Catalytic Oxidation of Ethylene to Acetaldehyde. Palladium Chloride–Active Charcoal Catalyst

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With palladium chloride supported on active charcoal, ethylene was catalytically oxidized by oxygen to acetaldehyde in the vapor phase. Selectivity and activity were very high. Steam was essential for the formation of acetaldehyde and the rate increased markedly with rise in steam concentration but decreased with rise in temperature, providing an apparent activation energy of −18 kcal/mol. Small ratios of butenes and carbon dioxide were formed but the selectivity of acetaldehyde was about 99% under the determined optimum condition. The kinetics suggest that the catalysis of the reaction consisted of the reduction of palladium salt by ethylene and water to give acetaldehyde and reduced palladium and reoxidation of reduced palladium by oxygen with the catalysis of active charcoal. Reduction of palladium chloride by ethylene and water, which gives acetaldehyde, is considered to proceed along a path that is substantially the same as that of liquid homogeneous systems. Oxidation of reduced palladium is considered to take place by dissociatively adsorbed oxygen on active charcoal. Reaction of other olefins was also studied; the main products were methyl ketones. Reactivity was in the following order: ethylene > propylene > 1-butene ≃ *cis*-2-butene > *trans*-2-butene.

Oxidation of olefins by metal ions is a novel method for the synthesis of carbonyl compounds. For example, palladium ion oxidation in the liquid phase provides saturated methyl ketones or aldehydes in the presence of water.

Smidt, *et al.* (1959), made a new homogeneous catalyst of olefin oxidation which is composed of palladium chloride, cupric chloride, and hydrochloric acid. Recently, Evnin, *et al.* (1973), have revealed a new heterogeneous catalyst of a vapor phase oxidation of ethylene in the presence of steam. This catalyst is composed of Pd^{2+} and vanadium pentoxide matrix. Both of them are evidently redox catalysts composed of palladium(II) ion and second metallic ions.

We have already reported (Fujimoto, *et al.*, 1972) that palladium salts adsorbed on active charcoal are excellent heterogeneous catalysts of ethylene oxidation in the presence of steam and the catalysis is a kind of redox consisting of palladium ion and active charcoal. This paper reports details and the kinetics of ethylene oxidation on palladium chloride–active charcoal catalysts.

Experimental Section

Catalysts used in this study were palladium chloride adsorbed on active charcoal from aqueous hydrochloric solution of palladium(II) chloride. The properties of catalysts are given in Table I. Details of the catalyst preparation have been described previously (Fujimoto, *et al.*, 1972).

Experimental apparatus and procedures, conditions of experiments, and analytical methods were the same as in the previous paper.

Results and Discussion

1. Synthesis of Acetaldehyde. Palladium chloride in the catalysts is one of the active components and consequently the catalyst activity depends on the content of palladium. Figure 1 shows that catalyst activity increases almost linearly with increase in palladium content up to about 0.5 wt %, but the selectivity of acetaldehyde is low when the palladium content is high owing to the formation of butenes. The activity of carbon dioxide formation is almost independent of the palladium content. If a catalyst contained too much palladium, for example 5 wt % or more, the activity was very low, and further, it lost its activity fairly rapidly during reaction. The optimum content of palladium lies in the range from 0.5 to 1.0 wt %. The low activity of a high palladium catalyst is proved to be due to a small amount of effective palladium ion which is caused by the aggregation of palladium chloride.

The reaction on $PdCl_2$-A.C. catalyst was strongly influenced by temperature, and its effects were very characteristic. Figures 2 and 3 show the effect of temperature on the reaction, and the parameter X is the steam content in the reaction mixture. Contrary to the usual oxidation of olefins, the conversion of ethylene decreases with a rise in temperature. The selectivity of acetaldehyde also sharply decreases and that of butenes increases with temperature, but when there is a sufficient amount of steam in the reaction mixture, the conversion of ethylene and selectivity of acetaldehyde is kept at a higher level until higher temperatures. Under the reaction conditions shown here, selectivity of carbon dioxide was less than 1 mol %. The results in Figure 2 and 3 are explained as follows. Formation of acetaldehyde is proved to be strongly accelerated by water molecules and that of butenes is suppressed (shown later). On the other hand, the amount of water which is adsorbed on a catalyst surface is considered to decrease with a rise in temperature. Consequently, the formation rate and the selectivity of acetaldehyde decrease with a rise in temperature due to the decrease in an effective amount of water molecules on a catalyst. However, they are kept at high levels when the water content in reaction mixture is high because the amount of water on a catalyst is kept at a considerably high level even when the temperature is high.

Reaction rates and product selectivities are also affected by the oxygen to ethylene molar ratio. Figure 4 shows the results which were obtained by varying the oxygen to ethylene molar ratio while keeping the partial pressure of steam constant. The maximum production rate of acetaldehyde is obtained when the oxygen to ethylene molar ratio is close to 1:4. The selectivity of butene is high at a high ethylene ratio and that of carbon dioxide is high at a high oxygen ratio. Thus maximum selectivity of acetaldehyde is obtained at an oxygen to ethylene molar ratio of about 1.5:3.5. As a whole the optimum molar ratio of oxygen to ethylene lies from 1:4 to 2:3.

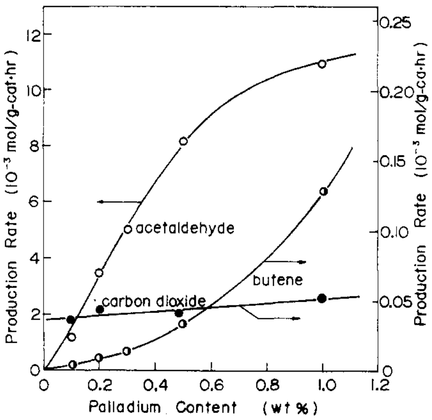


Figure 1. Catalyst properties *vs.* palladium content in $PdCl_2$-A.C. catalyst; active charcoal: made of wood, steam activation, 1380 m^2/g; C_2H_4:O_2:H_2O = 4:1:6, 100°C.

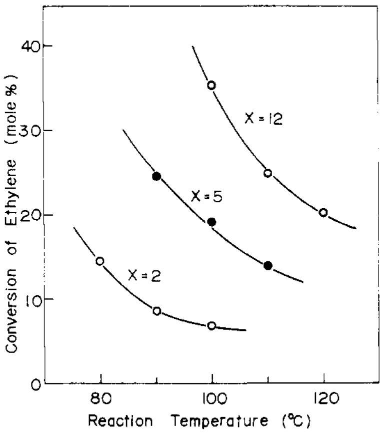


Figure 2. Effect of reaction temperature on ethylene conversion; catalyst A, C_2H_4:O_2:H_2O = 4:1:X, W/F = 22.

Table I. Properties of Catalysts

	Catalyst		
	A	B	C
Active component	$PdCl_2$	$PdCl_2$	$PdCl_2$
Palladium content (wt %)	1.0	3.0	0.5
Specific surface area (m^2/g)	1500	1500	1380
Average particle size (mm)	1.5	1.5	1.0
Source of active charcoal	Wood	Wood	Wood
Method of activation	Steam	Steam	Steam

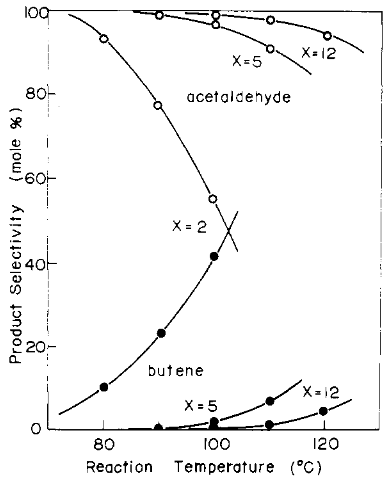


Figure 3. Effect of reaction temperature on products selectivity; same reaction conditions as in Figure 2.

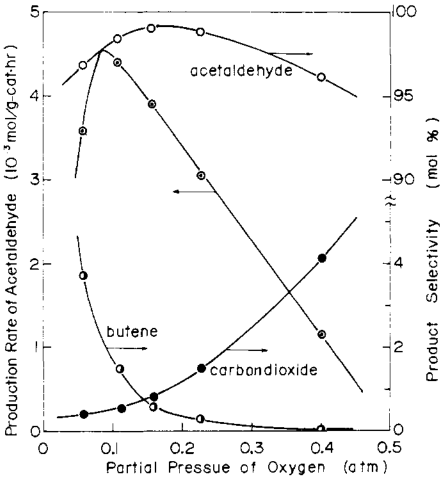
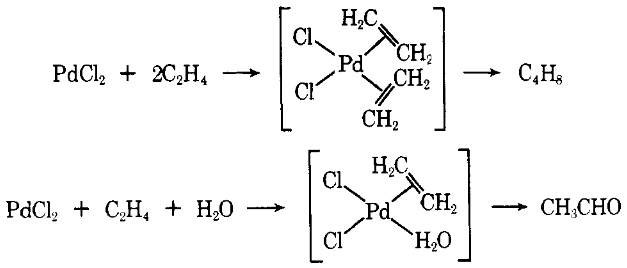


Figure 4. Effect of ethylene oxygen mole ratio on reaction; catalyst A, P_{H_2O} = 0.5 atm, P_{O_2} + $P_{C_2H_4}$ = 0.5 atm, 100°C.

Steam concentration has profound effects on the reaction. From Figures 5 and 6 it is apparent that the production rate of acetaldehyde is markedly accelerated with an increase in steam, while that of butene is suppressed. The behavior of carbon dioxide formation is similar to that of acetaldehyde. Thus the higher the steam concentration is, the better is the result obtained. The acceleration effect by steam indicates the similarity of the reaction mechanism to those proposed for the liquid homogeneous reaction system (Dozono and Shiba, 1963; Henry, 1964). The suppression of butene formation by steam is considered as follows. The formation of butene requires coordination (or adsorption) of two molecules of ethylene to an active site (Ketley, *et al.*, 1967). The chance of it increases with an increase in ethylene concentration and thus the rate of butene formation increases (shown in Figure 4). On the other hand, water molecules which coordinate to the same site competitively with ethylene, reduce the chance of ethylene-ethylene coordination.



Consequently, the formation of butene is suppressed and that of acetaldehyde is accelerated by steam. Carbon dioxide is considered to be formed mainly from an oxidative decomposition of acetaldehyde. Table II and Figure 7 show the effect of contact time on product yield. High yield of acetaldehyde is easily obtained with high selectivity. The decrease in butene yield with contact time is apparently due to a successive oxidation to methyl ethyl ketone.

Table III shows the results obtained by oxidizing various olefins with $PdCl_2$-A.C. catalyst. Product distributions and reactivities are about the same as those which have been reported by Smidt, *et al.* (1962). Similarities of reactivity and product patterns suggest the similarity of the reaction mechanism to that of liquid homogeneous reaction.

Table II. Reaction of Ethylene on Catalyst A (Reaction Temperature 100°C)

Contact time, g of cat. hr/mol	Mole ratio			Yield of products, mol % on ethylene			
	C_2H_4	O_2	H_2O	CH_3CHO	CO_2	C_4H_8	$C_2H_5COCH_3$
4.5	4	1	6	13.5	0.062	0.053	0.005
8.9	4	1	6	20.3	0.099	0.075	0.011
14.9	4	1	6	33.4	0.183	0.120	0.023
24.3	4	1	6	39.1	0.225	0.075	0.070
37.4	4	1	6	42.0	0.294	0.076	0.110
4.5	2	1	3.6	14.1	0.079	0.037	0.002
8.9	2	1	3.6	21.1	0.157	0.053	0.005
14.9	2	1	3.6	35.9	0.283	0.089	0.011
24.3	2	1	3.6	45.4	0.398	0.068	0.025
37.4	2	1	3.6	53.5	0.520	0.038	0.053

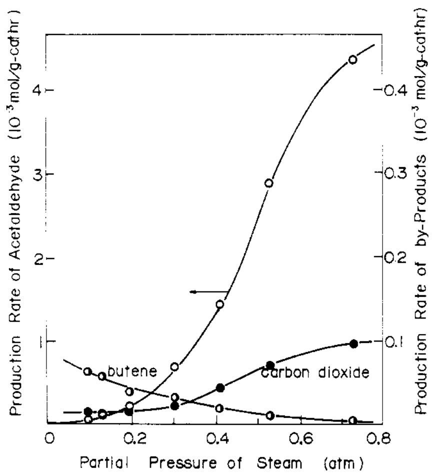


Figure 5. Partial pressure of steam *vs.* production rate; catalyst A, 100°C, $P_{C_2H_4}$ = 0.2 atm, P_{O_2} = 0.1 atm, W/F = 11 g of cat hr/mol.

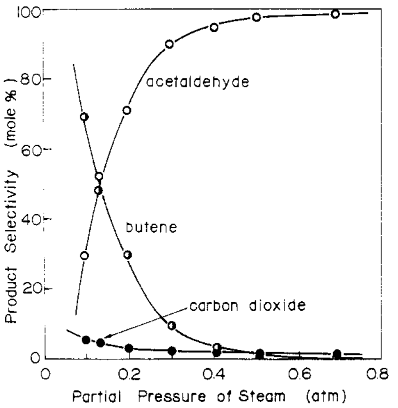


Figure 6. Partial pressure of steam *vs.* products selectivity; same conditions as in Figure 5.

Table III. Oxidation of Olefins on Catalyst B[a]

Olefin	Olefin conversion, mol %	Product selectivity, mol %		
		Aldehyde	Ketone	Carbon Dioxide
Ethylene	52	98	. . .	0.9
Propylene	28	10	89	0.5
1-Butene	10	4	93	0.9
trans-2-Butene	7	tr	96	2.6
cis-2-Butene	10	tr	97	2.1

[a] 105°C, W/F = 25 g of cat · hr/mol. Olefin:O_2:H_2O = 2.5:1:7.

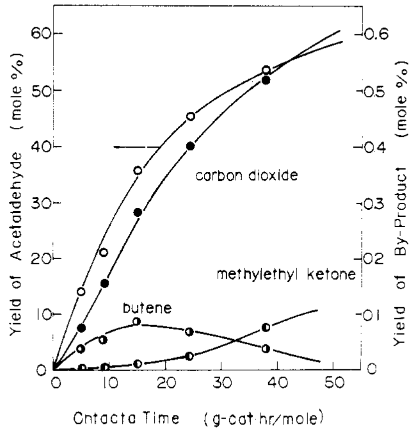


Figure 7. Contact time *vs.* products yield; catalyst A, 100°C, C_2H_4:O_2:H_2O = 2:1:3.6.

2. Kinetic Study. Kinetics of homogeneous palladium ion oxidations have been studied by several persons to clarify the mechanism (Dozono and Shiba, 1963; Henry, 1964). The kinetics are summarized as follows. The reaction rate is proportional to the partial pressure of the olefin and the concentration of the palladium ion and is inversely proportional to the concentration of the hydronium ion and two powers of halide ion concentration.

The kinetic study of this heterogeneous catalyst has an advantage in that the reaction is performed in a simple system which consists of palladium chloride and active charcoal only. Furthermore, it is possible in the system to clarify the kinetic effect of water which has been impossible to study in the liquid phase reaction, whereas the participation of water molecules in the formation of the carbonyl compound has been suggested (Smidt, *et al.*, 1959). It is believed that the kinetics of this catalyst can clarify the difference or the similarity of the reaction mechanism between the homogeneous and heterogeneous systems.

The possibilities were checked concerning the diffusion of reactants or products within micropores or in the boundary layer of a catalyst surface being the rate-determining step. Catalyst activities were measured with catalysts which had an average diameter from 0.3 to 3.2 mm. Reaction rates were at substantially the same level with those catalysts. The effect of linear gas velocity on reaction rate was checked by varying the linear velocity of the reactant gas mixture from 0.5 to 10 cm/sec while keeping

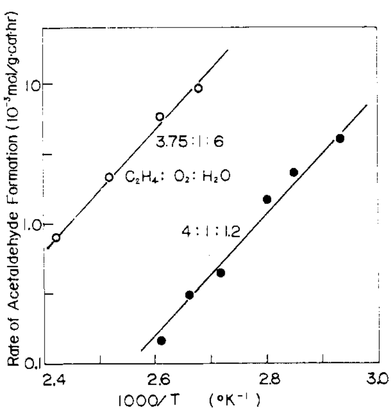


Figure 8. Arrhenius plots of acetaldehyde formation; catalyst C.

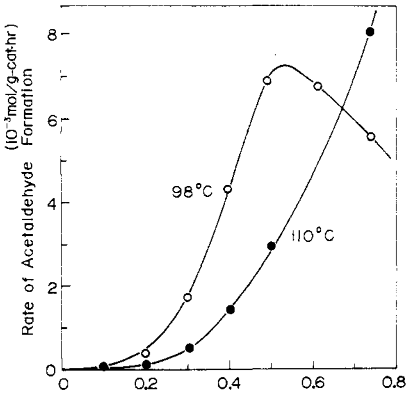


Figure 9. Partial pressure of steam *vs.* reaction rate (1); catalyst C, 100°C, $P_{C_2H_4} = 0.2$ atm, $P_{O_2} = 0.1$ atm.

the contact time constant. Substantially the same rates were obtained. Thus, it was concluded that the diffusion process of reactants or products was not the rate determining step of this reaction. Kinetic data were obtained by a differential method in which the conversion of reactants was less than 10%.

Figure 8 shows the effect of temperature on reaction rate. Apparently the rate increases with temperature decrease, but if the temperature decreases below the dew point the rate falls suddenly to about zero (not shown) and further, the catalyst activity is not restored to its original value even when the temperature is raised above the dew point. Below the dew point micropores of catalyst are filled with liquid water and thus the rate-determining step of the reaction is considered to be the diffusion of reactants or products in water within the micropores, the rate of which is about 1/1000 or lower as fast as that in gas phase. The irreversible deactivation of catalyst during the reaction below the dew point is proved to be caused by aggregation and precipitation of palladium metal which occur within micropores filled with water.

Arrhenius plots of the results shown in Figure 8 provide an apparent activation energy of about −18 kcal/mol. This value fluctuates within 5 kcal/mol with various active charcoals, but it differs greatly from the value of liquid phase reaction of 10.4 kcal/mol (Dozono and Shiba, 1963). The reason for this has been already suggested (in Figure 2) and will be discussed in more detail later.

The effect of each reactant pressure, steam, ethylene, and oxygen on reaction rate are measured and the results are shown in Figures 9, 10, 11, and 12. Partial pressures of reactants were changed independently while others were kept constant by balancing with nitrogen.

In Figure 9 a decrease in reaction rate with increase in steam pressure is observed above 0.5 atm at 98°C while at 110°C, the phenomenon is not observed. Cohan (1938) has pointed out that pores which have a small diameter are filled with condensed liquid above its dew point because of the surface tension of the liquid. The relation between the vapor pressure of a liquid and the radius of pores in which condensation of the liquid occurs at any temperature is represented by Kelvin's equation

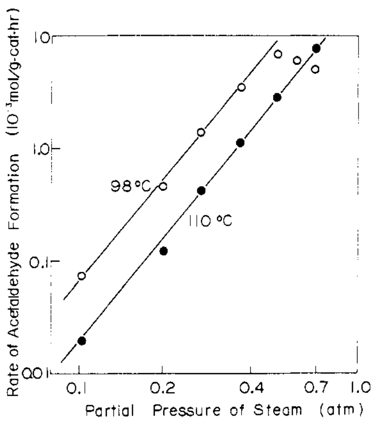


Figure 10. Partial pressure of steam *vs.* reaction rate (2); same conditions as in Figure 9.

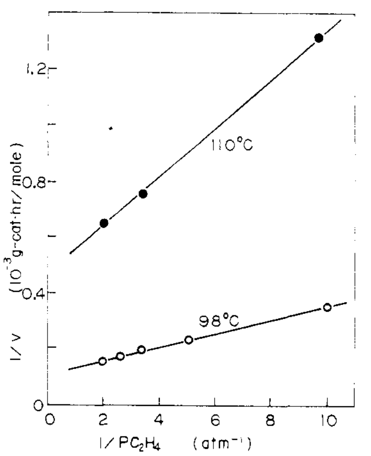


Figure 11. Partial pressure of ethylene *vs.* reaction rate; catalyst C, $P_{O_2} = 0.1$ atm, $P_{H_2O} = 0.5$ atm.

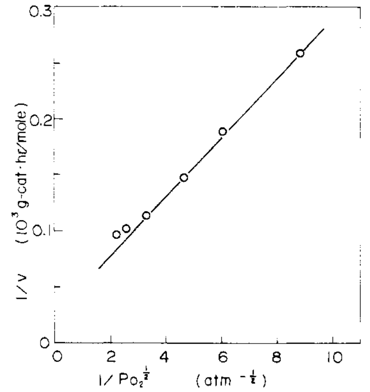


Figure 12. Partial pressure of oxygen *vs.* reaction rate; catalyst C,100°C, $P_{C_2H_4} = 0.3$ atm, $P_{H_2O} = 0.5$ atm.

$$\ln \frac{P_0}{P} = \frac{2\sigma\bar{V}}{rRT} \tag{1}$$

where P_0 is the saturated vapor pressure of a gas at temperature T, P is the vapor pressure of the gas, $\bar{V}$ is the

Table IV. Maximum Pore Diameter Filled with Condensed Water[a]

	P_{H_2O}		
	0.5 atm	0.6 atm	0.7 atm
98°C	18 Å	26 Å	48 Å
110°C	11 Å	13 Å	19 Å

[a] By Kelvin's equation assuming $\cos \alpha = 1$.

molar volume, R is the gas constant, T is the temperature of the gas and r is the maximum radius of pores in which the gas condenses. If the contact angle between the solid and liquid is α then the surface tension σ is modified by $\cos \alpha$. $D(= 2r)$ is calculated with respect to 98°C and 110°C for steam pressures of 0.5, 0.6, and 0.7 atm assuming a contact angle equal to zero, and the results are shown in Table IV. Considering the average pore diameter of this catalyst being about 30 Å, it is apparent that at 98°C and 0.6 atm about half of pores are filled with water and at 0.7 atm almost all of pores are filled with water, while at 110°C only a small amount of the pores are filled with water even at 0.7 atm of steam pressure. As mentioned above, palladium chloride in pores filled with water is far less effective than in dry pores and therefore, the catalyst in which considerable portions of pores are filled with water exhibits a lower activity than that expected from partial pressure of steam. Consequently, reaction rate is considered to decrease with an increase in steam pressure at 98°C. If the capillary condensation in the micropores is negligible, the reaction rate is expressed by

$$v \propto P_{H_2O}{}^3 \tag{2}$$

The effect of ethylene pressure on reaction rate is shown in Figure 11 and is expressed by

$$v \propto \frac{AP_{C_2H_4}}{B + P_{C_2H_4}} \tag{3}$$

Figure 12 shows how oxygen partial pressure affects the reaction rate. The rate concerning oxygen partial pressure is expressed by

$$v \propto \frac{N\sqrt{P_{O_2}}}{M + \sqrt{P_{O_2}}} \tag{4}$$

As concluded in the previous paper, the catalysis is believed to proceed by two unit reactions.

$$PdCl_2 + C_2H_4 + H_2O \xrightarrow{k_1} Pd + 2HCl + CH_3CHO \tag{5}$$

$$Pd + 2HCl + 1/2\,O_2 \xrightarrow{k_2} PdCl_2 + H_2O \tag{6}$$

The rates of reactions 5 and 6 are represented by eq 7 and 8, respectively.

$$v_1 = k_1[PdCl_2]f_1(P_{C_2H_4})f_2(P_{H_2O}) \tag{7}$$

$$v_2 = k_2[Pd]f_3(P_{O_2}) \tag{8}$$

wherein $[PdX_2]$ and $[Pd]$ represent concentrations of palladium(II) and palladium(0) on active charcoal, respectively, and f_1, f_2, and f_3 represent functions of partial pressures of ethylene, steam, and oxygen. Since the total amount of palladium on active charcoal is constant, eq 9 is obtained.

$$[PdCl_2] + [Pd] = \text{constant } (= 1) \tag{9}$$

In the steady state, the rates of reactions 5 and 6 are equal; therefore $v_1 = v_2 = v$ (apparent reaction rate). From eq 7, 8, and 9 the apparent reaction rate is represented by

$$v = \frac{k_1k_2f_1f_2f_3}{k_1f_1f_2 + k_2f_3} \tag{10}$$

From eq 8 and 9 the concentration of palladium(II) ion during reaction is expressed by

$$[PdCl_2] = \frac{k_2f_3}{k_1f_1f_2 + k_2f_3} \tag{11}$$

Equation 11 suggests that the concentration of $PdCl_2$ increases with increasing oxygen concentration and if the partial pressure of oxygen is infinite the concentration of $PdCl_2$ is unity.

The reciprocal of eq 10 provides

$$\frac{1}{v} = \frac{1}{k_2f_3} + \frac{1}{k_1f_1f_2} \tag{12}$$

If the partial pressures of ethylene and steam are constant, eq 12 is rewritten as

$$\frac{1}{v} = \frac{1}{k_2f_3} + \alpha \tag{13}$$

Comparison of eq 4 with eq 13 gives

$$\frac{1}{k_2f_3} + \alpha = \frac{1}{N} + \frac{M}{N\sqrt{P_{O_2}}} \tag{14}$$

Thus, eq 15 is obtained.

$$k_2f_3 = \frac{N\sqrt{P_{O_2}}}{M + (1 - N\alpha)\sqrt{P_{O_2}}} = \frac{N\sqrt{P_{O_2}/M}}{1 + (1 - N\alpha)\sqrt{P_{O_2}/M}} \tag{15}$$

Equation 15 is rewritten into

$$k_2f_3 = \frac{k_2\sqrt{K}\sqrt{P_{O_2}}}{1 + \sqrt{K}\sqrt{P_{O_2}}} \tag{16}$$

where $N = [\sqrt{k_2}(\sqrt{k_2 + 4} - \sqrt{k_2})]/2$ and $M = 2/[\sqrt{K}(\sqrt{k_2 + 4} + \sqrt{k_2})]$. Equation 16 suggests that palladium which is reduced in reaction 5 is oxidized with dissociatively adsorbed oxygen on active charcoal.

$$O_2(g) + 2\theta \overset{K}{\rightleftarrows} 2\theta - O \ (\theta\text{: active charcoal}) \tag{17}$$

$$\theta - O + (Pd + 2HCl) \xrightarrow{k_2} PdCl_2 + H_2O + \theta \tag{18}$$

If oxygen exists sufficiently in the gas phase it is apparent from Figure 12 that the reaction rate is not determined by reoxidation of palladium any longer and consequently the apparent rate is nearly equal to the rate of reaction 5 (oxidation of ethylene by palladium(II) ion). The results in Figures 9 and 10 are, from their conditions, considered to be able to be analyzed on the assumption above.

The mechanism of reaction 5 in the liquid phase is proposed by several workers (Dozono and Shiba, 1963; Henry, 1964) and is summarized as follows.

$$PdCl_4{}^{2-} + C_2H_4 \rightleftarrows PdCl_3(C_2H_4)^- + Cl^- \tag{19}$$

$$PdCl_3(C_2H_4)^- + H_2O \rightleftarrows PdCl_2(C_2H_4)(H_2O) + Cl^- \tag{20}$$

$$PdCl_2(C_2H_4)(H_2O) + H_2O \rightleftarrows PdCl_2(C_2H_4)(OH)^- + H_3O^+ \tag{21}$$

$$PdCl_2(C_2H_4)(OH)^- \xrightarrow{\text{slow}} \sigma\text{-complex} \tag{22}$$

$$\sigma\text{-complex} \xrightarrow{\text{fast}} Pd^0 + 2Cl^- + CH_3CHO + H^+ \tag{23}$$

Since the active species of our catalyst is not $PdCl_4{}^{2-}$ but

$PdCl_2$ (Fujimoto, *et al.*, 1972), the mechanism may be modified as shown below.

$$\begin{tikzcd}
PdCl_2 \arrow[r, shift left, "C_2H_4"] \arrow[d, shift left, "K_2"] & PdCl_2(C_2H_4) \arrow[l, shift left, "K_1"] \arrow[d, shift left, "H_2O"] \\
PdCl_2(H_2O) \arrow[u, shift left, "H_2O"] \arrow[r, shift left, "K_4"] & PdCl_2(C_2H_4)(H_2O) \arrow[u, shift left, "K_3"] \arrow[l, shift left, "C_2H_4"] \arrow[d, shift left, "H_2O"] \\
 & PdCl_2(C_2H_4)(OH^-) + H_3O^+ \arrow[u, shift left, "K_5"] \arrow[d, "H_2O", "k"'] \\
 & \sigma\text{-complex} \arrow[d, "\text{fast}"'] \\
 & \text{products}
\end{tikzcd}$$

(24)

Assuming that conversion of the palladium chloride–ethylene–hydroxy complex to the σ-complex is the rate-determining step and is accelerated by a water molecule, the rate is expressed by

$$v_1 = k[PdCl_2(C_2H_4)(OH^-)][H_2O] \tag{25}$$

Equation 25 is rewritten into a Langmuir type equation (26), since all species other than the σ-complex are at equilibrium concentration.

$$v_1 = \frac{kK_1K_3K_5P_{C_2H_4}P_{H_2O}^3}{(1 + K_1P_{C_2H_4} + K_2P_{O_2} + K_1K_3P_{C_2H_4}P_{H_2O} + K_1K_3K_5P_{C_2H_4}P_{H_2O}^2/[H_3O^+])[H_3O^+]} \tag{26}$$

If equilibrium constants K_2 and K_3 are very small, that is the coordinative force of water is very weak, then eq 27 is obtained.

$$v_1 = \frac{kK_1K_3K_5P_{C_2H_4}P_{H_2O}^3}{(1 + K_1P_{C_2H_4})[H_3O^+]} \tag{27}$$

As suggested previously, at the conditions shown in Figures 10 and 11, the apparent reaction rate is nearly equal to v_1 (rate of carbonyl formation); thus

$$v = \frac{kK_1K_3K_5P_{C_2H_4}P_{H_2O}^3}{(1 + K_1P_{C_2H_4})[H_3O^+]} \tag{28}$$

is obtained. When the partial pressure of steam is kept constant the rate is expressed by eq 29.

$$v = \frac{XP_{C_2H_4}}{W(1 + K_1P_{C_2H_4})} \tag{29}$$

On the other hand, if the partial pressure of ethylene is constant, then the rate is expressed as

$$v = \frac{ZP_{H_2O}^3}{Y[H_3O^+]} \tag{30}$$

Equations 29 and 30 which are derived from the theoretical mechanism are substantially identical with experimental equations 2 and 3, respectively. Consequently, the mechanism of carbonyl formation in the gas-solid system is concluded to be exemplified by eq 24, which is analogous to that of liquid phase oxidation, and also, the water molecule is confirmed empirically to play an important role as suggested by theories.

The apparent activation energy which is obtained by Arrhenius plots of reaction rates is theorized as follows. Arrhenius derivation of the reaction rate, which is shown in eq 28, gives

$$\Delta E_a = RT^2\left(\frac{\partial \ln v}{\partial T}\right)_p = RT^2 \frac{\partial}{\partial T}\left\{\frac{kK_1K_3K_5P_{C_2H_4}P_{H_2O}^3}{(1 + K_1P_{C_2H_4})[H_3O^+]}\right\} \tag{31}$$

$$\Delta E_a = RT^2\left\{\frac{\partial \ln k}{\partial T} + \frac{\partial \ln K_3}{\partial T} + \frac{\partial \ln K_5}{\partial T} + \frac{\partial \ln K_1}{\partial T}\left(1 - \frac{K_1P_{C_2H_4}}{1 + K_1P_{C_2H_4}}\right)\right\} \tag{32}$$

Thus

$$\Delta E_a = \Delta E^* + \Delta H_4 + \Delta H_5 + \Delta H_1\left(1 - \frac{K_1P_{C_2H_4}}{1 + K_1P_{C_2H_4}}\right) \tag{33}$$

is obtained. In which ΔE_a = apparent activation energy, ΔE^* = real activation energy of π-complex to σ-complex conversion which is considered to be the rate-determining step, ΔH_1 is the heat of coordination of ethylene, and ΔH_4 and ΔH_5 are the heats of coordination of water molecules, respectively. ΔE^* is generally positive (but not so large) while the heats of coordination ΔH_1 ΔH_4 and ΔH_5 are negative; thus ΔE_a which is the sum of ΔE^*, ΔH_4, ΔH_5, and $\Delta H_1[1 - K_1P_{C_2H_4}/(1 + K_1P_{C_2H_4})]$ is considered to be negative. Consequently, the temperature characteristic of the reaction is negative and provides an apparent activation energy of about −18 kcal/mol.

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