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KINETIC STUDIES OF THE SYSTEM TUNGSTEN HEXACHLORIDE/ TETRAMETHYLTIN (DIETHYL ETHER)/C_5-OLEFINS; DETERMINATION OF THE INITIAL REACTION STEPS

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Summary

The initial steps in the catalyst system tungsten hexachloride/ tetramethyltin/C_5-olefins have been studied kinetically. UV–vis spectroscopic examinations have shown that the first alkylation step proceeds as a second-order reaction with the low activation energy of 26.1 kJ mol^{-1}. The reaction between tungsten hexachloride and C_5-olefins leads quantitatively to tungsten pentachloride which is formed as a stable intermediate compound. This reaction, which is much slower than the alkylation step, is of great importance in the presence of high olefin concentrations, and especially in the case of cyclic olefins.

Introduction

Vagueness about the mechanism of metathesis, as well as regarding the elemental reactions which take place in the catalyst system, motivated us some six years ago to carry out exhaustive investigations of the catalyst. Subsequently it was decided to follow the course of the reactions in a common metathesis catalyst system. Knowledge of the reactions occurring in the catalyst system offers not only a basis for the optimization of the catalyst, but also helps in the identification of the active species involved.

The tungsten hexachloride/tetraethyltin system

As a starting point for the examination of the catalyst, we employed the reaction scheme suggested in the literature [1] (Scheme 1). It was planned to study the first alkylation step by UV spectroscopy, by observing the decrease in the absorbency (extinction) of tungsten hexachloride. Additional information concerning the consumption of a second mole of tetraalkyltin was expected from IR measurements, while GC methods were employed for kinetic studies of gas evolution. Tungsten pentachloride was also synthesized and used as the initial product.

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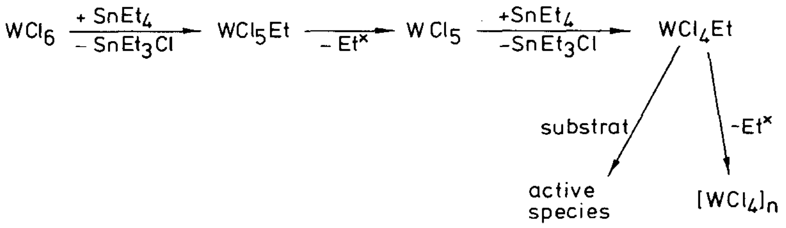
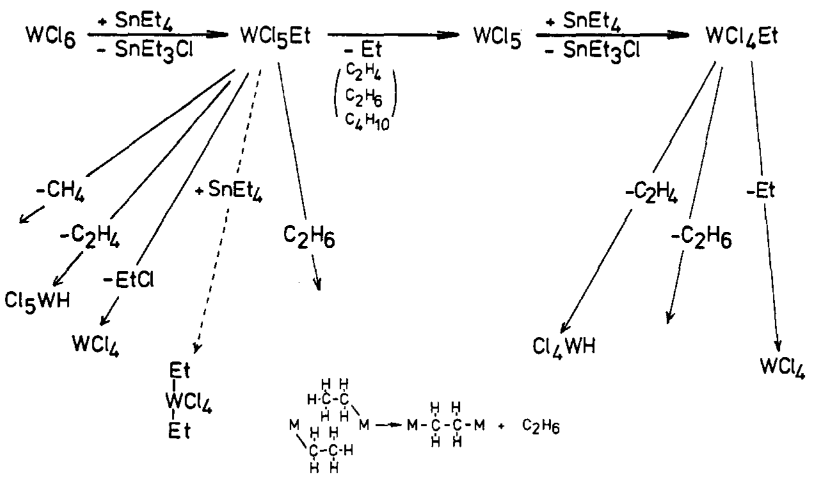


Scheme 1.

Our investigations on the catalyst system tungsten hexachloride/ tetraethyltin showed that the course of the reaction is more complex than presented in Scheme 1, with parallel reactions as well as consecutive ones occurring [2] (Scheme 2). The disproportionation of the ethyl group is not the only process responsible for the evolution of ethane and ethene. During the initial stages of the reaction more ethene was produced than ethane, and the formation of tungsten hydride is probably responsible for this fact. At the end of the reaction only ethane (and no ethene) evolution was observed, probably as a result of the formation of a dimetalloalkane structure. The existence of such compounds has been demonstrated in Ziegler–Natta systems [3]. Methane and ethyl chloride were also detected among the gaseous products evolved.

The extremely high reaction rate observed during alkylation and during the degradation of the intermediate products compelled us to use tetramethyltin instead of tetraethyltin as the alkylating agent. As rapid spectroscopic UV measurements show [4], the initial alkylation step with tetraethyltin was completed within ⩽0.04 s at a tungsten hexachloride

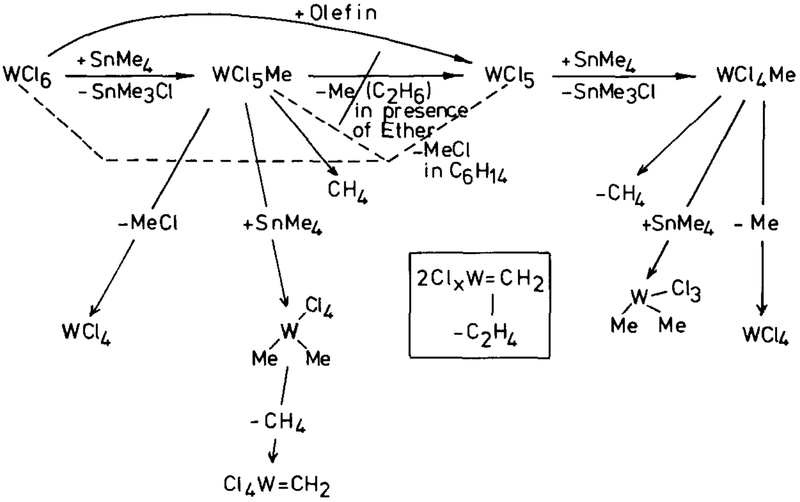


Scheme 2.

concentration of 5×10^{-4} mol l^{-1} when toluene was used as the solvent and the reaction was conducted at room temperature.

The tungsten hexachloride/tetramethyltin system

The reaction pattern obtained for the tungsten hexachloride/ tetramethyltin system shows that the course of the reaction on the whole is also quite complex [2] (Scheme 3). During the initial step two reactions are already taking place, *i.e.* the alkylation of tungsten hexachloride with tetramethyltin and the chlorination of the olefin by tungsten hexachloride. Since the alkylating agent is generally added in the presence of the olefin for metathesis, the influence of the olefin is important in this reaction as well.



Scheme 3.

It has also been demonstrated that the addition of ether has a significant influence on the direction of the reaction pathways. In the absence of ether the alkylation of tungsten pentachloride proceeds faster than the alkylation of tungsten hexachloride. In contrast, in the presence of ether the alkylation of tungsten pentachloride is slower. This behaviour is attributed to the generation of tungsten pentachloride monoetherate [5]. Furthermore, it is interesting that in the presence of ether evolution of ethene and ethane is strongly suppressed at the start of the reaction.

In order to determine the course of the various reactions quantitatively (or at least the course of the primary reactions), the next step in the investigation of this system is the establishment of the kinetics of the elemental reactions. This paper deals with the kinetics of the initial steps.

Method of examination

Since UV spectroscopy has proved to be a satisfactory method for the determination of the tungsten components in the reaction, and since the processes to be studied are in part rapid conversions with half-life periods measured in seconds [6], a high-speed UV spectrophotometer was preferred for the measurements presented in this report. Recording and interpretation of the spectra was achieved with the aid of a process-control computer [7].

UV–vis characterization of tungsten hexachloride

A special feature of the metathesis when tungsten hexachloride is employed as the catalyst is that the most important degradation product, tungsten oxytetrachloride, is also readily alkylated and acts as a very active metathesis catalyst as well [8]. Hence, in order to carry out the planned kinetic investigations, it therefore became necessary to ensure the absolute purity of the tungsten hexachloride used, the latter being checked by means of its initial UV spectrum (Fig. 1).

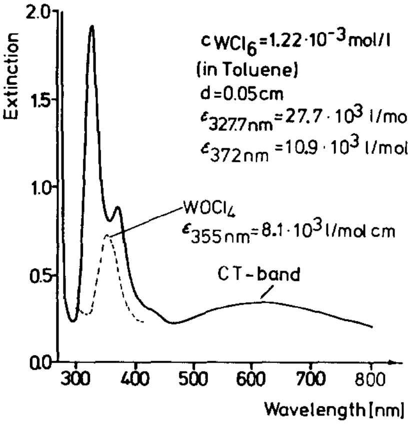


Fig. 1. UV–vis spectra of solutions of WCl_6 + $WOCl_4$ in toluene. Determination of the extinction coefficients was achieved through the use of the base line method.

UV–vis spectroscopic determination of the reaction between tungsten hexachloride and tetramethyltin

The results of a high-speed UV–vis spectroscopic investigation of the reaction between tungsten hexachloride and tetramethyltin are depicted in Fig. 2. The time-dependent alteration of the absorbency (extinction) spectrum of tungsten hexachloride was followed over the spectral range 280 - 420 nm. The occurrence of an isosbestic point is a peculiarity of this spectrum, this point persisting until the tungsten hexachloride band has vanished completely. The existence of an isosbestic point during the reaction is indicative of the formation of a stable intermediate, whose existence helps to simplify the subsequent evaluation of the kinetic data.

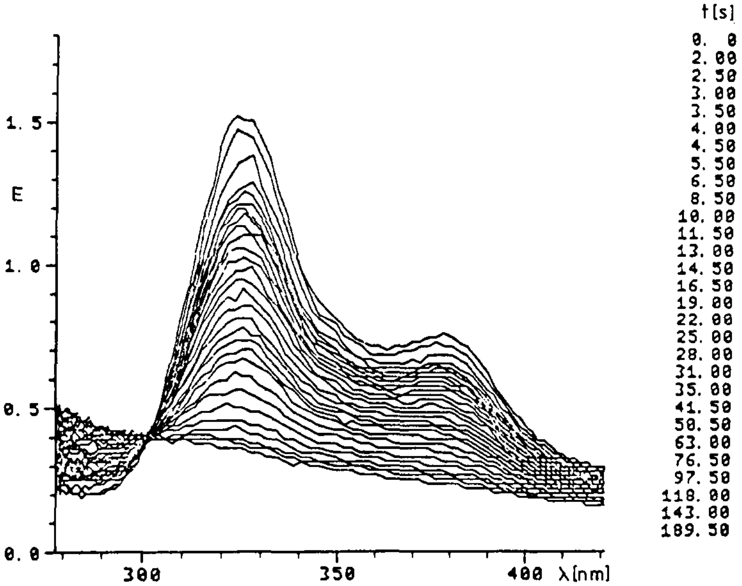


Fig. 2. High-speed UV–vis spectrophotometric examination of the reaction between WCl_6 and $SnMe_4$ (in a 1:2 ratio) in toluene. Initial concentration of WCl_6, $c_{WCl_6} = 1.01 \times 10^{-3}$ mol l^{-1}; reaction temperature, 293 K.

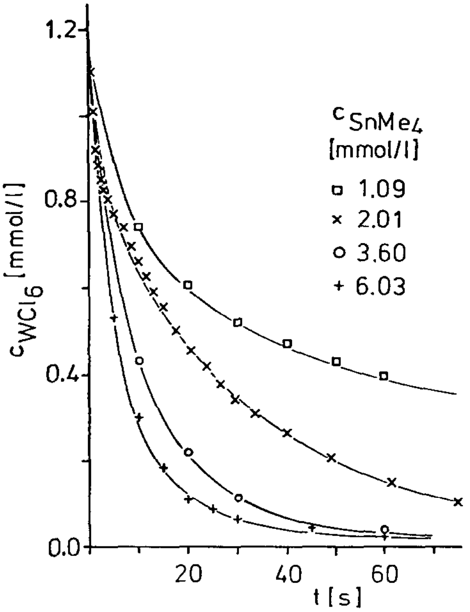
Evaluation of the experimental results

The concentration *versus* time curves resulting from experiments where the initial concentration of tungsten hexachloride was kept constant, while the concentration of tetramethyltin was varied, are illustrated in Fig. 3. As can be seen, the half-life of the reaction decreases sharply with increasing concentration of tetramethyltin, *i.e.* the reaction rate is dependent upon the concentration of tetramethyltin. The concentration *versus* time curves for different tungsten hexachloride/tetramethyltin ratios, but with equal initial concentrations of tetramethyltin, demonstrate (Fig. 4) that the alkylation rate is also a function of the tungsten hexachloride concentration. What is notable here is that the half-lives are equal, indicating that the reaction is first order with respect to the tungsten hexachloride concentration.

Determination of the order of the reaction

To determine the reaction order the initial rate of reaction was evaluated as a function of the initial concentration of the respective components, keeping the initial concentration of the other component constant [9]. Such experiments confirmed that the reaction is first order with respect to the two catalyst components (Fig. 5). Hence, for the initial alkylation step in toluene the conventional relationship for a second-order reaction may be employed, *i.e.*

$$-\frac{dc_{WCl_6}}{dt} = kc_{WCl}c_{SnMe_4}$$



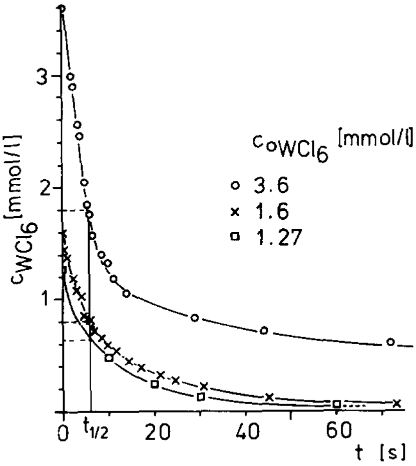


Fig. 3. Concentration *versus* time curves arising from experiments where the initial concentration of WCl_6 was kept constant (1.15×10^{-3} mol l^{-1}) while the concentration of $SnMe_4$ was varied.

Fig. 4. Concentration *versus* time curves for different $WCl_6/SnMe_4$ ratios, but with equal initial concentrations of $SnMe_4$ (3.5×10^{-3} mol l^{-1}).

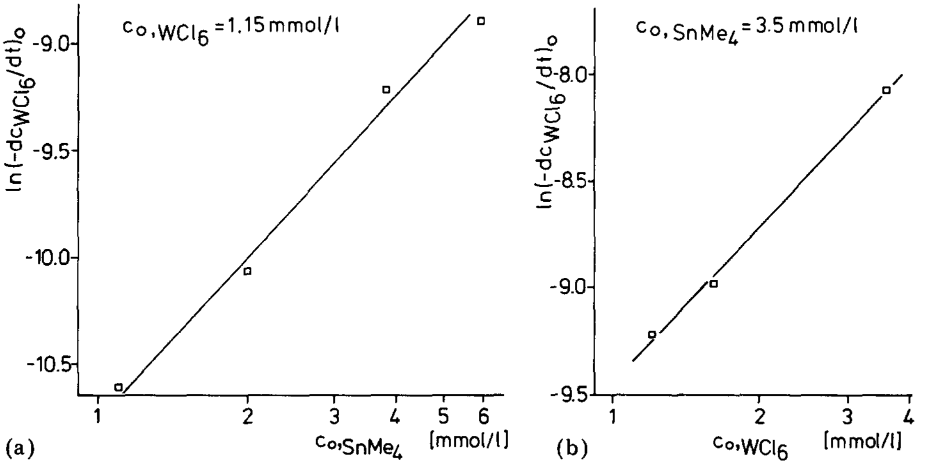


Fig. 5. Determination of the reaction order. (a) Plot of the initial rate of reaction *versus* the initial concentration of $SnMe_4$; (b) plot of the initial rate of reaction *versus* the initial concentration of WCl_6.

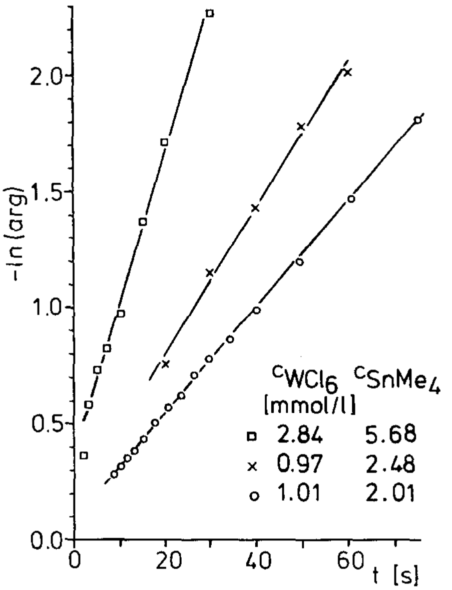


Fig. 6. Evaluation of the experimental values for a second-order reaction. In this plot of ln (arg) *versus* time, arg is equal to $c_{0,\mathrm{SnMe_4}} c_{\mathrm{WCl_6}} / [c_{0,\mathrm{WCl_6}}(c_{0,\mathrm{SnMe_4}} - c_{0,\mathrm{WCl_6}} + c_{\mathrm{WCl_6}})]$.

Figure 6 illustrates the evaluation of the experimental values for a second-order reaction.

As can be seen, the data fall very well on a straight line over the range presented in the figure. However, at high conversions (90%), deviations occur from this linear plot and this effect has been taken into consideration in determining the rate constant, insofar that measured concentrations lower than 10% of the initial concentration were discarded.

Determination of the activation energy

For the determination of the activation energy, rate constants were measured over a wide temperature range. From the resulting Arrhenius plot of the experimental values (Fig. 7), an activation energy with the low value of 26.1 kJ mol^{-1} was determined.

Consideration of the secondary reactions

The very good conformity of the experimental values with a second-order rate law is no longer valid in the final stages of the reaction when *ca.* 90% of the tungsten hexachloride had been consumed. For this reason it was checked whether a different kinetic formula would result in a better description of the experimental data, and in order to achieve this the kinetic formulation was expanded to include consecutive (secondary) reactions.

The possibilities presented in Scheme 4 for the subsequent reactions of the methyltungsten pentachloride formed in the intermediate stage include consecutive reactions with tetramethyltin; methyltungsten penta-

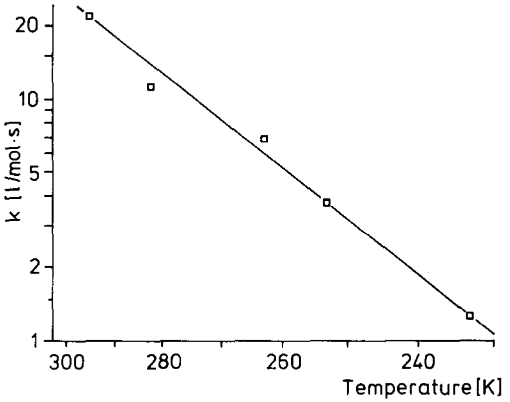
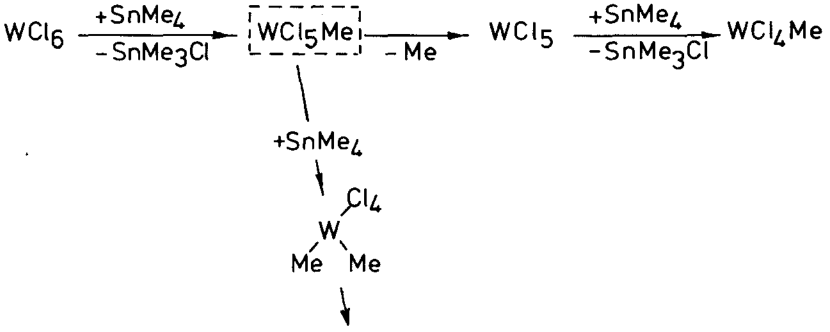
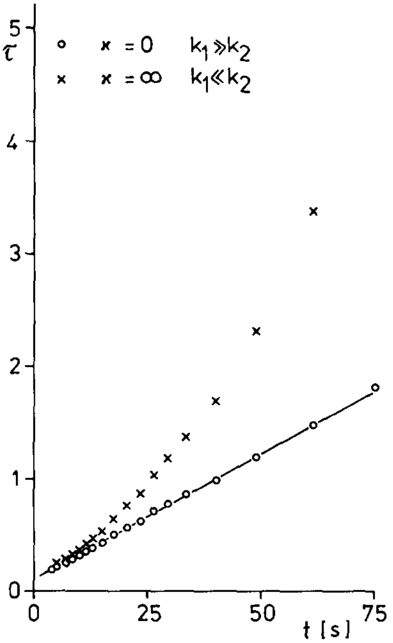


Fig. 7. Determination of the activation energy for the $WCl_6 + SnMe_4$ reaction. Arrhenius plot of the reaction rate constants, ln *k*, as a function of the inverse absolute temperature, 1/*T*.



Scheme 4.

chloride is either alkylated directly or tungsten pentachloride is formed by splitting off a methyl group and this also reacts with tetramethyltin. For this reason the experimental data were examined with the aid of a kinetic model, in which tungsten hexachloride and tetramethyltin react with each other via a second-order reaction, and the resulting tungsten component reacts further with the tetramethyltin. The study was limited to the two borderline cases, *viz.* where the consecutive reaction was much slower than the initiating reaction and, alternatively, where the consecutive reaction was much faster than the initiating reaction. All other cases between these two extremes would not have led to the occurrence of an isosbestic point in the spectral series (Fig. 2). A plot of the calculated values *versus* the reaction time should give a straight line of slope k_1c_{0,WCl_6} and, as can be seen from Fig. 8, in order to



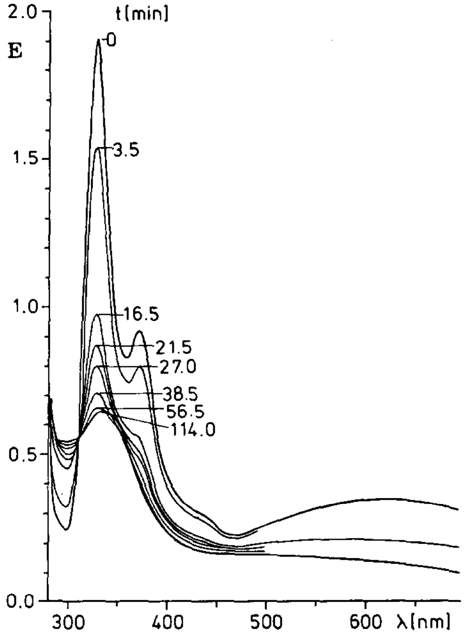


Fig. 8. Evaluation of the experimental values for a second-order reaction when consecutive reactions occur in the system. The following situations are depicted:

for $k_1 \gg k_2$, $\tau = \ln(\beta + 1)/2\beta$ where $\beta = c_{\mathrm{WCl_6}}/c_{0,\mathrm{WCl_6}}$;

for $k_1 \ll k_2$, $\tau = \dfrac{1}{2}\left(\dfrac{1}{\beta} - 1\right)$ and $\tau = c_{0,\mathrm{WCl_6}} \cdot k_1 \cdot t$.

Fig. 9. UV–vis spectra obtained during the WCl_6 + *cis*-/*trans*-2-pentene reaction. Initial concentration of WCl_6, $c_{0,\mathrm{WCl_6}} = 1.22 \times 10^{-3}$ mol l^{-1}; W/olefin ratio = 1:200; reaction carried out in toluene at a temperature of 293 K.

achieve this the consecutive reaction of tetramethyltin must be much slower than the rate of the first alkylating step.

Verification of these results may be obtained from IR measurements, the disappearance of the second mole of tetramethyltin being *ca.* 10^2 times slower than the disappearance of the first mole (in relation to the half-life) [6]. Because the alkylation of tungsten pentachloride with tetramethyltin is much faster in comparison to tungsten hexachloride, as shown by our results [4, 7], the kinetic findings suggest that if tungsten pentachloride is formed in toluene (in the absence of olefin) this occurs by a very slow secondary reaction or not at all.

Kinetic studies of the reaction between tungsten hexachloride and C_5-olefins

The reaction between tungsten hexachloride and olefin has been studied for 2-pentene (*cis* and *trans*) and cyclopentene. As UV–vis spectroscopic examinations show, tungsten hexachloride is converted quantitatively in the presence of olefin to tungsten pentachloride. Figure 9 depicts the decrease in the extinction bands for tungsten hexachloride in the presence of *cis-/trans*-2-pentene as a function of time.

The final spectrum corresponds to that of tungsten pentachloride. Again, an isosbestic point is observed for this reaction, indicating the non-appearance of an intermediate stage or its occurrence in negligible concentration. The stoichiometric conversion of tungsten hexachloride to tungsten pentachloride was also demonstrated by mass balance involving 2-pentene; thus for 1 mol tungsten hexachloride only 0.5 mol monochlorpentene (two isomers) was formed in addition to hydrogen chloride.

Figure 10 illustrates the decrease in reaction rate for the series *trans*-2-pentene, *cis-/trans*-2-pentene and *cis*-2-pentene, the fastest reaction being observed between cyclopentene and tungsten hexachloride. The course of

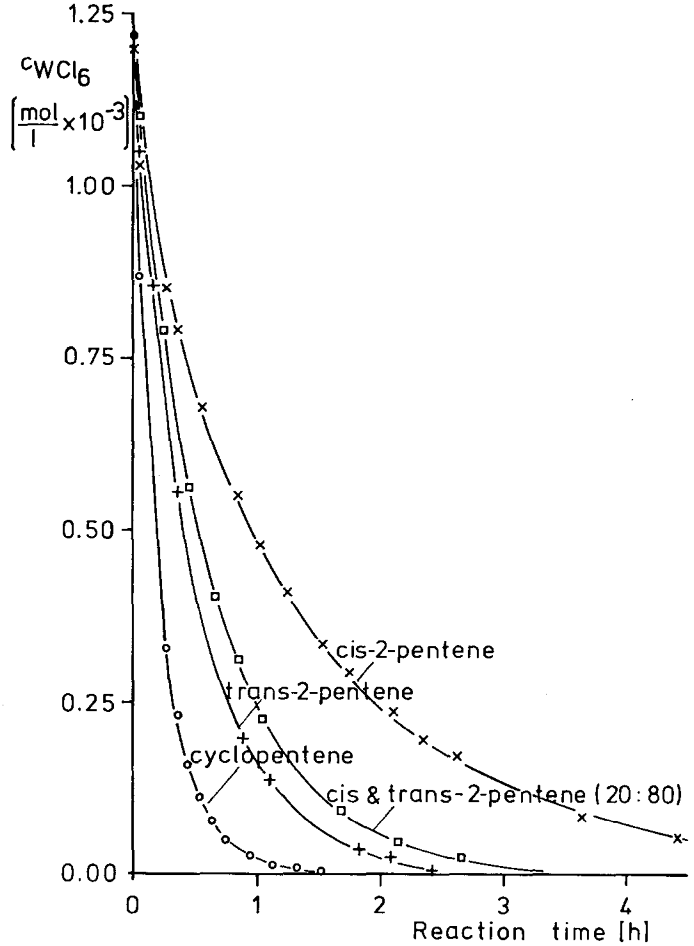


Fig. 10. The kinetics of the reaction between WCl_6 and C_5-olefins. Initial concentration of WCl_6, $c_{0,WCl_6} = 1.22 \times 10^{-3}$ mol l^{-1}; W/olefin ratio = 1:200; reaction carried out in toluene at a temperature of 293 K.

the reaction between cyclopentene and tungsten hexachloride is similar to that between tungsten hexachloride and 2-pentene. In this connection it should be mentioned that the formation of a 1:1 complex between tungsten hexachloride and cyclopentene, as reported by Amass [10], could not be detected. Amass examined the region between 450 and 700 nm, *i.e.* the charge-transfer band, using tungsten hexachloride and cyclopentene in stoichiometric ratios. To prove that the alteration in the charge-transfer range is based on the conversion of tungsten hexachloride, the reaction was further studied by high-speed spectroscopy in the 360 - 640 nm range. The appropriate extinction *versus* time diagram (Fig. 11) shows clearly that the decrease in the charge-transfer band occurred simultaneously with the reaction of tungsten hexachloride.

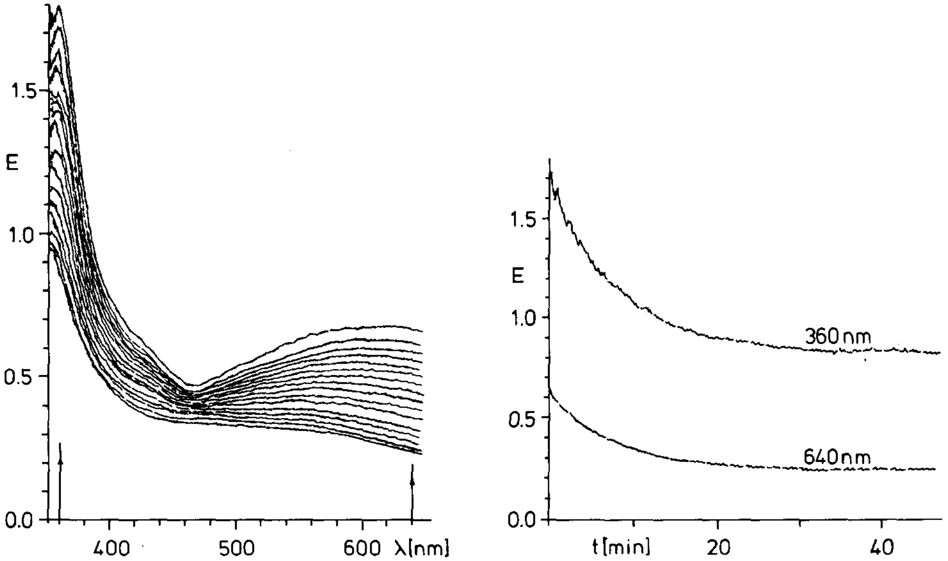


Fig. 11. High-speed UV–vis spectrophotometric examination of the reaction between WCl$_6$ and cyclopentene in the 360 - 640 nm spectral region. Initial concentration of WCl$_6$, $c_{0,\mathrm{WCl_6}} = 3.2 \times 10^{-3}$ mol l^{-1}; W/olefin ratio = 1:129; reaction carried out in toluene at a temperature of 293 K.

Evaluation of the experimental kinetic data showed that the reaction is first order with respect to tungsten hexachloride. An order regarding the olefin cannot be stated, however, since this must always be present in excess.

Conclusions

In conclusion it may be stated that although the alkylation reaction is much faster than the reaction between tungsten hexachloride and C$_5$-olefins, the influence of the olefin should not be neglected, especially at high olefin concentrations and for cyclic olefins.

Our examinations of the catalyst system tungsten hexachloride/ tetraalkyltin are still proceeding. Using the reaction scheme established to date and which has to be completed, the course of the reaction can be directed by the modification of the catalyst in a particular way.

Experimental

Investigations of the catalyst system were carried out under conditions commonly applied for metathesis reactions, using toluene as the solvent and employing a tungsten component concentration between 10^{-3} and 10^{-4} mol l^{-1}.

The spectroscopic measurements were performed using rotating cuvettes [11] with argon as the inert gas. The kinetic measurements were made using a rapid UV–vis spectrophotometer type T13/3 (Howaldtswerke, Kiel). Characterization of the starting materials was carried out with a Cary 14 spectrophotometer (Applied Physics Corp., Monrovia).

Acknowledgement

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