases during the reaction. In the presence of an excess of the ester its final concentration reaches the value of the initial concentration of WCl_6. The figures in the last column of the Table III give the number of moles of the ester bound in the complex per mole of WCl_6 charged at the beginning. It is evident that independently of the fact whether a part or all WCl_6 has been transformed to $WOCl_4$, the resulting complex contains both components mostly in the ratio one-to-one, but at a larger excess of the ester it can be even higher.

The same products, *i.e.* the complex, acyl chloride and methyl chloride are obtained in the reaction of WCl_6 with methyl 10-undecenoate. In this case, a complex resulting from the π-coordination of the double bond should also be formed. However, for reasons given above its presence could not be proven accurately, although in contrast to methyl palmitate, the absorption band at $1\,610-1\,620\,\mathrm{cm}^{-1}$, which is indicative of this type of coordination, was present in all cases. A little decrease of intensities of the bands at 910 and $992\,\mathrm{cm}^{-1}$ of the $\delta_{\mathrm{C-H}}$ in the free vinyl group was also evident. After longer reaction times, the IR spectra of the products of the reactions of WCl_6 with esters displayed another weak band at $1\,575\,\mathrm{cm}^{-1}$, characteristic of the C—O stretching vibration in the carboxylate ion.

The interaction of $WOCl_4$ with esters leads merely to the formation of complexes characterized by the same bands as are those which have been found with WCl_6 (Tab. II). At the molar ratio of methyl palmitate to tungsten oxychloride equal to 4, and for $c_W^0 = 20\,\mathrm{mmol\,l}^{-1}$, the formation of acyl chloride was not observed even after a ten days reaction at $20°\mathrm{C}$, followed by 75 h warming at $50°\mathrm{C}$. On the other

hand the reactions of esters with WCl_5 result both in formation of the complexes and in liberation of acyl chloride, the latter indicating the formation of equivalent amounts of $WOCl_3$.

EPR *spectra*. The courses of the reactions of WCl_6, WCl_5 and $WOCl_4$, respectively, with methyl palmitate and methyl undecenoate were followed at various ester-to-tungsten molar ratios. In most cases the IR spectra or UV-VIS spectra were also recorded simultaneously. The reactions of both esters with $WOCl_4$ did not afford at molar ratios ester/W < 100 any paramagnetic particles. However, during the interaction of WCl_6 with methyl undecenoate the spectrum shows after different reaction times depending on the concentration and temperature a singlet at $g = 1\cdot767$ with $\Delta H = 7\cdot8$ mT which increases to a constant value. At very high ester-to-tungsten molar ratios (> 100) and after long reaction times a slight decrease of its intensity can be observed. For instance, at the molar ratio ester/$WCl_6 = 80$ and for $c_W^0 = = 20$ mmol l^{-1} the first indication of the signal appeared after two hours, and then its intensity increased steadily during 24 h to a limit corresponding to about one half of WCl_6 added at the beginning. A signal with the same parameters appears also when any ester is added to the solution of WCl_5. Its intensity grows also very slowly to a constant value corresponding to about $20-40\%$ of the original WCl_5 concentration. Since WCl_5 in benzene solution is dimeric and due to the spin pairing

TABLE III

IR analysis of the products of the reactions between WCl_6 and methyl palmitate (MP). Benzene, $20°C$, concentrations in mmol l^{-1}; PCl denotes palmitoyl chloride

$[WCl_6]_0$	$\dfrac{[MP]}{[WCl_6]_0}$	t, h	ΔMP^a	[PCl]	$\dfrac{[PCl]}{[WCl_6]_0}$	$\dfrac{\Delta MP - [PCl]}{[WCl_6]_0}$
30·3	1	90	22	5·7	0·19	0·54
30·3	1	110	30·3	8·7	0·29	0·71
24	2	53	43·6	18·3	0·76	1·0
34	2	130^b	64	31	0·91	0·97
34	2	150^c	64	33	0·97	0·91
15	4	70	24	10	0·64	0·89
27	4	120	50	24	0·9	0·96
27	4	144	47	23	0·85	0·9
50	5	2	77	0	—	1·5
50	5	18	81	18	0·36	1·26
50	5	45	98	23	0·46	1·46

^{a} The consumption of methyl palmitate ($[MP]_0 - [MP]_t$); ^{b} 15 h at 40°C, ^{c} 30 h at 40°C.
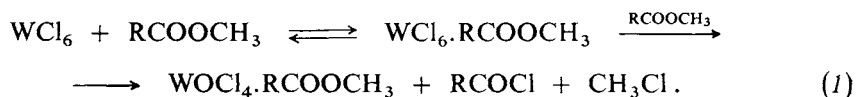
it shows no EPR signal, the origin of the above EPR line can be attributed to the paramagnetic complex WCl_5.ester (or even $WOCl_3$.ester), arising from a slow dissociation of the dimer due to the coordination of the ester group. Reduction of W(V) to paramagnetic W(III)-containing compounds, which has been observed by Ceausescu and coworkers in the course of the reaction of WCl_6 with cycloolefins[10], is not likely to take place in this case.

A weak signal at the above g-value appears also when WCl_6 is allowed to react with methyl palmitate at elevated temperature for several days (60°C). Its intensity is badly reproducible. Most probably it can be attributed to the side reactions of WCl_6 with benzene[11], and/or to a partial chlorination of the aliphatic chain of methyl palmitate, both reactions resulting in reduction of W(VI) to W(V)-species. All these reactions are photocatalytic which explains their poor reproducibility in the common experimental procedure.

DISCUSSION

The results of the individual spectroscopic methods can be compared only qualitatively because the concentrations and the molar ratios of the components required for a particular method are rather different. However, they provide a good evidence of the nature of the reactions taking place in the systems under study. The extent of their participation in a given case will depend on the reaction conditions used.

The electronic, as well as the IR spectra of the reaction mixtures of WCl_6 with acid esters reveal that the primary complexes WCl_6.ester, formed as initial products of the interactions between both components, undergo further transformations. As it follows from the continuous increase of the concentration of the acyl chloride in mixtures of WCl_6 with any ester, one product of these transformations is $WOCl_4$ which also forms with the excessive ester a complex exhibiting the same electronic and IR absorption bands as that one of WCl_6. The EPR and IR spectroscopic investigations of the model mixtures of $WOCl_4$ with methyl palmitate and methyl undecenoate, respectively, point to a considerable stability of this complex, since no EPR signal, as well as no IR bands of acyl chlorides have been detected even after a period of several weeks. The conversion of WCl_6 to $WOCl_4$ in the reaction with a saturated methyl ester (which is quantitative after sufficiently long reaction time) is described by the equation:

$$WCl_6 + RCOOCH_3 \rightleftharpoons WCl_6.RCOOCH_3 \xrightarrow{RCOOCH_3}$$

$$\longrightarrow WOCl_4.RCOOCH_3 + RCOCl + CH_3Cl. \qquad (1)$$

The capability of tunsten halides to abstract oxygen from various oxygen-containing compounds is well known[9,12]. The formation of $WOCl_4$ in the WCl_6-based

catalysts for metathesis of the esters of unsaturated acids has been postulated also by Van Roosmalen and coworkers[13].

A different situation arises when methyl undecenoate is used. In this case, the oxygen abstraction reaction competes with the reduction of WCl_6 to WCl_5, while simultaneously the double bond is chlorinated, affording mono- and dichlorooundecanoates (as shown by GLC-MS). Tungsten pentachloride is again partially complexed with the ester. From the EPR-data it is apparent that the final concentration of paramagnetic particles in the system WCl_6-methyl undecenoate corresponds to the amount of several tens % of the initial concentration of WCl_6. With regard to a low dissociation degree of WCl_5-dimer in the presence of the esters (as follows from the comparatively low equilibrium concentration of the paramagnetic complex in the mixtures of WCl_5 with esters), it may be concluded that the reduction of WCl_6 prevails over the oxygen abstraction. The presence of the complex WCl_5.ester in reaction mixtures cannot be proven by means of electronic or IR spectra due to the coincidence of its bands with those of analogical complexes of WCl_6 or $WOCl_4$. However, in addition to the EPR spectroscopic evidence, the formation of this complex is also supported by a shift of the main absorption maximum of WCl_5 at 345 nm to 352 nm after the addition of ester.

The complexes of WCl_5 with methyl undecenoate (again formed through coordination of both C=O and C=C bonds) are subjected to similar reactions as those of WCl_6, *i.e.* to the oxygen abstraction from the ester molecule giving $WOCl_3$, and to the reduction by the double bond to a lower-valence tungsten species which has not been identified so far. In the electronic spectrum this reduction is manifested by the decrease of the absorption band at 352 nm and by a simultaneous increase of the band at 300 – 305 nm. The same products are likely to account also for the two weak bands at 600 and 900 nm appearing in the reactions of methyl undecenoate with both WCl_6 and WCl_5. The formation of $WOCl_3$ could not be proven from the EPR spectra as the signal of W(V) in the system WCl_5–undecenoate, after its initial increase, remained constant for a long time whilst the IR spectrum showed the presence of the acyl chloride.

All the above discussed reactions are very slow in comparison with those occuring between the components of the most frequently used catalyst WCl_6–$(CH_3)_4Sn$. Therefore, if the ester is charged as the last component of the reaction system, they need not be taken into account in metathesis. On the other hand, if tetramethyltin is dosed at a certain time after mixing WCl_6 with the ester, the resulting activity of the catalyst may be considerably influenced. For instance, the formation of $WOCl_4$ (as a result of the interaction of WCl_6 with the ester group) explains the increase of the catalytic activity when WCl_6 is allowed to react for a suitable time before addition of $(CH_3)_4Sn$. For the same reason, it can be understood that very pure WCl_6 does not afford under inert conditions an active catalyst in metathesis of olefins[14], but a fairly active one in metathesis of unsaturated esters. In this latter case, the real

precursor of active centres $(i.e.$ $WOCl_4)$ is formed *in situ*. On the basis of the results obtained up to now it is not clear why the catalyst activity drops with prolongation of the forerunning reaction WCl_6–ester over the optimum time. According to the IR and EPR data, obtained under conditions used commonly in metathesis, the reaction mixtures of WCl_6 with esters should contain mainly the complexes of $WOCl_4$ and WCl_5, so that the conditions for the formation of an active catalyst are fulfilled. Presumably, a deeper carboxylation of the oxychlorides and coagulation of the products of the reduction of WCl_5 may be responsible for this effect.

REFERENCES

1. Lappert M. F.: J. Chem. Soc. *1961*, 817.
2. Ichikawa K., Watanabe O., Takagi T., Fukuzumi K.: J. Catal. *44*, 416 (1976).
3. Verkuijlen E.: *Thesis*. University of Amsterdam, 1980.
4. Otton J., Colleuille Y., Varagnat J.: J. Mol. Catal. *8*, 313 (1980).
5. Balcar H., Dybal J.: React. Kinet. Catal. Letters, in press.
6. Balcar H., Dosedlová A., Hanuš V., Petrusová L., Matyska B.: This Journal *49*, 1736 (1984).
7. Novikov G. I., Andreeva N. V., Polyachenok O. G.: Zh. Neorg. Khim. *9*, 1019 (1961).
8. Funk V. H., Weiss W., Mohaupt G.: Z. Anorg. Allgem. Chem. *304*, 238 (1960).
9. Walton R. A.: Progress Inorg. Chem. *16*, 1 (1972).
10. Ceausescu E., Cornilescu A., Nicolescu E., Popescu M., Coca S., Belloiu C., Oprescu C., Dimonie M., Hubca Gh., Dragutan V., Chipara M.: J. Mol. Catal. *28*, 351 (1985).
11. Günter P., Haas F., Marvede G., Nützel K., Oberkirch W., Pampus G., Schön N., Witte J.: Angew. Makromol. Chem. *14*, 87 (1970).
12. Funk H., Hoppe H. R.: Z. Chem. *8*, 31 (1968).
13. Van Roosmalen A. J., Polder K., Mol J. C.: J. Mol. Catal. *8*, 185 (1980).
14. Mocella M. T., Rovner R., Muetterties E. L.: J. Amer. Chem. Soc. *98*, 4689 (1976).