Tetrahedron Letters No. 29, pp 2531 - 2534, 1977. Pergamon Press. Printed in Great Britain.

HYDROGENATION OF AROMATICS WITH SALICYLALDEHYDE COMPLEXES AS CATALYSTS

Pradyot Patnaik and Samir Sarkar[\$]
Department of Chemical Engineering,
Indian Institute of Technology, Bombay -400 076,
India.

(Received in UK 13 May 1977; accepted for publication 2 June 1977)

The salicylaldehyde complexes of copper and nickel are known[1,2] to absorb hydrogen in solution. The catalytic activity of cuprous chelate in quinoline in the homogeneous hydrogenation of quinone was discovered by Calvin[3] in 1938. However, these chelates have not been reported to be active in the hydrogenation of aromatic rings. In our search for coordination catalysts for aromatic ring saturation by hydrogenation we found some salicylaldehyde complexes as active catalysts. These catalysts are of two groups, viz. (i) the complexes without any combination with a reductant and (ii) those in combination with a reductant such as lithium aluminium hydride (LAH). The first group consists of (1) Bis-(salicylaldehydato)cobalt(II)dihydrate (abbreviated, Cosal) and (2) Bis(Salicylaldehydato)nickel(II) dihydrate (abbreviated , Nisal) whereas the second group consists of (3) Cosal-LAH, (4) Nisal-LAH and (5) Bis(salicylaldehydato)copper(II) (abbreviated, Cusal)- LAH. The catalyst systems constituting the second group are more active than the other. The activity of the second group is comparable to that of the acetylacetonate complexes reduced by trialkyl aluminium[4] or LAH[5] and also of acetylacetone-ethylenediimino complexes reduced by LAH[6].

The complexes were prepared by the method of Tyson and Adams[7]. The hydrogenation experiments were carried out in a horizontal rotary autoclave of 500 ml capacity. Neither the complexes nor their combination with lithium aluminium hydride were soluble in the substrates used. However, a solvent like tetrahydrofuran or dioxan dissolved both the catalyst systems. After the reaction was over a black precipitate was always found, from which the liquid was filtered off and the substrate analysed. The precipitate could be reused several times with pronounced activity.

The catalysts hydrogenated benzene, toluene and xylenes into the corresponding naphthenes; the activity decreased with the degree of substitution in the ring, for example, conversion was 95 %, 44 % and 15 % with benzene, toluene and xylenes, respectively, under identical conditions.

Table 1 : Activity of Catalysts
(Substrate : 500 mmole of benzene ; temperature : 204°C ;
cold H_2 pressure : 60 kgf/cm^2 ; 1st group catalysts : 3 mmole ;
2nd group catalysts : 2 mmole of complexes and metal to Al ratio : 1:5)

Catalyst	Time[8], min	Conversion, % saturate (v/v)
Cosal	90	61
Nisal	90	95
Cosal - LAH	30	96
Nisal - LAH	30	96
Cusal - LAH	90	95

Cusal is inactive without combination with LAH.

Table 2 : Effect of Temperature
(Substrate : 500 mmole of benzene ; cold H_2 pressure : 60 kgf/cm^2 ;
catalyst : 3 mmole).

Catalyst	Temperature, °C	Time, min	Conversion, % saturate (v/v)
Nisal	235	15	97.5
	203	90	97.0
	186	90	42.0
	172	90	28.0
Cosal	235	90	95.0
	203	90	61.0
	186	90	14.0

Table 3 : Effect of Catalyst Concentration
(Substrate: 500 mmole benzene ; catalyst: Cosal-LAH; temp.: 200°C ;
cold H_2 pressure : 60 kgf/cm^2; metal to Al ratio in catalyst : 1:8)

Cosal, mmole	Time, min	Conversion, % saturate (v/v)
1.00	30	98
0.66	65	100
0.50	130	97
0.33	140	95

Table 1 shows the activity of the salicylaldehyde complexes of cobalt, nickel and copper with and without LAH, using benzene as the substrate. Tables 2 to 4 illustrate the effect of temperature, catalyst concentration and the transition metal to aluminium atomic ratio on the activity of the catalysts. Pronounced catalyst activity was noted under the following conditions: Temperature = 200°C and above ; Catalyst concentration (per 500 mmole substrate)=3 mmole of chelate in the case of 1st group catalysts and 1-2 mmoles of chelate in the case of 2nd group catalysts; Metal to aluminium ratio = 1:4 and less. Pressure has no special role beyond what is required by the stoichiometry, the temperature and volume of the reaction system and the convenience of carrying out the reaction without refilling the reactor with hydrogen. A cold H_2 pressure of 60kgf/cm^2 was convenient in a half-litre autoclave.

Table 4 : Effect of Metal to Aluminium Ratio
(Catalyst : Nisal-LAH ; substrate : 500mmole benzene ;
temperature : 204 °C ; cold H_2 pressure : 60 kgf/cm^2)

Ni:Al atomic ratio	Time, min	Conversion, % saturate (v/v)
1:1	90	88
1:2	90	96
1:3	35	98
1:4	30	98
1:5	25	96
1:6	20	98
1:7	20	97

A few other factors affecting the catalytic activity are the method of preparation, the nature of solvent, the presence of impurities, etc. In the absence of a solvent, the chelates were active both with and without LAH. However when a solvent (tetrahydrofuran or dioxan) was used only the systems containing LAH were active.

The mechanism of the catalytic hydrogenation reported here is not clearly understood. It appears to be different with the two different groups of catalysts.

In the presence of a reductant (2nd group catalyst), it is proposed that a transition metal hydride species is formed as a reaction intermediate by the reduction of the complex with lithium aluminium hydride. Depending upon the presence or absence of a solvent, it could be a case of homogeneous catalysis or " heterogenised" homogeneous catalysis with LAH behaving as both reductant and support. When no reductant is used (1st group catalyst), the system appears to be heterogeneous in nature. Concrete evidence is lacking for this entire hypothesis.

REFERENCES AND NOTES

1. G.N. Tyson, Jr., and R.E. Vivian , J.Am.Chem.Soc., 63, 1403-5 (1941).
2. M.A. Fobes and G.N. Tyson, Jr., J.Am.Chem.Soc., 63, 3530 (1941).
3. M. Calvin, Trans.Farad.Soc., 34, 1181-91 (1938).
4. S.J. Lapporte and W.R. Schuett , J.Org.Chem., 28, 1947 (1963).
5. N.Murugesan and S. Sarkar, J. Catal., 31, 469 (1973).
6. P. Patnaik and S. Sarkar, Paper presented at the IInd National Symbosium on Catalysis, IIT Kharagpur, India, Dec.1975.
7. G.N. Tyson, Jr., and S.C. Adams , J.Am.Chem.Soc., 62, 1228 (1940).
8. It is the time noted from the attainment of the required temperature till there was no pressure drop in the autoclave or 90 minutes after the attainment of the reaction temperature, whichever was shorter.
9. W.R. Kroll, J.Catal., 15, 281 (1969).
10. N. Murugesan and S. Sarkar, Indian J.Chem., 14(A), 107-11, 1976.