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NEW HOMOGENEOUS COBALT CATALYSTS FOR HYDROGENATION

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Considering the current interest in homogeneous catalysis (1) we would like to report some results of the remarkable effectiveness of a new catalyst system based on the reaction of lithium tri-t-butoxyaluminium hydride or di-t-butoxyaluminium hydride with various salts of iron, nickel, cobalt and other transition metals.

The introduction of alkoxy groups into lithium aluminium hydride modifies its reducing characteristics. At the same time the alkoxy groups enhance the Lewis acidity of aluminium which seems to be linked to the metal hydride formed.

We found that by using these reducing systems the activity in the hydrogenation of olefins and diolefins was actually multiplied by a factor of 10^2 to 10^3 compared with known heterogeneous systems (2) and by a factor of more than 10 compared with homogeneous systems (1). Neither the influence of the anion of the metal salt nor the ratio of the reducing agent to the cobalt salt when this ratio is higher than 4 seems to affect the rate of the reaction. However, at very low cobalt concentration, impurities may inhibit the catalyst when the ratio is close to 4.

In addition to cyclopentene the following olefins were also hydrogenated : cyclohexene, styrene, 2-methyl 1-butene, 1-pentene, 2-pentene, isoprene and 1,3-cyclooctadiene but not benzene. The rate of hydrogenation is enhanced by pressure. In an autoclave experiment we were able to hydrogenate 40 ml of cyclopentene (c = 2.86 M) at 20°C (between 225 and 140 psi pressure) at an initial rate of 0.088 M min^{-1} with only 0.0033 mmoles of cobalt or a concentration of $2.09.10^{-5}$ M. The results at low pressure are shown in Table 1.

TABLE 1

Hydrogenation of cyclopentene with soluble catalysts[a]

Transition metal Compound	Reducing agent[b]	Ratio[c]	Conc.[d] $M.10^3$	Temp. °C	Rate[e] $M.min^{-1}$	Conversion %
$CoBr_2$	$LiAlH(OR)_3$[g]	50	0.232	20	0.358	100
$CoBr_2L_2$[f]	$LiAlH(OR)_3$	30	0.376	20	0.460	100
$CoBr_2L_2$	$NaAlH(OR)_3$	20	0.570	20	0.515	100
$Co(acac)_2$	$LiAlH(OR)_3$	25	0.450	20	0.212	100
Co $(Acetate)_2$ + 6L	$LiAlH(OR)_3$	15	0.470	20	0.347	100
$NiBr_2L_2$	$LiAlH(OR)_3$	40	0.519	20	0.033	100
$FeCl_3$	$AlH(OR)_2$	3	2.32	40	0.075	100
$TiCl_2(C_5H_5)_2$	$LiAlH(OR)_3$ + AlH_3	30 + 15	0.916	40	0.485	100

a) Reactions were carried out with 40 mmoles of cyclopentene in heptane with 1 or 2 ml of tetrahydrofuran with 16 psi constant pressure in a glass reactor mechanically agitated and fitted with a serum cap allowing the injection of reagents. The sequence of introduction for the cobalt system was : reducing agent, solvent, olefin and metal compound. The volume of solution was 40 ml. The absorption of hydrogen was recorded and the alkane analysed by glc. b) $LiAlH(OR)_3$ was synthesised as usual and dissolved in THF. $AlH(OR)_2$ was synthesised without isolation by mixing 2 moles of tert-butyl alcohol and 1 mole of AlH_3 synthesised as indicated by Brown (3). c) Ratio of reducing system to transition metal. d) Based on transition metal. M = mol l^{-1}. e) The rate is generally constant during 80 to 90 % of the conversion and is expressed in mol $H_2.l^{-1}.min^{-1}$. f) L = $PO(C_8H_{17})_3$. g) OR = tert-butoxy.

More complete kinetic results were obtained on cobalt catalysts and proved the very high activity and stability of this type of catalyst. The further scope of this reaction is corrently under investigation.

REFERENCES

(1) M.F. Sloan, A.S. Matlack, and David S. Breslow, J. Amer. Chem. Soc., 85, 4014 (1963)
Katechits and F.K. Shmidt, Kinetika i Kataliz, Vol. 7, n° 4, 614 (1966)

(2) H.C. Brown and C.A. Brown, J. Amer. Chem. Soc., 85, 1003 (1963)

(3) H.C. Brown and Nung Min Yoon, J. Amer. Chem. Soc., 88, 1464 (1966).