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Olefin Disproportionation by Rhenium, Tungsten, and Molybdenum Based Catalysts. Effect of the Addition of Oxygen

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$ReCl_5$ was activated with Et_3Al and oxygen to give a catalyst effective for the disproportionation of α-olefins as well as internal olefins. The catalyst species was deactivated by excess oxygen. The catalyst system consisting of either WCl_6 or $MoCl_5$ and Et_3Al exhibited disproportionation activity in a short range of Al/M (M=W or Mo) molar ratio. The activity decreased with the increase in the Al/M ratio, but was restored by the introduction of oxygen.

A number of Ziegler-Natta type catalysts have been reported to be effective for olefin disproportionation. These catalysts were derived from WCl_6–$EtAlCl_2$,[1,2] WCl_6–$EtAlCl_2$–EtOH,[1),2] WCl_6–*n*-BuLi,[3] and nitrosyl complexes $L_2Cl_2(NO)_2M$ (M=Mo or W; L= Ph_3P, C_5H_5N, Ph_3PO, *etc.*)-alkylaluminum halides.[4,5] We wish to report a disproportionation catalyst consisting of $ReCl_5$, Et_3Al, and oxygen, which effected the disproportionation of α-olefins as well as internal olefins. The catalyst system of WCl_6 and Et_3Al, reported to convert 2-pentene into unknown oligomers,[3] exhibited disproportionation in a short range of Al/W molar ratio. Though disproportionation activity decreased with the increase in the ratio, it was restored by the introduction of oxygen. $MoCl_5$ behaved like WCl_6 upon treatment with Et_3Al and oxygen. Catalysts consisting of rhenium oxide on alumina are notable for their disproportionation activity at relatively low temperatures.[6,7] Ziegler-Natta type catalysts containing rhenium compounds do not seem to have been reported in detail, although a patent[8] has been claimed.

Experimental

Materials and Procedures. All the reactions were carried out with a Schlenk-type tube under nitrogen. The reaction mixtures were stirred at room temperature and atmospheric pressure. Analysis by gas-liquid partition chromatography(glpc) was performed on a Shimadzu Model GC-3AH chromatograph, using a 3 m stainless-steel tube column packed with Silicone SE 30 fluid on 60—80 mesh Diasolid M.

Chlorobenzene and benzene were dried and distilled under a nitrogen stream. Organoaluminum compounds were used after dilution to about 8 wt%. All the transition metal chlorides were commercially obtained. WCl_6 was used after removal of more volatile contaminants, $WOCl_4$ and WO_2Cl_2, by sublimation under a nitrogen stream at about 180°C. Molybdenum(III) acetylacetonate was prepared by the method of Larson and Moore.[9] Commercial olefins were used after degassing in a vacuum. When olefins purified by distillation in the presence of WCl_6 were

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[3] J. L. Wang and H. R. Menapace, *J. Org. Chem.*, **33**, 3794 (1968).

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used, the catalytic activity was higher than that with unpurified olefins.

Reaction of 2-Pentene with $ReCl_5$–Et_3Al–O_2. $ReCl_5$ (0.1 mmol) and 2 m*l* of chlorobenzene were treated with 0.4 mmol of Et_3Al (chlorobenzene solution) at *ca.* −30°C. The reduction was carried out for 30 min at ambient temperature and then 9.3 mmol (0.65 g) of 2-pentene purified by adding WCl_6 was injected by a syringe. The reaction mixture was degassed and a calculated amount of oxygen was introduced. Reaction times given in the tables were estimated from the time of introduction of oxygen. After 30 min, the reaction vessel was filled with nitrogen. Glpc analysis was carried out at 75°C and 20 cc/min of helium flow rate employing a chlorobenzene standard, and indicated the presnece of 2-butene, 3-hexene, and unreacted 2-pentene in the reaction mixture. All peaks in the chromatograms were identified by comparison of their retention times with those of authentic samples. The olefin yield in the tables is mol% of each olefin to the staritng olefin.

Reaction of 1-Pentene with $ReCl_5$–Et_3Al–O_2. The catalyst was prepared as described above except that oxygen was introduced 16 hr after the addition of Et_3Al. Glpc analysis showed the presence of olefins ranging from C_2 to C_8. The analytical conditions were the same as described above. Mass spectral data confirmed identification.

Reaction of 2-Pentene or 1-Pentene with WCl_6–Et_3Al (–O_2). A mixture of 0.1 mmol of WCl_6, 2 m*l* of chlorobenzene, and either 9.3 mmol of 2-pentene or 9.1 mmol of 1-pentene was treated with Et_3Al at *ca.* −30°C. Oxygen was subsequently introduced in some cases.

Reaction of 2-Pentene or 1-Pentene with $MoCl_5$–Et_3Al (–O_2). The catalyst was prepared as described above except that $MoCl_5$ was used in place of WCl_6.

Results and Discussion

Catalyst from $ReCl_5$. Treatment of $ReCl_5$ with Et_3Al in chlorobenzene gave a reddish brown solution, to which 2-pentene and oxygen were added. During the reaction a black precipitate was gradually deposited. Glpc analysis after 2 hr indicated the presence of 2-butene, 3-hexene, and unreacted 2-pentene; no additional products other than ethylene were detected. In order to determine the optimum O_2/Re ratio and to obtain information on the stoichiometry of the catalyst-formation reaction, a series of runs was made increasing the amount of added oxygen while the concentrations of $ReCl_5$ and Et_3Al were kept constant. At Al/Re=4, good results were obtained at O_2/Re=6—10. The Al/Re molar ratio was varied without adding oxygen. No disproportionation took place. The products after 20 hr consisted 25% of 2-butene, 50% of 2-pentene, and 25% of 3-hexene, indicating that a thermodynamic equilibrium was reached in each experiment. The data are collected in Table 1. At $O_2/Re \geqq 3.5$, the catalytic activity disappeared after 20 hr. It seems that at such large O_2/Re molar ratios, the disproportionation catalyst species was destroyed by excess oxygen.

When α-olefins were used as substrates, two competing processes occurred, namely disproportionation and double-bond migration. As shown in Table 2, 1-pentene gave a mixture of olefins ranging from C_2 to C_8. Only double-bond migration occurred before

Table 1. $ReCl_5$–Et_3Al–O_2 catalyst with 2-pentene[a)]

Olefin yield, mol%	O_2/Re molar ratio					
			2 hr			20 hr
	2.6	5.0	7.3	9.3	12.5	2.6—12.5
C_4H_8	16	23	25	24	22	25
C_5H_{10}	67	54	51	52	56	50
C_6H_{12}	16	23	25	24	21	25
$(C_4+C_6)/C_5$	0.48	0.85	0.98	0.92	0.77	1.0

a) Al/Re=4, 2-pentene/Re=93. 1-Pentene was purified by adding WCl_6.

Table 2. $ReCl_5$–Et_3Al–O_2 catalyst with 1-pentene[a)]

Al/Re Molar ratio	O_2/Re Molar ratio	Reaction time, hr	Olefin yield,[b)] mol%				
			C_4	C_5	C_6	C_7	C_8
4.0	2.0	2	3.5	93	2.1	1.1	0.0
	5.2		7.9	77	7.0	3.3	1.1
	11.4		15	53	14	5.9	3.6
4.0	1.0	72	1.0	98	1.0	0.2	0.0
	2.0		14	59	14	5.5	1.3
	2.5		20	25	18	12	7.3
	3.5		23	29	20	11	4.4
	5.2		20	42	17	9.4	4.4
	15.3		15	54	15	6.5	1.5
7.0	4.0	76	9.5	73	8.4	3.9	0.9
	5.1		18	43	17	7.3	4.3
	7.6		7.0	79	7.0	2.7	1.2

a) 1-Pentene/Re=60.
b) Ethylene and propylene were also detected.

the addition of oxygen. In this catalyst system the disproportionation of internal olefins proceeded at a fairly higher rate than the disproportionation and double-bond migration of α-olefins. Glpc analyses after 72 hr showed that at Al/Re=4, good results for disproportionation were obtained at O_2/Re=*ca.* 2.5. At Al/Re=4 and O_2/Re=2.6, the catalyst system was still active in the disproportionation of additional 1-pentene after 72 hr. This indicates that at a small O_2/Re ratio, the catalyst was probably long-lived. Thus 1-pentene was continually disproportionated little by little and 2-pentene which resulted from the slow double-bond migration of 1-pentene was rapidly disproportionated. But at a large O_2/Re ratio, the disproportionation catalyst was deactivated by excess oxygen present in the system before 2-pentene was gradually formed and the slow disproportionation of 1-pentene proceeded to a considerable extent. According to analyses after 72 hr, good results were obtained at relatively small O_2/Re ratios. At Al/Re=7, the optimum ratio was larger than that at Al/Re=4. At Al/Re=1 and O_2/Re=1, alkylation products were exclusively formed. The first three experiments in Table 2 indicate that in the early stage of the reaction, the high conversion of 1-pentene was attained at relatively large O_2/Re molar ratios. It seems that this was due to the slow catalyst-formation at small molar ratios. The result that large ratios are preferred (Table 1) could be similarly elucidated.

Glpc analyses of the 2-pentene reaction solutions after 96 hr showed the presence of small amounts of C_7 olefins (1—2%), which can be attributed to double-bond migration followed by disproportionation. This catalyst in combination with 1-hexene afforded a mixture of olefins ranging from C_2 to C_{10}. 2-Hexene gave a mixture of olefins ranging from C_4 to C_8 (Table 3). The formation of each olefin, as described in Tables 2 and 3, requires the interaction of a combination of α- and internal olefins.

In these catalyst systems olefins should be added after the reduction of $ReCl_5$ by Et_3Al, since $ReCl_5$ itself can promote the moderate alkylation of aromatic compounds and the oligomerization of olefins.[10] Aromatic compounds were suitable as solvent. Olefins were not disproportionated with tetrahydrofuran as a solvent. When three moles of PPh_3 per mole of $ReCl_5$ were present in the system before oxygen was introduced, the system showed no disproportionation activity. $ReCl_3$ showed none upon treatment with Et_3Al and oxygen.

Table 3. $ReCl_5$-Et_3Al-O_2 catalyst with 1-hexene or 2-hexene[a]

Olefin yield, mol%	Reactant	
	1-Hexene	2-Hexene
$Al/O_2/Re$ Molar ratio	4/2/1	4/2/1
Reaction time, hr	74	64
C_4H_8	b)	19
C_5H_{10}	12	7.0
C_6H_{12}	52	45
C_7H_{14}	12	6.8
C_8H_{16}	1.5	20
C_9H_{18}	8.3	
$C_{10}H_{20}$	3.6	

a) Olefin/Re=50.

b) Ethylene, propylene, and butene were present. However, they were not estimated.

Catalyst from WCl_6. Wang and Menapace[3] reported that with a WCl_6–Et_3Al catalyst system, 100% conversion into unknown oligomers was obtained. The catalyst system WCl_6 and Et_3Al, however, exhibited disproportionation activity for 2-pentene in a short range of Al/W molar ratio. The optimum ratio was *ca.* 0.5. Though the catalyst activity decreased with the increase in the ratio, it was restored by the introduction of oxygen into the system. At Al/W=2.6, good results were obtained at O_2/W=1.2—1.7. Traces of oligomerization and Friedel-Crafts alkylation products were observed in the reaction mixture.[11] Glpc analyses after 96 hr indicated the presence of C_7 olefins.

In the reaction of α-olefins by the catalyst system of WCl_6–Et_3Al, unknown oligomerizasion took place considerably accompanied by disproportionation and double-bond migration. Although both oligomerization and disproportionation activities disappeared with the increase in the Al/W ratio and the double-bond migration activity was not much influenced, introduction of oxygen into this system recovered only the disproportionation activity. Addition of PPh_3 to WCl_6–Et_3Al system also suppressed the oligomerization activity and effected disproportionation and double-bond migration. The results are given in Table 4. The disproportionation activity of the catalyst WCl_6–Et_3Al–O_2 was dependent on the mixing order of the catalyst components. Preparation of the active catalyst was favored by the presence of olefin when WCl_6 was treated with Et_3Al and then oxygen.

Catalyst from Molybdenum Compounds. The catalyst system of $MoCl_5$ and Et_3Al also exhibited catalytic activity for olefin disproportionation in a narrow range of Al/Mo ratio. This system appeared to be less active than the tungsten system. The disproportion activity was reduced by the increase in the Al/Mo ratio but restored by the introduction of oxygen into the system. In the reaction of α-olefins with $MoCl_5$–Et_3Al, oligomerization occurred accompanied by disproportionation and double-bond migration. The results are summarized in Table 5.

Molybdenum(III) acetylacetonate also exhibited disproportionation activity for 1-pentene upon treatment with Et_3Al and oxygen. At Al/Mo=7 and O_2/Mo=2, the system exhibited a slight activity. At Al/Mo=4, only double-bond migration and dimerization were observed with a change of O_2/Mo.

As a reducing agent, other organoaluminum compounds were also investigated. Several systems were found to form disproportionation catalysts. Pertinent data are given in Table 6.

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[11] J. R. Graham and L. H. Slaugh, *Tetrahedron Lett.*, **1971**, 787.

TABLE 4. WCl_6-$Et_3Al(-O_2)$ CATALYST[a]

Reactant	Al/W Molar ratio	O_2/W Molar ratio	Reaction time, hr	Olefin yield,[c] mol%				
				C_4	C_5	C_6	C_7	C_8
2-Pentene	0.6[b]	0	0.5	24	49	25		
	0.5	0	2	20	43	20		
	2.6	0	2	0	98	0		
	2.6	1.2	2	22	56	22		
	2.6	4.5	2	14	73	13		
1-Pentene	0.7	0	2	2.6	21	3.0	1.1	0.1
	2.6	0	12	0.9	96	0.6	3.0	0.0
	2.6	2.3[d]	2	11	59	11	5.3	3.5
	1.2	1.0[e]	44	19	26	20	11	4.4

a) 2-Pentene/W=93, 1-pentene/W=91.

b) In this reaction 2-pentene purified by adding WCl_6 was used. 2-Pentene/W=270.

c) When the reactant was 1-pentene, ethylene and propylene were also present. Although chlorophenylpentane was detected, the amount of alkylation products was so small that we could employ chlorobenzene as an internal standard in the glpc analysis.

d) Oxygen was added 12 hr after the reduction by Et_3Al.

e) PPh_3 was used in place of O_2. 1-Pentene was purified by adding WCl_6.

TABLE 5. $MoCl_5$-$Et_3Al(-O_2)$ CATALYST[a]

Reactant	Al/Mo Molar ratio	O_2/Mo Molar ratio	Reaction time, hr	Olefin yield,[b] mol%				
				C_4	C_5	C_6	C_7	C_8
2-Pentene	0.3	0	20	4.7	86	4.8		
	2.1	0	48	0.5	95	0.5		
	2.1	1.7[c]	2	5.1	86	4.8		
1-Pentene	0.3	0	20	0.3	18	0.4	1.0	0.0
	2.0	1.6[d]	2	4.0	71	4.0	3.1	0.2

a) 2-Pentene/Mo=93, 1-pentene/Mo=91.

b) Traces of chlorophenylpentane were also detected. When the reactant was 1-pentene, ethylene and propylene were present.

c) Oxygen was added 48 hr after the reduction by Et_3Al and the reaction was continued for another 2 hr.

d) Oxygen was added 12 hr after the reduction.

TABLE 6. MCl_n-$Et_2AlCl(-O_2)$ CATALYST WITH 2-PENTENE[a]

Metal chloride	Al/M Molar ratio	O_2/M Molar ratio	Reaction time, hr	Olefin yield,[b] mol%		
				C_4	C_5	C_6
WCl_6	3	0	24	0.7	59	0.7
$MoCl_5$	6	4	22	3.8	75	3.5
$ReCl_5$	7	5	24	1.0	80	1.0

a) 2-Pentene/M=93.

b) Traces of phenylpentane were also detected.

The Reaction Intermediate. Wang and Menapace[3] described the disproportionation of 2-pentene by a catalyst system of WCl_6 and *n*-BuLi. They reported that a conversion of 50% and a selectivity of 100% were obtained at Li/W=2, results not being good with other ratios. Thus they suggested a W-(IV) catalytic intermediate. Hughes[12] proposed a zero-valent molybdenum compound as the active species in the $L_2Cl_2(NO)_2Mo$-R_xAlCl_{3-x} catalyst.

In our catalyst systems starting metal chlorides, which demonstrate moderate Friedel-Crafts alkylation activity,[10,11] can be reduced to various oxidation states according to an added amount of Et_3Al. At Al/W=*ca.* 0.6, WCl_6 can be reduced to an appropriate oxidation state and exhibits disproportionation activity. Subsequently added oxygen can re-oxidize the low-valent complex and realize a favorable oxidation state for disproportionation. If oxygen was present in excess, the activity species would be further oxidized and destroyed. When three moles of PPh_3 per mole of $ReCl_5$ were present in the system before the introduction of oxygen, PPh_3 could stabilize the low-valent metal species and prevent it from re-oxidation. However, it is difficult to assume the precise oxidation state of the active species.

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