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The Mechanism of the Palladium-Catalyzed Synthesis of Vinyl Acetate from Ethylene in a Heterogeneous Gas Reaction

SEISIRO NAKAMURA AND TERUO YASUI

From the Research and Development Department, Kurashiki Rayon Company, Sakazu, Kurashiki, Japan

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The catalytic effect of palladium on the synthesis of vinyl acetate from ethylene has been studied. The study led us to the following conclusions: (1) Ethylene and acetic acid are activated as the result of the abstraction of hydrogen by palladium, and this abstraction occurs even in the absence of oxygen for ethylene, whereas for acetic acid it occurs only when oxygen is present; (2) vinyl acetate is produced as the result of combination of dissociatively adsorbed acetic acid with dissociatively adsorbed ethylene, and this surface reaction is the rate determining step in industrially important reaction conditions; (3) co-catalysts such as potassium or other alkali metals promote the abstraction of hydrogen from acetic acid and weaken palladium-oxygen bonds in dissociatively adsorbed acetic acid.

INTRODUCTION

Vinyl acetate has been commercially prepared from acetic acid and acetylene. However, a large quantity of ethylene is cheaply available as a result of the recent development of the petroleum chemical industry, and great efforts have been made to obtain vinyl acetate from ethylene. The studies of this synthesis are classified into two groups: the liquid phase process with redox system using palladium salts and cocatalysts, and the gas phase process with heterogeneous catalysis on metallic palladium. The former method was studied first by I. I. Moiseev in 1960 (*1*), and this process has been industrialized by Imperial Chemical Industries Co. (*2*). The latter method has been disclosed in a Belgian patent of Farbenfabriken Bayer AG. (*3*). Kurashiki Rayon Co. had developed this method independently of Farbenfabriken Bayer AG., and the first commercial plant was put into operation in 1968. We propose a mechanism of this process based on the experimental data obtained in the development of this synthesis.

EXPERIMENTAL

Catalyst Preparation

Supported palladium catalyst was prepared by impregnating a carrier with an aqueous solution of palladium chloride and by evaporating it to dryness. It was reduced with an alkali hydrazine hydrate solution, washed with distilled water until chloro ions disappeared, impregnated with a potassium acetate solution or other metal salt solution and dried.

Palladium black was prepared by adding the alkali hydrazine hydrate solution to the aqueous solution of palladium chloride. Precipitated palladium black was washed with distilled water until chloro ions disappeared and dried.

Palladium acetate, commercially available pure grade, was purified by boiling in acetic acid for 5 hr and dried under reduced pressure.

Reagents

Ethylene and propylene were pure grade products for polymerization (purity being superior to 99.5%).

TABLE 1
THE AMOUNT OF PRODUCTS FORMED FROM ETHYLENE ON PALLADIUM

Reaction[a] time (min)	Product (mM/hr)[b]			
	C_2H_6	*trans* C_4H_8	*cis* C_4H_8	*n*-C_4H_8
1–9.5	0.42	0.0024	0.0016	trace
11–18.5	0.16	0.00097	0.0010	trace
27–40	0.096	0.00034	0.00034	—
50–58	0.067	trace	trace	—
77–85	0.041	—	—	—
132–135	0.052	—	—	—
207–210	0.028	—	—	—
600–603	0.019	—	—	—

[a] Reaction condition: C_2H_4, 0.73 1/hr(NTP) at 150°C.
[b] Catalyst: Pd 5.0 wt %$-Al_2O_3$ (Neobead 900°C).

Procedure and Analysis

All experiments were performed using a flow system. A reactor consisting of a 12 mm ID hard glass tube was used at atmospheric pressure, and a 10 mm ID stainless steel tube was used at 2–5 pressure. Acetic acid was fed into an evaporator with a micro feeding pump. Ethylene and oxygen were passed through the evaporator into the reactor.

Products were analyzed by gas chromatography. Surface structure of catalysts and adsorbed species were examined with X-ray and infrared measurements. A Rigaku Denki X-ray diffractometer with Ni-filtered Cu-Kα radiation was used to obtain X-ray diagrams. Infrared spectra were obtained by the KBr disk techniques with a Hitachi infrared spectrometer EPI-G_2.

RESULT

Products from Ethylene on Palladium

The reactor was packed with 8.2 g of the catalyst consisting of Pd 5.0 wt %–Al_2O_3 (Neobead[1] calcinated at 900°C), and then water was removed from the catalyst by passing nitrogen gas through the reactor at 7.5 1/hr(NTP) at 150°C for 95 min. Ethylene was passed over the catalyst at 0.73 1/hr(NTP) at 150°C. Ethane and butene were formed as shown in Table 1. Freshly and ethylene treated palladium catalysts were examined by X-ray measurement. The diffraction angle 2θ of (111) plane was 40.2° for fresh palladium, but it was 39.0° after the treatment of ethylene at 150°C. By passing oxygen over the ethylene treated palladium catalyst, the diffraction angle 2θ changed from 39.0° to 40.2°. This means that the ethylene treated palladium catalysts occlude hydrogen atoms (*4*). From the following observations it is seen that palladium easily abstracts hydrogen from ethylene: (1) Ethylene treated palladium occludes hydrogen atoms; (2) ethane was formed by passing ethylene over palladium.

The catalytic activity for ethane formation was decreased with reaction time, but the poisoned catalyst could be reactivated easily by passing oxygen over the catalyst as shown in Fig. 1.

Activation of Acetic Acid on Palladium

No vinyl acetate was formed from ethylene and acetic acid in the absence of oxygen under various conditions. This result indicates that acetic acid is not activated in the absence of oxygen, whereas ethylene is activated even if oxygen does not exist as described in Section 1.

In order to study the mechanism of activation of acetic acid, the chemical structure of palladium black after the treatment with gas including or not including

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[1] Product of Mizusawa Kagaku Co., Japan.

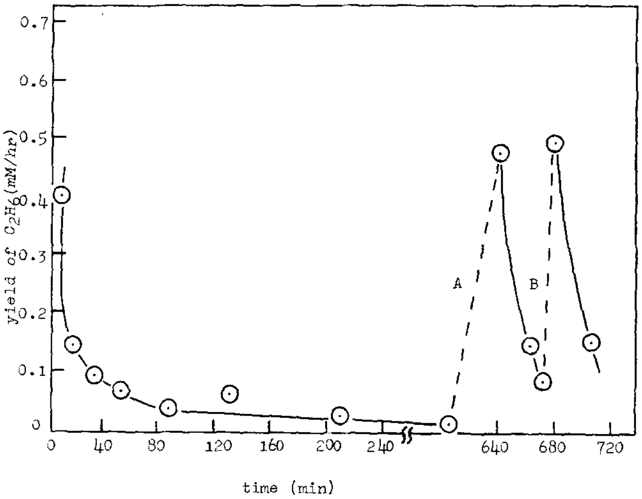


FIG. 1. Reactivation of palladium catalyst for ethane formation from ethylene. (A) treatment with O_2(0.55–0.70 l/hr(NTP) at 150°C, 45 min). (B) treatment with O_2(0.53 l/hr(NTP) at 150°C, 5 min). Cat: Pd 5.0 wt %$-Al_2O_3$ (Neobead 900°C calcination). Reaction condition: flow rate of C_2H_4; 0.73 l/hr(NTP); temp = 150°C.

oxygen was examined with X-ray and infrared measurements. From X-ray data, as shown in Fig. 2 (a), it can be seen that palladium black after the treatment with acetic acid including oxygen showed the lines at $2\theta = 10.6°$, $11.0°$, $12.0°$, $12.5°$, $13.0°$, $13.5°$, $14.8°$, $15.0°$ ($2\theta = 10–15°$). They were identical with lines belonging to palladium acetate. From Fig. 3 (a) we note that the palladium black exhibited strong adsorption bands at 1600, 1575, 1420 cm^{-1} and weaker bands at 620, 650, 695 cm^{-1}.

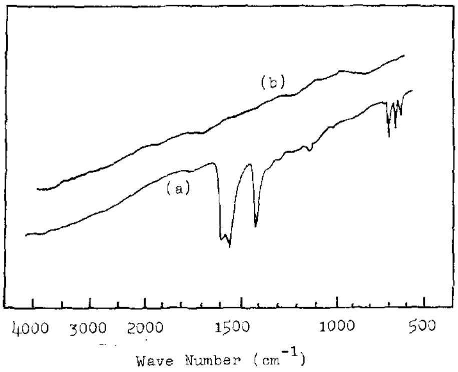


FIG. 2. X-ray diffraction patterns of Pd black treated with gas including CH_3COOH. (a) Pd black; N_2:O_2:CH_3COOH = 63:23:14, 40 hr at 105°C. (b) Pd black; N_2:CH_3COOH = 80:20, 72 hr at 105°C.

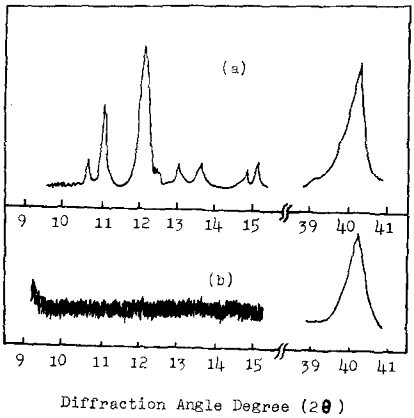


FIG. 3. Infrared absorption spectra of Pd black treated with gas including CH_3COOH. (a) Pd black; N_2:O_2:CH_3COOH = 63:23:14, 40 hr at 105°C. (b) Pd black; N_2:CH_3COOH = 80:20, 72 hr at 105°C.

These bands at 1575, 1420, 650, and 620 cm^{-1} are due to ionized COO stretching, whereas 1600 and 695 cm^{-1} are due to coordinated COO stretching (*5*). These observations led to the conclusion that palladium acetate is formed by treating palladium with acetic acid including oxygen. The infrared spectrum data suggest that palladium acetate has two types of Pd—O bond. X-ray and infrared spectrum data show that in the absence of oxygen palladium acetate is not formed by treating palladium with acetic acid (see Fig. 2 (b) and Fig. 3 (b)).

Palladium black on which palladium acetate was formed was evacuated at 10^{-3} mmHg–10^{-4} mmHg pressure at 120°C for 10 hr. It was sealed in nitrogen gas, and ethylene was passed over it at 160°C. Vinyl acetate was detected in the effluent gas by gas chromatography. Vinyl acetate also was formed from palladium acetate $Pd(OCOCH_3)_2$ by passing ethylene over it at 160°C. From these results it can be seen that oxygen is necessary for the abstraction of hydrogen from acetic acid, and once acetic acid is adsorbed dissociatively on palladium, vinyl acetate can be formed by passing ethylene on it.

Palladium acetate $Pd(OCOCH_3)_2$ including potassium acetate was easily reduced with ethylene (Section 3) and $Pd(OCOCH_3)_2$ was not detected in the catalyst after the reaction of vinyl acetate from ethylene (X-ray diagram). These observations suggest that the intermediate of the reaction is dissociatively adsorbed acetic acid Pd—$(OCOCH_3)$, and $Pd(OCOCH_3)_2$ does not exist in the working state.

TABLE 2
INFLUENCE OF ACETATES OF VARIOUS METALS ON THE CATALYTIC ACTIVITY[a]

Metal ion	VAc STY (g/cat. 1/hr)[b]
Cs^+	26
Rb^+	25
K^+	25
Na^+	19
Li^+	15
Cu^+	5
Ba^+	5
Mg^+	3
Zn^+	15
no addition	3

[a] Cat.: Pd 1.0 wt % (carrier; Neobead C calcinated at 900°C) metal ion; metal/Pd = 2 (M/M).

[b] Reaction condition: SV 600 hr^{-1}, C_2H_4:O_2:CH_3COOH = 80:10:10, temp = 120°C.

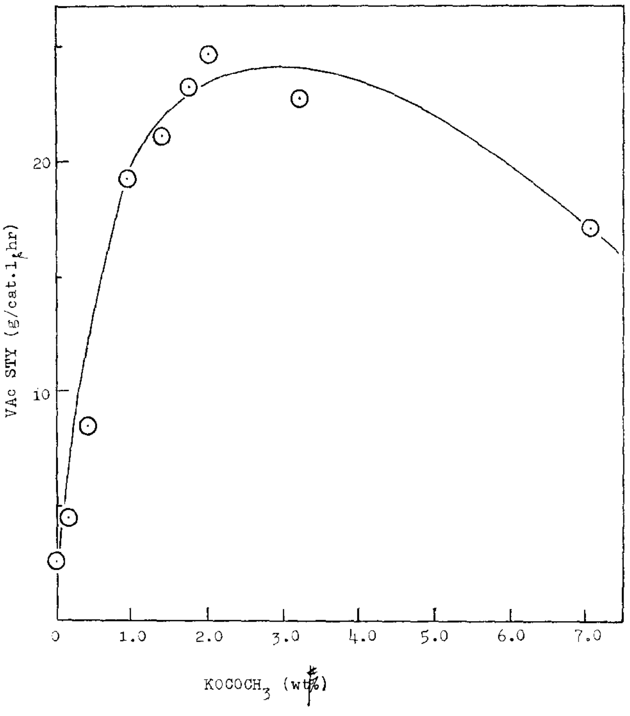


FIG. 4. Influence of concentration of potassium acetate on the catalytic activity. Cat: Pd 1.0 wt % – Al_2O_3 (Neobead 900°C calcination) reaction condition: SV 800 hr^{-1}, C_2H_4:O_2:CH_3COOH = 80:10:10, temp = 120°C.

Effect of Potassium or Other Metals as Co-catalyst

Potassium acetate impregnated catalyst promotes the formation of vinyl acetate as shown in Fig. 4. The influence of acetates of various metals on the catalytic activity is outlined in Table 2. The impregnation of alkali metal acetates was found to be more effective than that of other metals.

The influence of potassium anions on the catalytic activity also was examined. Table 3 indicates that the constant activity of vinyl acetate production does not depend on anions where anions are easily replaced with acetate ion, although the activity at the beginning of the reaction is less than the constant activity. Such an anion was found in products as the acid corresponding to the anion and the vinyl ester of the acid at the beginning of the reaction. As shown in Table 4, in addition to vinyl acetate, propionic acid and vinyl propionate were formed from ethylene, acetic acid and oxygen with potassium propionate impregnated catalyst at the beginning of the reaction. Similarily, in addition to vinyl propionate, acetic acid and vinyl acetate were formed from ethylene, propionic acid and oxygen with the potassium acetate impregnated catalyst at the beginning of the reaction. Vinyl acetate is not formed with the catalyst impregnated with potassium anions such as potassium chloride, which is not easily replaced with acetate ion of acetic acid.

TABLE 3

INFLUENCE OF ANIONS OF POTASSIUM ON THE CATALYTIC ACTIVITY[a]

Anion	VAc STY (g/cat. 1/hr)[b]
$—OCOCH_3$	25
$—OCOC_2H_5$	25
$—OCO(CH_2)_3CH_3$	21
$—C_2O_4$	25
—OH	25
$—CO_3$	25
$—SiO_3$	11
—Cl	0

[a] Cat.: Pd 1.0 wt %-Al_2O_3 (Neobead C calcinated at 900°C), potassium salt; K/Pd = 2(M/M).

[b] Reaction condition: SV 600 hr^{-1}, C_2H_4:O_2:CH_3COOH = 80:10:10, temp = 120°C.

Palladium black including potassium acetate (I) and not including one (II) were treated with the gas (N_2:O_2:CH_3COOH = 63:23:14) at 3 1/hr(NTP) at 120°C for 2 hr. X-ray measurement shows that after the treatment the diffraction angle 2θ of (111) plane of the catalyst (II) was 40.2°, which was identical with that of fresh palladium, whereas 2θ of (111) plane of the catalyst (I) was 39.0°. During the treatment, carbon dioxide was produced with the catalyst (I), but was not produced with the catalyst (II). From these results, it is considered that potassium ionizes associatively acetic acid and promotes the abstraction of hydrogen from adsorbed acetic acid.

Palladium acetate $Pd(OCOCH_3)_2$ including potassium acetate (III) and that not including it (IV) were treated with the

TABLE 4

PRODUCTS FORMED FROM ETHYLENE, ACETIC ACID AND OXYGEN WITH Pd CAT. INCLUDING $KOCOC_2H_5$[a]

	Product (mM/hr)[b]		
Reaction time (min)	propionic acid	vinyl propionate	vinyl acetate
0–40	0.87	0.27	0.11
40–80	0.66	trace	3.15
80–120	trace	trace	3.46
total, 0–120	1.53	0.27	6.72
	degree of recovery	51.5%	

[a] Cat.: Pd 1.5 wt %, 6.8 cc (6.1 g), Pd 0.57 mM, Carrier; Neobead 900°C, potassium propionate 3.5 mM add.

[b] Reaction condition: C_2H_4:O_2:CH_3COOH 80:10:10, SV 515 =hr^{-1}, temp = 130°C.

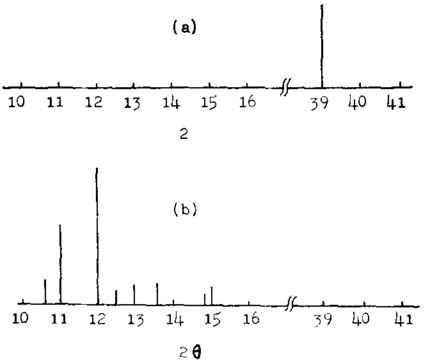


Fig. 5. X-ray diffraction patterns of (b) $Pd(OCOCH_3)_2$ and (a) $Pd(OCOCH_3)_2$ – $KOCOCH_3$, treated with ethylene. ($KOCOCH_3/Pd(OCOCH_3)_2$ = 2, $C_2H_4:CH_3COOH:O_2$ = 71:19:10, 1 1/hr (NTP), 2 hr, temp = 120°C.

gas ($C_2H_4:CH_3COOH:O_2 = 71:19:10$) at 1 1/hr(NTP) at 120°C for 2 hr (see Fig. 5). X-ray measurement shows that palladium acetate (III) was easily changed to palladium black by the foregoing treatment and vinyl acetate was formed, while palladium acetate (IV) did not react. A similar result was obtained by the treatment of pure ethylene gas at 120°C. From these observations, it can be seen that potassium weakens palladium-oxygen bonds in palladium acetate in addition to the promotion of the hydrogen abstraction from adsorbed acetic acid.

The amount of ethane formed from ethylene did not differ between potassium free catalyst and that containing catalyst, which means that potassium or other alkali metals do not affect the abstraction of hydrogen from ethylene.

Kinetic Data for Vinyl Acetate Formation from Ethylene

The influence of the partial pressure of ethylene and acetic acid on the rate of formation of vinyl acetate is shown in Fig. 6 and Fig. 7. In these reaction conditions the catalytic activity did not decrease and the influence of gas-film resistance on the reaction rate was not observed.

Products from Propylene, Acetic Acid and Oxygen on Palladium

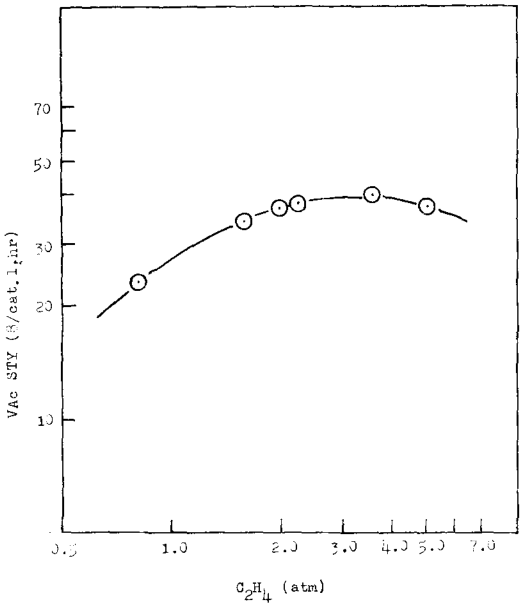


Fig. 6. Dependence of reaction rate on partial pressure of ethylene. Cat: Pd 1.0 wt %–$KOCOCH_3$ – 3 wt %–Al_2O_3 (Neobead 900°C calcination). Reaction condition: SV 1000 hr^{-1}, total pressure; 5.23 ata, O_2; 0.12 atm, CH_3COOH; 0.11 atm, N_2 dillution, temp = 110°C.

Propylene was reacted with acetic acid and oxygen on various supported palladium under the following condition; $C_3H_6:CH_3COOH:O_2 = 80–60:10–30:10$, SV 600 hr^{-1}, temp 100–160°C. The products were allyl acetate and a trace of carbon dioxide.

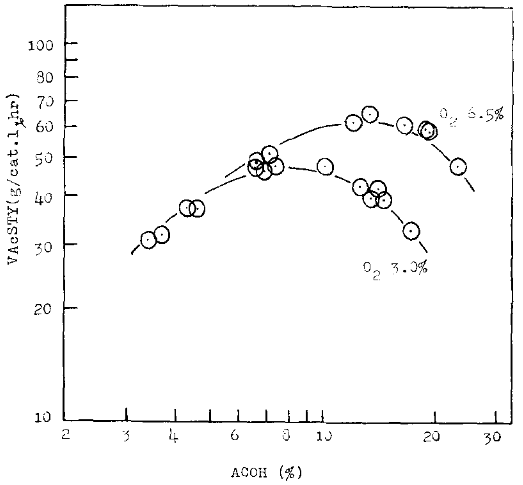


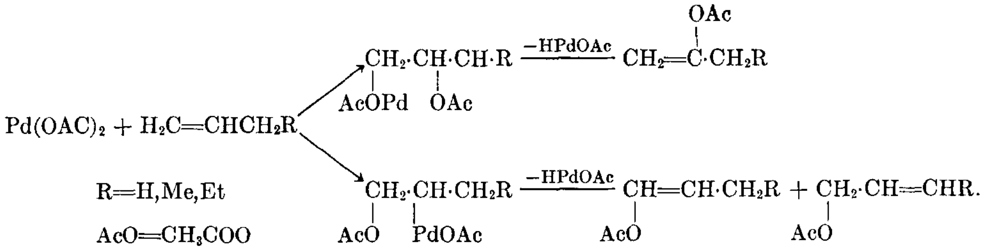
Fig. 7. Dependence of reaction rate on partial pressure of acetic acid. Cat: Pd 1.0 wt %–$KOCOCH_3$ – 3 wt %–Al_2O_3 (Neobead 900°C calacation). Reaction condition: SV 1000 hr^{-1} Total pressure; 3.0 ata, C_2H_4; 2.2 ata, N_2 dillution, temp = 120°C.

Neither iso-propenyl acetate nor *n*-propenyl acetate were detected by gas chromatography, in accordance with a patent of Farbenfabriken Bayer AG. (*6*).

The mixed gas of propylene and ethylene were reacted with acetic acid and oxygen on palladium catalysts under the condition, $C_2H_4:C_3H_6:CH_3COOH:O_2 = 75:5:10:10$, SV 600 hr^{-1}, temp 120°C. Allyl acetate and a trace of carbon dioxide were formed, and vinyl acetate was not detected. This means that propylene is much more reactive than ethylene. The diffraction angle 2θ of (111) plane of palladium treated with propylene at 150°C was 39.0°, which is equal to the diffraction angle of ethylene treated palladium.

DISCUSSION

Allyl acetate is selectively formed from propylene, acetic acid and oxygen with metallic palladium in a gas phase, whereas in a liquid phase, in addition to allyl acetate, iso-propenyl acetate and *n*-propenyl acetate were formed with palladium salt and suitable co-catalysts (*7–11*). This result shows that the mechanism differs between a gas phase reaction and a liquid phase one. For the liquid phase W. Kitching *et al.* proposed the following mechanism:



$$\mathrm{Pd(OAC)_2 + H_2C{=}CHCH_2R} \nearrow \underset{\mathrm{AcOPd}}{\mathrm{CH_2}}\cdot\underset{\mathrm{OAc}}{\mathrm{CH}}\cdot\mathrm{R} \xrightarrow{-\mathrm{HPdOAc}} \mathrm{CH_2{=}}\overset{\mathrm{OAc}}{\mathrm{C}}\mathrm{\cdot CH_2R}$$

$$\searrow \underset{\mathrm{AcO}}{\mathrm{CH_2}}\cdot\underset{\mathrm{PdOAc}}{\mathrm{CH}}\cdot\mathrm{CH_2R} \xrightarrow{-\mathrm{HPdOAc}} \underset{\mathrm{AcO}}{\mathrm{CH}}\mathrm{{=}CH\cdot CH_2R} + \underset{\mathrm{AcO}}{\mathrm{CH_2}}\mathrm{\cdot CH{=}CHR}.$$

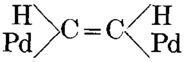
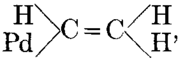
R=H,Me,Et

$AcO=CH_3COO$

Y. Kunugi *et al.* suggested from kinetic data available that the gas phase reaction proceeds similarly to the liquid phase reaction and the rate determining step is the abstraction of hydrogen from $H—Pd—C_2H_4OCOCH_3$ in the presence of dissociatively adsorbed oxygen (*12*).

However, we suggest that in the gas phase reaction vinyl acetate is produced as the result of combination of dissociatively adsorbed ethylene with dissociatively adsorbed acetic acid, based on the following results: (1) Palladium abstracts hydrogen from ethylene with ease even in the absence of oxygen; (2) acetic acid is activated as the result of the abstraction of hydrogen on palladium in the presence of oxygen; (3) allyl acetate is selectively formed from propylene, acetic acid and oxygen on palladium.

As described in Section 5, allyl acetate was the main product formed from ethylene, propylene, acetic acid and oxygen with metallic palladium even if the partial pressure of propylene was much less than that of ethylene. This result can be rationalized in a way that dissociation energy of C-H bond of propylene is less than that of ethylene.[2]

Many suggestions have been made for the structures of adsorbed species of olefins (*13–19*). For the dissociatively adsorbed species of ethylene, L. H. Little *et al.* proposed the di-adsorbed species of formula  $\mathrm{{}^{H}_{Pd}{>}C{=}C{<}^{H}_{Pd}}$ from the comparison of the adsorbed species of acetylene by a infrared spectra method (*13*). However, we propose mono-adsorbed species of formula  $\mathrm{{}^{H}_{Pd}{>}C{=}C{<}^{H}_{H}}$, based on the following results: (1) In vinyl acetate synthesis, acetylene poisoned palladium catalyst to an extreme degree; (2) acetylene was adsorbed on palladium to form the di-adsorbed species of the type Pd-CH=CH-Pd (*13*); (3) the catalytic activity of vinyl acetate production did not decrease by the pretreatment of pure ethylene for 100 hr. In the case of adsorbed propylene, it is considered to form allyl complex on palladium.

The amount of ethane formed from

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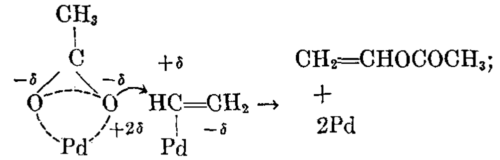
[2] The dissociation energy of C-H bond is 104 Kcal/mol for ethylene and it is 77 Kcal/mol for the methyl group of propylene (*20*).

ethylene on palladium decreased with reaction time. This observation has been explained in terms of the accumulation of acetylene residues on palladium by S. J. Stephens, which is formed by self-hydrogenation (*14*). The catalyst poisoned by acetylene residues was reactivated by passing oxygen on palladium (Section 1).

From the experimental results obtained (Sections 1–5), it is suggested that the reaction of vinyl acetate synthesis from ethylene proceeds as the following mechanism: (1) Ethylene is dissociatively adsorbed on palladium as the result of abstraction of hydrogen; (2) oxygen is dissociatively adsorbed on palladium (*21*); (3) acetic acid is associatively adsorbed on palladium; (4) in the presence of adsorbed oxygen, hydrogen is abstracted from associatively adsorbed acetic acid by palladium; (5) vinyl acetate is produced as the result of the combination of dissociatively adsorbed acetic acid with dissociatively adsorbed ethylene; it may possibly proceed as follows:



$(+2\delta = 1)$

(6) abstracted hydrogen reacts with dissociatively adsorbed oxygen; (7) some of dissociatively adsorbed ethylene and acetic acid are oxidized to carbon dioxide with dissociatively adsorbed oxygen.[3] The mechanism is summarized as follows:

Main reaction

$$C_2H_4 + 2Pd \underset{k'_1}{\overset{k_1K_1}{\rightleftarrows}} CH_2{-}CH{-}Pd + PdH \quad (1)$$

$$O_2 + 2Pd \underset{k'_2}{\overset{k_2,K_2}{\rightleftarrows}} 2Pd{-}O \quad (2)$$

$$CH_3COOH + Pd \underset{k'_3}{\overset{k_3K_3}{\rightleftarrows}} Pd{-}CH_3COOH_{ad.} \quad (3)$$

$$Pd{-}CH_3COOH_{ad.} + PdO \underset{k'_4}{\overset{k_4,K_4}{\rightleftarrows}} Pd{-}OCOCH_3 + Pd{-}OH \quad (4)$$

$$Pd{-}OCOCH_3 + CH_2CH{-}Pd \underset{k'_5}{\overset{k_5,K_5}{\rightleftarrows}} Pd{-}CH_2CHOCOCH_{3\,ad.} + Pd \quad (5)$$

$$Pd{-}CH_2{\cdot}CHOCOCH_{3\,ad.} \underset{k'_6}{\overset{k_6,K_6}{\rightleftarrows}} Pd + \text{vinyl acetate} \quad (6)$$

$$Pd{-}OH + PdH \underset{k'_7}{\overset{k_7,K_7}{\rightleftarrows}} Pd{-}H_2O_{ad.} + Pd \quad (7)$$

$$Pd{-}H_2O_{ad.} \underset{k'_8}{\overset{k_8,K_8}{\rightleftarrows}} Pd + H_2O \quad (8)$$

Side reaction

$$CH_2{-}CH{-}Pd + Pd{-}O \underset{k'_9}{\overset{k_9,K_9}{\rightleftarrows}} Pd{-}CO_{2\,ad.} + Pd{-}H_2O_{ad.} \quad (9)$$

(followed by (8))

$$Pd{-}CO_{2\,ad.} \underset{k'_{10}}{\overset{k_{10},K_{10}}{\rightleftarrows}} Pd + CO_2 \quad (10)$$

$$Pd{-}OCOCH_3 + Pd{-}O \underset{k'_{11}}{\overset{k_{11},K_{11}}{\rightleftarrows}} Pd{-}CO_{2\,ad.} + Pd{-}H_2O_{ad.} \quad (11)$$

(followed by (10), and then by (8))

From the kinetic data we suggest that the rate determining step is the combination of dissociatively adsorbed acetic acid with dissociatively adsorbed ethylene (Eq. 5). In this case the rate of the vinyl acetate formation is given by the following equation:

$$R_{VAC} = \frac{k_5K_1K_2^{\frac{1}{2}}K_3K_4p_{C_2H_4}p_{O_2}^{\frac{1}{2}}p_{CH_3COOH}}{(1 + K_1p_{C_2H_4} + (K_2p_{O_2})^{\frac{1}{2}} + K_3p_{CH_3COOH})^2}.$$

$(p = \text{atm}, R_{VAC} = \text{g/l. hr})$

This equation well fits the experimental

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[3] It can be considered that carbon dioxide is mainly formed from ethylene as follows: (1) Selectivity of vinyl acetate formation increases with increase of the ratio of acetic acid to ethylene; (2) ethylene is oxidized to carbon dioxide by palladium more easily than acetic acid.

values given in Figs. 6 and 7, putting $K_1 = 0.93$, $K_2 = 6.27$, $K_3 = 11.9$, and $K_5 = 439$, with a standard deviation 3.7 $(t/m^3 \cdot D)$.

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