Homogeneous Olefin Hydrogenation over Oxidized Rhodium Complexes

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Summary Hydrogenation of the previously reported oxides obtained from oxidation of [Rh(Ph_3P)Cl] in ethanol and benzene gives materials capable of olefin hydrogenation but double-bond isomerization occurs during the reaction: hydrogenation of these species in the presence of Ph_3P gives catalysts which are not only much more active toward olefin hydrogenation but also inhibit isomerization.

IN previous work it was found that oxygen was involved in the double bond isomerization frequently observed during olefin hydrogenations over tris(triphenylphosphine)-chlororhodium [Rh(Ph_3P)Cl] (**1**).[1] It was further shown that (**1**) was oxidized readily in solution but that the product obtained was markedly dependent on the solvent in which the oxidation was run.[2] Since it was felt that these oxidized species, or something very similar to them, were involved in the olefin isomerization process, these species were investigated as potential hydrogenation catalysts.

The material obtained from the oxidation of (**1**) in ethanol[2] was hydrogenated in a benzene–ethanol solution. At room temperature and atmospheric pressure five equiv. of hydrogen were taken up in 10—20 h. G.c. analysis of the reaction mixture showed the presence of small amounts of cyclohexane evidently arising from the hydrogenation of some of the benzene solvent. Evaporation of the solution gave a residue which, after washing, gave analytical data indicating a Rh : P ratio of 2 : 1. The hydrogenation of hept-1-ene over this reduced species occurred at 28° and one atmosphere at a rate of 4·7 ml/mol Rh/min. Extensive double-bond isomerization was observed during this hydrogenation.

Hydrogenation of the material obtained from the oxidation of (**1**) in benzene[2] occurred much more readily with 10—23 equiv. of hydrogen being absorbed in a relatively short time. Cyclohexane was formed in proportion to the amount of hydrogen taken up. Unfortunately, neither of these oxidized species was capable of prolonged benzene hydrogenation. Since the species finally obtained after hydrogenation do not promote this reaction, it must be assumed that an intermediate in the reduction process is responsible for the hydrogenation of the benzene.

The product obtained from the material oxidised in benzene hydrogenated hept-1-ene at a rate of only 2·2 ml/mol Rh/min, and, again, with extensive isomerization.

When the material oxidised in either ethanol or benzene solution was hydrogenated in the presence of one equiv. of triphenylphosphine 2·5 equiv. of hydrogen were taken up very quickly and the reaction stopped. No cyclohexane formation was observed. The resulting materials showed i.r. bands at 1980 and 1995 cm^{-1} respectively, an area characteristic of Rh–H absorption.[3] Similar bands were absent in the spectra of the compounds obtained from reduction in the absence of phosphine.

The most important difference between the species obtained from hydrogenations with and without added triphenylphosphine, however, was made evident when the phosphine-treated products were used to hydrogenate hept-1-ene. The rates of reaction were markedly increased (30 and 76 ml/mol Rh/min for the species oxidised in ethanol or benzene solution respectively) with no double-bond isomerization taking place.

These data serve to indicate why isomerization occurs readily during hydrogenations over (**1**) in alcoholic solutions but not in benzene or benzene–hydrocarbon solvents even in the presence of oxygen. The presence of even small amounts of ethanol in benzene will prevent the dissociation of (**1**) to give triphenylphosphine.[4] Thus, the oxidized species which is formed in this solution is further hydrogenated in the absence of phosphine and isomerization occurs. In benzene, however, phosphine is present[4] and isomerization is prevented. The reason for this inhibition of isomerization by triphenylphosphine could be electronic and/or steric by nature.

(*Received, April 1st*, 1970; *Com.* 439.)

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[1] R. L. Augustine and J. F. Van Peppen, *Chem. Comm.*, 1970, 495.

[2] R. L. Augustine and J. F. Van Peppen, *Chem. Comm.*, 1970, 497.

[3] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[4] R. L. Augustine and J. F. Van Peppen, *Chem. Comm.*, 1970, 497.