

FACILE HETEROGENEOUS CATALYTIC HYDROGENATION OF BENZENE AND CYCLOHEXENE

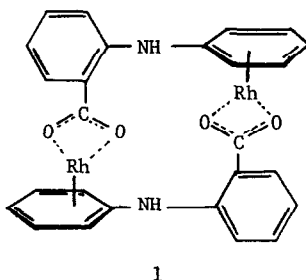
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The DMF-soluble rhodium (I) complex of N-phenylanthranilic acid (1) is a remarkably active hydrogenation catalyst. It readily converts benzene to cyclohexane at room temperature and 1 atm of hydrogen.¹ The only other homogeneous catalyst displaying similar activity is $n^3\text{-C}_3\text{H}_5\text{Co[P(OCH}_3)_3]_3$, but this catalyst is considerably more difficult to prepare and has an



additional disadvantage in that it is more air sensitive.² However, because of the difficulties of catalyst recovery and product contamination, the N-phenylanthranilic acid catalyst is not particularly attractive to industry; these problems suggested attachment to a polymer.³

The methyl ester of N-phenylanthranilic acid was prepared in refluxing methanol and sulfuric acid. An excess of the ester was then stirred with chloromethylated polystyrene beads (Rohm and Haas XAD-4 Amberlite, chloromethylated with chloromethyl methyl ether, 10.02% chlorine). A mildly exothermic reaction occurred immediately, but the mixture was stirred for three days to ensure complete incorporation. The protecting methyl group was removed by refluxing the beads for three hours in 10% aqueous sodium hydroxide. After washing thoroughly with water, the beads were stirred with an excess of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in absolute ethanol and an excess of sodium borohydride was added. There was an immediate change of color of the beads to black; after washing the beads thoroughly with ethanol they were air-dried for a few minutes. Adding 0.300g of the beads prepared in this fashion to 20 ml of cyclohexene and hydrogenation

at 30-50 psi resulted in no detectable cyclohexane formation after 8 hours.

In view of this failure we decided to change the ligand incorporated into the beads. It seemed attractive to choose a ligand that would retain the same functionalities present in N-phenylanthranilic acid; thus, the parent compound, anthranilic acid, was selected.

To 0.2383g (0.67×10^{-3} g-atom Cl) of the chloromethylated beads suspended in 10 ml of ether was added 0.3081g (2.25×10^{-3} mol) of anthranilic acid. The mixture was stirred for two days. After tritulating the beads thoroughly with absolute ethanol, 0.3000g (1.92×10^{-3} mol) of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 5 ml of absolute ethanol was added and the beads were stirred for 24 h. Sodium carbonate, 0.1g, was added and the mixture stirred for 30 minutes. The beads were thoroughly washed with ethanol, then suspended in 5 ml of ethanol and 0.10g (2.5×10^{-3} mol) of sodium borohydride was added; the beads immediately turned black. After 0.5 hr. the beads were washed with ethanol and air-dried for twenty min., yield 0.2635g (Anal. N-0.4%, 7.5×10^{-5} g-atom; Rh-5.15%, 1.3×10^{-4} g-atom).

To a pressure bottle was added 0.2201g of the prepared beads and 20 ml of cyclohexene. Upon hydrogenation for 8 h at room temperature and 30 psig, gas chromatographic analysis indicated a 40% conversion to cyclohexane. This represented approximately 540 catalytic cycles per rhodium atom. Starting with 6.00 g of catalyst, 20 ml of benzene, and 50 psig hydrogen, the conversion to cyclohexane was > 99% complete after 18 h. The rate of benzene hydrogenation is comparable to the most active previously known heterogeneous catalysts.⁴

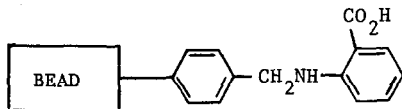
ESCA analysis of the catalyst revealed the presence of C, Cl, Na, O, and Rh. Narrow scan analysis of the Rh(3d) lines showed a broad spectrum peaking at 308 eV and a shoulder at 312 eV. It would be inappropriate at this time to make specific assignments concerning the environment of the rhodium, but the ESCA studies do demonstrate that the oxidation state of the metal is +1. The binding energies are in agreement with those for the $3d_{5/2}$ (308 eV) and the $3d_{3/2}$ (312 eV) lines observed in several other Rh(I) complexes.⁵

The hydrogenation of cyclohexene is largely independent of solvent effect; this was shown for 20% cyclohexene solutions in the solvents listed in the Table.

Table. Relative Rate of Hydrogenation as a Function of Solvent

<u>Solvent</u>	<u>Relative Rate</u>
acetonitrile	1.8
dimethylformamide	1.5
ethyl ether	1.0
cyclohexane	1.0

We were interested in investigating models of this catalyst that did not involve incorporation on the beads. From a microscopic viewpoint, the complex most closely approximating the structure on the beads would be the catalyst derived from N-benzylanthranilic acid.



Treating N-benzylanthranilic acid with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, followed by reduction with sodium borohydride, resulted in a black microcrystalline powder that was insoluble in DMF - quite unlike the catalyst prepared from N-phenylanthranilic acid. Furthermore, after 8 h at 20-50 psig hydrogen there was no trace of benzene hydrogenation, and at the same conditions just a trace of cyclohexane was evidenced from cyclohexene. Apparently the catalyst reversibly accepts hydrogen because bubbles are observed to emerge from the catalyst upon release of the pressure. By repressurizing and releasing, this process could be repeated. It is not entirely surprising that this material did not display attractive catalytic behavior since the activities of supported catalysts often differ from non-supported analoges.⁶

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