

CATALYTIC HYDROGENATION OF OLEFINS, ACETYLENES AND ARENES BY RHODIUM
TRICHLORIDE AND ALIQUAT-336 UNDER PHASE TRANSFER CONDITIONS

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The ion pair formed from aqueous rhodium trichloride and aliquat-336 in dichloroethane catalyzes hydrogenation of a variety of unsaturated compounds. Aromatics are reduced to cyclohexane derivatives under exceedingly mild conditions.

In a previous study¹ we have shown that the solvated ion pair $[(C_8H_{17})_3NCH_3]^+ [RhCl_4]^-$ formed from rhodium trichloride and methyltrioctylammonium chloride (Aliquat-336) is an excellent isomerization catalyst and can be recycled in many successive runs.

We now find this catalyst able to promote also hydrogenation of a variety of unsaturated compounds, including aromatics, at room temperature and under atmospheric pressure. Since many of the current arene hydrogenation catalysts require high pressure and temperature, and those which operate under less severe conditions often give irreproducible results,^{2,3} the present system is of considerable practical value. The only homogeneous catalysts reported, so far, to promote selective arene hydrogenation under such mild conditions are $\eta^3-C_2H_5Co[P(OCH_3)_3]_3$ and some analogous phosphine and phosphite complexes. Unfortunately the lifetimes of these catalysts are very short⁴. [See, however, reference 5].

Olefins and acetylenes were hydrogenated at atmospheric hydrogen pressure by injection of 1 mmol of the substrate into a mixture of 0.02 mmol of $RhCl_3 \cdot 3H_2O$ in 1 ml of water and 0.025 mmol of Aliquat-336 in 0.5 ml of 1,2-dichloroethane (pretreated for 20 min with 1 atm. H_2 at 30 °C). Typical initial reduction rates of 0.148, 0.140, 0.080, 0.071 and 4.8×10^{-4} mmol ml⁻¹ min⁻¹ were recorded for 1-tetradecene, cyclohexene, cyclooctene and diphenylacetylene, respectively. The conversion of the olefins was usually quantitative after 20-30 min. In the absence of the quaternary ammonium salt metallic rhodium separated within 5 min and considerably lower rates were observed. Deuterium labeling experiments indicated that the water hydrogen atoms are not incorporated in the saturated products. However, the presence of water is essential: a dried dichloroethane solution of $[(C_8H_{17})_3NCH_3]^+ [RhCl_4]^-$ was found completely inactive. The pretreatment of the catalyst with H_2 assured immediate hydrogen uptake on addition of the substrate. Otherwise the process was preceded by a long induction period.

The maximum rate of toluene hydrogenation was 3×10^{-3} mmol ml⁻¹ min⁻¹. Almost identical rates were recorded for the other arenes listed in Table I except for those having unsaturated

Table I. Hydrogenation of Arenes Catalyzed by RhCl_3 -Aliquat-336 under Comparable Conditions.^a

Substrate	Conversion, % ^b	Products (yield, % ^b)
Benzene	51	cyclohexane (100)
Toluene	16	methylcyclohexane (100)
Ethylbenzene	13	ethylcyclohexane (100)
<i>p</i> -Xylene	38	<i>cis</i> -1,4-dimethylcyclohexane (68), <i>trans</i> -1,4-dimethylcyclohexane (32)
Styrene	100	ethylbenzene (94), ethylcyclohexane (6)
Diphenylacetylene	19	<i>cis</i> -stilbene (78), <i>trans</i> -stilbene (22)
Naphthalene	34	tetralin (99), <i>cis</i> -decalin (1)
Fluorobenzene	72	fluorocyclohexane (39) ^c , cyclohexane (59), cyclohexene (2)
Chlorobenzene	74	benzene (22), cyclohexane (78)
Phenol	56	cyclohexanol (27), cyclohexanone (67), cyclohexane (6)
Thiophenol	27	benzene (69), cyclohexane (28), cyclohexene (3)
<i>N,N</i> -Dimethylaniline	71	<i>N,N</i> -dimethylcyclohexylamine (100)
Anisole	55	methoxycyclohexane (92)
Acetophenone	87	methylcyclohexyl ketone (43), 1-cyclohexylethanol (43), 1-phenylethanol (14)
Methyl benzoate	70	methyl hexahydrobenzoate (89), cyclohexylmethanol (10), benzyl alcohol (1)

^a Reaction conditions: a mixture of 5.7×10^{-2} mmol $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 1 ml H_2O , 6.1×10^{-2} mmol Aliquat-336 in $(\text{CH}_2\text{Cl})_2$ and 1 mmol substrate was vigorously stirred for 5 h under 1 atm. H_2 at 30 ± 0.5 °C. ^b Determined by GC analysis. ^c The relative yield of fluorocyclohexane increased considerably by lowering the reaction temperature.

side chains. Thus, it can be concluded that the electronic nature of the substrate affects the duration of the induction period rather than the reaction rate. However, the rate was shown to be sensitive to steric effects. Durene e.g., consumed only 4% of the theoretical amount of hydrogen after 22 h. The hydrogenation of hexamethylbenzene was even slower.

Table I indicates that alkylbenzenes, *N,N*-dimethylaniline and anisole form exclusively fully hydrogenated cyclohexanes. Two cyclohexene derivatives were, however, formed from the heavily substituted durene.

Aromatic ketones and esters yielded phenyl- and cyclohexyl-carbinols in addition to the cyclohexyl carbonyl compounds. The isolation of benzene from thiophenol and chlorobenzene suggests hydrogenolysis of the Cl and SH groups prior to ring hydrogenation.

Fluorobenzene gave fluorocyclohexane which proved to decompose slowly into cyclohexene and HF at the reaction temperature.⁶ The formation of cyclohexanone from phenol can be explained by tautomerization of the cyclohexenol intermediate.

Although acetylenes were shown to be reduced much more slowly than olefins, phenylacetylene was neither converted directly into ethylbenzene nor formed any cyclohexane derivative. The primary product, styrene, was further reduced only after complete consumption of the acetylene, and ring hydrogenation of the ethylbenzene did not begin as long as any olefin was present. This and similar experiments suggest that each of the unsaturated compounds is hydrogenated via a different organometallic intermediate and eventually the acetylene and olefin complexes interfere with the reductions of the less unsaturated compounds. This assumption was supported by competitive experiments in which styrene was added to a reacting system of toluene and hydrogen. The ring hydrogenation stopped and rapid reduction of the styrene began. Upon addition of phenylacetylene to this mixture the formation of ethylbenzene discontinued and slow reduction of the triple bond started. Hydrogenation of the styrene resumed when all the acetylene was consumed and toluene reduction started again when no more styrene was present. When the concentration of toluene and ethylbenzene became equal it was expected that both arenes will react at a similar rate. In fact, the toluene was reduced 44 times faster. This observation indicates the existence of different mechanisms for hydrogenation of arenes in the presence and absence of olefins.

Thus, it can also be concluded that the reversible coordination and activation of the unsaturated substrate precedes the interaction with hydrogen (which is apparently the rate determining step). The order of stability for the various rhodium-substrate complexes must, therefore, be Rh-acetylene > Rh-olefin > Rh-arene.

A clear preference for *cis*-hydrogenation was observed. As shown in Table I diphenylacetylene and *p*-xylene gave *cis*-stilbene and *cis*-1,4-dimethylcyclohexane, respectively, as the major hydrogenation products. Tetralin formed at 40% conversion over 90% of *cis*-decalin.

During olefin and acetylene reduction both liquid phases were perfectly homogeneous throughout the entire process. However, when arenes were hydrogenated *small* quantities of black solid particles precipitated during the first 50 min of the process.⁷ With the aid of an internal filter device (glass coated teflon or a micropore filter) the solids, which showed hardly any catalytic power, could be removed and the remaining dark filtrate was highly active. Two methods were applied to prove the homogeneity of the system: (i) Maitlis' test for detection of heterogeneous components⁸, (ii) light scattering experiments of laser beams (using a Spectrophysics Model 112A He-Ne laser and an EG & G 550-1 radiometer).

Finally we found that arene hydrogenation on a preparative scale is best carried out under slightly positive pressure. The respective cyclohexane derivatives were obtained in 90-95% yield when a mixture of 10 g of the aromatic substrate, 0.2 g of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 0.44 g of Aliquat-336, 10 ml of water and 10 ml of dichloroethane was shaken under 2 atm. H_2 for 20 h at room temperature in a Paar hydrogenation apparatus. The catalyst system could be used in numerous runs provided the products were removed by distillation under reduced pressure and the new batches of substrate injected into the reaction vessel without exposure to air.

Acknowledgements. We thank Professor Muetterties and Professor Maitlis for useful discussions and the United States-Israel Science Foundation (BSF) for financial support.

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(Received in UK 14 June 1983)