Some Recent Developments in the Homogeneous Catalyzed Hydrogenation of Olefins

ROBERT L. AUGUSTINE and JAN F. VAN PEPPEN, Chemistry Department,
Seton Hall University, South Orange, N.J. 07079

Abstract

It has been found that the amount of double bond isomerization accompanying homogeneous olefin hydrogenations over tris (triphenylphosphinechlororhodium is markedly influenced both by the duration of hydrogen presaturation of the catalyst and the presence of oxygen in the reaction mixture. These results are compared to those obtained over a heterogeneous catalyst, 5% rhodium on charcoal.

Introduction

The hydrogenation of olefins over tris (triphenylphosphine) chlororhodium (I) has been investigated and utilized rather extensively over the past few years. The mechanism proposed originally for this reaction (Fig. 1) (1) has been extended and modified in recent years (2,3). The first reaction in the sequence, the dissociation of I into $(\emptyset_3P)_2RhCl$ (II) and triphenylphosphine, was proposed on the basis of several relatively sound observations. The most important of these was that an osmometric molecular weight determination indicated that the molecular weight of I was about one half of that expected. This conclusion has been questioned since it was found by the use of NMR techniques that this dissociation proceeds only to the extent of about 5% (4). Repetition of the molecular weight determination again indicated complete dissociation (4). Even with this dichotomy, the dissociation step is considered to be essential in all mechanistic discussions of the reaction (2,3,5,6).

The second reaction proposed for the hydrogenation sequence involves the reaction of II with hydrogen to give the dihydride, III, which was fully characterized by NMR and IR data (1). Here, too, later work has shown that some modification of this proposal is needed. It was considered originally that the reaction of II with olefins would give a species which was catalytically inactive. This assumption was based on the finding that the ethylene complex, IV, did not take up hydrogen (1). Recently, it has been found that IV is a catalytically active species (2). This observation led to the proposal of two competing routes from II for olefin hydrogenation (Fig. 2). The nature of the solvent was considered to be the primary factor involved in determining whether the reaction proceeded through the hydride or the unsaturate route (2).

The third step in the reaction sequence (Fig. 1) was considered on the basis of kinetic studies to be the rate determining step of the reaction sequence (1). In the final step the simultaneous transfer of the two hydrogens to the olefin to give alkane was proposed. This simultaneous transfer proposal was based primarily on two lines of evidence: (a) no metal alkyl, which would be expected to be a stable entity if formed, was observed in low temperature NMR studies; (b) no double bond isomerization was observed in the recovered olefin.

Since the report of the initial studies on this reac-

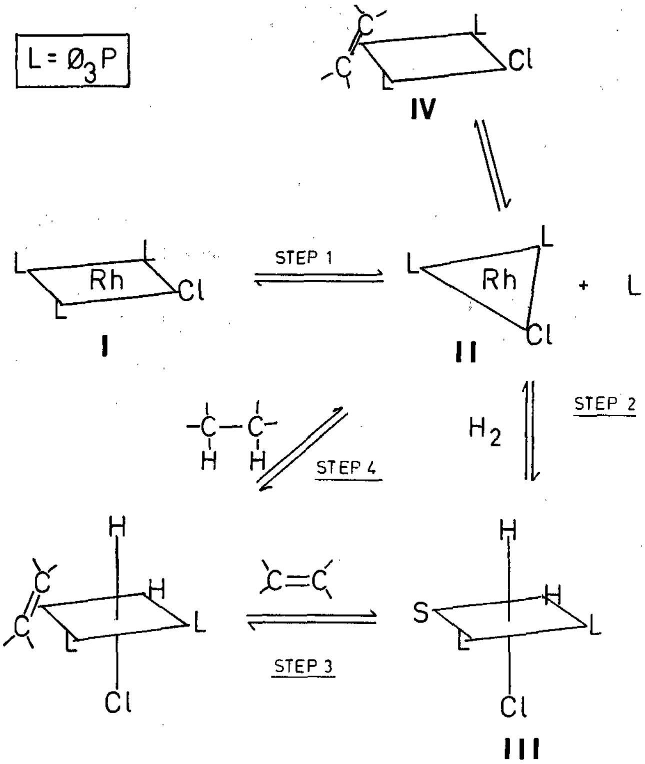

FIG. 1. Mechanism for olefin hydrogenation over $(\emptyset_3P)_3RhCl$ (1).

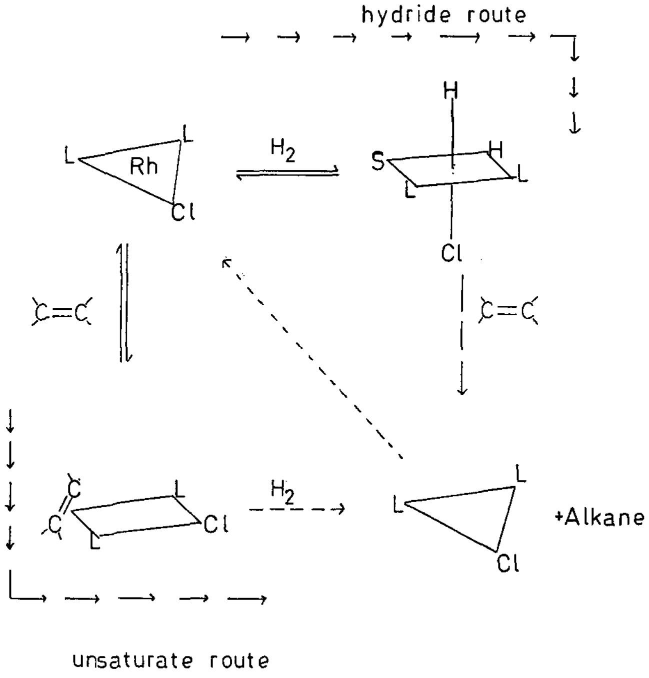

FIG. 2. Hydride and unsaturate route for olefin hydrogenation (2).

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[1] One of 10 papers to be published from the Symposium "Hydrogenation," presented at the AOCS Meeting, New Orleans, April 1970.

tion other workers have shown that double bond isomerization can, indeed, occur over I during hydrogenation (5–8). As a result of one of these observations the reaction mechanism has been modified to include a two-step transfer of hydrogen (3). Even with this modification, it was stated that for all practical purposes the two transfer steps would occur simultaneously except when a trisubstituted or bulky disubstituted olefin was hydrogenated (3). Other work has shown, however, that isomerization of 1-pentene occurred on hydrogenation over I (6). It appears, therefore, that the factors involved in double-bond isomerization during hydrogenation are more complicated than mere olefin substitution.

Investigation of the data reported in the literature on the hydrogenation of olefins over I led to a rather interesting observation. The isomerization of double bonds during the reaction appeared to be influenced by two factors: (a) the extent of pre-saturation of I with hydrogen prior to the addition of the olefin, and (b) the nature of the solvent used. When I was thoroughly presaturated with hydrogen no isomerization was observed while in the absence of presaturation isomerization was reported often. In these latter reports when the hydrogenations were run in benzene or benzene-hydrocarbon solvents no isomerization occurred while when an alcohol was present isomerization took place. This solvent effect also appeared to affect deuteration reactions over I. In benzene, deuterium was reported to add directly to the double bond with no scrambling observed (9) while in the presence of ethanol deuterium scrambling occurred (3).

A solvent effect on the rate of reaction has been noted previously in at least two references. In one case it was assumed to be involved in assisting the dissociation of I (3) and in the other in differentiating between the unsaturated and the hydride routes proposed for the reaction (2). It has recently been established that the solvent is involved in the dissociation reaction but that the effect of alcohol appears to be one of inhibition of dissociation and not of assistance (10). This finding casts some doubt on the validity of the so-called unsaturate route proposed for the reaction (Fig. 2).

To shed more light on the problem of double bond isomerization during the hydrogenation reaction it was believed necessary to check whether the factors mentioned above were actually influential in determining whether isomerization occurred. To this end the hydrogenation of 1- and 2-heptene over I was studied under a variety of reaction conditions. When the reaction was run in benzene no isomerization of recovered olefin was observed either with or without prior saturation of I with hydrogen. In benzene-ethanol, however, presaturation of the catalyst was influential in preventing isomerization. These latter data are shown in Table I. It can be seen that not only isomerization but also the rate of the reaction is markedly influenced by this presaturation. In an attempt to understand the effect of this presaturation on the reaction it was thought that this process might be removing some of the dissolved oxygen from the reaction media. If this were true, then one could conclude that the presence of oxygen is necessary for isomerization to occur. This hypothesis was tested and shown to be correct. The resulting data are shown in Table II. In benzene no isomerization was observed even in the presence of added oxygen. In ethanol, the addition of oxygen to the hydrogen pretreated catalyst gave a system in which isomerization occurred readily. Here, as in the hydrogenation of cyclohexene over I (11), the addition of oxygen markedly increased the rate of the hydrogenation. This solvent effect has recently been shown to be due to the influence of the solvent on the dissociation of I (10,12).

TABLE I

Heptene Hydrogenation Over [Rh(Ph$_3$P)$_3$Cl] in Benzene-Ethanol

Olefin	Catalyst	Time, min	% Heptane	% Heptene -1-	% Heptene *cis*-2-	% Heptene *trans*-2-
Hept-1-ene						
	NPS[a]	15	13	56	12	19
		30	17	47	16	20
		70	22	32	17	29
	PS[b]	3	18	81	....	1
		7	29	70	....	1
		16	40	57	....	3
Hept-2-ene						
	NPS[a]	0	....	....	79	21
		15	12	....	41	47
		30	14	....	43	43
		90	18	9	11	42

[a] [Rh(Ph$_3$P)$_3$Cl] not presaturated with H$_2$.

[b] [Rh(Ph$_3$P)$_3$Cl] presaturated with H$_2$ for 60 min prior to addition of olefin.

TABLE II

Effect of Oxygen on the Hydrogenation of 1-Heptene

Solvent	mmole $O_2 \times 10^2$	Rate mlH$_2$/mmoleRh/min	% Isomerization
Benzene	0	69	<2
Benzene	0.6	120	<2
Benzene	1.2	85	<2
1:1 Benzene Ethanol	1.2	128	17
2:1 Benzene Ethanol	Excess	24	55

In addition to double bond isomerization one of the most common methods used in studying the mechanism of heterogeneous hydrogenation of olefins is the variation of product stereochemistry with pressure (13). This variation can be expected as a result of the currently accepted Horiuti-Polanyi mechanism for the reaction (Fig. 3) (14). The initial interaction of catalyst and olefin (Step 2) results in the formation of a pi-complex whose stereochemistry resembles that of the olefin. In Step 3 a diadsorbed sigma-complex in which the bonds are eclipsed is produced. In Step 4 the half-hydrogenated state (V) is formed. This

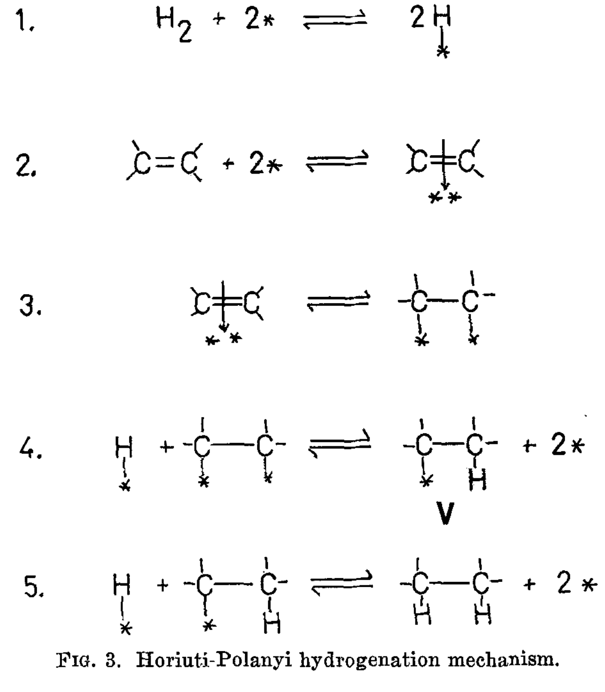


FIG. 3. Horiuti-Polanyi hydrogenation mechanism.

species with a stereochemistry which approaches that of the product is the counterpart of the sigma-bonded metal-alkyl intermediate proposed in some mechanisms for homogeneous hydrogenation. The last step in the Horiuti-Polanyi mechanism is usually reversible only at high temperatures or low hydrogen pressures or both. On the other hand, Steps 2 to 4 can be reversed under normal conditions. If these reversals involve other carbon atoms adjacent to the adsorbed carbon in V olefin isomerization occurs. The reversibility of these steps, however, can be controlled by changing the hydrogen availability to the catalyst by modifications of the pressure, rate of agitation, catalyst quantity, etc. Under conditions of high hydrogen availability Step 3 (Fig. 3) is product determining while under low hydrogen availability the nature of the product is determined by the reversibility of Step 4, i.e., the relative stabilities of the various half-hydrogenated states available to the system. This variation in hydrogen availability is made manifest by the change in product stereochemistry on hydrogenation of certain olefins on changing the hydrogen pressure. It has been found that in the hydrogenation of VI over platinum the amount of *cis* product formed, VII, decreased with increasing pressure (13,15). This has been attributed to a shift in the rate determining step of the reaction by increasing pressure as discussed above. The transition states for the hydrogenation of VI are depicted as X and XI (13). X shows the transition state for the formation of the half-hydrogenated state of VI (Step 4) while in XI is depicted the diadsorbed alkane involved in Step 3. These transition states control the ratio of *cis* and *trans* product formation. The mode of adsorption shown in XI leads to the *cis* product, VII, but because of the planar nature of the organic segment in this species adsorption from the opposite face of the olefin is also possible to give the *trans* isomer, VIII. Transition state X yields only the *cis* product.

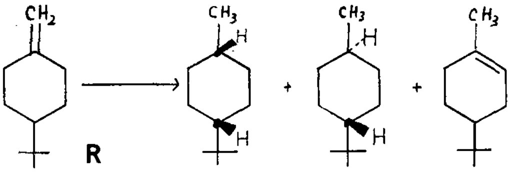
With these factors well understood in heterogeneous catalysis it was believed that additional information concerning the homogeneous hydrogenation of olefins over I could be obtained by studying the effect of pressure on the hydrogenation of VI over I in benzene-ethanol solvents. With pre-saturated I no isomerization nor pressure effect on product composition was observed. However, with nonpresaturated I extensive isomerization to IX as well as a marked pressure effect on product stereochemistry occurred. These results are shown in Table III. This pressure effect suggested that a correlation between heterogeneous and homogeneous hydrogenation catalysts was feasible and Table IV shows the comparison of product stereochemistry data utilizing both 5% rhodium on charcoal and nonpresaturated I. [The product stereochemistry differences found on hydrogenation of VI over various heterogeneous catalysts has already been discussed (8).] These data show a rather close correlation between these two catalysts and give further support to the idea that one might be able to utilize data from homogeneous hydrogenations to understand the results of the heterogeneous reactions and vice versa. It is obvious, though, that considerably more work in this area is called for.

TABLE III

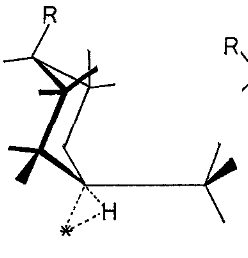
Hydrogenation of 1-Methylene-4-t-Butylcyclohexane Over [Rh(Ph$_3$P)$_3$Cl]

Catalyst	Pressure, atm.	% 1-Methyl-4-*t*-butylcyclohex-1-ene (IX)	% 1-Methyl-4-*t*-butylcyclohexane	
			Cis	*Trans*
NPS[a]	1	47	39	14
	20	7	77	16
	93	4	82	14
PS[b]	1	....	66	34
	90	....	67	33

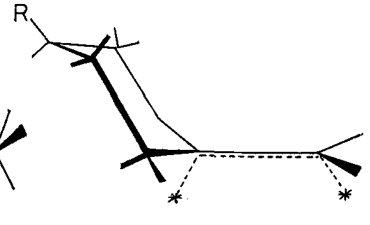
[a,b] See footnotes to Table I.



VI VII VIII IX



X



XI

Experimental Procedures

Gas chromatographic analyses (GLC) were carried out on a Varian Aerograph Autoprep Model A-100 gas chromatograph. The column employed was a 45 ft. × ¼ in. o.d. copper tubing filled with 10% ethylene glycol succinate on chromosorb P. At a column temperature of 70 C and a flow rate of 20 ml of helium per minute the following retention times were recorded: heptane, 42 min; heptene-1, 48 min; heptene-2, 52 min. At a column temperature of 125 C and a flow rate of 47 ml of helium per minute, the following retention times were recorded: *trans*-4-*tert*-butyl-methylcyclohexane, 38 min; *cis*-4-*tert*-butyl-methylcyclohexane, 44 min; 4-*tert*-butyl-methylenecyclohexane, 55 min; 4-*tert*-butyl-methylcyclohexene-1, 60 min.

High pressure hydrogenations were carried out in an Autoclave Engineers Inc., Magnedrive Autoclave. Low pressure hydrogenations were made in a Parr apparatus. For atmospheric pressure hydrogenations and oxidations the reactor described below was employed.

The benzene used was spectral grade, the ethanol was absolute, pure. All solvents were degassed before use by refluxing and subsequent cooling under nitrogen. Heptene-1, puriss, obtained from the Aldrich Chemical Co., Inc., was distilled before use. 4-*Tert*-butyl-methylenecyclohexane (VI) was prepared from triphenylphosphinemethylene and 4-*tert*-butylcyclohexanone by the Wittig reaction (16) and by a modified Wittig reaction (18). Tris(triphenylphosphine)chlororhodium (I) was prepared from tri-

TABLE IV

Hydrogenation of 4-*Tert*-Butylmethylenecyclohexane

Pressure, atm.	% *Cis*-4-*tert*-butylmethylcyclohexane[a]	
	5% RH/C	(ø$_3$P)$_3$RhCl[b]
1	75	74
20	77	83
93	80	85

[a] Calculated from the amount of *cis* product in the saturated species present.

[b] Nonpresaturated catalyst.

phenylphosphine and rhodium trichloride trihydrate by a method described by Wilkinson (1).

General Procedure for the Gas-Liquid Reactions

The reactor used in this work permitted the observation of small quantities of gas uptake. This apparatus consisted of a 125 ml flat bottom flask with a 24/40 ground joint. The flask had three side arms connected to the upper part of the flask. One side arm was comprised of a water manometer, one arm was sealed by a serum cap allowing addition or sampling, and a third arm was connected to a syringe of desired volume. The water level in the manometer was maintained by moving the plunger of the syringe. The absorption of gas in a reaction was read from the position of the plunger. The apparatus was totally submerged in a water bath. Thus, the reaction as a whole was at a controlled temperature. The reaction mixture was agitated by a teflon coated magnet, driven by a magnetic stirrer motor positioned underneath the water bath. The speed of agitation was such that it was not a rate controlling factor in the reactions. The hydrogenations were carried out with Dry Grade Hydrogen from The Matheson Company.

Heptene Hydrogenations Over 1

Presaturated Catalyst. The 125 ml hydrogenation vessel containing 23 mg (2.5×10^{-2} mmole) of I was carefully filled with nitrogen. To the reaction vessel 20 ml of degassed benzene was added. The nitrogen was evacuated and replaced by hydrogen three times and the mixture stirred for 1 hr. At this time 0.4 ml (2.8 mmole) of heptene was added and hydrogenated. The hydrogenation and isomerization were monitored by the GLC of samples withdrawn periodically.

Nonpresaturated Catalyst. The general procedure described above was followed except that the benzene solution of I was initially stirred under nitrogen for 1 hr. The nitrogen was replaced by hydrogen and the heptene added immediately.

Effect of Oxygen. The above experiments were repeated with varying amounts of oxygen added at the beginning of the 1 hr stirring under nitrogen.

Hydrogenation of 4-Tert-Butyl-1-Methylenecyclohexane Over I

The hydrogenation of 4-tert-butyl-methylenecyclohexane (VI) was carried out in benzene and in ethanol-benzene at various hydrogen pressures over I. I was predissolved under hydrogen for 1 hr, or predissolved under nitrogen containing air for 1 hr. In this procedure the autoclave was charged with 20 ml of the catalyst solution and about 410 mg (2.7 mmole) of 4-tert-butyl-methylenecyclohexane. The autoclave was pressurized. The hydrogenation and isomerization were monitored by GLC of samples withdrawn during the experiment. The hydrogenations over 5% Rh/C were carried out in the same manner.

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