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# HOMOGENEOUS CATALYTIC HYDROGENATION AND EXCHANGE OF STYRENES WITH TRIS(TRIPHENYLPHOSPHINE)CHLORORHODIUM (I)

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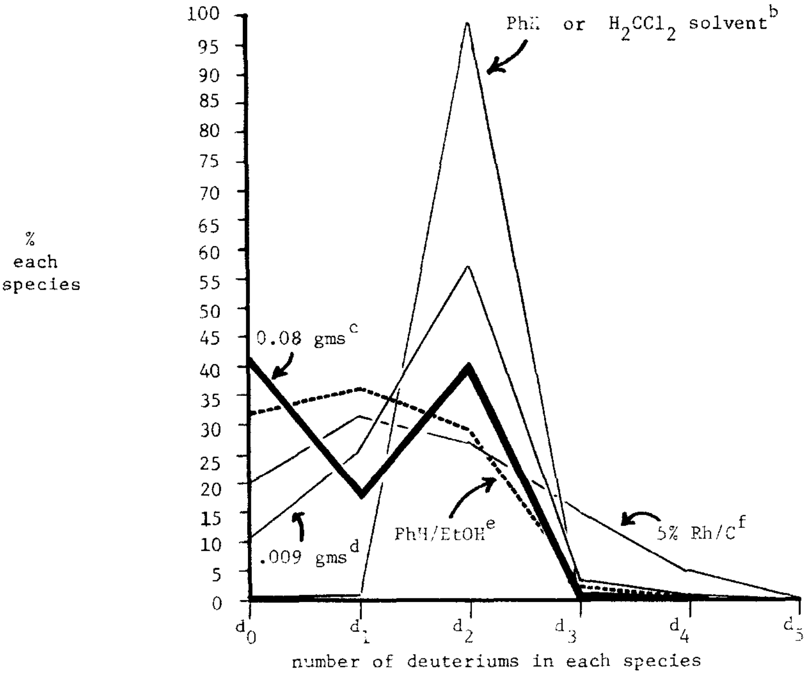
Tris(triphenylphosphine)chlororhodium (I) is a well demonstrated catalyst for the hydrogenation of certain olefins (1,2,3,4). Original evidence suggests essentially simultaneous cis addition of two hydrogens (deuteriums) across the double bond (1a, b, 2a, b) but other work seems to indicate stepwise addition (5,6). Recent careful hydrogenations support the latter view (7,8). We wish to disclose evidence that both mechanisms may be correct but two different competing catalyst systems are operating.

We have previously studied the hydrogenation and exchange of certain α,β-unsaturated compounds over metal surfaces (9) and are now comparing the results with the same reactions catalyzed by homogeneous metal complexes. Partial deuteriogenation of styrene in chloroform yields a novel product distribution, Figure 1, apparently due to 1) an olefin exchange-addition reaction leading to exchanged styrene and light ethylbenzene and 2) a straight addition reaction leading to 1,2-dideuteroethylbenzene. We thought this might reflect chloroform exchange and, indeed, using benzene as the solvent changes the results to give virtually pure 1,2-dideuteroethylbenzene; however, deuterochloroform solvent produces results identical to those obtained with light chloroform, benzene/ethanol gives similar results and methylene-chloride gives only $d_2$. The possibility of rhodium metal precipitating and heterogeneously catalyzing the exchange was excluded by adding small quantities of thiophene or mercury as poisons. Although thiophene does not completely poison rhodium metal, the exchange pattern in ethylbenzene is identical to that from unpoisoned rhodium and distinctly different from the homogeneous rhodium catalyst. Hg kills all catalytic properties of rhodium metal. Pentafluorostyrene and para-methoxystyrene yield still different results and demonstrate that a solvent effect is not the exclusive variable.

We propose that the unique exchange pattern of ethylbenzene coupled with the solvent and substituent effects signal the presence of more than one catalyst system. One catalyst

DISTRIBUTION OF ETHYLBENZENES OBTAINED FROM DEUTERIOGENATION OF STYRENE WITH $(Ph_3P)_3RhCl$[a]



a) Experiments performed at atmospheric pressure in standard hydrogenation apparatus[9]; substrate (1 ml), catalyst (0.08 gm) and solvent (4 ml) added first except as mentioned elsewhere. Reactions were run to 8-12% reduction.

b) Nearly pure 1,2-dideuteroethylbenzene forms in both benzene and methylenechloride and no styrene exchange occurs. If, however, the catalyst, chloroform and $D_2$ are shaken for 24 hrs. and the chloroform is replaced with benzene, then styrene exchange is extensive at 11.3% reduction and the ethylbenzene exchange pattern is similar to that in chloroform, i.e. $d_0$ is 22.1%, $d_1$ is 36.0%, $d_2$ is 39.3%, $d_3$ is 2.34% and $d_4$ is 0.21% (compare to curves c, d and f). Slightly more 1,2-dideutero products are formed in methylenechloride and the reactions are much faster.

c) The thickness of this line is the maximum variation from three separate experiments using 0.08 gms of catalyst from three sources, Strem Chemical, K.C. Dewhirst[10] and a fresh preparation in this laboratory. The Strem catalyst was used in the other experiments except for curve e in which the fresh catalyst was also used.

d) Catalyst concentration was lowered to 0.009 gms.

e) 3 ml of benzene and 1 ml of ethanol mixture was the solvent[7]; the line represents two experiments using the Strem catalyst and the fresh preparation to give identical results.

f) The heterogeneous catalyst (rhodium-on-charcoal donated by Engelhard Industries) gives a typical pattern characterized by high $d_3$ and $d_4$.

system accomplishes the addition of two deuteriums only (1,2); the other(s) causes deuteriums to add reversibly with exchange (6,7). Certain olefins complex in one catalyst system only, but others may complex in both, and solvent and substituent effects influence the extent to which each catalyst system is favored. Increasing catalyst concentration decreases $d_2$ and increases $d_0$ suggesting formation of a dimer as the exchange catalyst. The dimer forms under such conditions (1); however, our preparation of it was only slightly catalytically active. That some equilibrium is involved is shown by mixing the catalyst, $D_2$ and $HCCl_3$ and shaking for one hour before adding styrene. The resulting ethylbenzene is richer in $d_0$ and poorer in $d_2$ suggesting loss of the catalytically active monomer and enrichment in the exchange catalyst system.

The contrast between these results and the heterogeneous results (9) demonstrates the need for caution in transferring information from one system to another. We are continuing to use these model compounds to identify and investigate the differences and similarities between homogeneous and heterogeneous catalytic hydrogenation.

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