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Preliminary communication

CATALYTIC ACTIVITY OF "SOLVATED" RHODIUM ATOMS IN THE HYDROGENATION OF OLEFINIC AND AROMATIC COMPOUNDS UNDER MILD CONDITIONS

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Summary

Co-condensation of rhodium vapours and toluene at liquid nitrogen temperature followed by warming to about −50°C gives a red-brown solution which is a good catalyst for the hydrogenation of olefins and aromatics under mild conditions.

One of the most significant recent developments in the field of metal vapour synthesis is the preparation of "solvated" metal atoms and their application in catalysis [1]. The method consists of co-condensing metal vapours with various organic solvents (toluene, tetrahydrofuran, alkanes, etc.), usually at liquid nitrogen temperature, to obtain on melting weakly stabilized compounds which are of potential interest as new catalysts [2].

We have found that the co-condensation products from Rh atoms and toluene on warming up give a red-brown solution which can be conveniently used for the catalytic hydrogenation of olefinic and aromatic compounds under very mild conditions. Hex-1-ene, styrene and toluene were used as substrates (see Scheme 1).

In a typical experiment rhodium vapour (40—50 mg), obtained by resistive heating of tungsten filaments surface coated with electrodeposited rhodium, was co-condensed with toluene (40 ml) at liquid nitrogen temperature during 20—30 min in a conventional metal-atom reactor [3] to give a red-brown matrix. This was warmed to about −70°C and the resulting homogeneous solution siphoned out in a Schlenk tube and handled at low temperature (< −50°C). After the addition of the olefin (10 ml) the mixture was allowed to warm slowly to room temperature under hydrogen at atmospheric pressure.

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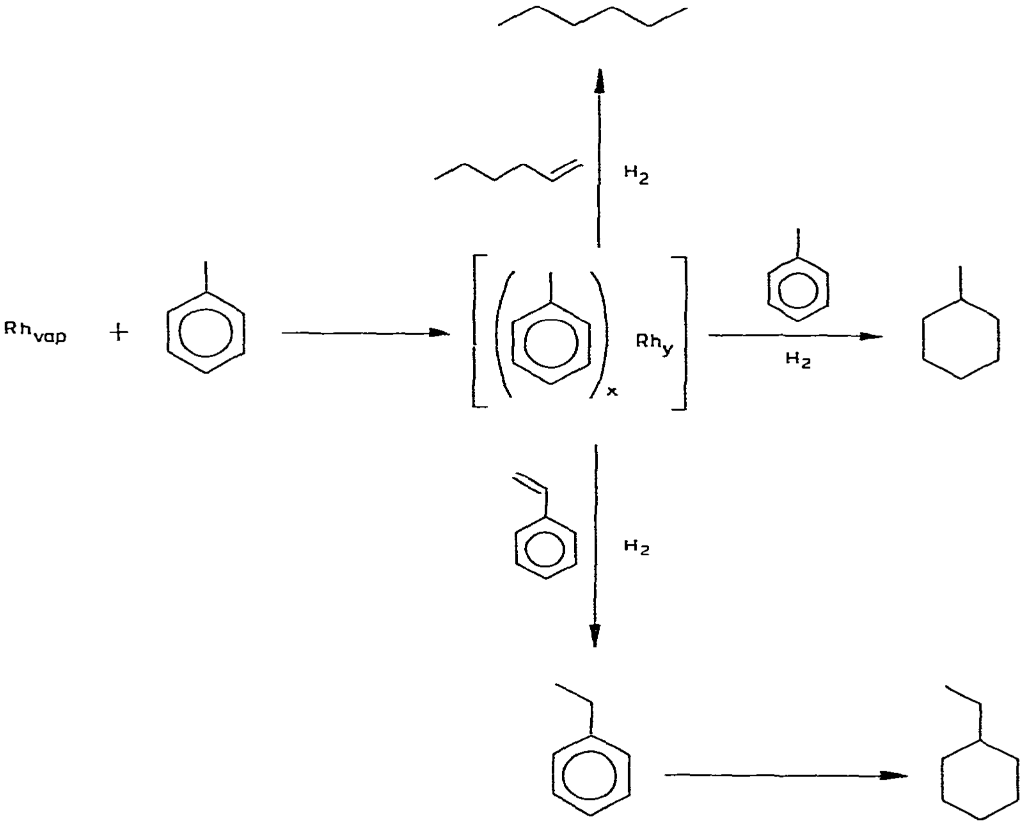

SCHEME 1. Hydrogenations with toluene solvated Rh atoms; room temperature, 1 atm of H_2, toluene as solvent.

Hex-1-ene hydrogenation proceeds readily under these conditions, with a H_2 uptake of $\simeq 4$ cm^3 min^{-1}. When all olefin has reacted, a brown precipitate is formed, the solution becomes colourless, and hydrogenation of toluene to give methylcyclohexane takes place with a H_2 uptake of $\simeq 1$ cm^3 min^{-1}. In experiments performed without adding olefin, toluene was fully hydrogenated in the heterogeneous phase to methylcyclohexane with this same H_2 uptake of $\simeq 1$ cm^3 min^{-1}. In no case were methylcyclohexenes or methylcyclohexadienes detected among the products even when the reaction had not gone to completion. When the olefinic double bond and the aromatic ring are present in the same molecule as in styrene, the double bond is selectively hydrogenated in the homogeneous phase to give ethylbenzene, with a H_2 uptake rate comparable with that observed for hex-1-ene, the solution remaining red-brown; then hydrogenation of both ethylbenzene and toluene takes place, after formation of the brown precipitate, to give the corresponding substituted cycloalkanes. The precipitate has been isolated and has been found to be active by itself as heterogeneous catalyst for the hydrogenation of aromatic compounds at room temperature and atmospheric pressure.

Some comments can be made about the nature of the catalytic species involved in the above hydrogenations. Several transition metals have been recently reported to produce in co-deposition reactions with toluene highly labile π-arene complexes possessing at least one strongly bound η^6-toluene and at least one weakly bound solvating toluene molecule [4]. Similar species are probably formed in the reaction of Rh vapours with toluene, and may act as active homogeneous catalyst or catalytic precursor in the hydrogenation of olefins.

The brown precipitate which is formed under hydrogen in the absence of olefins or when all the olefin has reacted, is the effective catalyst in the hydrogenation of aromatics. Its extreme reactivity makes definite characterization difficult; but elemental analysis, indicates the presence of significant amounts of carbon and hydrogen ($\simeq$ 12 and 4% respectively) suggesting the formation of metal cluster species containing organics, as found for toluene-solvated nickel atoms [5]. It seems that the presence of olefin prevents the cluster formation so preserving the soluble π-toluene complex which is the selective catalyst for the homogeneous hydrogenation of the olefin.

It is also noteworthy that although metallic Rh on carbon or alumina is known to be an efficient catalyst for the hydrogenation of aromatics [6], the possibility of obtaining Rh cluster species is of interest for preparing very active heterogeneous catalytic systems which have a higher surface area and a greater proportion of the rhodium in the catalytically active low valent state than is the case in the conventional systems [7].

Preliminary work shows that the Rh-toluene solution is a very versatile catalytic precursor: selective hydroformylation of olefins, for example, can be performed with high yields under mild conditions, such as room temperature and fairly low pressures of H_2/CO (20—60 atm).

These results indicate the considerable potential of solvated metal atoms, which, when subjected to controlled melting, can give catalytic systems whose efficacy and versatility can rival that of some of the best conventional catalysts.

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