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Cobalt and Nickel Acetylacetonates–Lithium Aluminum Hydride as Hydrogenation Catalysts for Aromatics

A number of transition metal compounds combined with organometallics have been found to be soluble catalysts for the hydrogenation of olefins and aromatics (*1–3*). Transition metal compounds reduced by lithium aluminum hydride have been found to be good catalysts for the hydrogenation of olefins (*4–6*). Recently, nickel chloride reduced by sodium borohydride has also been reported to catalyze the hydrogenation of olefins (*7*). In the present note we report the facile hydrogenation of aromatic compounds catalyzed by bis(acetylacetonato) cobalt(II) dihydrate and bis(acetylacetonato) nickel(II) dihydrate in combination with lithium aluminum hydride.

One gram of complex was taken in 50 ml of tetrahydrofuran. Lithium aluminum hydride was added to this solution; an exothermic reaction took place and a dark brown solution was formed. To this, 250 mmole of the aromatic compound was added. This solution was charged into a 500 ml stainless steel rotary autoclave and filled with hydrogen after flushing. The cold pressure of hydrogen was 60 kg/cm^2 gauge. The autoclave was rotated at 85 rpm. It was heated to 200°C over a period of 1 hr. During heating the pressure rose to a maximum of 90 kg/cm^2 gauge and then slowly fell. The autoclave was maintained at 200°C for 1 hr, at the end of which time both heating and rotating were stopped. When the autoclave was cool, the charge was taken out. The autoclave contained a black precipitate which slowly settled whereupon, a clear solution was obtained by filtration. The solution was freed from tetrahydrofuran by treatment with water in a separating funnel. The remaining organic layer was dried and the solution was analyzed by the sulfuric acid–phosphorous pentoxide absorption method (*8*).

Table 1 shows the variation of catalytic activity with the change in the cobalt/nickel: aluminum atomic ratio in the hydrogenation of benzene. In all the cases there was no substantial decrease in the autoclave pressure after 10 min at 200°C. The optimum ratio was found to be 1:3 for the cobalt complex and 1:2 for the nickel complex.

Table 2 gives the time required for the completion of the hydrogenation of benzene, toluene and xylene using these catalyst systems with the optimum atomic ratios. It may be observed that both the cobalt and nickel complexes show similar activity.

TABLE 1
EFFECT OF COBALT/NICKEL: ALUMINUM RATIO ON THE CATALYTIC ACTIVITY[a]

Complex	Cobalt/nickel: aluminum atomic ratio	Saturates (%)
Bis(acetylacetonato) cobalt(II) dihydrate	1:1	0
	1:2	65
	1:3	98
	1:4	96
	1:5	96
	1:6	96
Bis(acetylacetonato) nickel(II) dihydrate	1:1	77
	1:2	99
	1:3	97
	1:4	97
	1:5	97
	1:6	97

[a] Substrate: benzene.

TABLE 2
TYPICAL RESULTS OF HYDROGENATION WITH OPTIMUM ATOMIC RATIOS

Complex	Cobalt/nickel: aluminum atomic ratio	Substrate	Time (min)	Saturates (%)
Bis(acetylacetonato) cobalt(II) dihydrate	1:3	Benzene	10	97
	1:3	Toluene	40	95
	1:3	Xylene	70	91
Bis(acetylacetonato) nickel(II) dihydrate	1:2	Benzene	10	99
	1:2	Toluene	40	95
	1:2	Xylene	70	93

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