

STUDIES ON HOMOGENEOUS OLEFIN DISPROPORTIONATION CATALYSTS

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Carbon monoxide increases the activity of catalysts composed of tungsten and molybdenum halide complexes and EtAlCl_2 for the disproportionation of olefins. Hexacarbonyls as final products and halo carbonyls as intermediates were isolated from the reaction mixtures.

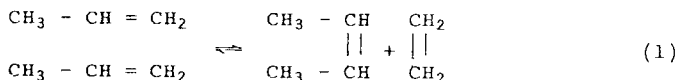
INTRODUCTION

The disproportionation of olefins has undergone a very fast but contradictory development during the last 12 years since the first patent application. The heterogeneous propylene disproportionation is already at present an industrial process, while the disproportionation of longer chain olefins will still remain at the level of laboratory experiments for probably a long time, because of the simultaneous double bond isomerization leading to a low selectivity of the reaction. An increase of catalyst selectivity by the blocking of acidic centres is accompanied with a rapid decrease in activity [1, 2].

The development of the homogeneous catalytic process seems to be somewhat faster; the disproportionation of terminal and internal olefins has been achieved in the last few years [3, 4, 5]. Numerous new catalytic combinations and metals (Ti, Rh, Fe, Co,

etc.) [6, 7] have been reported, in addition to those based on molybdenum and tungsten which were applied from the beginning. However, although a large number of active catalysts are already known, only a few investigations on the catalytic mechanism have so far been reported.

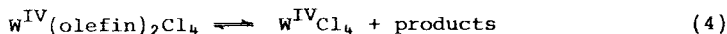
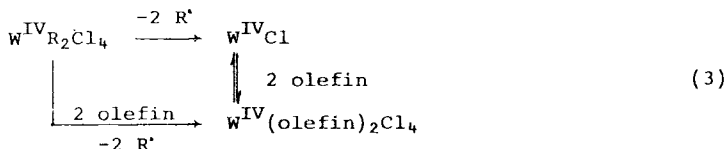
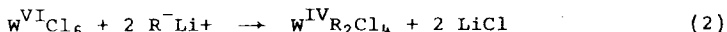
Following the first successful disproportionation experiments a trans alkylidenation mechanism was proposed for propylene disproportionation



This general scheme was confirmed by the disproportionation of 2-propene-¹⁴C [9]. However, it still remained a problem, that the "quasi cyclobutane intermediate" state proposed for this reaction requires thermally forbidden electron transitions according to the HOFFMAN-WOODWARD rule [10]. This problem could be solved by the assumption that since the trans alkylidenation has to take place partly or entirely within the co-ordination sphere of the transition metal, the d orbitals of the transition metal also have to be considered in these calculations. The Hoffman-Woodward rule extended in this sense was found to be applicable for the disproportionation of olefins: the process can be described by the combination of the d orbitals of one transition metal and the pi orbitals of two olefins [11].

The homogeneous catalysts used for the disproportionation of olefins are generally composed of a transition metal compound (such as WCl₆) and a cocatalyst such as EtAlCl₂ or BuLi [12]. The cocatalyst probably functions partly to produce free co-ordination sites which can be used by the olefin molecules and partly to maintain the necessary electron concentration for the reaction. According to the proposed mechanism, at least two co-ordination sites are required on the transition metal. The experimental observations that disproportionating activity is shown by catalyst combinations with an Al(Li)/W(Mo) ratio of ≥ 2 are in accordance with this theory.

Very little is known about the formation of the catalytically active species. Suggestions for this process were first made by MENAPACE et al. [12] for the two component $WCl_6 + BuLi$ catalyst system:



According to the schema above, the free co-ordination sites are formed by the decomposition of dialkyltungsten tetrachloride. Following this the trans alkylidenation takes place by an intramolecular transformation of the bis olefin complex. Some suggestions were made regarding the oxidation and co-ordination states of the transition metal in Equations (2)-(4), but no experimental proof was presented. The experiments described in this paper were directed towards the isolation of stable derivatives of these intermediates to elucidate some steps of the disproportionation mechanism.

RESULTS AND DISCUSSION

For all experiments cis,trans-2-pentene was chosen as model olefin. Using CALDERON'S $WCl_6 + EtOH + EtAlCl_2$ catalyst it was observed that this was very sensitive to air and moisture, whereas Ar, N_2 , H_2 or CO and small quantities of PPh_3 or pyridine did not alter its activity appreciably and CO even increased its selec-

activity [13]. It was, therefore, concluded that CO, phosphines and pyridine may function as ligands of the transition metal in these catalytic systems.

In order to eliminate the moisture sensitive WCl_6 at first Mo and W compounds were sought that were not sensitive to air and which combined with $AlEtCl_2$ would give active disproportionation catalysts. When 2-pentene was added to the benzene solution of a $AlEtCl_2$ and a ML_2Cl_4 type compound (where $L = Py, PPh_3$ or $1/2 C_2H_4(PPh_2)_2$; $M = Mo$ or W) the olefin was consumed by a Friedel-Crafts type reaction for the alkylation of benzene in a few minutes and the disproportionation reaction could not be studied under such conditions [14]. However, using chloro benzene as a solvent (which is more difficult to alkylate than benzene), a homogeneous master solution could be prepared which had the desired disproportionating catalytic activity and was not disturbed by the alkylation of the aromatic ring. The activity of these catalysts significantly increased under CO and approached that of the CALDERON system [15].

Investigating the $WPY_2Cl_4 + EtAlCl_2 + 2$ -pentene + chloro benzene reaction mixture by IR spectroscopy, a very strong, sharp absorption band could be observed at 1980 cm^{-1} in addition to some smaller peaks in the ν_{CO} range. This strong band indicated the presence of $W(CO)_6$ which was proved by the subsequent isolation of $W(CO)_6$ from these reaction mixtures. The yield of $W(CO)_6$ reached about 30 per cent and thus surpassed the yield of some of the previously known high pressure syntheses.

By comparing the $W(CO)_6$ content and the catalytic activity of catalyst master solutions (Fig.1) it was shown that an increase of $W(CO)_6$ leads to a decrease of activity. The increase of catalytic activity under carbon monoxide could not, therefore, be attributed to the $W(CO)_6$ formed in the reaction mixture, but to tungsten derivatives having oxidation states between IV and 0. It was assumed that the formation of the free sites necessary for co-ordination of olefin (in the catalytic reaction) or carbon monoxide (in metal carbonyl formation) to the metal atom is a result of alkylation (5) and the subsequent decomposition of metal alkyls (6):

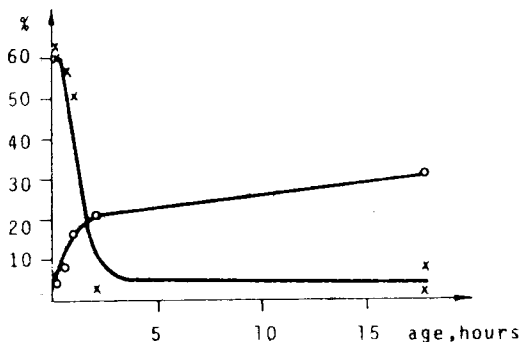
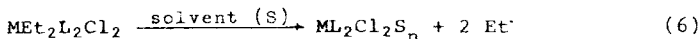
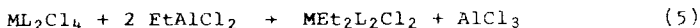
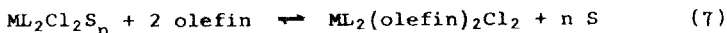


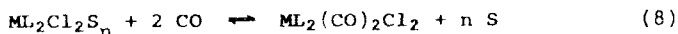
Fig.1. Yield of $W(CO)_6$ and disproportionation activity as functions of the age of the catalyst master solution. o - yield of $W(CO)_6$; x - conversion of 2-pentene in 3 minutes reaction time



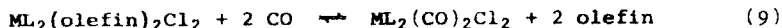
These free co-ordination sites can then be occupied either by olefins:



or by carbon monoxide:



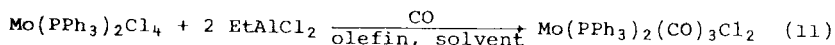
If olefin and CO is also present at the same time the following equilibrium must be taken into account:



Such types of VIB metal-halo-carbonyls are already known. Some of these derivatives (like $L = PPh_3$) are "CO carriers" [16]:



To confirm the probability of the above reactions $ML_2(CO)_2Cl_2$ or rather $ML_2(CO)_3Cl_2$ type complexes had to be detected during the disproportionation reaction carried out under carbon monoxide. Although the formation of such compounds was observed in the WPY_2Cl_4 containing systems, their isolation in a pure state failed. Efforts were more successful in the case of the catalyst composed of $Mo(PPh_3)_2Cl_4$ and $AlEtCl_2$:

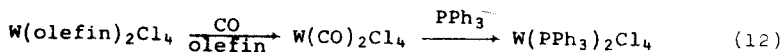


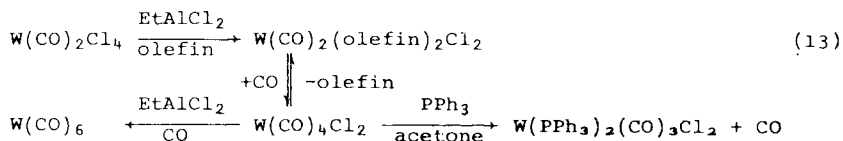
The isolation of these complexes supports the assumption that the active catalyst combination contains a low (but not 0) oxidation state transition metal atom having available co-ordination sites. However, the formation of free co-ordination sites does not require the presence of olefins, since the appropriate halo carbonyl complexes can also be prepared from the CO-treated catalyst master solutions in the absence of olefin with good yield.

The halo molybdenum and tungsten carbonyls were prepared previously only by the oxidative transformation of the corresponding carbonyls. Our qualitative observations have been developed to a preparative method which enables the preparation of halo carbonyls by reductive carbonylation with 30-35 per cent yields.

Based on these results, the method described above was also applied in the study of the highly active catalysts derived from $WOCl_4$ or WCl_6 and $AlEtCl_2$ at a molar ratio of $W/Al = 1/4$. The formation of intermediate unsubstituted halo carbonyls and $W(CO)_6$ was also observed here. $W(CO)_4Cl_2$ was isolated from these reaction mixtures in the form of its stable triphenylphosphine derivative $W(PPh_3)_2(CO)_3Cl_2$. Molybdenum halides reacted similarly [17].

As a matter of fact, all of these results confirm the Menapaces hypothesis and complete it by the reactions occurring under CO atmosphere:





Carbon monoxide is generally known as a catalyst poison and behaves here similarly: it expels the olefins from the catalyst. Despite this the rate of disproportionation is increased in its presence, which suggests the $\text{M(PPh}_3)_2(\text{CO})_n\text{Cl}_2$ ($n = 2, 3$) type compounds ("the poisoned catalysts") formed in these reaction mixtures are also good catalysts in combination with EtAlCl_2 or AlCl_3 . This assumption was confirmed experimentally: the mixtures of $\text{ML}_2(\text{CO})_n\text{Cl}_2$ (where $L = \text{PPh}_3$ or AsPh_3 and $M = \text{Mo}$ or W) and EtAlCl_2 or AlCl_3 ($\text{Al/M} = 4/1$) in chlorobenzene solvent catalyzed the disproportionation of 2-pentene present in a 2-500 fold excess of the equilibrium olefin mixture within 3-5 min [18].

EXPERIMENTAL

General. All manipulations were carried out under Ar or CO at room temperature. Hexane, benzene and cis, trans-2-pentene (Fluka) were distilled from K-Na alloy, chlorobenzene and methylene chloride (Reanal) from phosphorous pentoxide before use. All were stored under Ar.

Molybdenum and tungsten complexes were prepared from pure WCl_6 and MoCl_5 (Koch-Light)(Fluka) as described in literature [19, 20]. EtAlCl_2 was prepared from Et_3Al and AlCl_3 and purified by distillation [21].

The IR spectra were recorded on a double-beam Carl Zeiss UR 20 spectrophotometer.

Catalytic experiments

a) A solution (5 ml) of cis-2-pentene in n-pentane (1/1) and 0.05 ml EtAlCl₂ was added to a suspension of 29 mg WPy₂Cl₄ in 5 ml chlorobenzene. After 1 hour, the mixture was hydrolyzed and analyzed by GLC. Based on the quantity of cis-2-pentene introduced, the reaction product contained 14.1 per cent cis, trans-2-butene, 45.7 per cent cis, trans-2-pentene and 27.3 per cent cis, trans-3-nexene. The rest of the olefins were converted to polymers.

b) Several parallel runs were performed with the above catalyst under Ar and CO. After a 15 minute reaction, the conversions of 2-pentene ranged between 7-22 per cent under Ar and 48-51 per cent under CO; since the equilibrium composition was reached under carbon monoxide, the rate of reaction must have been rather high. This was confirmed by utilizing even shorter reaction times: conversion of 2-pentene was 40.6 per cent after 1 minute, 41.8 per cent after 3 minutes and 47.2 per cent after 5 minutes.

c) To study the connection between W(CO)₆ content and catalytic activity, a master solution was prepared from 300 mg WPy₂Cl₄, 0.9 ml EtAlCl₂ and 50 ml chlorobenzene. This was stirred under CO and samples were taken at certain intervals. 5 ml of the sample was given to 5 ml of a mixture of n-pentane and 2-pentene (1/1) and the conversion of 2-pentene after 3 minutes reaction time was used as a measure of the activity. The concentration of W(CO)₆ was determined in another part of the sample by IR spectroscopy and an extinction vs. concentration curve using the extinction measured at 1980 cm⁻¹.

d) W[C₂H₄(PPh₂)₂]₂Cl₃, W[C₂H₄(PPh₂)₂]Cl₄ and Mo(PPh₃)₂Cl₄ behaved similarly to WPy₂Cl₄ under the conditions of a), b) and c).

e) 5 ml of a solution of cis-2-pentene in pentane (1/1) containing 0.05 ml EtAlCl₂ was added to a suspension of 0.05 g W(PPh₃)₂(CO)₃Cl₂ in 5 ml chlorobenzene under Ar. A homogeneous solution was formed. After 1 hour, the reaction mixture was hydrolyzed and GLC analysis indicated the presence of 13.4 per cent 2-

-butenes, 49.7 per cent 2-pentenes, 26.2 per cent 3-hexenes and traces of higher olefins.

Preparative Experiments

f) The master solutions made according to c) were steam distilled after 2-3 hours reaction time. $M(CO)_6$ ($M = Mo$ or W) precipitated on the wall of the condenser in the form of white crystals, before an appreciable distillation of chlorobenzene has started. Yield 10-30 per cent.

g) A solution of 0.05 ml $EtAlCl_2$ in 3 ml 2-pentene was given to a solution of 190 mg $Mo(PPh_3)_2Cl_4$ in 3 ml chlorobenzene. Rapid disproportionation reaction was observed. Adding pentane (5-10 ml) a precipitate formed due to the diminished solubility of the complexes. This solid portion of the product was separated and dissolved in a small quantity of acetone upon which 20-30 mg $Mo(PPh_3)_2(CO)_3Cl_2$ precipitated.

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РЕЗЮМЕ

Окись углерода в реакции диспропорционирования олефинов увеличивает активность используемого катализатора, состоящего из галогенидных комплексов вольфрама и молибдена и из EtAlCl_2 . Из реакционной смеси были выделены в качестве конечных продуктов гексокарбонилы и в качестве интермедиеров галогенкарбонилы.