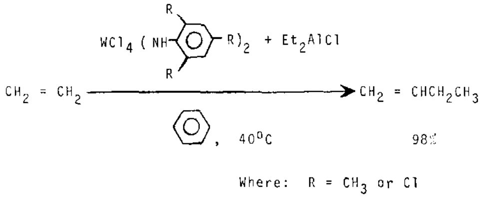
JOURNAL OF CATALYSIS 43, 371–372 (1976)

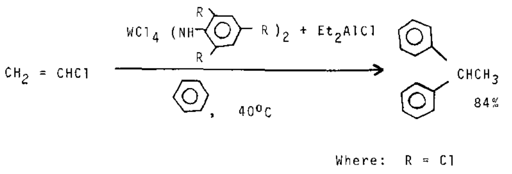
Mechanism Changes in the Tungsten-Catalyzed Reactions of Ethylene versus Vinyl Chloride in Benzene

The dimerization of ethylene to 1-butene in high selectivity and yield is accomplished catalytically with a reduced tungsten complex in benzene, i.e.,



The reaction is fast (the conversion of ethylene is 184,000 moles/mole of tungsten in 1 hr), and even with large excesses of reductant (up to Al/W = 80), no polymerization of ethylene (less than 1% 2-butene and 1% hexenes are formed when a constant pressure of 500 psig of dry ethylene is employed with 0.031 mmoles of the tungsten complex and 2.5 mmoles of diethyl aluminum chloride in 100 ml of sodium-dry benzene) or alkylation of benzene is observed (*1*), thus suggesting that the catalyst system does not exhibit appreciable Lewis acidity during the course of the reaction.

However, attempts to dimerize vinyl chloride with the same catalyst system result in a dialkylation reaction in which 1 molar equivalent of vinyl chloride reacts with 2 molar equivalents of benzene to give an 84% yield (based on vinyl chloride) of 1,1-diphenylethane; i.e.,



1,1-Diphenylethane was identified by its boiling point (284°C, lit. (*2*) 285°C), mass spectra, $C_{14}H_{14}$ (M^+ calcd., 182.1096; M^+ found, 182.1080, with the major fragmentation showing loss of $-CH_3$), and NMR spectrum in CCl_4 (TMS) (singlet at 7.15 δ (10H), quartet at 4.08 δ (1H), and a doublet at 1.06 δ (3H).

The reaction was carried out by metering vinyl chloride into a reactor at a rate of 30 g/hr under a pressure of about 20 psig. The reactor contained 0.066 mmoles of the tungsten complex and 2.5 mmoles of diethyl aluminum chloride in 100 ml of sodium-dried benzene. The conversion of vinyl chloride is 7360 moles/mole of tungsten in 1 hr. The tungsten complex is formed by refluxing a chlorobenzene solution of 2,4,6-trimethylaniline and tungsten hexachloride in a 2 to 1 molar ratio for 1 hr. Enough chlorobenzene is employed to keep the complex in solution.

When Et_2AlCl is employed without the tungsten complex in the benzene–vinyl chloride solution, the conversion of vinyl chloride is reduced by $\frac{2}{3}$, although the selectivity to 1,1-diphenylethane remains the same. This reduced tungsten–Et_2AlCl-catalyzed alkylation reaction parallels the $AlCl_3$-catalyzed alkylation of benzene with vinyl chloride (*3*) in which 1,1-diphenylethane is also produced; however, neither $AlCl_3$ (*4*) nor Et_2AlCl produces any appreciable 1-butene when ethylene and benzene are brought together.

The effected change in reaction mechanism by replacing a hydrogen atom on ethylene with a chlorine atom is ascribed to the greater ease with which vinyl chloride will form a stable carbonium ion in the presence of even a weak Lewis acid, possibly a tungsten or aluminum complex. Other reduced tungsten salts have been shown to catalyze Friedel–Crafts type alkylation reactions of benzene and toluene with olefins (*5*).

Tungsten complexes have also been shown to undergo a variety of mechanism changes by varying the reductant to tungsten ratio. Thus, changes from a metathesis to alkylation catalyst (*5*) and from a metathesis to dimerization catalyst (*6*) have been observed with olefins.

ACKNOWLEDGMENT

The authors are grateful to Dr. G. S. Benner for carrying out some of the catalyst preparations.

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Received November 18, 1975

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[1] Contribution No. 540.