

## ACTIVATION AND REACTIVATION OF CATALYST BY ORGANIC CHLORIDES IN THE RHODIUM-CATALYZED CODIMERIZATION OF $\alpha$ -OLEFIN AND CONJUGATE DIENES

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### SUMMARY

Organic chlorides with labile C-Cl bonds can be used to convert certain  $Rh^I$  complexes into a catalyst for the codimerization of  $\alpha$ -olefins and 1,3-dienes to form 1,4-dienes. In the presence of excess organic chlorides, the catalytic activity can be maintained indefinitely through continuous reactivation of decayed catalyst. This catalyst activation effect can be attributed to the ability of the organic chlorides to convert an inactive  $Rh^I$  species to an active  $Rh^{III}$  species by oxidative addition.

### INTRODUCTION

In transition metal catalyzed olefin dimerizations, oligomerizations, or polymerization reactions, the loss of the catalyst activity or "catalyst decay" in some instances<sup>1,2</sup> is associated with the reduction of the metal from a high oxidation state to a lower oxidation state (for example, due to homolytic cleavage of the carbon-metal bonds). Restoration of the original oxidation state by a proper oxidation process without destroying the catalytic site or sites should reactivate or "rejuvenate" the decayed catalyst. In this paper we wish to report the application of oxidative addition reactions to activate, reactivate, and maintain the activity of a Rh catalyst as demonstrated by the catalytic synthesis of 1,4-hexadiene from ethylene and butadiene.

### RESULTS AND DISCUSSION

Alderson<sup>3</sup> found that  $\alpha$ -olefins such as ethylene and conjugated dienes such as butadiene can be selectively converted under relatively mild conditions to 1,4-hexadiene using  $RhCl_3 \cdot 3H_2O$  as a catalyst. However, the catalyst becomes deactivated after prolonged reaction or after the removal of the products and monomers from the reaction mixture. Verbanc<sup>4</sup> discovered that most of the catalyst's original activity is restored on addition of some HCl. Cramer<sup>5</sup> showed that this activation involved addition of HCl to a  $Rh^I$  complex to form the active  $Rh^{III}$  complex.

It is well known that organic halides will add to lower valent transition metal derivatives oxidizing the metal to a higher valence state.<sup>6-10</sup> We have now shown that

certain activated organic chlorides, under suitable conditions, can have the same activation effect on the rhodium catalyst as that of HCl.

In a typical reaction, a catalytic amount of  $Rh^I$  complex such as  $[(C_2H_4)_2RhCl]_2$  is added to an autoclave containing measured amounts of ethylene and butadiene in an inert solvent. After more than 1 h at  $70^\circ$ , only traces of  $C_6$  product are formed. At this point an organic chloride, *e.g.*, benzotrichloride, is added. Immediately, the catalytic codimerization begins forming 1,4-hexadiene as a major product. The catalytic property and by-products formed are essentially the same as that described by Alderson<sup>3</sup> and Cramer<sup>5</sup>. The results are shown in Table 1.

TABLE I

CATALYST ACTIVATION BY  $PhCCl_3$ <sup>a</sup>

Time (min)	$C_6$ Diene (g)	1,4-Hexadiene (%)
0	0	
30	Traces	
60	Traces	
(Add 50 mmoles $PhCCl_3$ )		
90	15	99
120	62	90
150	120	80

<sup>a</sup> Starting reaction conditions:  $70^\circ$ ; 1 l toluene, 20 ml DMAC, 180 g butadiene pressured with ethylene to 140 lbf/in<sup>2</sup>; 1 mmole  $[(C_2H_4)_2RhCl]_2$ ;  $\approx$  50 mmoles  $PhCCl_3$  was added after 60 min of reaction.

The above procedure was used to compare the effectiveness of various organic chlorides in the oxidative activation of the  $Rh^I$  catalyst. The reactions are most conveniently carried out in inert non-polar solvents such as toluene containing some mild electron donor such as THF, acetone, or *N,N*-dimethylacetamide<sup>\*\*\*</sup>, or in solvents of weak donor ability such as ethers or glyme. The results are shown in Table 2. We found that, in general, allylic chlorides, benzylic chlorides,  $\alpha$ -chloroethers, and those chlorides with C-Cl bonds adjacent to a carbonyl group such as hexachloroacetone are effective activators. Aliphatic and aromatic chlorides except  $CCl_4$ <sup>\*\*\*</sup>, are not effective activators. Certain vinylchlorides, such as  $\begin{matrix} C \\ | \\ C=C-Cl \end{matrix}$ , are moder-

\* In completely nonpolar solvents the catalyst is not very active. The presence of some mild donor ligands greatly increases catalyst activity, it is believed that the donor converts associated rhodium complexes into more active monomeric forms without blocking the catalytic site. The effect of ligands in controlling not only the activity but also the stereoselectivity of the Rh catalyst will be reported in detail in a separate paper.

\*\* The activation reaction can also be carried out in protic solvents such as alcohols. Aprotic solvents were used throughout this work to ensure that the activation process results from the interaction of  $Rh^I$  with R-Cl and is not due to the presence of small amounts of HCl which might be generated *in situ* if some proton source were present. Under these aprotic conditions, the rhodium catalyst is stable in the presence of many common metals; thus the reaction can be carried out in stainless steel equipment instead of the glass or silver-lined equipment required with alcoholic media<sup>3-5</sup>.

\*\*\*  $CCl_4$  is effective only if it constitutes the bulk of the solvent system.

TABLE 2

CATALYTIC ACTIVITY OF  $[(C_2H_4)_2RhCl]_2/RCl$  CATALYST SYSTEM<sup>a</sup>

RCl	Hexadiene produced (g) at			
	15 min	30 min	60 min	120 min
CH <sub>3</sub> O-CH <sub>2</sub> Cl	25	60	110	
Crotyl-Cl	15	30	60	
PhCCl <sub>3</sub>	6	15	30	60
PhCCl <sub>3</sub> <sup>b</sup>		21	50	
Cl <sub>3</sub> CCOCCl <sub>3</sub>	2-3	6	20	50
Ph <sub>3</sub> CCl	Traces	4	14	70
CCl <sub>4</sub> <sup>c</sup>	Traces			30
1-Chloro-2-methylpropene <sup>d</sup>	Traces	2	6	15
Chloroprene	Traces	Traces	3	10

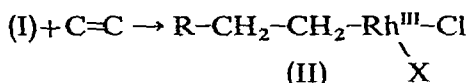
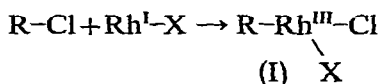
<sup>a</sup> Reaction conditions same as described in Table 1 except that 1/2 mmole (1 mg-atom in Rh) of the Rh<sup>I</sup> complex and 100 mmoles of the organic chloride are used. They are added to the reactor simultaneously.

<sup>b</sup> Acetone (20 ml) instead of DMAC was present in the solvent. <sup>c</sup> CCl<sub>4</sub> was used as solvent. <sup>d</sup> Glyme was used as solvent instead of toluene; no other electron donor was added.

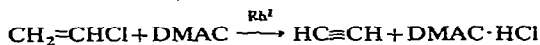
ately effective as activators, while vinyl chloride\*, vinylidene dichloride, and 1,2-dichloroethylene are not.

The effectiveness of an organic chloride in activating the Rh catalyst appears to be related to the lability of the C-Cl bond. Figure 1 depicts reaction curves obtained when organic chlorides of various activation ability were used. The most effective compounds, CH<sub>3</sub>OCH<sub>2</sub>-Cl and crotyl-Cl, show no induction period, indicating fast formation of the active species.

We believe that the activation reaction described above is a result of oxidative addition reactions between the organic chlorides and a Rh<sup>I</sup> complex\*\*. The reactions are analogous to those described by Cramer<sup>3</sup> for the activation of  $[(C_2H_4)_2RhCl]_2$  with HCl.



\* Addition of vinyl chloride to a reaction mixture containing some mildly basic electron donor such as dimethylacetamide (DMAC) converts the Rh<sup>I</sup> complex to an active catalyst. We found that this was not due to direct oxidation of Rh<sup>I</sup> by vinyl chloride, but rather to the oxidation of Rh<sup>I</sup> by HCl generated by the interaction between vinyl chloride and dimethylacetamide catalyzed by Rh<sup>I</sup>:



We have isolated the salt DMAC·HCl and detected the equivalent quantity of acetylene in the reaction mixture. When a weaker base such as ether or alcohol was used instead of dimethylacetamide, no activation was observed.

\*\* Heck<sup>8</sup> has shown that interaction of RX with Rh<sup>I</sup>Cl(R<sub>3</sub>P)<sub>2</sub>(CO) results in the oxidized product R-Rh<sup>III</sup>XCl(R<sub>3</sub>P)<sub>2</sub>CO. In the present case, in the absence of ligands such as phosphine and CO, the intermediate oxidized complex is expected to be very unstable and to further react with olefins to form the active catalyst species.



TABLE 3

RECYCLIZATION OF CATALYST MIXTURE<sup>a</sup> AND CATALYST REACTIVATION

	Butadiene conversion <sup>b</sup> (%)	Total C <sub>6</sub> dienes (g) <sup>b</sup>	1,4-Hexadiene (g)	2,4-Hexadiene (g) <sup>c</sup>	3-Methyl-1,4-pentadiene
Initial run	≈ 66	160	117	31	≈ 1
1st recycle	≈ 7	19	≈ 19	Traces	Traces
2nd recycle <sup>d</sup>	≈ 50	123	102	20	≈ 1
3rd recycle	≈ 46	114	95	18	≈ 1
4th recycle	≈ 44	109	91	17	≈ 1
5th recycle	≈ 46	114	95	18	≈ 1

<sup>a</sup> Starting catalyst:  $(C_4H_7)_2Rh_2Cl_4 \cdot C_4H_6$  (1 mmole); reaction time, 2 h. <sup>b</sup> Initial butadiene 180 g. Butadiene conv. = wt. butadiene used/wt. Initial butadiene. The yield of C<sub>6</sub> diene with respect to butadiene converted decreased with increasing conversion. See Experimental for more detail. <sup>c</sup> The amount of 2,4-hexadiene produced as a result of isomerization of 1,4-hexadiene increased with increasing conversion of butadiene. <sup>d</sup> Addition of 200 mmoles PhCCl<sub>3</sub>.

## EXPERIMENTAL

*Equipment*

All our reactions were carried out in a 2 l Hastelloy B steel autoclave connected to an ethylene source. The detailed design and operation of the autoclave have been described previously<sup>13,14</sup>.

All the product analyses were done using a Perkin-Elmer Model 800 GLC unit. The type of column used, the retention times of the various C<sub>6</sub> dienes, and their quantitative determination have also been described previously<sup>14</sup>.

*General procedure for 1,4-hexadiene synthesis*

All reactions were carried out under an inert atmosphere.

Dry toluene (900 ml) containing 20 ml of dimethylacetamide (DMAC)\* was charged into the reactor and cooled to below  $-20^\circ$ . About 180 g of butadiene, previously purified by passing through a column of molecular sieves, was distilled into the cooled reactor which was then heated up to  $70^\circ$ . Purified ethylene was then charged into the reactor to a total pressure of 140 lbf/in<sup>2</sup>. A fixed quantity of internal standard for GLC analysis (usually either cyclohexane or hexane) and the desired quantity of organic chloride were injected into the reactor followed by a solution containing 0.5–1 mmole of either  $C_4H_7Rh_2Cl_4 \cdot C_4H_6$ <sup>15</sup> in chlorobenzene or  $[(C_2H_4)_2RhCl]_2$ <sup>6</sup> in toluene. Ethylene was fed as required to maintain a reactor pressure of 140 lbf/in<sup>2</sup> the gas flow was monitored by a rotameter. The reactor temperature was maintained by a hot water bath heated by steam passing through a copper coil. The steam feed was controlled by a solenoid valve connected to a Shell Thermotral unit\*\*, which opens or closes the solenoid valve to maintain a constant bath temperature.

\* When solvents of weak donor property such as THF or glyme were used instead of toluene, the addition of DMAC was unnecessary.

\*\* Hallikainen Thermotral Model 1053A (115 v), Hallikainen Instrument Co., Richmond, California.

The reaction was stopped by cooling the reactor to below room temperature or by addition of some triethylamine to the reaction mixture, and the products were isolated in the same manner as described previously<sup>13</sup>.

#### *Catalyst reactivation and recyclization procedure*

One liter of toluene, 20 ml of DMAC, and 180 g of butadiene were introduced into the reactor which was constantly supplied with ethylene. At a pressure of 140 lbf/in<sup>2</sup> and temperature of 70°, 1 mmole of (C<sub>4</sub>H<sub>7</sub>)<sub>2</sub>Rh<sub>2</sub>Cl<sub>4</sub>·C<sub>4</sub>H<sub>6</sub> was added and the reaction continued for 2 h. The reactor was cooled to 20° (reaction stopped at this temperature) and the excess monomer, the C<sub>6</sub> products, and 90% of the solvent removed under reduced pressure. The reactor was replenished with fresh solvents and monomers until the content was the same as the initial run. The reactor was warmed quickly to 70° and the reaction proceeded for another 2 h (first recycle). The recycling procedure was repeated. At the beginning of second cycle, 200 mmoles of PhCCl<sub>3</sub> were added and remained in the reaction mixture throughout the rest of the recyclizations.

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