Low Temperature, Liquid Phase Disproportionation Catalysts Using Metal–Metal Bonded Complexes

The discovery of the olefin disproportionation reaction over heterogeneous catalysts (*1*) has led to widespread studies of this field in industry as well as in academic institutions. Shortly thereafter a number of very active homogeneous catalysts have been discovered and described (*2–5*). A recent review (*6*) covers both homogeneous and heterogeneous disproportionation catalysts.

Practically all the homogeneous disproportionation catalysts reported (*2–5*) start with molybdenum or tungsten halide derivatives which are then reacted with various organometallic compounds. Most of the published investigations discuss catalyst systems with high valent group VI transition metal halides (*2*, *3*), although more recently low valent nitrosyl derivatives of molybdenum have been successfully used (*5*). We have carried out disproportionation studies using exclusively low valent, metal–metal bonded group VI transition metal carbonyl derivatives which do not contain halogen or nitrosyl as a ligand. We discovered a unique way of activating such complexes for the low temperature disproportionation of olefins in the liquid phase.

The following general type of metal–metal bonded, ionic complexes were investigated:

$$A_n{}^+[(CO)_5M\text{–}M'(CO)_5]^{n-}$$

where $A =$ alkali metal, NR_4; $M =$ Mo, W; $M' =$ Mo, W, Mn, Re, and $n =$ charge of the dinuclear transition metal carbonyl anion ($2 \geq n \geq 1$). These complexes can be conveniently prepared from the commercially available metal carbonyls (*7–11*). They are generally only slightly soluble in aromatic or halogenated aromatic solvents; and, alone, they do not show any activity for olefin disproportionation in the liquid phase at ambient temperature. When they are contacted with an alkylaluminum chloride (e.g., alkylaluminum dichloride or alkylaluminum sesquichloride) a small amount of disproportionation is observed (Table 1). However, if a cocatalyst is present, typically a quaternary ammonium chloride (e.g., tetra-*n*-butylammonium chloride), a fast olefin disproportionation reaction takes place.

In a typical disproportionation experiment (Table 1) the metal–metal bonded complex is stirred with 5 ml of chlorobenzene, followed by the addition of 5 ml of pentene-1. Subsequently the cocatalyst, generally tetra-*n*-butylammonium chloride, is added followed by the addition of the methylaluminum dichloride activator. At this point the reaction starts, proceeding at ambient temperature, and can be followed by measuring the amount of ethylene formed. After 2 hr reaction time, the volatile products are flash distilled *in vacuo* and analyzed by GLC.

Upon addition of the activator, the reaction mixture appeared to be homogeneous with the exception of an occasional haziness. Only a small amount of work was carried out with tungsten complexes due to their lower solubility and reactivity. The data in Table 1 indicate the highest activity for the Mo–Mo system, regardless of whether it was used as a sodium salt or as a tetra-*n*-butylammonium salt. The Mo–Re system is slightly less active; whereas the Mo–Mn system shows substantially less activity. The octenes reported in Table 1 are octene-4 *trans* and *cis* isomers (ratio of 2.6–3.3:1). Other octene isomers were also found, however, only in trace amounts.

The new catalyst system was found effective also in the disproportionation of other types of olefins as, e.g., 4-methylpentene-1 and heptene-3. The disproportionation of octadiene-1,7 gave cyclohexene and ethylene in 99%+ selectivity (Table 1).

TABLE 1
DISPROPORTIONATION REACTION OF PENTENE-1 AT AMBIENT TEMPERATURE[a]

Cation A^+	Metal complex (mM) M–M′	Cocatalyst NR_4 Cl(mM)	Conversion to octenes (% wt)[b]	Remarks
NR_4	W–W (0.25)	0.25	36	—[c]
NR_4	Mo–Mo (0.50)	—	4	—[ce]
NR_4	Mo–Mo (0.125)	0.155	60	—[c]
Na	Mo–Mo (0.129)	0.125	61	—[cf]
Na	Mo–Re (0.125)	0.126	53	—[d]
NR'_4	Mo–Re (0.127)	0.133	51	—[d]
NR_4	Mo–Mn (0.124)	0.126	17	—[d]
Na	Mo–Mo (0.125)	0.06	53	—[c]
Na	Mo–Mo (0.248)	0.12	44	—[cg]

[a] $R = n\text{-}C_4H_9$; $R' = C_2H_5$; activator: CH_3AlCl_2 (2.5 mM).

[b] Material balance indicates practically no polymerization. Conversion data represent the solvent free percentage of octenes in the distillate.

[c] $n = 2$.

[d] $n = 1$.

[e] One hour reaction time; 4 mM CH_3AlCl_2 activator.

[f] Same catalyst and conditions as in *f* gave 44% conversion of octadiene-1,7 to cyclohexene.

[g] Co-disproportionation of 5 ml of *cis*-octene-4 and 5 ml of butene-2(*cis* + *trans* mixture) for 3 hr at 6 psi. Conversion indicated is to hexene-2.

The novel catalyst is also quite active in co-disproportionation reactions, e.g., between octene-4 and butene-2 to give hexene-2 (Table 1).

Studies are underway to determine the functions of the activator and the cocatalyst. These studies will also clarify whether the metal–metal bond is broken in the activation step.

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W. R. KROLL*
G. DOYLE

Corporate Research Laboratories
Esso Research & Engineering Company
Linden, New Jersey 07036
Received May 18, 1971

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* To whom correspondence should be sent. Present address: BASF, Olefin Abteilung, 6700 Ludwigshafen, Germany.