

Tritium Exchange Using Homogeneous Hydrogenation Catalysts

I. Chlorotris(triphenylphosphine)rhodium(I) As A Hydrogen-Exchange Catalyst

The complex $\text{RhCl}(\text{Ph}_3\text{P})_3$ is under active investigation as an homogeneous hydrogenation catalyst (1-4). Wilkinson and co-workers (5) were able to observe the growth and subsequent decay of an intermediate hydridic species. With one exception (1) (where 1-hexene was hydrogenated with a 1:1 H_2 - D_2 mixture and $\text{C}_6\text{H}_{13}\text{D}$ was formed along with C_6H_{14} and $\text{C}_6\text{H}_{12}\text{D}_2$, suggesting a H_2 - D_2 exchange reaction), there has been no exchange observed accompanying these hydrogenations.

We have investigated the hydrogenation of cyclohexene using H_2 - T_2 mixtures. Freshly purified (by gas-liquid chromatography) cyclohexene (0.5 ml) was added to 5 ml of a benzene solution of the complex ($10^{-3} M$) which was then degassed by two freeze-thaw cycles with pumping. A small amount (~ 40 mc) of tritium was admitted to the frozen solution, followed by hydrogen (reversal of this procedure did not effect the results). The ampoule (approximately 60 ml volume) was sealed and shaken until no further distribution of activity (as shown by subsequent analysis) took place. Experiments were carried out at 30°C , and at 60°C . A dark-brown precipitate slowly appeared. The products were analyzed on a PYE gas-liquid chromatograph connected in series with an ionization chamber.

Results are listed in Table 1. It is seen that exchange occurs along with hydrogenation. This exchange reaction has not previously been reported for this catalyst, although Cramer (6) reports similar reactions with other rhodium complexes. No exchange with benzene was observed.

Attempts to label cyclohexane by the same method were unsuccessful.

We believe that exchange was not noticed prior to this communication for two rea-

sons. Firstly no experiments have been carried out at elevated temperatures (60°C in our case), and secondly, at 30°C a five-fold increase in catalyst concentration was found to eliminate (or conceal) exchange. It can be seen from the table that relative

TABLE 1
REACTION OF CYCLOHEXENE AND HYDROGEN
IN THE PRESENCE OF
CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I)

H_2 Press. (cm Hg)	Temp. ($^\circ\text{C}$)	Mass % C_6H_{12} (molar)	% T_2 in products	% T_2 in C_6H_{10}
60	60°	89	98	7
50	60°	85	98	13
40	60°	74	99	17
30	60°	58	100	20
20	60°	44	100	24
10	60°	20	100	28
0	60°	0	100	0
60	30°	72	72	13
50	30°	56	65	12
40	30°	43	62	11
30	30°	29	58	10
20	30°	16	42	7
10	30°	4	23	7
0	30°	0	100	0

to hydrogen exchange, hydrogenation is more favored at 60°C than at 30°C . This suggests that the energy of activation for exchange is higher than for hydrogenation. Further experiments in other solvents are in hand.

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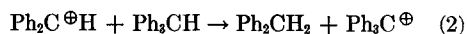
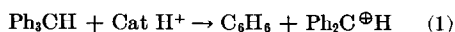
Mechanism of Triphenylcarbonium Ion Formation on the Silica-Alumina Surface

Leftin and Hall (1) noted that the triphenylcarbonium ion formed spontaneously from triphenylmethane on silica-alumina, but they were unable to ascertain unambiguously the fate of the H^- which is stoichiometrically removed in the process. However, they showed that it was not evolved as H_2 by reaction with catalyst protons, nor was it transferred to a carbonium ion formed from an olefinic impurity. Since treatment of the catalyst with H_2 at 500° had no effect on the reaction, they argued that oxidation of triphenylmethane to triphenylcarbinol was not a necessary prerequisite for carbonium ion formation. On the basis of this information, they suggested that the hydride ion was abstracted and held by the silica-alumina surface, presumably by strong Lewis acid sites which had been frequently postulated.

Recently, Hirschler (2, 3) presented evidence purporting to show that ion formation did indeed result from oxidation to triphenylcarbinol. This question was re-examined by Porter and Hall (4) who refuted this claim by demonstrating that the oxidation is photolytic; it could not have been responsible for the results of Hall and co-workers, although it might have been a factor in Hirschler's work. Since conclusive proof has been lacking, the authors maintained their respective positions in a later exchange (5, 6).

The fate of the H^- has now been ascer-

tained; the triphenylcarbonium ion results from the following Friedel-Crafts chemistry:



The pretreatments of catalyst and chemisorption procedures are detailed elsewhere (4). The procedures for qualitative and quantitative determination of benzene, diphenylmethane, and triphenylcarbinol were as follows: (1) The catalyst cell was placed on a vacuum line via a break-seal and the volatile benzene fraction was distilled into a trap at -195° . Benzene was identified by its PMR and its mass spectra. It was quantitatively determined by calibrated GLC and PMR. (2) The catalyst was transferred to a Soxhlet and extracted for several days with wet cyclohexane. The separation, identification, and quantitative determination of products were accomplished by GLC calibrated with authentic samples. The diphenylmethane fraction was purified by preparative GLC and its identity was confirmed by mass spectrography.

According to Eqs. (1) and (2), equimolar quantities of benzene, diphenylmethane, and triphenylcarbinol should be formed. The experimental results are summarized in Table 1, where this was established. The values for diphenylmethane and triphenyl-