Investigation of the catalyst system tungsten hexachloride/ tetramethyltin; reduction of tungsten hexachloride during the alkylation step

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Abstract

The alkylation steps in the catalyst system tungsten hexachloride/tetramethyltin have been studied kinetically. FTIR examinations in combination with UV and GC results have shown that the alkylation of tungsten hexachloride is accompanied by a reduction of the tungsten component. Ether addition increases the amount of the tungsten chloride which is reduced.

Introduction

In the conventional metathesis catalyst system many competing parallel and consecutive reactions occur, so that only a small portion of the catalyst components which were initially used is converted into the active species. The long-term goal of our investigations is to determine the reaction paths in the system 'tungsten hexachloride/tetramethyltin (diethyl ether)' to optimize the production of active species. To achieve this, several steps are necessary:

- (1) consideration of all reactions in the system;
- (2) quantitative determination of the individual steps;
- (3) identification of the reactions that produce the catalytically active species.

Analysis of the reaction steps in the catalyst system tungsten hexachloride/ tetramethyltin by UV spectroscopy, head space GC and conventional IR spectroscopy [1–5] enabled us to establish the mechanism shown in Fig. 1. Since the alkylating agent is generally added in the presence of the olefin, the influence of the olefin is important as well [4, 6]. As shown in the Figure, even in the initial stage, several reactions are taking place. Tungsten hexachloride is alkylated by tetramethyltin, the olefin is chlorinated by tungsten hexachloride and probably tungsten hexachloride is reduced to tungsten pentachloride. Our experiments with hexane as solvent show that the reduction of tungsten hexachloride competes with the alkylation step [2].

The alkylation steps have been studied kinetically by looking at the change in the concentration of the tungsten compound with time [2, 4, 5] using UV-spectroscopy. Kinetic measurements of the tin component were also necessary to complete the quantitative description.



Fig. 1. Reaction pattern obtained for the WCl₆/SnMe₄ system.

This paper deals in particular with the investigation of the conversion of tetramethyltin to trimethyltin chloride during the reaction.

Experimental

The investigations were carried out in all-glass vessels with argon purified of traces of oxygen and water as inert gas under conditions commonly applied for metathesis reactions. Benzene as the solvent was purified [8]. The absolute purity of the tungsten hexachloride used was verified by means of its UV spectrum.

The kinetic measurements were performed using flow-through cuvettes (KBr cuvettes; Spectra-Tech Inc.) coupled with a glass reaction vessel (Fig. 2) using benzene as the solvent and employing a tungsten hexachloride concentration of 5.5×10^{-3} mol l⁻¹. The tungsten hexachloride:tetramethyltin ratio was 1:2. The mixing time was 2 s. As FTIR spectrophotometer a Nicolet 20 SXB instrument was used.

Method of examination

IR spectroscopy is very well suited to observe the conversion of tetramethyltin to trimethyltin chloride [1]. Tetramethyltin has a strong band at 527 cm^{-1} , while trimethyltin chloride has a band about half as strong at 544 cm^{-1} (Fig. 3). Since the alkylation steps are in part rapid conversions with half-life periods measured in seconds [2, 4, 5], a FTIR spectrophotometer was preferred since it was able to record a spectrum from $580-490 \text{ cm}^{-1}$ every 1.5 seconds. Benzene was used as solvent in preference to toluene since it does not have interfering bands in this region. The reaction vessel used, analogously to the UV-measurements [2, 4-6], was a double-jacketted glass vessel connected to a flow-through IR cell (Fig. 3).



Fig. 2. Double-jacketted reaction vessel containing a flow-through cell for UV-vis or IR measurements.

Fig. 3. IR spectra of SnMe₄ and SnMe₃Cl in benzene.

Results and discussion

Determination of the reaction between tungsten hexachloride and tetramethyltin

The results of the FTIR spectroscopic investigation of the reaction between tungsten hexachloride and tetramethyltin (1:2) are depicted in Fig. 4. The spectra of tetramethyltin and trimethyltin chloride are given for comparison. Figure 4 shows that the final spectrum is the same as the spectrum of trimethyltin chloride. This is in accordance with our earlier results obtained with a conventional IR spectrometer. Thus only one alkylgroup of the tetramethyltin is exchanged for a chlorine; dimethyltin dichloride was not found [1, 2]. The occurrence of an isosbestic point, which remained until all tetramethyltin was consumed, also shows that tetramethyltin is converted quantitatively to trimethyltin chloride.

Figure 5 shows the decrease in tetramethyltin and concomitant increase in trimethyltin chloride with time. The initial phase is shown in the inset graph. As can be seen, the consumption of tetramethyltin occurs essentially in three steps. The first step is very fast, followed by a slow phase of tetramethyltin consumption. After that the reaction accelerates again. Furthermore, the FTIR results show that more tetramethyltin than necessary for equimolar conversion reacts in the first step. This overconsumption indicates that a product is formed that also reacts with tetramethyltin.

With the proposed reaction scheme (Scheme 1) this result can be explained. Tungsten hexachloride reacts in benzene via the intermediate methyltungsten pentachloride. This reaction is relatively fast and competes with the alkylation of tungsten hexachloride. Although this side-reaction



Fig. 4. FTIR spectroscopic examination of the reaction between WCl_6 and $SnMe_4$ (WCl_6 :SnMe_4 = 1:2).



Fig. 5. FTIR spectroscopic examination of the reaction between WCl₆ and SnMe₄ (WCl₆:SnMe₄ = 1:2). Concentration vs. time curves for SnMe₄ (\times) and SnMe₃Cl (\bigcirc).

reduces the amount of tungsten hexachloride that can be alkylated, it produces tungsten pentachloride (Scheme 2). Our investigations show that tungsten pentachloride reacts even faster with tetramethyltin than does tungsten

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 $WCl_{6} \xrightarrow{SnMe_{4}} WCl_{5}Me \xrightarrow{} WCl_{5}Me \xrightarrow{} WCl_{5} + WCl_{5}Me \xrightarrow{} WCl_{5} + MeCl \xrightarrow{} WCl_{5} + WCl_{5} + WCl_{5} + WCl_{5} + MeCl \xrightarrow{} VCl_{6} + SnMe_{4} \xrightarrow{} MeWCl_{5} + SnMe_{3}Cl \xrightarrow{} 2 WCl_{5} + MeCl \xrightarrow{} 2 WCl_{5} + MeCl \xrightarrow{} 2 WCl_{5} + SnMe_{4} \xrightarrow{} MeWCl_{4} + SnMe_{3}Cl \xrightarrow{} 2 WCl_{5} + SnMe_{4} \xrightarrow{} MeWCl_{4} + SnMe_{3}Cl \xrightarrow{} 2 WCl_{5} + (1 + x)SnMe_{4} \xrightarrow{} WCl_{5} + (1 + x)SnMe_{4} \xrightarrow{}$

Scheme 2.

hexachloride [2]. Since for every molecule of tungsten hexachloride used in the reduction two molecules of tungsten pentachloride are produced, the overconsumption of tetramethyltin is explained.

The two steps of the consumption of the second mol tetramethyltin $(c/c_0 = 0.5-0;$ Fig. 5) are attributed to the second alkylations of monomethyltungsten(V) and monomethyltungsten(VI) chlorides.

Evidence of the reduction step

The overconsumption of tetramethyltin can be explained by the reduction of tungsten hexachloride. Thus, we had to prove that this reaction really takes place. The detection of the byproduct methyl chloride would prove the occurrence of this side reaction.

 $WCl_6 + WCl_5Me \longrightarrow 2WCl_5 + MeCl$

UV measurements show that tungsten hexachloride is completely consumed within 30 s. Since tungsten hexachloride takes part in the reaction, the corresponding amount of methyl chloride must also be present after 30 s. FTIR spectroscopy failed to detect methyl chloride, because the concentration was too low, and head-space GC was unsuitable, because it is too slow for the determination of events within the first minute. However, gas chromatographic analysis of the liquid phase confirmed that methylchloride is produced in the initial stages of the reaction [7].

The mass balance for the reaction products is remarkably good, and therefore the good agreement between UV, IR and GC results. While about 0.25 mol methyl chloride per mol tungsten hexachloride was detected by gas chromatography. The overconsumption of tetramethyltin, as determined

WCl ₆ +	SnMe ₄	MeWCl ₅ +	SnMe3Cl
0.75 mol		0.75mol	0.75mol
WCl ₆ +	MeWCl ₅	2 WCl ₅ +	MeCl
0.25 mol	0,25mol	0.50 mol	0.25 mol
WCl ₅ + 0.50 mol	SnMe ₄	MeWCl ₄ +	SnMe ₃ Cl 0.50 mol
W Cl ₆ +	1.25SnMe₄+	0.50 MeV 0.50 MeV 1.25 SnM 0.25 MeC	VCl ₅ + VCl ₄ + 1e ₃ Cl + Cl

Scheme 3.



Fig. 6. FTIR spectroscopic examination of the reaction between WCl₆ and SnMe₄ in the presence of ether (WCl₆:SnMe₄:EtOEt = 1:2:2). Concentration vs. time curves for SnMe₄ (×) and SnMe₃Cl (\bigcirc). UV results for WCl₆ consumption are added for comparison.

by FTIR spectroscopy, is also 0.25 mol per mol tungsten hexachloride (Scheme 3).

Study of the reaction between tungsten hexachloride and tetramethyltin in the presence of ether

As is well known, in the system tungsten hexachloride/tetramethyltin useful activities for metathesis can only be achieved by adding ether. Therefore we were interested in the question:"what influence does the addition of ether have on the alkylation of tungsten hexachloride with tetramethyltin".

As is the case without addition of ether, in the presence of ether $(WCl_6:SnMe_4:EtOEt = 1:2:2)$ tetramethyltin is also converted quantitatively to trimethyltin chloride [8]. In Fig. 6 the decrease in tetramethyltin and the simultaneous increase in trimethyltin chloride are plotted against time. The expanded plot shows the course of the reaction during the first minute; the UV results are included for comparison.

(1) WCl₆ + SnMe₄
$$\xrightarrow{k_1}$$
 MeWCl₅ + SnMe₃Cl
1-x
(2) WCl₆ + MeWCl₅ $\xrightarrow{k_2}$ 2 WCl₅ + MeCl
x
(3) WCl₅ + SnMe₄ $\xrightarrow{k_4}$ MeWCl₄ + SnMe₃Cl
(4) WCl₅·EtOEt + SnMe₄ $\xrightarrow{k_4}$ MeWCl₄·EtOEt +
SnMe₃Cl
k₄« k₁, k₂
WCl₆ + (1-x)SnMe₄ \xrightarrow{EtOEt}

Scheme 4.

It is remarkable that in the first fast step, when tungsten hexachloride is completely consumed, only about half of the equimolar amount of tetramethyltin is reacted (*cf.* $SnMe_4$ and WCl_6 consumptions during the first minute; Fig. 6). Responsible for this fact is again the reduction of tungsten hexachloride, with the formation of methyltungsten pentachloride as a side reaction.

In the presence of ether, tungsten pentachloride exists as a one to one complex with ether and does not contribute to a rapid decrease in the amount of tin component. Moreover, our investigations show that tungsten pentachloride—monoetherate is alkylated much more slowly than tungsten hexaor pentachloride (Scheme 4) [2, 9]. Because a part of the added tetramethyltin is consumed in the side reaction, our earlier observation that the optimum ratio of tungsten hexachloride to tetramethyltin is greater than 1:2, is explained [10]. Furthermore, the FTIR investigations yield the important result that the alkylation of tungsten hexachloride in the presence of ether does not proceed selectively, that is, the second alkylation step already takes place before the first step is completed.

Conclusion

The FTIR investigations of the catalyst system tungsten hexachloride/ tetramethyltin in conjunction with UV and GC results show that the alkylation of tungsten hexachloride is always accompanied by a reduction of tungsten hexachloride. Monomethyltungsten(VI) pentachloride is involved in the reduction reaction. For every mol of tungsten hexachloride which is reduced, one mol monomethyltungsten(VI) chloride is dealkylated and cannot participate in the formation of the dimethylalkyltungsten component. This means that for the catalyst system 'Tungsten hexachloride/tetramethyltin/(ether)' to be active the ratio of tetramethyltin to tungsten hexachloride must be greater than two. Assuming that the metathetically active species is formed from a dimethyltungsten compound, an assumption supported by our results [11], it follows that a maximum yield of dimethyltungsten species is desirable. Because the dimethyltungsten compound is an intermediate in a chain of consecutive reactions, the selectivity of the alkylation reaction must be high. Since the addition of ether is necessary for stabilisation of the metathetically active species, and the alkylation of tungsten hexachloride in the presence of ether does not proceed selectively, it can be concluded that the addition of diethyl ether must occur after the first alkylation step is completed.

Acknowledgement

The authors gratefully acknowledge financial support from the DFG (Deutsche Forschungsgemeinschaft; Th 307/3-1) and FC (Fonds der chemischen Industrie).

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