

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 olefins¹⁻⁵. 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 $\text{W}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}_2$ 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 $\text{W}[\text{C}_2\text{H}_4(\text{PPh}_2)_2]_2\text{-Cl}_3$ 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 $\text{W}[\text{C}_2\text{H}_4(\text{PPh}_2)_2]_2\text{-Cl}_3 + \text{EtAlCl}_2$ 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.

REFERENCES

- 1 N. CALDERON, HUNG YU CHEN AND K. W. SCOTT, *Tetrahedron Lett.*, (1967) 3327.
- 2 N. CALDERON, E. A. OFSTEAD, J. P. WARD, W. A. JUDY AND K. W. SCOTT, *J. Amer. Chem. Soc.*, 90 (1968) 4133.
- 3 E. A. ZUECH, *Chem. Commun.*, (1968) 1182.
- 4 J. L. HÉRISSON, Y. CHAUVIN, NHU HUNG PHUNG AND G. LEVEBRE, *C.R. Acad. Sci. Ser. C*, 269 (1969) 661.
- 5 E. A. ZUECH, W. B. HUGHES, D. H. KUBICEK AND E. T. KITTLEMAN, *J. Amer. Chem. Soc.*, 92 (1970) 528.

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