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DISPROPORTIONATION OF OLEFINS WITH TUNGSTEN CARBONYL DERIVATIVES AS HOMOGENEOUS CATALYSTS

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SUMMARY

Carbon monoxide increases the catalytic activity of mixtures of tungsten halide complexes with $EtAlCl_2$ towards disproportionation of olefins. Probably tungsten carbonyl complexes are formed.

INTRODUCTION

Halide complexes of tungsten in combination with $EtAlCl_2$ or $AlCl_3$ have been reported to be homogeneous catalysts for the disproportionation of olefins[1-5]. We have now found that carbon monoxide increases the activity of some catalyst systems of this type, presumably through formation of tungsten carbonyl derivatives.

RESULTS AND DISCUSSION

A solution (5 ml) of *cis*-2-pentene in n-pentane (1/1) and 0.05 ml of $EtAlCl_2$ was added to a suspension of 29 mg WPy_2Cl_4 in 5 ml benzene. After 1 h, the mixture was hydrolyzed and analysed by GLC. Based on the quantity of *cis*-2-pentene introduced, the reaction product contained 14.1% 2-butene, 45.7% 2-pentene and 27.3% 3-hexene. The rest of the olefin was converted to polymers.

Several parallel runs were performed with the same catalyst under Ar and CO. After 15 min reaction the conversions of 2-pentene ranged between 7–22% under Ar and 48–51% under CO; since the equilibrium composition was reached under carbon monoxide the rate of reaction must be rather high. This was confirmed by use of even shorter reaction times: conversion of 2-pentene was 40.6% after 1 min, 41.8% after 3 min and 47.2% after 5 min.

The infrared spectra of the reaction mixtures (or those of blank experiments without olefin) always showed strong absorption bands in the 2100–1800 cm^{-1} region, pointing to the formation of tungsten carbonyl derivatives. This suggested that tungsten carbonyl complexes might also be active as disproportionation catalysts. Accordingly, 5 ml of a solution of *cis*-2-pentene in pentane (1/1) containing 0.05 ml $EtAlCl_2$ was added to a suspension of 0.05 g $W(CO)_3(PPh_3)_2Cl_2$ in 5 ml chlorobenzene under Ar. A homogeneous solution was formed, the colour of which changed from blue through green and yellow to red. At the same time a number of C–O stretching bands appeared between 2060 and 1890 cm^{-1}. These bands do not belong to the original tungsten carbonyl complex, since this is insoluble in chlorobenzene. After 1 h, the reaction mixture was hydrolyzed and GLC analysis indicated the presence of 13.4% 2-butene, 49.7% 2-pentene, 26.2% 3-hexene and traces of higher olefins.

Carbon monoxide not only increased the rate of disproportionation, but also had a beneficial effect on the selectivity of the catalyst system, especially when a terminal olefin was used. Thus the catalyst system obtained from $W[C_2H_4(PPh_2)_2]_2Cl_3$ and $EtAlCl_2$ (molar ratio 1/10) at 0° transformed 90% of the initial 1-pentene in 15 min to a mixture of gaseous and liquid olefins, the latter composed of about equal quantities of 2-pentenes, hexenes, heptenes and octenes. When the same catalyst was used under Ar, a strong isomerising activity was observed, giving mainly *trans*-2-pentene; only about 2% of the original olefin reacted by disproportionation.

The reactions leading to the active catalysts seem to be rather complex. It was found, for example, that if the $W[C_2H_4(PPh_2)_2]_2Cl_3 + EtAlCl_2$ catalyst solution was stored under CO for some time before use, it completely lost its activity for disproportionation of terminal olefins and became a very active polymerisation catalyst.

These marked effects of introducing carbonyl ligands into the catalytic complexes are being further investigated.

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