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Oxychlorination of Propylene on Supported Palladium and Other Platinum Group Metal Catalysts

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Oxychlorination of propylene was studied on platinum groups metal catalysts. Main product was allyl chloride on all catalysts studied. The catalylic activity was in the following order: Rh > Pd > Pt > Ir > Ru. Details of the reaction were studied on palladium catalysts. Byproducts were isopropyl chloride, 1,2-dichloropropane, chloropropenes and carbon dioxide. Isopropyl chloride and 1,2-dichloropropane were formed parallel to allyl chloride and major part of carbon dioxide was formed successively from allyl chloride. Among others active charcoal was the best support for the palladium catalyst. The high efficiency of active charcoal support is explained by its catalytic action for palladium oxidation. Hydrogen chloride was chemically adsorbed on the catalyst in the presence of oxygen and a significant amount of palladium chloride was formed during the reaction. The concentration of palladium chloride under working conditions was measured by a novel method. The $PdCl_2$ concentration reached a steady state, which was controlled by the feed composition. On a fully chlorinated palladium catalyst little allyl chloride was formed and 1,2-dichloropropane was formed instead. Allyl chloride was considered to be formed through a reaction of π-allyl species of propylene on the reduced palladium with the chlorides of palladium.

I. INTRODUCTION

Palladium metal has been known as an useful catalyst of the vinyl acetate synthesis from ethylene, acetic and oxygen (*1*). In the reaction a hydrogen atom of ethylene is oxidatively substituted by an acetate anion to give vinyl acetate and water. When the reaction is carried out using propylene an allyl hydrogen is oxidatively substituted to yield allyl acetate and water (*2*).

$$CH_2{=}CH{-}CH_3 + CH_3COOH + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CH{-}CH_2OCOCH_3 + H_2O. \quad (1)$$

We considered that the reaction is a general oxidative substitution of allylic hydrogen of propylene by a nucleophilic reagent with active hydrogen and tried to develop new reactions using other nucleophilic reagents such as hydrogen halide, water (*3*) and alcohols (*4*).

Conventional oxychlorination of aliphatic olefins are catalyzed by copper chloride and give addition products (dichloro paraffins) but no substituted products. Thus the main product of the oxychlorination of propylene on copper chloride is 1,2-dichloropropane. A patent has revealed that a supported copper catalyst which contains palladium gives allyl chloride and 1,2-dichloropropane in the temperature range from 250°C to 350°C (*5*). We discovered that supported palladium and other platinum group metals were excellent catalysts of the allylic oxychlorination of propylene in the abscence of copper.

We report in this paper the details and the mechanism of the allylic oxychlorination of propylene over supported palladium and other platinum group metal catalysts. The overall reaction stoichometry is expressed as follows:

$$CH_2{=}CH{-}CH_3 + HCl + \tfrac{1}{2}O_2 \rightarrow CH_2{=}CH{-}CH_2Cl + H_2O. \qquad (2)$$

II. EXPERIMENTAL METHODS

1. Catalyst Preparation

Catalysts were prepared by an impregnation method. A calculated amount of metal chloride was dissolved into dilute aqueous hydrogen chloride. Into the solution a determined amount of dried granular carrier was poured and evacuated at room temperature for about 1 hr. The resultant mixture was let stand for more than 24 hr. Then the mixture was heated to dryness on a water bath and further dried *in vacuo* for 2 hr at about 160°C. The product was stored in a desiccator. When the reaction was carried out with a reduced catalyst the product was reduced by flowing hydrogen at about 450°C for 3 hr before use.

2. Apparatus

The apparatus used was a conventional flow-type reaction system equipped with devices for measuring and controlling the reaction temperature and flow rate of reactants. Reactions were carried out at atmospheric pressure by balancing with nitrogen. The reactor was made of Pyrex glass tube (500 mm long and 16 mm inner diameter) which had a thermocouple sheath along the central axis. The catalyst bed was a fixed bed and charged with several grams of catalyst particles. Above and below the bed, glass spheres were packed.

3. Materials

Oxygen and nitrogen were commercially available ones and fed from compressed gas cylinders. Propylene was a polymerization grade ones supplied by Tonen Petrochemical Co. Ltd. It was fed from liquified gas cylinders. Hydrogen chloride was fed from liquid hydrogen chloride cylinders manufactured by Tsurumi Soda Co. Ltd. Water used in the reaction was deionized water.

4. Analysis

Gaseous products and liquid organic products were analyzed with gas chromatographs. Column: Porapac Q for gaseous products and polyethylene glycol 1500 for liquid products. Unreacted hydrogen chloride was determined by a titration method after being absorbed in water.

5. Determination of Oxidation State of Palladium

When the oxychlorination reaches a steady state the reactor is purged with oxygen-free nitrogen at the reaction temperature for about 1 hr. This period has been proved experimentally to be enough to remove free hydrogen chloride from the catalyst. After that the temperature is lowered to 100°C under nitrogen flow and then propylene, oxygen and steam are fed in a predetermined ratio. The rate of acetone formation is determined at the steady state. The ratio of the rate of acetone formation to the rate obtained on the fresh $PdCl_2$/active charcoal catalyst corresponds to the specific palladium chloride concentration.

6. Determination of Metal Particle Size

The particle size of supported metals were determined from the amount of chemisorbed carbon monoxide. The method and the apparatus for measuring the amount of chemisorbed carbon monoxide are similar to those of Scholten and Van Montfoort (*6*).

III. RESULTS AND DISCUSSION

Table 1 gives the results obtained with supported platinum group metal catalysts and the heat of formation of each metal chloride (*7*). Allyl chloride was the main product on any catalysts used under the

TABLE 1

Oxychlorination of Propylene on Group 8 Metal Catalysts[a]

Metal	$\Delta Hf^{\circ b}$ (kcal/mol)	$\Delta Hf^{\circ *c}$ (kcal/mol)	Rate of formation (10^{-4} mol/g cat hr)		
			Allyl chloride	Isopropyl chloride	Carbon dioxide
Fe	−96.8	−32.3	0.21	18.5	0.77
Co	−77.8	−38.9	0.16	11.0	0.62
Ni	−75.5	−37.8	0.19	6.55	0.50
Ru	−63.0	−21.0	2.14	14.2	1.55
Rh	−56.0	−18.7	18.5	3.25	1.74
Pd	−45.4	−22.7	9.37	7.30	1.32
Ir	−61.5	−20.5	6.86	9.30	3.05
Pt	−35.5	−17.8	9.18	3.65	2.33

[a] 3 wt% Metal/A.C.; reaction temperature = 200°C; W/F = 7.4 g cat hr/mol; $C_3H_6:O_2:HCl:H_2O = 4:2:1:10$.

[b] ΔHf°: Heat of formation of metal chloride.

[c] $\Delta Hf^{\circ *}$: Heat of formation of metal chloride per one chloride atom.

standard reaction condition. Important by-products were isopropyl chloride and carbon dioxide. The formation of chloropropenes such as 1-chloropropene and 2-chloropropene and dichloropropanes were very small. As shown in Table 1, while every platinum group metal exhibits a significant catalytic activity for allyl chloride formation the activities of other transition metal catalysts (Fe, Co, and Ni) are far less than those of platinum group metals. Isopropyl chloride was the main product on those catalysts. The catalytic activity is in the following order: Rh > Pd > Pt > Ir > Ru ≫ Fe ≃ Co ≃ Ni.

The high activity of the platinum group metal catalyst is interpreted as follows: It has been pointed out that in the oxychlorination of ethylene with copper chloride and other metal chloride catalysts, chloride atoms of metal chloride react with ethylene to give dichloroethane and metal chlorides of lower valence state. The metal chloride of lower valence is then reoxidized to higher valence state by hydrogen chloride and oxygen (*8*).

$$y\mathrm{MCl}_x + \mathrm{C_2H_4} \rightarrow y\mathrm{MCl}_{x-z} + \mathrm{CH_2ClCH_2Cl} \quad (3)$$

(where $y \cdot z = 2$),

$$y\mathrm{MCl}_z + 2\mathrm{HCl} + \tfrac{1}{2}\mathrm{O_2} \rightarrow y\mathrm{MCl}_x + \mathrm{H_2O}. \quad (4)$$

It has been shown that the reactivity of the chloride atom of which metal–chloride bond dissociation energy is low (*9*) is higher. From Table 1 the heat of formation of platinum group metal chloride per one chloride atom is smaller by about 10 kcal/mol than those of other transition metal chlorides. It suggests the high reactivity of chloride atoms of platinum group metals. But if the reoxidation of lower valence metal chloride [Eq. (4)] is too slow, the overall reaction rate is determined by it and the apparent activity is low. Generaly, metals of which metal–chloride atom bond dissociation energy are low are slow in being oxidized because of the small thermodynamical driving force (*9*). However, it has been pointed out that the platinum group metals on active charcoal are rapidly oxidized by HCl and O_2 (*10*). Consequently, it is considered that the platinum group metals of which metal–chloride atom bond dissociation energy are low exhibit high catalytic activity when they are supported on active

TABLE 2

Oxychlorination on Supported Palladium[a]

Support	Surface area[b] (m^2/g)	Mean particle diameter[c] of Pd (Å)	Rate of formation (10^{-4} mol/g cat hr)	
			Allyl chloride	Isopropyl chloride
Active charcoal	1300	60	4.2	0.61
Silica gel	460	148	0.73	2.2
γ-Alumina	150	55	0.66	1.4

[a] 1 wt% Pd; reaction temperature = 230°C, W/F = 12 g cat hr/mol; $C_3H_6:O_2:HCl:H_2O$ = 4:2:1:10.
[b] By BET method at liquid nitrogen temperature.
[c] By CO chemisorption at room temperature.

charcoal. The reason why rhodium is most active within platinum group metals is not clear.

Catalytic Activity of Palladium on Several Supports

Table 2 gives the catalytic activity of palladium catalysts supported on active charcoal (AC), γ-alumina and silica gel and some other properties of the catalysts. The data show that active charcoal is most effective as a support. The effectiveness of active charcoal as a carrier is considered to arise from the catalysis of active charcoal for palladium oxidation by hydrogen chloride and oxygen.

$$Pd + 2HCl + \tfrac{1}{2}O_2 \xrightarrow{AC} PdCl_2 + H_2O. \quad (5)$$

As discussed above it is considered that palladium is partially chlorinated during the reaction (the details are discussed below in Sect. 2) and the chloride reacts easily with propylene to yield allyl chloride. Thus, the higher the rate of oxidation of palladium, the higher is the surface concentration of palladium chloride and consequently, the overall catalytic activity is higher. This interpretation is supported by the fact that the catalytic activity of a Pd/γ-alumina catalyst increased greatly by the addition of oxidizing catalyst or oxidizer of reduced palladium such as cupric chloride or nitric acid as shown in Table 3. The catalysis and the reaction stoichometry of $CuCl_2$ and HNO_3 are expressed by the following equations.

$$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl, \quad (6)$$

TABLE 3

Oxychlorination of Propylene on Modified Palladium/γ-Alumina Catalysts[a]

Catalyst	Rate of formation (10^{-4} mol/g cat hr)			
	Allyl chloride	Isopropyl chloride	1,2-Dichloropropane	Carbon dioxide
Pd–NaCl[b]	1.2	0.35	Tr	0.81
Pd–NaCl–$CuCl_2$[c]	8.4	0.23	3.2	0.95
Pd–NaCl[d]	3.7	0.48	Tr	1.40
Pd	1.4	0.81	Tr	0.92

[a] Temp, 260°C; catalyst:Pd 1 wt% on γ-alumina; $C_3H_6:O_2:HCl:H_2O$ = 4:2:1:10.
[b] Pd/Na = 1:1 (atom ratio).
[c] Pd/Na/Cu = 1:1:0.5 (atom ratio).
[d] HNO_3 was added to the reactant, HCl/HNO_3 = 1:1 (mole ratio).

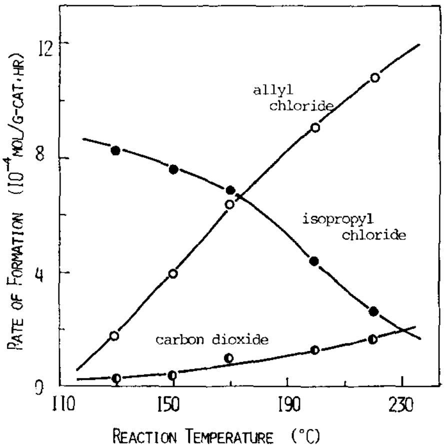


FIGURE 1

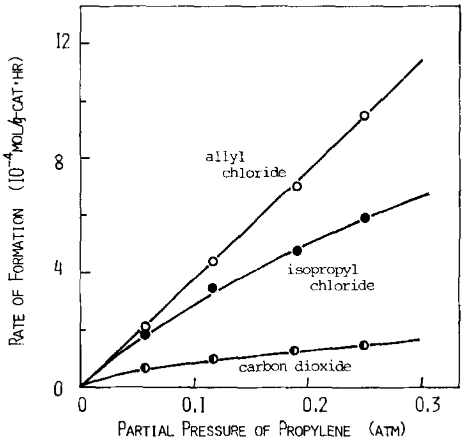


FIGURE 2

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \rightarrow 2CuCl_2 + H_2O, \quad (7)$$

$$Pd + 2HCl + NO_3^- \rightarrow PdCl_2 + H_2O + NO_2^-. \quad (8)$$

The acceleration of isopropyl chloride formation on the γ-alumina and the silica gel supported catalysts is attributed to the surface acidity of them and it is suppressed by the addition of alkali metal ion (see Table 3).

OXYCHLORINATION OF PROPYLENE OVER PALLADIUM/ACTIVE CHARCOAL CATALYSTS

1. Several Factors Which Have Important Effects on the Reaction

Figure 1 shows the effect of reaction temperature on the rate of product formation. While the formation of allyl chloride and carbon dioxide increase almost linearly with the rise in reaction temperature, the formation of isopropyl chloride decreases markedly with the rise in reaction temperature.

Figure 2 shows the effect of propylene pressure. The rate of allyl chloride formation is proportional to propylene pressure (reaction order is 1.0 with respect to propylene). But reaction orders of isopropyl chloride and carbon dioxide with respect to propylene are smaller than unity.

Figure 3 shows the effect of oxygen pressure on the product formation. The formation of allyl chloride and carbon dioxide are nearly proportional to the oxygen pressure. Surprisingly, the rate of isopropyl chloride formation is promoted by oxygen.

Figure 4 shows the effect of the partial pressure of hydrogen chloride on the reaction. The rate of isopropyl chloride formation approaches to a saturated value at fairly low partial pressure.

Steam in the reactant was inert in terms of the catalytic activity. However, it was observed that if the feed of steam

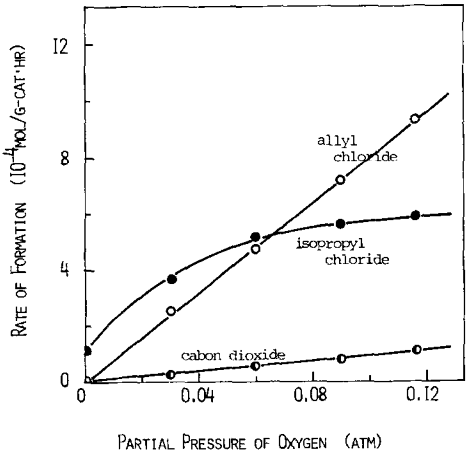


FIGURE 3

was stopped the rate of allyl chloride formation decreased gradually with time and after several hours little allyl chloride was formed. Thus steam is necessary to keep the activity constant.

Figure 5 shows the effect of contact time. While the yield of allyl chloride approaches to a saturated value those of carbon dioxide and chloropropenes increase acceleratory with the contact time. The yield of isopropyl chloride increases almost linearly with the contact time.

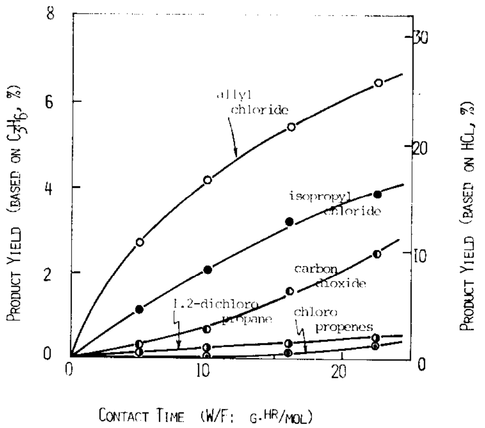


FIGURE 5

2. *Oxidation State of Palladium/Active Charcoal Catalysts*

The oxidation state of a palladium catalyst under working conditions was measured with a novel method. Palladium chloride supported on active charcoal has been proved to be an excellent catalyst of the olefin oxidation in the presence of steam ("Wacker" reaction) and the catalytic activity is proportional to the concentration of palladium chloride up to about 1 wt% of active charcoal (*10*).

Figure 6 shows the variation of product formation in the oxychlorination on Pd and $PdCl_2$/active charcoal catalysts as a function of the reaction time. There are two points which should be noted. The first point is that, whereas when a palladium chloride catalyst is used about 30 min is necessary for the attainment of a steady state, when a reduced palladium catalyst is used a steady states is attained within several minutes. Both catalysts exhibit about the same activity and selectivity at the steady state. The second point is that on the palladium chloride catalyst the main product at an early period is 1,2-dichloropropane and little allyl chloride is formed. The first point suggests that there exists the steady state of the catalyst which is not controlled by the initial state of the catalyst but by the reaction condition. The second point indicates that reduced palladium is necessary for the formation of allyl chloride.

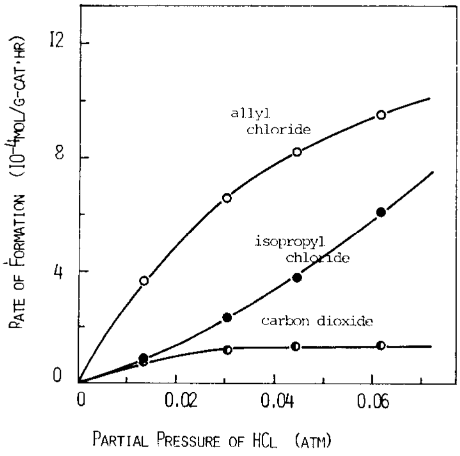


FIGURE 4

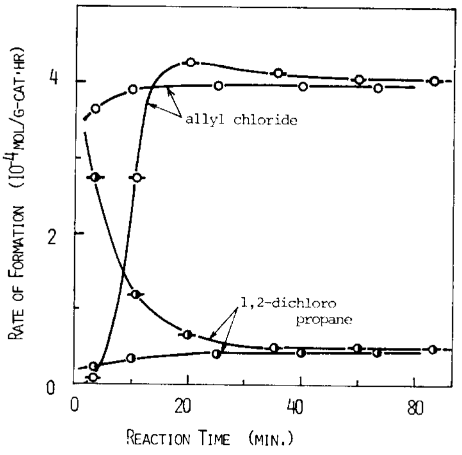


FIGURE 6

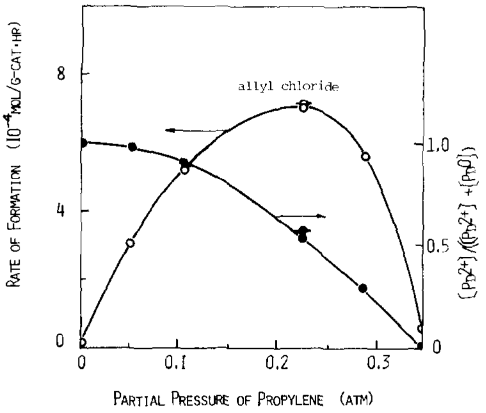


Figure 7

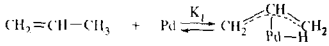
Figure 7 shows the rate of allyl chloride formation and the specific concentration of palladium chloride determined by the method described above as a function of oxygen to propylene feed ratio. It is apparent from Fig. 7 that while the rate of allyl chloride reaches a maximum when the feed ratio of oxygen to propylene is close to 2:1 the concentration of palladium chloride increases with the increase in oxygen to propylene feed ratio. The specific concentration of palladium chloride under a steady state is the same for each catalyst.

Figure 8 shows the rate of allyl chloride formation and the specific concentration of palladium chloride as a function of propylene to hydrogen chloride feed ratio. The specific concentration of palladium chloride is kept at high level if small amount of hydrogen chloride is present in the gas phase. However, the reaction rate increases almost linearly with the increase in propylene pressure despite of the gradual decrease in palladium chloride.

The results shown in Figs. 6 to 8 suggest that palladium on active charcoal is fairly easy in being oxidized to palladium chloride under the reaction condition and also reduced by propylene. At the steady state the specific concentration of palladium chloride is controlled by the rate of oxidation and reduction. Apparently oxygen and hydrogen chloride are oxidants and propylene is a reductant. Especially, hydrogen chloride is an effective oxidant.

3. Reaction Mechanisms

a. Allyl chloride and 1,2-dichloropropane. It is possible that four isomers are formed during the substitutive oxychlorination of propylene, however, as apparent from Fig. 5 allyl chloride is the primary product and other chloropropenes are formed successively from it. Formary, we postulated a π-allylic intermediate in the oxidative acetoxylation (*2*) and oxidative hydration (*3*) of propylene in order to explain allylic products.



(9)

The formation of π-allylic intermediate during the oxidation of propylene on platinum group metals has been suggested in several cases (*11*). Further, π-allyl palladium chloride complex of propylene has been known to thermally decompose to give allyl chloride (*12*). Consequently, it is reasonable that π-allylic adsorbend of propylene is assumed as the active intermediate of the reaction. The high reactivity of the terminal carbon atom of π-allyl complex has been proved by a

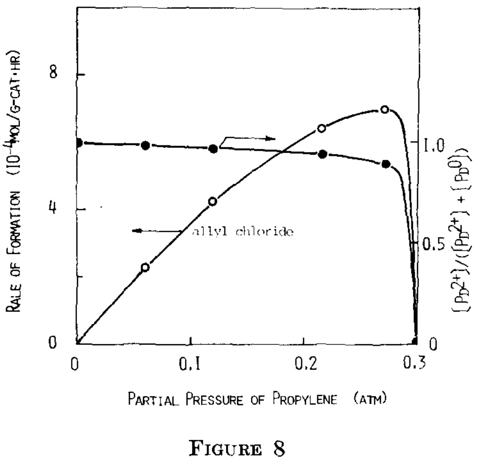
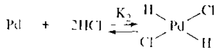
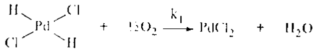


Figure 8

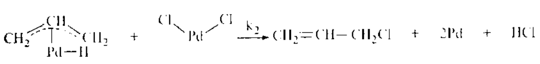
quantum chemical calculation (*13*). The abstraction of allyl hydrogen from propylene is considered to be conducted by metallic palladium is supported by the formation of β-phase of palladium during the oxidation of propylene (*14*). The idea of the activation of propylene by reduced palladium is also supported by the fact that as shown in Fig. 6 when the reaction is carried out on a $PdCl_2$/AC catalyst little allyl chloride is formed and after a significant amount of palladium is reduced by propylene, which gives 1,2-dichloropropane, then allyl chloride is formed.

It is apparent from Figs. 7 and 8 that palladium is partially chlorinated to $PdCl_2$ during the reaction.

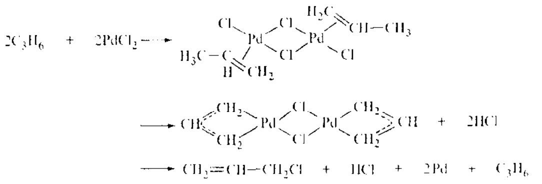

(10)


(11)

Palladium chloride on active charcoal is proved experimentally to react with propylene at above 140°C to give allyl chloride and 1,2-dichloropropane. Therefore, it is considered that the main route of allyl chloride formation is the reaction of palladium chloride and allyl complex of propylene.


(12)

Another possible route is the direct reaction of palladium chloride and propylene via the formation of π- and π-allyl complex (*12*).


(13)

However, this mechanism is not consistent with the fact that the main product is not allyl chloride but 1,2-dichloropropane in the oxychlorination on a $PdCl_2$/active charcoal catalyst (shown in Fig. 6).

Thus the important unit reactions of allyl chloride formation consist of Eqs. (9), (10), (11), and (12). From Eq. (12) the reaction rate is expressed by

$$r_a = k_2[\pi\text{-allyl}][PdCl_2], \tag{14}$$

where r_a is the rate of allyl chloride formation. From Eq. (9) and the results shown in Fig. 2,

$$[\pi\text{-allyl}] = K_1[Pd]P_{C_3H_6}. \tag{15}$$

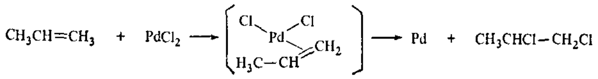
Consequently the rate of allyl chloride formation is expressed by

$$r_a = k_2 \cdot K_1[PdCl_2][Pd]P_{C_3H_6}. \tag{16}$$

Palladium chloride is formed by the oxidative chlorination of Pd [Eqs. (10) and (11)] and consumed by the reaction with activated propylene [Eq. (12)]. When a steady state is attained each rate of Eqs. (11) and (12) are equal and [$PdCl_2$] and [Pd] in Eq. (16) are the functions of the partial pressures of propylene, hydrogen chloride and oxygen. The functions are very complicated and difficult to express by a simple form. However, the results suggested by Eq. (16) are quite consistent with the results shown in Figs. 2, 3, 4, 7, and 8.

In conclusion, the oxychlorination of propylene on palladium catalysts is a kind of redox reaction which is composed of Pd^0 and Pd^{2+} and both species are necessary to the formation of allyl chloride.

1,2-Dichloropropane is formed directly from palladium chloride and propylene, perhaps through π-complex.


(17)

b. Isopropyl chloride (IPC). Isopropyl chloride (IPC) is apparently formed directly from hydrogen chloride and propylene. It is a stable product and not a precurcer of allyl chloride. The formation of IPC is catalyzed by both active charcoal and palladium chloride (Table 4) and the latter is more catalytically active. Thus the main part of IPC formation is attributed to the catalysis of $PdCl_2$ which is formed during the oxychlorination.

Results shown in Figs. 2, 3, and 4 lead to the rate equation expressed by

$$r_1 = k_1'[PdCl_2]P_{C_3H_5}P_{HCl} + k_2'P_{C_3H_6}P_{HCl}. \quad (18)$$

The saturation of the IPC formation at high propylene pressure is interpreted by the decrease in $[PdCl_2]$ caused by the reductive action of propylene. Acceleration by hydrogen chloride and oxygen is due to the increase in $[PdCl_2]$ by the reactions (10) and (11). The decrease in the IPC formation with the rise in the reaction temperature is caused by the equilibrium limitation.

$$CH_3—CH=CH_2 + HCl \rightarrow CH_3—CHClCH_3 \quad \Delta H = +17 \text{ kcal/mol.} \quad (19)$$

TABLE 4

Catalytic Activity of Isopropyl Chloride Formation[a]

Catalyst	Rate of formation (10^{-4} mol/g cat hr)
Active charcoal	1.8
3 wt% Pd–active charcoal	2.4
5 wt% $PdCl_2$–active charcoal	13.6

[a] Reaction temperature = 200°C; C_3H_6:HCl:H_2O = 4:1:10.

c. Carbon dioxide. From Fig. 5 carbon dioxide is apparently formed successively from allyl chloride. In fact when 0.02 atm of allyl chloride is added to the reactant instead of propylene and passed over the catalyst at 200°C about 0.36 mol of carbon dioxide is formed/mol of allyl chloride fed.

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