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Catalyst Systems Derived from Transition Metal Acetylacetonates for the Hydrogenation of Aromatics

N. MURUGESAN & S. SARKAR
Department of Chemical Engineering, Indian Institute of Technology, Bombay

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Acetylacetonate complexes of iron, cobalt and nickel on reduction with lithium aluminium hydride or sodium borohydride yield highly active catalyst systems for the hydrogenation of aromatic compounds. Cobalt and nickel based systems are more active than the iron based one. The systems derived from lithium aluminium hydride are much more active than those from sodium borohydride. The activities of the catalyst systems show a dependence on the ratio of the transition metal to the reducing agent. In the case of lithium aluminium hydride, solvents like tetrahydrofuran and diethyl ether lower the amount of the reducing agent required for the optimum catalytic activity. Using tetrahydrofuran as the solvent, the effect of different variables, viz. [catalyst], temperature, pressure and additives, on the catalytic activity has been investigated. It has been possible to regenerate the lithium aluminium hydride derived catalysts after hydrogenation reactions. Based on the study of the infrared spectra of the precipitates from the reaction systems and also various other studies, a mechanism involving a transition metal hydride moiety has been suggested for the catalytic hydrogenation.

CATALYSIS by coordination compounds is now a recognized field of both theoretical and applied importance[1,2]. A survey of transition metal complex catalysts shows that there are only a few catalysts available for the hydrogenation of aromatic compounds[3-14]. Of these, the costlier rhodium complexes are active at room temperature and one atmosphere pressure. Dicobalt octacarbonyl is not active for isolated benzene rings. The Ziegler-Natta catalysts are active at high temperature and pressure; moreover they require the use of organoaluminium compounds which need special care in handling. In an earlier note[15] we reported the use of lithium aluminium hydride (LAH) as a useful alternative reducing agent for preparing catalysts similar to Ziegler-Natta type for the hydrogenation of benzene. In the present paper, are presented further details on this newly developed catalyst system and also another system prepared by using sodium borohydride in place of LAH. The systems, bis (acetylacetonato) cobalt(II) dihydrate-LAH and bis (acetylacetonato) nickel(II) dihydrate-LAH were investigated in greater detail.

Materials and Methods

Cyclohexene (LR), benzene (AR), toluene (LR), xylene (LR) and naphthalene (LR) were used as substrates. Lithium aluminium hydride (E. Merck) and sodium borohydride (E. Merck) were used as the reducing agents. The additives were of reagent grade.

The following acetylacetonate complexes prepared in the laboratory according to literature method[16-19] were used: tris(acetylacetonato) iron(III), bis (acetylacetonato) cobalt(II) dihydrato, tris (acetylacetonato) cobalt(III) and bis (acetylacetonato) nickel(II) dihydrate.

All the solvents, viz. tetrahydrofuran, diethylether, and 1,4-dioxane were dried over sodium wire and freshly distilled over LAH.

Commercial grade hydrogen supplied by the Indian Oxygen Limited was used without purification for all the reactions in the autoclave. Its approximate composition was given as: H_2, 99·5%, O_2, 0·2%, CO_2, 25 ppm and H_2O, 500 ppm. However, for reactions at room temperature and one atmosphere pressure, this hydrogen was purified using an active copper catalyst[20] and then dried by passing through phosphorus pentoxide.

Procedure for hydrogenation at room temperature and one atmosphere pressure — The apparatus consisted of a flat-bottomed flask fitted with a three-way adaptor. One of the outlets was connected to the gas line. The second was closed with a stopper and the third was fitted with a pressure equilibrated addition funnel. The gas line connected a dibutyl phthalate-filled gas burette through a two-way stopcock. There was another two-way stopcock connecting the system to pure, dry hydrogen gas supply or vacuum. The other arm of the two-way stopcock of the gas burette connected it to a separate hydrogen supply line.

To start the experiment, the gas burette was filled with hydrogen. The gas burette stopcock was closed. In the flask, the solution of the transition metal complex in the solvent was taken. In the addition funnel, the substrate was taken. The system was filled with hydrogen by alternately evacuating and filling with hydrogen. Then the stopper in the system was opened with a continuous passage

of hydrogen through the system and LAH was added. When the reaction subsided, the stopper was closed and the stopcock of the gas burette opened to the system. When a steady reading was noted in the gas burette, the substrate was added to the solution in the flask. Any hydrogen absorption was noted. When required, the gas burette was refilled with hydrogen, without disturbing the system, through the separate hydrogen supply line. At the end of the reaction, the whole system was flushed with nitrogen and the solution in the flask was taken for further treatment.

Procedure for hydrogenation at medium temperature and high pressure — These experiments were carried out in a ½ litre rotary autoclave provided with heating at a controlled temperature.

The hydrogenation reactions using a solvent were performed in the following manner. The required amount of the transition metal complex was dissolved in the solvent (50 ml). The weighed amount of LAH was added to this. When the reaction subsided, usually yielding a black or brownish black solution for optimum complex to sodium hlyride ratio, the substrate was added and the flask closed. After 10 min, this solution was fed to the autoclave and the latter was closed with the lid. It was then flushed with hydrogen several times and finally filled with hydrogen up to the required pressure. All these operations required about 20 min. The rotating and heating of the autoclave were started. It took about 30 min to reach 100° from room temperature, about 45 min to reach 150° and about 55 min to reach 200°. The autoclave was maintained at the required temperature till the pressure drop stopped. The time required for this was noted. For slower reactions indicated by prolonged period of pressure drop, the autoclave was run for 2 hr. After the heating was stopped, the autoclave was kept overnight for cooling.

In hydrogenation reactions of naphthalene, the preparation of the reaction solution was slightly modified. The transition metal complex was reduced by LAH in tetrahydrofuran. This was added to the naphthalene already taken in the autoclave. Then the autoclave was closed and pressurized.

In hydrogenation experiments in the absence of solvent, the autoclave was filled in the following manner. The transition metal complex, the substrate and the saline hydride were placed in that order in the autoclave. In experiments where the requirement of hydrogen was more than the amount filled initially, the autoclave was repressurized with hydrogen.

For the reactions carried out to find out the effect of impurities on the catalyst system, the additive was incorporated first to benzene and then the mixture was introduced to the catalyst solution. However, in the case of water as the impurity, it was added to the reaction solution after the addition of benzene to it, owing to the immiscibility of the two.

Reactions were conducted for a period ranging from 10 min to 6 hr. By the reaction time is meant the time for which the experiment was conducted at a particular temperature. The time taken to reach the reaction temperature and then bring it back to the room temperature was neglected even though some reaction might have taken place during this time. The completion of reaction was indicated by the constancy of pressure.

Isolation of the products — After the hydrogenation, the reaction mixture, usually, had a black precipitate and a clear colourless solution. The clear solution at the end of the experiment was separated by filtration and washed with water to remove water-soluble solvents such as tetrahydrofuran and 1,4-dioxane. In the case of diethylether solvent, it was removed by careful evaporation. The product was finally dried over anhydrous calcium chloride. When no solvent had been used, the product was freed from the precipitate by filtration and thereafter dried. In a few cases when the reaction mixture had a black solution as well as a black precipitate, the solute was completely precipitated by adding some water to the solution.

Analysis of the products — When the substrate was benzene, toluene or xylene, the product was analysed for the amount of aromatics and olefins by absorption with phosphorous pentoxide-sulphuric acid absorption method[21]. In the case of cyclohexene and also the above mentioned substrates, the amount of olefin in the product was found by a similar method using 84% sulphuric acid. The percentage of saturates in the products was determined by the method of difference.

The hydrogenation products of naphthalene were analysed by gas liquid chromatography. The latter was not available in the benzene hydrogenation study which required a large number of experiments and formed the bulk of the present investigation.

The precipitates were isolated by centrifugation and washing with the solvent. The solvent was finally removed under reduced pressure and the precipitate dried in a vacuum desiccator over calcium chloride. For further reactions with this precipitate, no special care was taken to protect it from the atmosphere.

Results

The recovery of the hydrogenated product ranged from 80 to 85%. The saturated portion of the product was found to be cyclohexane when cyclohexene or benzene was used as the substrate. Olefins were totally absent.

All the catalyst systems derived by reaction with LAH were similar in many properties but slightly different in colour. The precipitates contained the particular transition metal as well as lithium and aluminium. Elemental analyses of the precipitate, both before and after exposure to atmosphere for a long time, showed the presence of carbon and hydrogen. But the values were not consistent and they varied widely from one analysis to another. The carbon content varied from 0·5 to 15·5% and the hydrogen content varied from 0·2 to 4·2%.

The catalytic activities of various catalyst systems employing different transition metal compounds

are given in Table 1. The activities of two selected systems at room temperature and one atmosphere pressure of hydrogen are given in Table 2.

The effect of the ratio of nickel to reducing agent, catalyst concentration, reaction temperature, cold pressure of hydrogen and additives on the catalytic activity were studied. The hydrogenation of some aromatic compounds other than benzene has also been achieved (Table 3).

Discussion

It is observed that the activity of the catalyst systems reported in this paper depended very much on: (a) the nature of the transition metal, (b) the nature of the ligands, (c) the nature of the reducing agent, (d) the ratio of the transition metal to the reducing agent, (e) the nature of solvent used, if any, and (f) the nature of additives, if any. The activity

TABLE 1 — EFFECT OF THE NATURE OF TRANSITION METAL COMPOUNDS IN THE CATALYST SYSTEMS

[acac = acetylacetonate anion; THF = tetrahydrofuran (50 ml); amount of transition metal = 3 millimoles; substrate = benzene, 250 millimoles for reactions with solvent and 500 millimoles for reactions without solvent; cold hydrogen pressure = 60 kgf/cm² gauge]

Sl No.	Catalyst system	Temp. °C	Reaction pressure (kgf/cm² gauge)	Time (min)	Saturates (vol. %)
1	$Fe(acac)_3+LiAlH_4$ in THF (1 : 10)	200	120-80	120	78
2	$Fe(acac)_3+LiAlH_4$ (1 : 12)	200	120-100	120	43
3	$CoCl_2+LiAlH_4$ in THF (1 : 6)	200	120-80	120	76
4	Cobaltnaphthenate+$LiAlH_4$ in THF (1 : 6)	150	110-40	120	95
5	$Co(acac)_2 2H_2O+LiAlH_4$ in THF (1 : 4)	150	105-40	10	99
6	$Co(acac)_2 2H_2O+LiAlH_4$ (1 : 11)	150	100-60[a]	25	100
7	$Co(acac)_2 2H_2O+NaBH_4$ in THF (1 : 7)	200	130	120	11
8	$Co(acac)_2 2H_2O+NaBH_4$ (1 : 12)	200	115-95	120	37
9	$Co(acac)_2+LiAlH_4$ in THF (1 : 4)	150	100-40	5	100
10	$Co(acac)_3+LiAlH_4$ (1 : 11)	150	90-60	30	99
11	$Co(acac)_3+LiAlH_4$ in THF (1 : 7)	150	100-40	10	98
12	$NiCl_2+LiAlH_4$ in THF (1 : 6)	200	120-90	120	62
13	$Ni(acac)_2.2H_2O+LiAlH_4$ in THF (1 : 3)	150	150-40	10	100
14	$Ni(acac)_2.2H_2O+LiAlH_4$ (1 : 10)	150	100-60[a]	25	100
15	$Ni(acac)_2.2H_2O+NaBH_4$ in THF (1 : 10)	200	125	120	13
16	$Ni(acac)_2.2H_2O+NaBH_4$ (1 : 12)	200	110-90	120	33
17	$Ni(acac)_2+LiAlH_4$ in THF (1 : 3)	150	100-40	5	100

(a) The autoclave was refilled during the course of the reaction.

TABLE 2 — ACTIVITY OF THE CATALYST SYSTEMS AT ROOM TEMPERATURE

[Solvent, 50 ml of tetrahydrofuran; temp., 30°; pressure, 1 atmosphere of hydrogen]

Catalyst system	Substrate	Hydrogen absorption* (ml/min)	Time (min)	Saturates (vol. %)
$Co^{II}(acac)_2.2H_2O+LiAlH_4$ (1 : 4)	Cyclohexene	16	370	98
$Co^{II}(acac)_2.2H_2O+LiAlH_4$ (1 : 4)	Benzene	4	360	8
$Ni^{II}(acac)_2.2H_2O+LiAlH_4$ (1 : 3)	Cyclohexene	16	360	99
$Ni^{II}(acac)_2.2H_2O+LiAlH_4$ (1 : 3)	Benzene	4	360	8

*Average rate of absorption in the first half an hour.

TABLE 3 — EFFECT OF AROMATIC SUBSTRATE

[Complex: 3 millimoles of bis(acetylacetonato) cobalt (II) dihydrate for experiment Nos. 1 to 4 and 3 millimoles of bis-(acetylacetonato) nickel (II) dihydrate for experiment Nos. 5 to 8; substrate concentration: 250 millimoles for experiment Nos. 1, 2, 5 and 6, 100 millimoles for experiment Nos. 3, 4, 7 and 8; solvent: 50 ml of tetrahydrofuran; cold pressure of hydrogen: 60 kgf/cm² gauge]

Sl No.	Cobalt/ Nickel: Aluminium atomic ratio	Substrate	Temp. °C	Reaction pressure (kgf/cm² gauge)	Time (min)	Product
1	1 : 4	Toluene	150	100-40	55	Saturates (97 vol. %)
2	1 : 4	Xylene	200	120-85	25	Saturates (95 vol. %)
3	1 : 6	Naphthalene	150	100-95	5	Tetralin (100 %)
4	1 : 6	Naphthalene	150	100-85	120	Decalin (*cis*+*trans*) (99%)
5	1 : 3	Toluene	150	100-40	50	Saturates (96 vol. %)
6	1 : 3	Xylene	200	120-85	30	Saturates (95 vol. %)
7	1 : 6	Naphthalene	150	100-95	10	Tetralin (100%)
8	1 : 6	Naphthalene	150	100-85	120	Tetralin (10%) +Decalin(*cis*+*trans*) (88%)

was noted over a wide range of temperature, viz. from room temperature to 200°.

The high activity of the catalyst systems is evident from Tables 1 and 2. Benzene could be hydrogenated to a perceptible extent even at room temperature and one atmosphere pressure.

For the systems derived from acetylacetonate complexes, the activity was found to be of the order: nickel $\simeq$ cobalt $\gg$ iron. At lower temperatures and lower concentrations, the cobalt containing system was less active than that containing nickel. This activity pattern resembles the one reported for Ziegler-Natta catalysts by other workers[8,10]. The reported activity in these cases was, however, in the order: nickel > cobalt > iron.

With lithium aluminium hydride as the reducing agent and tetrahydrofuran as the solvent, the hydrogenation of benzene was almost complete at the aluminium to nickel atomic ratio of 2:1 and above and at the aluminium to cobalt atomic ratio of 3:1 and above. With the iron catalyst, the maximum conversion was about 78% at the corresponding ratio of 9:1 and above.

In the case of sodium borohydride as the reducing agent and tetrahydrofuran as the solvent, the conversion was up to a maximum of 13% and there was no clear dependence of the catalytic activity on the ratio of the transition metal to sodium borohydride. This may be due to the caking of sodium borohydride under the prevailing reaction conditions. This difficulty was experienced even with finely powdered sodium borohydride.

It was found that the catalyst systems were active even without any solvent. In the case of lithium aluminium hydride, however, the use of tetrahydrofuran brought down the optimum ratio of reducing agent to the transition metal from 3:1 to 2:1. This may be attributed to the favoured formation of the catalytically active complex in the presence of tetrahydrofuran. Diethyl ether was also an equally good solvent while 1,4-dioxane was found to retard the catalytic activity. In contrast to lithium aluminium hydride reduced systems, sodium borohydride reduced systems were poisoned by the use of tetrahydrofuran (maximum conversion was about 35% without any solvent).

The study on the effect of [catalyst] on the hydrogenation of benzene shows that, up to 3 millimoles of the transition metal complex (based on the transition metal) for 250 millimoles of the substrate in 50 ml of tetrahydrofuran, the increase in [catalyst] resulted in a corresponding increase in the activity. Beyond 3 millimoles, the effect was less appreciable. According to an explanation given by Heinemann for a similar observation, an aggregation of the metal complex occurs at higher [catalyst] to give catalytically inactive and insoluble polymeric complexes of low surface area[22].

The cold pressure of hydrogen did not have much influence on the catalytic activity above 40 kgf/cm^2 gauge. The incomplete hydrogenation of the substrate at lower pressures was due to the insufficiency of hydrogen contained in the autoclave. The autoclave was not refilled during the hydrogenation in these experiments. The difference between the catalytic activities at one atmosphere and 100 kgf/cm^2 gauge pressures at room temperature (8 and 16% hydrogenation respectively) may be explained in terms of the increased solubility of hydrogen in the solvent at higher pressures.

The degree of hydrogenation increased with the temperature of the system and reached 99% at 100° and 125° with the Ni-based and the Co-based system respectively.

Among the additives used water, methanol, ethanol, actone and phenol did not affect the system while pyridine, aniline, acetic acid and nitrobenzene acted as poisons in the increasing order of activity. There was no hydrogenation when thiophenol, carbon tetrachloride and chloroform were added to the system. These observations were made with both Co-based and Ni-based systems in tetrahydrofuran, the concentration of the additives being 10 mmoles per 250 mmoles of benzene.

The results in Table 3 show that both the Co-based and Ni-based systems are active towards hydrogenation of toluene, xylene and naphthalene also. If sufficient time is allowed, decalin may be obtained from naphthalene in high yield.

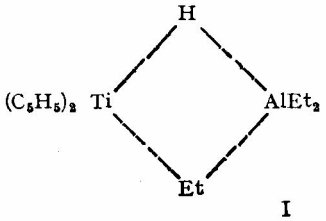
The catalyst systems reduced by lithium aluminium hydride initially contained a black solution and some unreacted lithium aluminium hydride. This solution remained as such under hydrogen atmosphere or on reactions with pure dry hydrogen at room temperature and one atmosphure pressure and also when a very high excess of lithium aluminium hydride was used in the autoclave. But with the normal amounts of the reducing agent, the product from the autoclave reactions invariably contained a clear solution together with a black precipitate. These observations are explainable on the basis of the following reaction scheme:

$$MX_n + LiAlH_4 \rightarrow \underset{\text{in solution}}{[\text{Active Species}]}$$

$$\underset{\text{in solution}}{[\text{Active Species}]} + H_2O \rightleftharpoons \text{Black precipitate}$$

The precipitate was formed by the presence of water and oxygen in the hydrogen used in the autoclave without purification. When large amounts of lithium aluminium hydride were used, the precipitation of the active species was prevented. Moreover, the resultant mixture from the anhydrous bis(acetylacetonato)nickel (II) lithium aluminium hydride contained a black solution with a precipitate and that the black solution yielded a further crop of precipitate on addition of water or exposure to air. All these happened in the absence of large excess of lithium aluminium hydride and thus lend support to the scheme given above.

The infrared spectrum of the precipitate did not show any transition metal-hydrogen terminal bond. The presence of a broad band around 800 cm^{-1} may be attributed to a bonding hydrogen between two or more metal atoms[23,24]. On the basis of this assumption, the absence of this absorption on exposure of the precipitate to atmosphere for a long time is attributable to the slow decomposition of such a bond.



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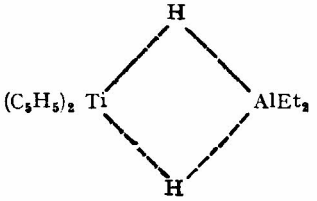

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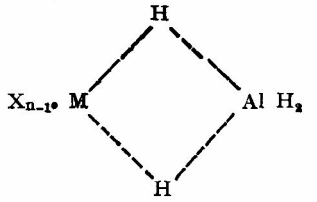

III

where M = transition metal and X = ligands

On the basis of these observations and also the recent literature report of the complexes (I) and (II) as the active species in the system bis(cyclopentadienyl) titaniumdichloride-triethylaluminium[25], the structure (III) may be suggested for the active species in the systems reported in this paper.

It is most likely that the transition metal is in a low valent state which favours the formation of a transition metal-hydrogen bond.

It is of interest to recall that Henrici-Olivé and Olivé have suggested a similar structure for the complex obtained by the reaction of lithium aluminium hydride with the dimeric complex $[(C_5H_5)_2(TiCl)_2]$ in tetrahydrofuran solvent[26].

The complete poisoning of the catalyst system by carbon tetrachloride and chloroform may be explained on the basis of the destruction of the transition metal-hydrogen linkage by the chlorinated hydrocarbons. The poisoning influence of thiophenol may be attributed to the blocking of the available coordination site by thiophenol since sulphur compounds strongly bond to the transition metals. The effect of other additives may be explained as a result of the formation of less active complexes by these additives. However, phenol did not poison these catalyst systems.

The catalyst systems reported in this paper compare favourably with the conventional heterogeneous catalysts like Raney nickel and are also similar in activity to the Ziegler-Natta catalysts reported by Lapporte[8] and by Lipovich *et al.*[10]. But the difficulty in handling the aluminium alkyls used in the Ziegler-Natta catalysts is absent in the present systems where lithium aluminium hydride and sodium borohydride are used instead. The catalyst systems are easily prepared and may be regenerated for further use. The catalyst systems without solvent possess good industrial prospects since these obviate one of the greatest disadvantages of the transition metal complex catalyst systems, namely the separation of the product.

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