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Metathesis of 2-pentene with the $W(CO)_6/CCl_4/h\nu$-system. Role and physical properties of the photogenerated precipitate

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Abstract

This paper describes the role and some characteristic properties of the precipitate formed upon irradiation of the $W(CO)_6/CCl_4$ catalyst system in the photoinduced methathesis of 2-pentene. It is shown that the precipitate is the active catalyst species and that the reaction therefore follows a heterogeneous pathway. Experiments show that CCl_4 is only a reactant in the formation of the precipitate and plays no role as a cocatalyst in the metathesis of 2-pentene. It is also demonstrated that infrared spectroscopy may give a misleading picture of the catalytically active intermediates in this reaction. Attempts have been made to identify and characterize the active solid; at present the structural information points to an unstable polymeric W–C–Cl species.

Introduction

The mechanism of the homogeneous metathesis of olefins has been the subject of many studies [1–3]. The active catalyst is generally obtained by interaction between a tungsten, molybdenum, or rhenium complex and a non-transition metal compound, the so-called cocatalyst. An exception is the metathesis of 2-pentene and 1-octene in the presence of a catalyst which is photochemically generated by reaction of $W(CO)_6$ and CCl_4. This reaction was first reported by Agapiou and McNelis [4] and Krausz et al. [5] and was recently reviewed by Szymanska–Buzar [6]. Some later reports focused on the activity and selectivity of the

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$W(CO)_6/CCl_4/h\nu$ catalyst system [7,8]. We decided to study this photoinduced metathesis because it seemed to us more insight into its mechanism might be obtained by performing the reactions at lower temperatures. Reactive intermediates might then be stabilized and characterized spectroscopically, thus providing valuable information about the reaction pathways. Such a study seemed even more promising because the photochemical behaviour of Group 6 carbonyls has already been studied in much detail [9].

A few spectroscopic observations have been reported [5,10–14], but they did not allow unambiguous elucidation of the reaction mechanism. A common feature of these studies was that a tungsten carbene complex was suggested to be the active intermediate in the metathesis reaction. This carbene mechanism, first proposed by Hérrison and Chauvin [15], is now well accepted in the wide range of olefin metathesis reactions. On the basis of a combination of literature data [13,16–18] the formation of a tungsten carbene in the photoinduced metathesis can be depicted as follows:

$$W(CO)_6 \overset{h\nu}{\rightleftharpoons} W(CO)_5 + CO$$

$$W(CO)_5 \xrightarrow{CCl_4} W(CO)_5Cl$$

$$W(CO)_5Cl \xrightarrow{h\nu/CCl_4} W(CO)_4Cl_2 + CO$$

$$W(CO)_4Cl_2 \xrightarrow{h\nu/CCl_4/:CCl_2} (CO)_m(Cl)_nW{=}CCl_2 + (4-m)CO$$

First, irradiation of $W(CO)_6$ produces the coordinatively-unsaturated complex $W(CO)_5$, which takes up a chlorine atom from CCl_4. Replacement of CO by Cl generates $W(CO)_4Cl_2$. The monochloride and dichloride tungsten complexes have been observed by infrared spectroscopy. The last step, which involves the (photochemical) formation of a tungsten dichlorocarbene, is, however, much more doubtful, since such a complex has never been observed spectroscopically. According to Brothers and Roper [19] it should not even be expected to be stable because of the difference in bonding properties between the (oxidized) tungsten fragment (singlet state) and the dichlorofragment (triplet state). The proposed formation of the tungsten-dichlorocarbene, and especially the formation of the CCl_2-fragment from the halide, fails also to explain the influence of the halide (AX_n) on the activity of the $W(CO)_6/AX_n/h\nu$ system. The role of the halide has extensively been studied and these investigations have led to the conclusion that the activity of the system is increased when stronger electron-withdrawing halides are used. Thus, the catalyst system showed a higher activity when $ZrCl_4$ or $TiCl_4$ was used instead of CCl_4 [13].

Another unsolved problem is the role of the precipitate formed upon irradiation of a solution of $W(CO)_6$ in CCl_4. Some authors briefly mentioned the formation of this precipitate. Although Tanielian et al. [8] emphasized the important role of the precipitate as the active species in the metathesis of 2-pentene, no attempts were made to characterize this solid and to relate the heterogeneous pathway to the above-mentioned carbene mechanism.

We report here our preliminary results of studies on the formation, isolation, catalytic activity and characterization of the precipitate formed upon irradiation of a solution of $W(CO)_6$ in CCl_4. The metathesis of 2-pentene: 2 2-pentene $\rightleftharpoons$ 2-butene + 3-hexene, was used as a model reaction.

Experimental

For the experiments which were focused on activity measurements and the photoproduction of the precipitate the irradiations were carried out under nitrogen in Pyrex Schlenk tubes. For the simultaneous collection of IR data for the tungstencarbonyl derivatives and the extents of conversion (by GLC) *cis*-2-pentene as a function of (irradiation) time, a specially constructed IR flow-cell was used (Fig. 1) [20]. This flow-cell forms a closed system that prevents contact between the IR solution and air. Such a contact cannot be avoided when samples are taken from a bulk volume with standard syringe techniques. The free access to the reaction mixture enables withdrawal of samples for GLC or other analyses. Photochemically-generated CO can easily escape from the flow-cell as the free volume above the solution is gently flushed with nitrogen when the cell-valve is opened.

Spectroscopic and photochemical measurements

IR spectra were recorded on a Nicolet 7199 B interferometer provided with a MCT liquid nitrogen cooled detector (32 scans, resolution 1 cm^{-1}). Gas-chromatographic analysis was performed on a Varian GC 3300 with a DB-5 liquid phase column. Irradiations were performed with a high-pressure mercury lamp (Oriel 6137, 200 W).

Chemicals

Tungsten hexacarbonyl (Strem) was used without further purification. *Cis*-2-pentene (Aldrich) was distilled from sodium. Carbon tetrachloride and all other solvents were purified by distillation and kept under nitrogen.

Results and discussion

Role of the precipitate

In order to establish the role of the precipitate in the metathesis of 2-pentene, the following key experiments were performed. A solution of 35 mg of $W(CO)_6$ in

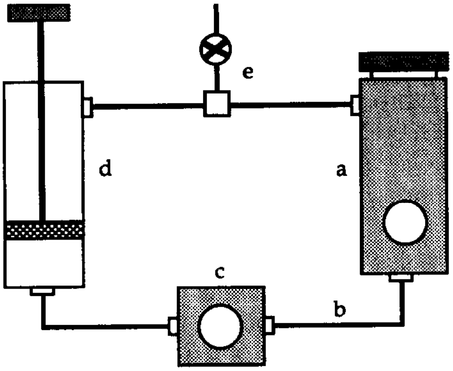


Fig. 1. Schematic representation of the IR flow-cells. (a) reaction vessel with quartz windows for irradiation; (b) tubes; (c) IR measure cell; (d) suction unit; (e) two-way valve.

10 ml of CCl_4 (10^{-2} mol l^{-1}) was irradiated for 45 min and then centrifuged (4000 rpm) for 10 min. The liquid was decanted. The activity of the isolated 'wet' brown precipitate was examined by the following procedures:

(*a*) 10 ml of CCl_4 and 200 μl of *cis*-2-pentene were successively added to the 'wet' precipitate. The stirred suspension showed metathesis activity in the dark for 30 min. Irradiation of the suspension did not affect the metathesis reaction. The liquid phase obtained after centrifugation did not show any activity.

(*b*) The isolated precipitate was thoroughly dried under vacuum and 10 ml of CCl_4 and 200 μl of *cis*-2-pentene then added. The suspension showed metathesis activity for the first 15 min. Compared with that with the 'wet' precipitate the conversion was considerably lower, and a further fall in activity was observed when the dried precipitate was first kept under nitrogen for more than 1 h.

(*c*) The IR spectra of the isolated precipitate showed the presence of unchanged $W(CO)_6$ and of traces of $W(CO)_4Cl_2$ as the only carbonyl complexes. In order to exclude its role as a catalyst, $W(CO)_6$ was removed by washing the precipitate twice with CCl_4. The 'wet' solid thus obtained showed, after addition of 10 ml of CCl_4 and 200 μl of *cis*-2-pentene, an initial metathesis conversion, although the catalytic activity was lower than that in the set-up described under (b).

(*d*) In order to find out whether carbon tetrachloride takes part in the metathesis after formation of the precipitate, n-hexane was added instead of CCl_4 to the isolated precipitate. For this purpose 10 ml of n-hexane and 200 μl of *cis*-2-pentene were successively added to the 'wet' precipitate. The stirred suspension showed metathesis activity for the first 30 min. Its activity was about the same as that observed under (a).

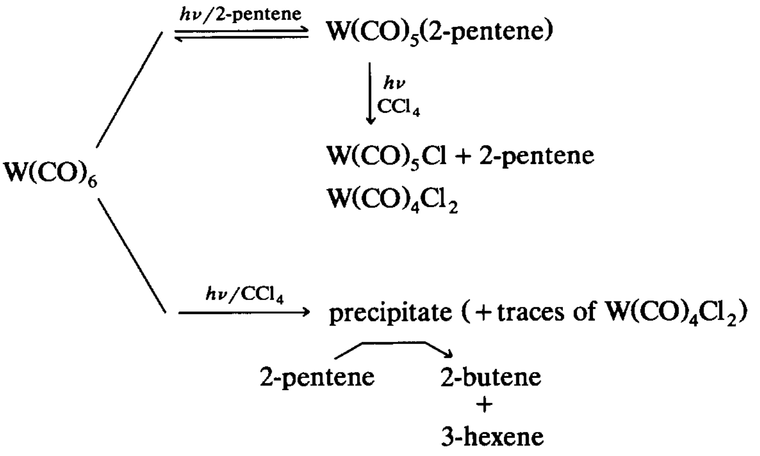
These experiments clearly show that the photochemical metathesis of *cis*-2-pentene into 2-butene and 3-hexene follows a heterogeneous pathway. These findings support those reported by Tanielian et al. [8], who were the first to demonstrate the heterogeneous character of the reaction. Other authors only briefly reported the formation of a precipitate or the colour change of the irradiated solution from colourless to dark brown via a yellow intermediate [4,17], but paid no attention to the possible catalytic role of the precipitate. A brownish 'solution' has also been observed in other photochemical systems similar to $W(CO)_6/CCl_4/h\nu$. Thus, Nagasawa reported the development of inhomogeneity when $AlCl_3$ and $TiCl_4$ were used as halides instead of CCl_4 [21]. Apart from traces of $W(CO)_4Cl_2$ the active precipitate does not contain a carbonyl complex. This means that a carbene mechanism such as proposed in the literature and depicted in the Introduction cannot proceed via a dichlorocarbene having the composition $(CO)_m(Cl)_nW{=}CCl_2$. The possible role of $W(CO)_4Cl_2$ will be discussed later.

It is also significant that CCl_4 only acts as a reactant in the photosynthesis of the precipitate without influencing the metathesis itself. This observation contradicts the suggestion by Tanielian et al. that CCl_4 acts as a cocatalyst in this reaction.

In contrast to the results described above, carbonyl containing complexes were formed when irradiation of $W(CO)_6$ in CCl_4 was carried out in the presence of *cis*-2-pentene. This became evident when a 50-fold excess of *cis*-2-pentene was added to the solution of $W(CO)_6$ in CCl_4 ($3.0 \cdot 10^{-3}$ mol l^{-1}) before irradiation. After 5 min of irradiation the brown/yellow solution became slightly turbid, and after 45 min the reaction mixture was completely converted into a dark brown suspension. Metathesis started after 30 min of irradiation.

During the first 15 min of irradiation $W(CO)_5$(2-pentene) was formed, as indicated by the appearance of its CO-stretching modes at 2078, 1956 and 1946 cm^{-1} in the IR spectrum (Fig. 2) [22]. Upon further irradiation (30 min) new CO bands showed up at 2105, 2098, 2045, 2039 and 2012 cm^{-1}, and at the same time the CO-stretching modes of $W(CO)_5$(2-pentene) decreased in intensity.

The bands at 2098 and 2012 cm^{-1} belong to *cis*-$W(CO)_4Cl_2$ [23]. The two other CO bands of *cis*-$W(CO)_4Cl_2$ ($\cong$ 1985, $\cong$ 1945 cm^{-1}) cannot be seen in Fig. 2 because they are overlapped by the strong CO band of unchanged $W(CO)_6$. The less intense bands at 2105, 2045 and 2039 cm^{-1} are assigned to $W(CO)_5Cl$. Although there is no clear proof for this assignment from literature data, similar high CO-stretching frequencies have been reported for $Cr(CO)_5I$ (2100, 2024 and 1988 cm^{-1} in CH_2Cl_2) [24]. The observed IR bands did not belong to the precipitate since the spectrum of the mixture hardly differed from that of the liquid phase obtained after centrifugation of the active suspension. The formation of *cis*-$W(CO)_4Cl_2$ and $W(CO)_5Cl$ is in agreement with earlier reports [4,10,13]. The obvious formation of $W(CO)_5$(2-pentene) has never been reported before, but this is not surprising since $W(CO)_5$(2-pentene) was converted into $W(CO)_5Cl$ and *cis*-$W(CO)_4Cl_2$ upon prolonged irradiation. These three carbonyl complexes are, however, only side-products. They have no influence on the metathesis reaction since the same catalytic activity was observed when *cis*-2-pentene was instead added to the solution after irradiation of $W(CO)_6$. The above results are summarized in the following scheme:



Concerning the photochemistry it is important to note that all irradiations were performed through a glass filter. This means that the emission spectrum of the mercury lamp is restricted to wavelengths between 320 and 600 nm and that photodissociation of CCl_4 into $Cl^\cdot$ and $CCl_3^\cdot$ radicals can thus be almost completely excluded ($\lambda_{abs}(CCl_4) < 280$ nm). The absence of these very reactive chlorine radicals permits the formation of $W(CO)_5$(2-pentene) after photogeneration of $W(CO)_5$. In the $W(CO)_5$(2-pentene) complex the olefin is weakly bonded to the tungsten atom because of its weak π-backbonding ability. Further irradiation

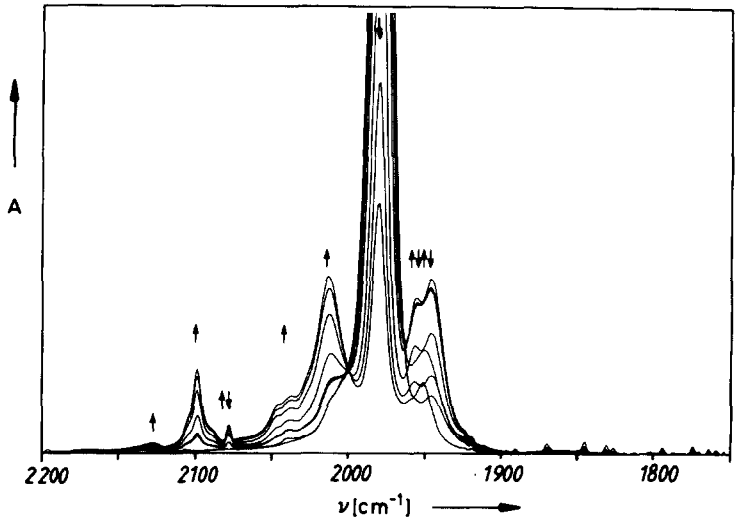


Fig. 2. Spectral changes in the infrared CO-stretching region upon irradiation of a CCl_4 solution containing $W(CO)_6$ and a 50-fold excess of *cis*-2-pentene. $[W(CO)_6] = 3.0 \cdot 10^{-3}$ mol l^{-1}.

apparently leads to the substitution of 2-pentene and of a second CO by chlorine atoms, resulting in the formation of $W(CO)_5Cl$ and *cis*-$W(CO)_4Cl_2$.

The formation of the precipitate takes place immediately after the irradiation is started. This process has no relationship to the photochemistry discussed above, but it can be seen as a yet unidentified but reproducible photoreaction of $W(CO)_6$ with CCl_4.

The formation of the precipitate was found to depend strongly on the $W(CO)_6$ concentration, the power of the mercury lamp, the irradiation efficiency, and whether pure CCl_4 or a CCl_4/hexane mixture was used as a solvent. For instance, after irradiation for 5 min of a 10^{-3} mol l^{-1} solution of $W(CO)_6$ in CCl_4 by the 200 W mercury lamp, a brown precipitate was formed, whereas in a CCl_4/hexane (1/100) mixture only a slight turbidity was observed after that time. Another important fact is the optical path length of the reactor used. A short path length may give a homogeneous optical appearance to a heterogeneous reaction. The small inhomogeneities do not give rise to any signal in the IR, UV-VIS and NMR spectra, and a heterogeneous reaction could therefore have been described as being homogeneous. This may be the reason why in the literature the role of the precipitate has so often been neglected. As soon as it became evident that the precipitate was in fact the catalyst in the photoinduced metathesis of 2-pentene, an attempt was made to identify and characterize it.

Structural analysis of the isolated precipitate

In order to obtain larger quantities of the precipitate for structural analysis the photochemical experiment was carried out on a larger scale. For this purpose a solution of 0.5 g of $W(CO)_6$ in 80 ml of CCl_4 was irradiated for 4 h. After filtration through a Schlenk filter the pale brown precipitate was washed with n-hexane to remove unchanged $W(CO)_6$ and finally thoroughly dried under vacuum. The physical data collected so far, are presented in Table 1. Reliable ^{13}C NMR

Table 1

Physical data for the precipitate

IR frequencies (cm^{-1}) (KBr pellet):

2094m, 2016vs, 1987m, 1943s, 969sh, 1000–500br

Maxima of FAB-mass signals (m / z):

521, 413, 395, 347, 323, 282, 256, 239, 217, 187, 165, 149, 131, 109, 91, 73, 57
- Higher mass signals show decreasing intensity
- The spectrum showed so called grass between m/z 1600 and m/z 521

Elemental analysis: $W_1C_{0.6}Cl_{0.9}$; formula corrected for $W(CO)_4Cl_2$

Powder diffraction: No significant signal, indicating an amorphous structure

Thermal analysis: No clear melting point below 1273 K. At 727 K an exothermic decomposition of the precipitate

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(THF-d_8 and solid phase) and Raman data could not be obtained because of decomposition of the compound during the measurements. To justify this synthesis method the IR, Fast Atom Bombardment (FAB) mass and elemental data were compared with those of the washed and dried precipitate isolated as described under (c). No significant differences were observed. Furthermore the activity of the obtained precipitate was examined. The wet filtered precipitate showed metathesis activity, whereas the washed and dried precipitate was inactive. This is consistent with the results of experiments (b) and (c).

The IR spectrum (400–3000 cm^{-1}) of the isolated precipitate (KBr pellet) showed a broad band between 600 and 900 cm^{-1} and several bands between 1900 and 2100 cm^{-1}. The former band is assigned to W–Cl vibrations because of its close similarity with the broad band of WCl_6 in this frequency region. The CO bands at 2094, 2016, 1987 and 1943 cm^{-1} (Fig. 3) can be ascribed to traces of the

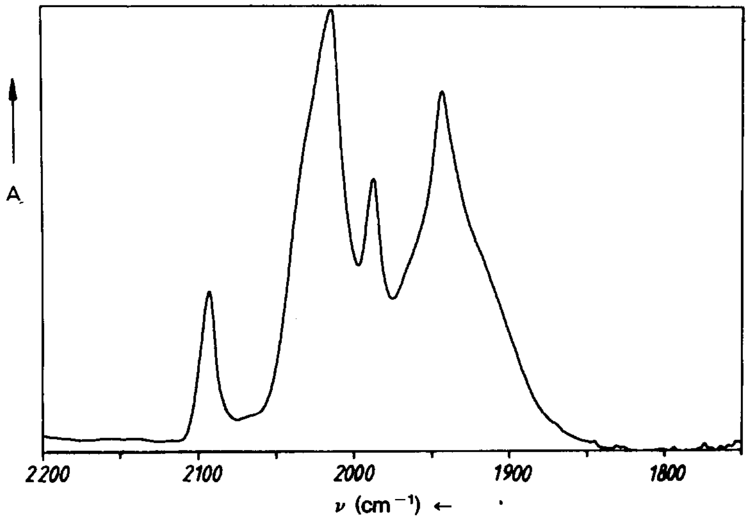

Fig. 3. IR spectrum in the CO-stretching region of the isolated precipitate (KBr pellet).

yellow $W(CO)_4Cl_2$ complex [23]. This was confirmed by separation of the precipitate on a silica column with methanol, as eluant, which resulted in the collection of a pale yellow fraction with the corresponding IR CO bands. Decomposition problems after isolation prevented the collection of more structural information from this fraction. It should be noted that the CO band at 1987 cm^{-1} may be partly owing to traces of $W(CO)_6$.

Elemental analysis of the washed precipitate gave, after correction for the presence of $W(CO)_4Cl_2$, the reproducible formula $(WC_{0.6}Cl_{0.9})_x$, which is different from that given by Tanielian et al. ($(WC_{2.1}Cl_4)_x$) [8]. Such a formula points to a polymeric tungsten structure, which is in good agreement with the very high melting point and the FAB-MS spectrum. Although the mass spectrum showed a significant maximum signal at m/z 521, the presence of many small peaks between m/z 521 and ±1600 indicates that the observed signals between m/z 0 and 521 can be assigned to fragments of a polymeric tungsten complex.

Thus, in addition to traces of $W(CO)_4Cl_2$ the precipitate contains a polymeric W–C–Cl compound. Up to now activity of $W(CO)_4Cl_2$ in the metathesis of 2-pentene has only been reported in chlorobenzene between 353 and 373 K [14,25] and not in CCl_4 under our circumstances. The metathesis activity of the precipitate is, therefore, probably owing to the polymeric tungsten compound, photochemically generated from $W(CO)_6$ and CCl_4. A polymeric and amorphous structure is consistent with the deactivation that occurs on exposing to vacuum and storing the precipitate; since these actions may disturb the superfacial structure of the solid particles and so cause deactivation of the active sites.

The heterogeneous pathway of the photochemical metathesis of 2-pentene agrees well with the lack of clarity about the mechanism in the literature. It does not for example exclude the donor–acceptor interpretation because the type of acceptor may influence the formation and activity of the precipitate. The formation of an active monomeric tungsten dichlorocarbene of the type $(CO)_m(Cl)_nW{=}Cl_2$, as described in the Introduction, can, however, now be completely rejected. A relationship between the polymeric structure of the precipitate and its activity can, however, hardly be defined. If one seeks to retain a carbene mechanism the question arises of how a tungsten carbene is formed at the surface of the precipitate. Well-known possible processes are α-hydrogen migration [26] in a [M]–alkyl bond ([M] denoting a metal centre) and the transformation of a [M]–olefin into a [M]–carbene bond [27,28]. This latter process can take place via a 2,1-hydrogen shift, via cleavage of a C=C bond with a bi- or polymetallic system, or via a π-allyl hydride and a metallacyclobutane. For all these processes the metal centre must be one that can easily change its coordination number. The unstable and amorphous structure of the precipitate may facilitate this process.

Conclusion

The above observations lead to the conclusion that the photocatalytic metathesis of *cis*-2-pentene with the $W(CO)_6/CCl_4$ system proceeds via a solid polymer formed by the photochemical reaction of $W(CO)_6$ and CCl_4. All carbonyl complexes showing up as the main photopfoducts in the IR spectra are catalytically inactive side-products.

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