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The Chemistry of Palladium Complexes

VI. Studies on the Palladium(II)-Catalyzed Decomposition of Vinyl Acetate*

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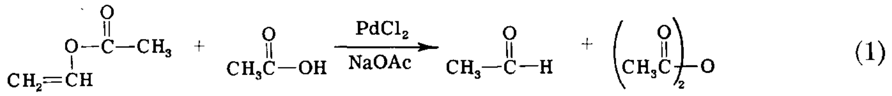
The kinetics and mechanism of the palladium(II)-catalyzed decomposition of vinyl acetate to give acetaldehyde and acetic anhydride were studied. The experiments were performed in acetic acid in the presence and absence of excess chloride, nitrile, and water, which served either as promoters or inhibitors for the decomposition reaction. Rate constants are plotted and tabulated for a variety of reaction conditions and a mechanism that is supported by deuterium studies is proposed.

INTRODUCTION

The secondary decomposition reaction of vinyl acetate in acetic acid, as catalyzed by palladium chloride and sodium acetate [Eq. (1)]

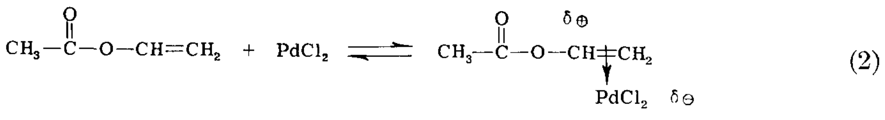


$$\underset{CH_2{=}CH}{O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3} + CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \xrightarrow[NaOAc]{PdCl_2} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + \left(CH_3\overset{\overset{\displaystyle O}{\|}}{C}\right)_2O \qquad (1)$$

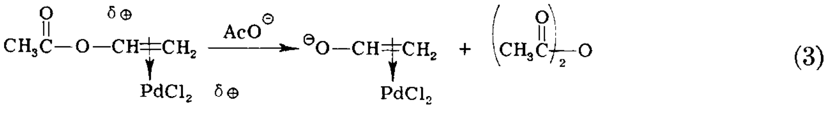
has been recognized for several years (*2*). In one study, Clement and Selwitz (*3*) established that both palladium chloride and sodium acetate were necessary in the catalysis of this reaction and that ethylidene diacetate was not an intermediate. The mechanism they proposed (*3*) is reproduced below [Eqs. (2)–(4)].

It is probable that this decomposition reaction is the major cause of the formation of the acetaldehyde found in the synthesis of vinyl acetate from ethylene in anhydrous acetic acid systems [Eq. (5)] (*4–6*).*

It should be noted that in the synthesis of vinyl acetate, all the agents necessary for its destruction are present. Additional acetaldehyde is undoubtedly formed from the reaction of ethylene with water (Wacker Reaction) that is formed during the regeneration of palladium [Eqs. (6a) (6b)].



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH{=}CH_2 + PdCl_2 \rightleftharpoons CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\underset{\underset{\displaystyle PdCl_2\ \ \delta\ominus}{\downarrow}}{CH{\doteq}CH_2}^{\ \delta\oplus} \qquad (2)$$



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\underset{\underset{\displaystyle PdCl_2\ \ \delta\oplus}{\downarrow}}{CH{\doteq}CH_2}^{\ \delta\oplus} \xrightarrow{AcO^{\ominus}} {}^{\ominus}O{-}\underset{\underset{\displaystyle PdCl_2}{\downarrow}}{CH{\doteq}CH_2} + \left(CH_3\overset{\overset{\displaystyle O}{\|}}{C}\right)_2O \qquad (3)$$

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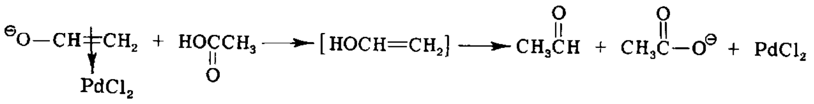
* Presented in part at the 153rd Meeting Am. Chem. Soc. Miami Beach, April 1967. *Div. Petrol. Chem. Preprints* 12(1), 139 (1967).

* The patent literature on the subject of vinyl acetate synthesis from ethylene has become voluminous in the last several years. Some key patents are listed in Ref. (*5*).



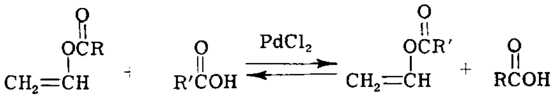
$$^{\ominus}\text{O}-\underset{\underset{\text{PdCl}_2}{\uparrow}}{\text{CH}}\!\!=\!\!\text{CH}_2 + \text{HO}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{CH}_3 \longrightarrow [\text{HOCH}{=}\text{CH}_2] \longrightarrow \text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{H} + \text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{O}^{\ominus} + \text{PdCl}_2 \qquad (4)$$

$$\text{CH}_2{=}\text{CH}_2 + \text{HOAc} + \text{PdCl}_2 \xrightarrow{\text{NaOAc}} \text{CH}_2{=}\text{CHOAc} + \underline{\text{Pd}} + 2\,\text{HCl} \qquad (5)$$

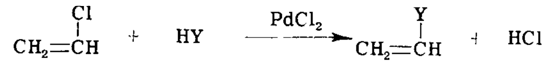
$$\underline{\text{Pd}} + 2\,\text{CuCl}_2 \longrightarrow \text{PdCl}_2 + 2\,\text{CuCl} \qquad (6a)$$

$$2\,\text{CuCl} + 2\,\text{HCl} + \tfrac{1}{2}\text{O}_2 \longrightarrow 2\,\text{CuCl}_2 + \text{H}_2\text{O} \qquad (6b)$$

Analogous palladium chloride catalyzed reactions, transvinylation (*7*) [Eq. (7)] and catalytic vinylation (*8*) [Eq. (8)], have also been reported.



$$\begin{matrix}\text{O}\\ \|\\ \text{OCR}\\ |\\ \text{CH}_2{=}\text{CH}\end{matrix} + \text{R}'\underset{}{\overset{\overset{\text{O}}{\|}}{\text{C}}}\text{OH} \overset{\text{PdCl}_2}{\rightleftarrows} \begin{matrix}\text{O}\\ \|\\ \text{OCR}'\\ |\\ \text{CH}_2{=}\text{CH}\end{matrix} + \text{R}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{OH} \qquad (7)$$



$$\begin{matrix}\text{Cl}\\ |\\ \text{CH}_2{=}\text{CH}\end{matrix} + \text{HY} \xrightarrow{\text{PdCl}_2} \begin{matrix}\text{Y}\\ |\\ \text{CH}_2{=}\text{CH}\end{matrix} + \text{HCl} \qquad (8)$$

$[\text{HY} = \text{HOR, HOOCR, H}_2\text{NR}]$

As part of our continuing study of the chemistry of palladium complexes (*1*), it was decided to investigate the decomposition reaction and some of the factors affecting it in greater detail.

EXPERIMENTAL METHODS

Materials. Palladium chloride (Engelhard Industries), palladium acetate (Matthey-Bishop Co.), reagent vinyl acetate (99.5%) and benzonitrile (both Matheson, Coleman, and Bell), and other reagent-grade nitriles (Eastman or Matheson, Coleman, and Bell) were all used without further purification.

Apparatus and measurement procedure. Reaction mixtures were prepared by mixing appropriate quantities of stock solutions of the palladium salts, additives, and solvents. These mixtures were placed in a small (2 dram) vial that was stoppered with a serum cap. Vinyl acetate (corresponding to 0.17 *M*) was then added through the serum cap with a syringe and the reaction mixture was allowed to stand at 25 ± 1°C. Samples of the liquid were periodically taken through the serum cap with a 10-μl syringe and injected directly into either a Perkin-Elmer model 154 gas chromatograph fitted with a ¼-in. × 6-ft Ucon 1715 on Teflon 6 column at 44°C or a F and M model 810 gas chromatograph fitted with a ⅛-in. × 10-ft Porapak Q column programmed from 80 to 150°C. Chromatographic data on vinyl acetate and acetaldehyde composition were corrected for varying sensitivity with the aid of a series of standards. The number of data points per experimental run varied from 4 to 17.

Interpretation of data. The kinetic data for each run were fit either to a pseudo-zero-order rate expression,

$$-\frac{d\,[\text{vinyl acetate}]}{dt} = k_{\text{obs}}, \qquad (9)$$

or a pseudo-first-order rate expression,

$$-\frac{d[\text{vinyl acetate}]}{dt} = k'_{\text{obs}}[\text{vinyl acetate}], \qquad (10)$$

and analyzed by a linear regression analysis on a CDC 6400 computer. Since catalyst precipitation occurred during the later stages of many of the runs, the final data points from each experimental run were successively removed and the data were reanalyzed by the computer. This procedure proved to be an effective test of the precision of the data points. Correlation coefficients for the 160 experimental runs ranged from 0.9913 to 0.9999, with the majority being greater than 0.9990 (corresponding to a precision of ±2%). No estimate of the accuracy of the computed rate constants can be given.

RESULTS

Measurements of the palladium(II)-catalyzed decomposition of vinyl acetate in acetic acid were performed in the presence and absence of excess chloride, acetate, nitrile, and water. Under the conditions of our experiments, the following general observations obtain: (a) In the absence of excess nitrile or other comparable neutral inhibitors, the reaction is zero order in vinyl acetate and inversely proportional to the chloride concentration. (b) In the presence of excess nitrile, the reaction is first order in vinyl acetate and inversely proportional to the nitrile concentration. (c) The reaction occurs in the absence of acetate ion. (d) The reaction rate is severely depressed in the absence of chloride ion. (e) In the presence of a large excess of acetate ion, the reaction is independent of the acetate ion concentration. (f) In the absence of nitrile, the reaction is first order in water (experiments to determine the order of water in the presence of nitrile were not performed).

As in many other areas of homogeneous catalysis, the determination of the nature and concentration of the specific palladium (II) species existing in the reaction medium was not an easy task. An attempt was made to sort out, *on the basis of kinetic measurements*, the various rate parameters of the decomposition reaction and to determine the kinetic effect of each of the major components of the system. The ensuing presentation of results will therefore be divided into five subsections: (i) nature of the initial palladium species, (ii) effect of chloride and acetate ions, (iii) effect of neutral inhibitors, (iv) effect of water, and (v) miscellaneous observations.

Nature of the initial palladium species. Palladium(II) chloride is a polymeric solid that is insoluble in acetic acid. Only with the addition of materials which are capable of splitting the chloride bridges can the palladium chloride be solubilized. Such bridge-splitting agents include halide, acetate, and other anions; and benzonitrile, dimethyl sulfoxide, and other neutral coordinating ligands. Alternatively, the solubilization problem can be eliminated by the use of sodium chloropalladate, Na_2PdCl_4, as the catalytic palladium (II) species. In this case, the necessary square-planar configuration is already present, no bridge-splitting is required, and the palladium compound is readily soluble in acetic acid. Clement and Selwitz indicated that acetate ion was necessary for the vinyl acetate decomposition reaction to occur (*3*). We have observed that added acetate ion is not necessary; the reported acetate effect must therefore be attributed to solubilization and not to cocatalysis.

Some question exists whether the palladium(II) species present are monomeric or dimeric. While Davies (*9*) and Henry (*7c*) have presented evidence for the dimeric nature of palladium(II) chloride in acetic acid in the absence of other coordinating ligands, Heck (*10*) has given evidence that monomeric palladium(II) species exist in the presence of a coordinating ligand such as acetonitrile. The kinetic evidence reported in this work could not distinguish whether monomeric complexes such as $[PdCl_3(CH_2{=}CHOAc)]^-$ or dimeric complexes containing chloride bridging systems such as $[Pd_2Cl_5(CH_2{=}CHOAc)]^-$ were the dominant palladium species in solution.

Effect of chloride and acetate ions. Chloride ion exhibited two different kinetic effects: at high concentrations $\{[Cl^-]_0 \gg [Pd]_0$, where $[Cl^-]_0$ and $[Pd]_0$ represent the *total* concentration of free and complexed chloride and palladium in the solution, re-

TABLE 1
Effect of Acetate and Chloride Ion on the Decomposition of Vinyl Acetate

Runs	System	Acetate conc. (M)	$k_{obs}(10^{-6}\ M\ sec^{-1})$ Anhydrous	$k_{obs}(10^{-6}\ M\ sec^{-1})$ With 0.27 M water
A	0.011 M $PdCl_2$	0.18	0.40	1.7
B	0.011 M $Pd(OAc)_2$	0.18	0.03	0.17
C	0.011 M $Pd(OAc)_2$ saturated with NaCl	0.18	0.60	2.0

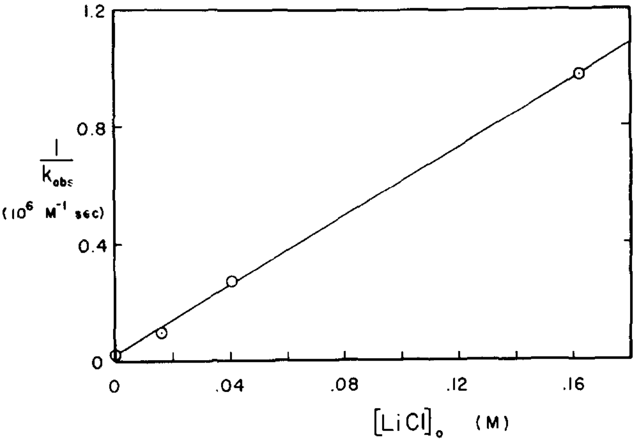


FIG. 1. Inverse of the pseudo-zero-order rate constant as a function of the concentration of added lithium chloride: $[\text{Na}_2\text{PdCl}_4]_0 = 0.0081\ M$ and $[\text{H}_2\text{O}]_0 = 2.62\ M$; the slope and intercept are $5.6 \times 10^6\ M^{-2}$ sec and $4.1 \times 10^3\ M^{-1}$ sec, respectively.

spectively}, it inhibited the reaction, whereas at low concentrations $\{[\text{Cl}^-]_0 \sim [\text{Pd}]_0\}$, it was an essential ligand. In the absence of chloride ions, the reaction proceeded very slowly. Table 1 illustrates the latter effect. Experimental runs A represent the "standard" palladium chloride–sodium acetate run in the absence and presence of $0.27\ M$ water, respectively. The total concentrations of vinyl acetate, palladium, acetate ion, and chloride ion were 0.17, 0.011, 0.18, and 0.022 M, respectively.

In the corresponding chloride-free systems (runs B), a significant but much lower rate of vinyl acetate decomposition was observed both in the absence and presence of water. Finally, when the systems corresponding to runs B were saturated with sodium chloride (ca. $0.013\ M$ free chloride ion), the decomposition reaction occurred at rates typical of the "standard" runs (runs C).

At higher concentrations $\{[\text{Cl}^-]_0/[\text{Pd}]_0 \geq 4\}$, chloride ion (added as the lithium salt) was a strong inhibitor for the vinyl acetate decomposition reaction. When the inverse of the observed zero-order rate constants were plotted against the excess chloride con-

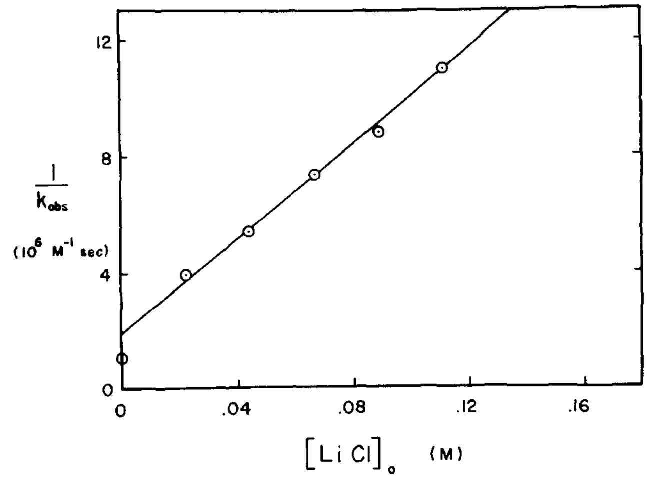


FIG. 2. Inverse of the pseudo-zero-order rate constant as a function of the concentration of added lithium chloride: $[\text{Na}_2\text{PdCl}_4]_0 = 0.0113\ M$ and $[\text{H}_2\text{O}]_0 = 0.00\ M$; the values of the slope and intercept are $7.9 \times 10^7\ M^{-2}$ sec and $2.1 \times 10^6\ M^{-1}$ sec, respectively.

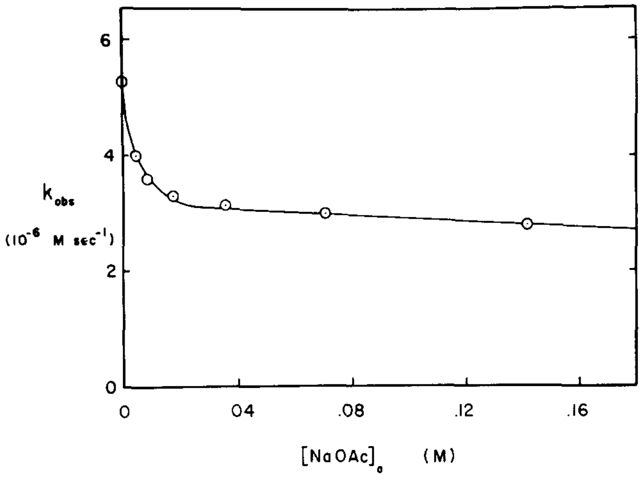


FIG. 3. Pseudo-zero-order rate constant as a function of the concentration of added sodium acetate: $[Na_2PdCl_4]_0 = 0.0090\,M$ and $[H_2O]_0 = 0.41\,M$.

centration at constant $[Pd]_0$, linear relationships were found both in the presence and absence of water (Figs. 1 and 2, respectively).

Acetate ion acted as a mild inhibitor for the decomposition reaction (Figs. 3 and 4). The observation that this inhibition reached a limiting value both in the presence and absence of water has interesting kinetic implications which are discussed below.

Effect of neutral inhibitors. It has been reported (*5*, *6*) that the ratio of vinyl acetate to acetaldehyde in the vinyl acetate *synthesis* reaction can be increased by the use of mixed-solvent systems containing acetic acid and neutral compounds such as dimethyl formamide, dimethyl sulfoxide, alkyl and aryl nitriles, trialkyl amines, and esters. This change is probably due to the suppression of the vinyl acetate decomposition reaction. To test this conclusion, several of these compounds were evaluated in our reaction system; the results are set forth in Table 2. Small quantities of acetic anhydride had essentially no effect on the decomposition rate (Table 3).

Since benzonitrile was the most effective inhibitor, further studies of the inhibition

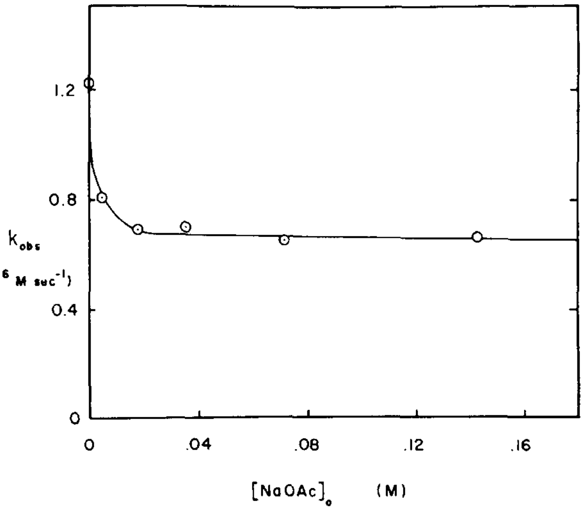


FIG. 4. Pseudo-zero-order rate constant as a function of the concentration of added sodium acetate: $[Na_2PdCl_4]_0 = 0.0090\,M$ and $[H_2O]_0 = 0.00\,M$.

TABLE 2

EFFECT OF NEUTRAL INHIBITORS ON THE VINYL ACETATE DECOMPOSITION REACTION[a]

Inhibitor	Conc. (M)	$k'_{obs}(10^{-6}\ sec^{-1})$	
		Anhydrous	With 0.27 M water
Dimethylformamide	4.80	5	20
Diethylene glycol dimethyl ether	4.80	4	8
Benzonitrile	4.80	0.7	3
	0.06	9	40

[a] Conc: 0.0113 M $PdCl_2$; 0.18 M NaOAc.

effect of a series of nitriles were conducted (Table 4). Though they were all effective in inhibiting the decomposition reaction, little difference was observed between individual nitriles with the exception of acrylonitrile, which also was very effective in inhibiting the vinyl acetate synthesis reaction (the other nitriles caused only a slight decrease in the vinyl acetate synthesis rate). The effect of varying concentrations of benzonitrile on the decomposition reaction was also studied; the results are presented in Figs. 5 and 6. Observable inhibition was noted even at benzonitrile levels as low as 0.06 M.

TABLE 3

EFFECT OF ACETIC ANHYDRIDE ON THE VINYL ACETATE DECOMPOSITION REACTION[a]

Conc. (M)	$k_{obs}(10^{-6}\ M\ sec^{-1})$
0.00	1.5
0.05	1.5
0.10	1.4
0.21	1.4

[a] Conc: 0.0113 M $PdCl_2$; 0.18 M NaOAc.

Apparently most nitriles are intermediate in π-bonding power between ethylene and vinyl acetate. That is, nitriles (with the exception of acrylonitrile) do not interfere with vinyl acetate synthesis but will preferentially complex with palladium chloride in the place of vinyl acetate. From such studies, these compounds can be arranged in a descending series of palladium complexing strengths:

$$CH_2{=}CHCN > CH_2{=}CH_2 > C_6H_5CN > CH_2{=}CHOCOCH_3 > CH_3COO^- \sim Cl^-$$

Effect of water. Low levels of water significantly increased the rate of vinyl acetate decomposition. At low water concentrations, a rapid and linear increase in the decomposition rate was observed (Figs. 7 and 8). At higher water concentrations, however, an increase in the amount of water actually decreased the decomposition rate (Fig. 9). At these high water levels, the effective competition by water for the ligand positions around the tetracoordinated palladium(II) seemed to reduce the probability of vinyl acetate and chloride ion being simultaneously present.

Miscellaneous observations. When deuteroacetic acid was employed as a solvent, the deuterium entered (as expected) exclusively into the methyl groups of the acetaldehyde formed [Eq. (11)].

Several side reactions were found during the course of the studies. The previously reported catalytic vinylation reaction [Eq. (8)] (*8*) was observed to be an equilibrium reaction [Eq. (12)].

In experimental runs that were relatively high in chloride ion, vinyl chloride was detected both in the gas and liquid phases within the stoppered vial. As the reaction proceeded with an irreversible consumption of vinyl acetate, the vinyl chloride concentration decreased with time and eventually vanished. An additional complication ob-

$$CH_2{=}CH{-}OAc + DOAc \xrightarrow[NaOAc]{PdCl_2} DCH_2CHO + Ac_2O \tag{11}$$

$$CH_2{=}CH{-}OAc + Cl^- \rightleftharpoons CH_2{=}CH{-}Cl + OAc^- \tag{12}$$

TABLE 4
INHIBITION OF THE VINYL ACETATE DECOMPOSITION REACTION BY NITRILES[a]

Inhibitor	Conc. (M)	k'_{obs} (10^{-6} sec^{-1}) Anhydrous	k'_{obs} (10^{-6} sec^{-1}) With 0.41 M water
		Alkyl nitriles	
CH_3CN	2.40	1.5	8.6
n-C_3H_7CN	2.40	1.1	4.4
t-C_4H_9CN	2.40	2.3	6.3
$C_6H_5CH_2CN$	2.40	2.5	12.
$CH_2{=}CHCN$	2.40	0.2	1.4
		Aryl nitriles	
C_6H_5CN	2.45	1.8	8.2
	0.49	4.4	19.
p-CH_3O-C_6H_4CN	0.52	4.0	11.
p-CH_3-C_6H_4CN	0.49	4.9	14.
p-F-C_6H_4CN	0.50	5.1	23.
p-Cl-C_6H_4CN	0.50	5.8	26.
p-CN-C_6H_4CN	0.45	6.2	31.
p-NO_2-C_6H_4CN	0.51	11.	27.
		Alkyl dinitriles	
NC-$(CH_2)_2$-CN	1.25	2.2	15.
NC-$(CH_2)_3$-CN	1.06	1.9	10.
NC-$(CH_2)_4$-CN	0.90	1.3	8.1
NC-$(CH_2)_5$-CN	0.90	1.2	7.7
NC-$(CH_2)_6$-CN	0.90	3.7	12.
NC-$(CH_2)_7$-CN	0.90	1.4	6.1
NC-$(CH_2)_8$-CN	0.90	1.1	6.7

[a] Conc: 0.011 M $PdCl_2$; 0.18 M NaOAc.

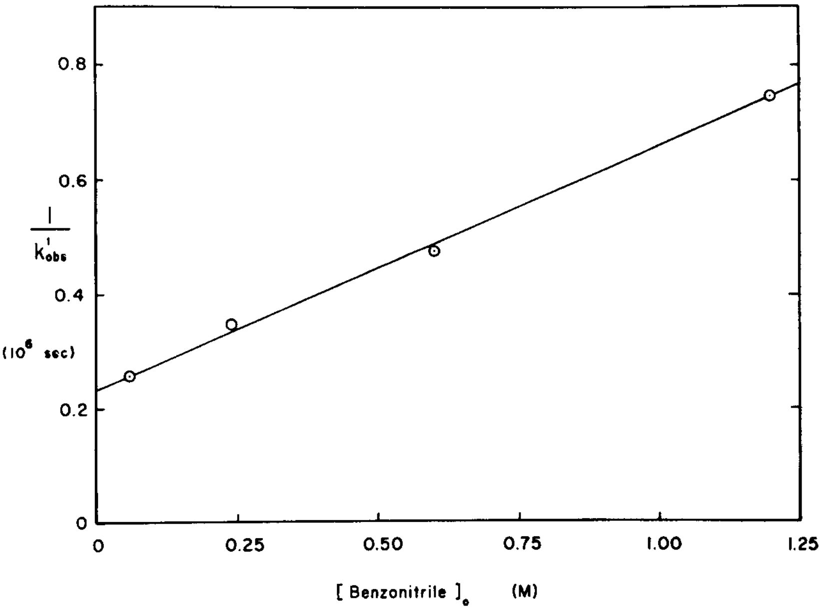


FIG. 5. Inverse of the pseudo-first-order rate constant as a function of the concentration of added benzonitrile: $[PdCl_2]_0 = 0.01\,M$, $[NaOAc]_0 = 0.18\,M$, and $[H_2O]_0 = 0.27\,M$. The slope and intercept are $4.2 \times 10^4\ M^{-1}$ sec and 2.4×10^4 sec, respectively.

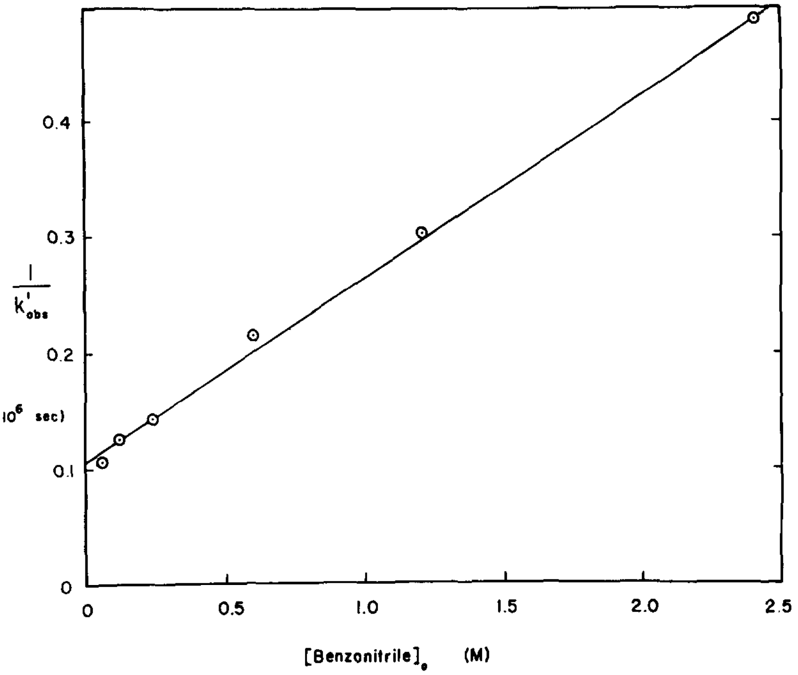


FIG. 6. Inverse of the pseudo-first-order rate constant as a function of the concentration of added benzonitrile. $[PdCl_2]_0 = 0.01\,M$, $[NaOAc]_0 = 0.18\,M$, and $[H_2O]_0 = 0.00\,M$. The slope and intercept are $1.6 \times 10^5\,M^{-1}$ sec and 1.1×10^5 sec, respectively.

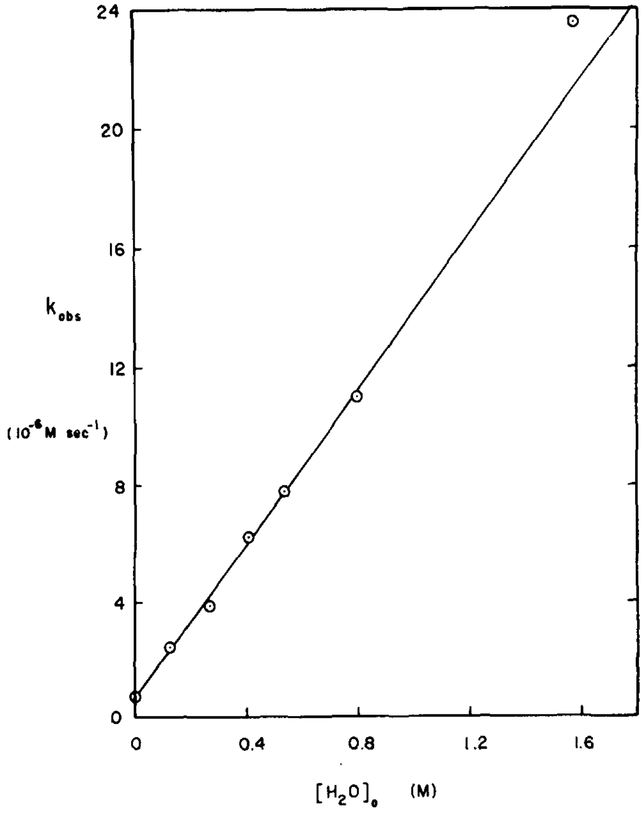


FIG. 7. Pseudo-zero-order rate constant as a function of the concentration of added water: $[Na_2PdCl_4]_0 = 0.0113\,M$. The slope and intercept are 1.3×10^{-5} sec^{-1} and $7.5 \times 10^{-7}\,M^{-1}$ sec^{-1}, respectively.

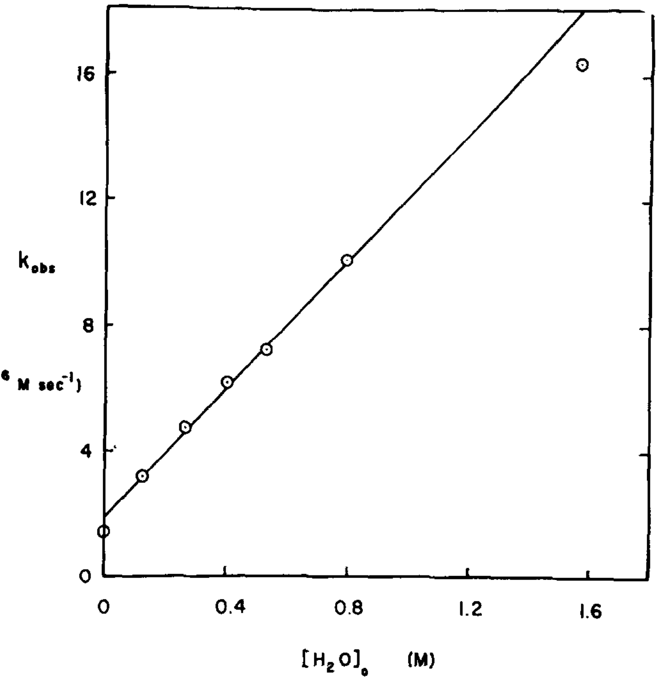


FIG. 8. Pseudo-zero-order rate constant as a function of the concentration of added water: $[PdCl_2]_0 = 0.0113$ *M* and $[NaOAc]_0 = 0.18$ *M*. The slope and intercept are 1.1×10^{-5} sec^{-1} and $1.7 \times 10^{-6} M^{-1}$ sec^{-1}, respectively.

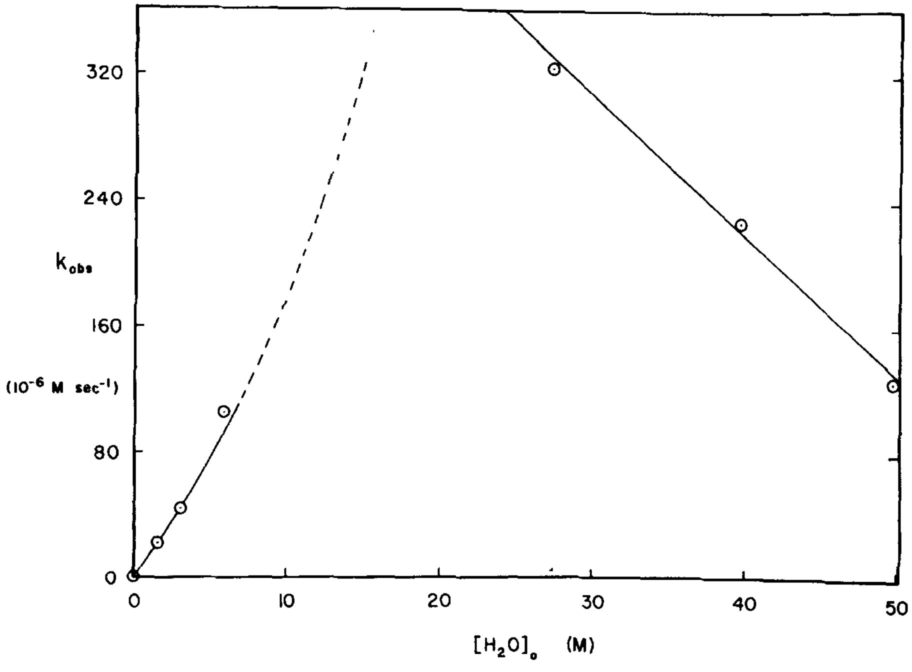


FIG. 9. Pseudo-zero-order rate constant as a function of the concentration of added water (high water concentrations): $[Na_2PdCl_4]_0 = 0.0113$ *M*.

served during the experimental runs (especially those containing water) was the slow formation of palladium metal. The precipitation of catalyst was also reflected in a decreasing reaction rate over long periods of time, an effect which complicated the theoretical analysis of the rate data for the nitrile runs. In a careful study of the reaction mixture, however, no products other than acetaldehyde and acetic anhydride were found. One possibility for this precipitation reaction is a Wacker-type process operating upon vinyl acetate [Eq. (13)].

$$CH_2{=}CH{-}OAc + H_2O + PdCl_2 \longrightarrow Ac_2O + 2\,HCl + \underline{Pd^0} \tag{13}$$

THEORETICAL

Any theoretical treatment of the observed kinetics of the vinyl acetate decomposition reaction must account for the general observations given in the results section. Since acetic acid is the solvent, it is impossible to directly determine the order with respect to acetic acid. The kinetic treatment given below, however, indicates that the reaction is probably first order in acetic acid.

In the absence of acetate ion and nitrile, the palladium(II)-catalyzed vinyl acetate decomposition reaction was zero order in vinyl acetate and inversely proportional to the chloride ion concentration at the palladium and vinyl acetate concentration levels employed in this study (0.011 and 0.17 M, respectively). These observations indicate that the dominant palladium(II) specie in solution is either $Cl_2PdCl(CH_2{=}CHOAc)^-$ or $Cl_2PdCl_2PdCl(CH_2{=}CHOAc)^-$, which are formed by the reaction of vinyl acetate with monomeric and dimeric palladium chloride $PdCl_4^{-2}$ and $Pd_2Cl_6^{-2}$ (*7c*). The inverse dependence upon chloride ion and direct dependence upon water are consistent with the following reaction sequence [assuming that the dominant palladium(II) specie is monomeric].

$$Cl_2PdCl(CH_2{=}CHOAc)^- + HOAc \overset{K_1}{\rightleftarrows} \underset{\text{I}}{Cl_2Pd(HOAc)(CH_2{=}CHOAc)} + Cl^- \tag{14}$$

$$Cl_2PdCl(CH_2{=}CHOAc)^- + H_2O \overset{K_2}{\rightleftarrows} \underset{\text{II}}{Cl_2Pd(H_2O)(CH_2{=}CHOAc)} + Cl^- \tag{15}$$

$$\text{I} \xrightarrow{k_1} \text{Products} \tag{16}$$

$$\text{II} \xrightarrow{k_2} \text{Products} \tag{17}$$

where

$$K_1 = \frac{[Cl_2Pd(HOAc)(CH_2{=}CHOAc)][Cl^-]}{[Cl_2PdCl(CH_2{=}CHOAc)^-][HOAc]} \tag{18}$$

$$K_2 = \frac{[Cl_2PdCl(H_2O)(CH_2{=}CHOAc)][Cl^-]}{[Cl_2PdCl(CH_2{=}CHOAc)^-][H_2O]} \tag{19}$$

and Ac represents an acetyl group. Since $CH_2{=}CHOAc$ and $Cl_2PdCl(CH_2{=}CHOAc)^-$ were the dominant vinyl acetate and palladium species in solution, the rate law is simply

$$\begin{aligned} \text{Rate} &\approx -\frac{d[CH_2{=}CHOAc]}{dt} = k_1(\text{I}) + k_2(\text{II}) \\ &= \frac{\{k_1K_1[HOAc] + k_2K_2[H_2O]\}[Pd]_0}{[Cl^-]} = k_{\text{obs}} \end{aligned} \tag{20}$$

Excess acetate ion inhibited the decomposition reaction both in the presence and absence of water, but when there was a large excess of acetate, the reaction became independent of the acetate ion concentration.

This behavior is consistent with the following additional reaction steps,

$$Cl_2PdCl(CH_2{=}CHOAc)^- + OAc^- \overset{K_3}{\rightleftharpoons} \underset{\text{III}}{Cl(OAc)PdCl(CH_2{=}CHOAc)^-} + Cl^- \tag{21}$$

$$\text{III} + HOAc \overset{K_4}{\rightleftharpoons} \underset{\text{IV}}{Cl(OAc)Pd(HOAc)(CH_2{=}CHOAc)} + Cl^- \tag{22}$$

$$\text{III} + H_2O \overset{K_5}{\rightleftharpoons} \underset{\text{V}}{Cl(OAc)Pd(H_2O)(CH_2{=}CHOAc)} + Cl^- \tag{23}$$

$$\text{IV} \xrightarrow{k_4} \text{Products} \tag{24}$$

$$\text{V} \xrightarrow{k_5} \text{Products} \tag{25}$$

and rate law,

$$\begin{aligned} -\frac{d[CH_2{=}CHOAc]}{dt} &= k_1(\text{I}) + k_2(\text{II}) + k_4(\text{IV}) + k_5(\text{V}) \\ &= \left(\frac{k_1K_1[HOAc] + k_2K_2[H_2O]}{[Cl^-] + K_3[OAc^-]}\right)[Pd]_0 + \left(\frac{k_4K_4[HOAc] + k_5K_5[H_2O]}{[Cl^-] + K_3[OAc^-]}\right)\frac{K_3[OAc^-][Pd]_0}{[Cl^-]} \end{aligned} \tag{26}$$

In the presence of a large excess of acetate, Eq. (26) simplifies to

$$-\frac{d[CH_2{=}CHOAc]}{dt} \approx \frac{\{k_4K_4[HOAc] + k_5K_5[H_2O]\}[Pd]_0}{[Cl^-]} = k_{\text{obs}} \tag{27}$$

The studies with nitriles were all performed in the presence of excess acetate ion. All of the nitriles acted as competitive inhibitors according to the following reaction,

$$\text{III} + RCN \overset{K_6}{\rightleftharpoons} \underset{\text{VI}}{Cl_2Pd(OAc)(RCN)^-} + CH_2{=}CHOAc \tag{28}$$

Reaction (28), together with reactions (22) through (25), leads to a rate expression that is inversely proportional to the nitrile concentration,

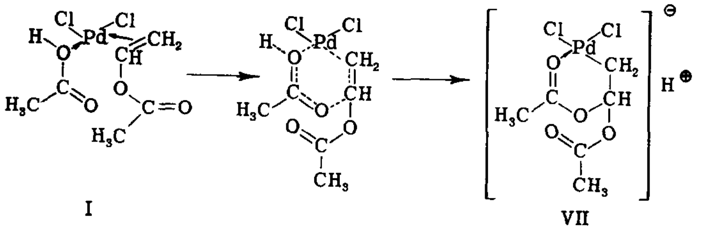
$$-\frac{d[CH_2{=}CHOAc]}{dt} = \frac{\{k_4K_4[HOAc] + k_5K_5[H_2O]\}[Pd]_0[CH_2{=}CHOAc]}{K_6[RCN][Cl^-]} = k'_{\text{obs}}[CH_2{=}CHOAc] \tag{29}$$

Neutral disubstituted vinyl acetate and nitrile palladium(II) species such as $Cl(OAc)Pd(RCN)_2$, $Cl(OAc)Pd(CH_2{=}CHOAc)(RCN)$, and $Cl(OAc)Pd(CH_2{=}CHOAc)_2$ did not appear to be present in appreciable concentrations. If the dominant palladium(II) specie is $Cl_2PdCl_2PdCl(CH_2{=}CHOAc)^-$, the initial palladium concentration $[Pd]_0$, in Eqs. (20), (26), (27), and (29) must be replaced by $\frac{1}{2}[Pd]_0$. Otherwise, the rate equations remain unchanged.

DISCUSSION

Mechanism of the reaction. A mechanism has previously been proposed (*3*) for the decomposition of vinyl acetate by palladium chloride [Eqs. (2–4)]. On the basis of our current studies and other more recent work on the mechanism of palladium-catalyzed reactions of olefins (*1, 6, 11*), it is now possible to propose a more detailed pathway for this reaction [Eqs. (16) and (30–34)].

While several alternate possibilities for the pathway of the reactions are not excluded by the results reported in this paper, the mechanism proposed below is preferred, being both consistant with all the observations and bearing the greatest analogy to other observations in palladium chemistry. The reaction is written below as involving a monomeric palladium species but it is obvious that a similar series of transformations could be written in which dimeric species are involved. The pathways proposed are given in detail to point out some

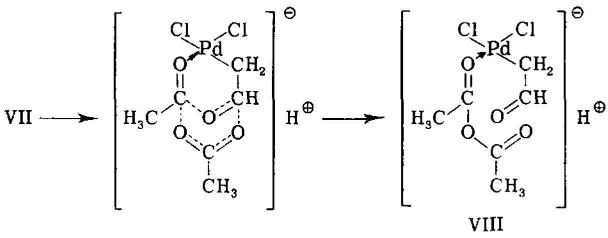


(30)

$$\underset{\text{I}}{\text{Cl}_2\text{Pd(HOAc)(CH}_2\text{=CHOAc)}} \longrightarrow \underset{\text{VII}}{[\text{Cl}_2\text{PdCH}_2\text{CH(OAc)}_2]^{\ominus}\ \text{H}^{\oplus}} \qquad (30a)$$

of the analogies involved. Each reaction step is summarized below the detailed formulation.

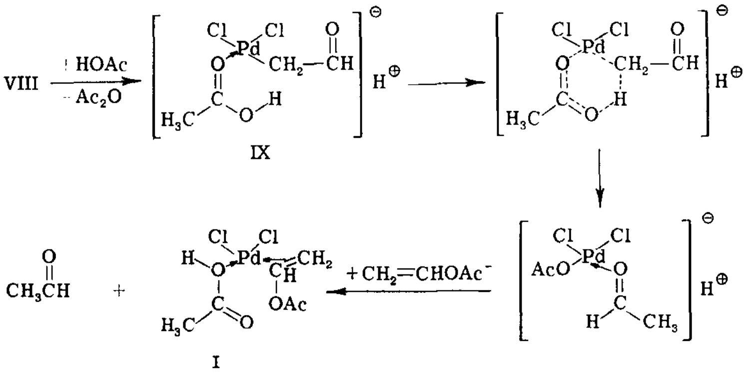
After a series of pre-equilibrium reactions (see "Theoretical" section), a species (I) capable of the catalytic decomposition of vinyl acetate is formed. This species first undergoes an intramolecular insertion reaction to form a palladium-substituted ethylidene diacetate (VII) (Eqs. 30 and 30a), (Species VII is not ethylidene diacetate nor would it be expected to form directly from ethylidene diacetate.) Species VII then undergoes a rearrangement reaction [Eq. (31)] in which coordinated acetic anhydride and a palladium-substituted acetaldehyde (VIII) are formed,



(31)

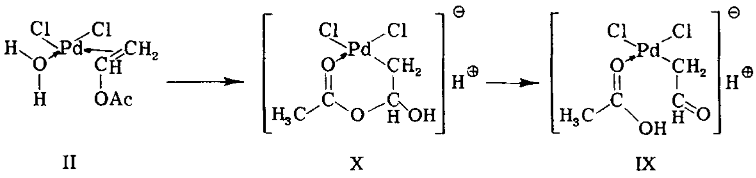
$$\underset{\text{VII}}{[\text{Cl}_2\text{PdCH}_2\text{CH(OAc)}_2]^{\ominus}\ \text{H}^{\oplus}} \longrightarrow \underset{\text{VIII}}{[\text{Cl}_2\text{PdCH}_2\text{CHO(Ac}_2\text{O)}]^{\ominus}\ \text{H}^{\oplus}} \qquad (31a)$$

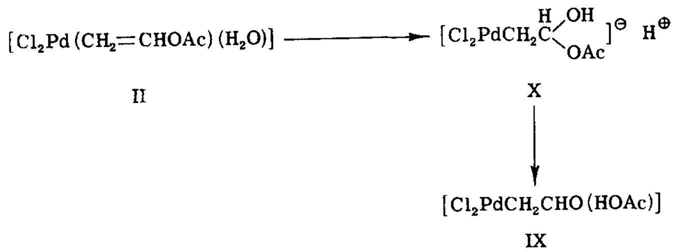
Displacement of the acetic anhydride by acetic acid, followed by intramolecular rearrangements [Eq. (42)] yields free acetaldehyde,

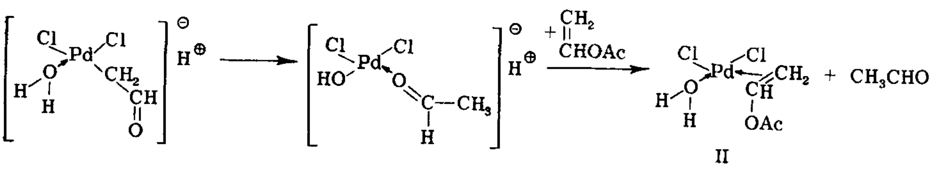


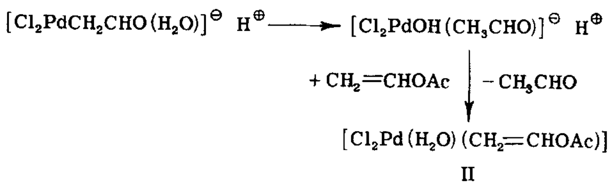
(32)

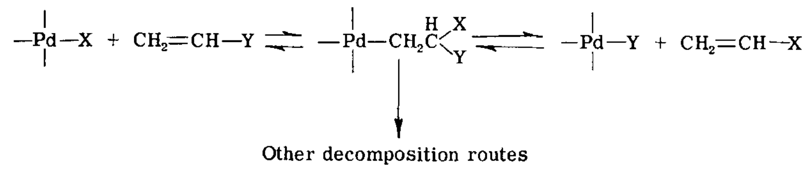
$$\begin{tikzcd} \text{VIII} \arrow[r, "+\text{HOAc}", "-\text{Ac}_2\text{O}"'] & {[\text{Cl}_2\text{PdCH}_2\text{CHO(HOAc)}]^{\ominus}\ \text{H}^{\oplus}} \arrow[r] & {[\text{Cl}_2\text{PdOAc(CH}_3\text{CHO)}]^{\ominus}\ \text{H}^{\oplus}} \arrow[d, "+\text{CH}_2\text{=CHOAc}"', "-\text{CH}_3\text{CHO}"] \\ & & \text{I} \end{tikzcd} \qquad (32a)$$


(33)


(33a)


(34)


(34a)

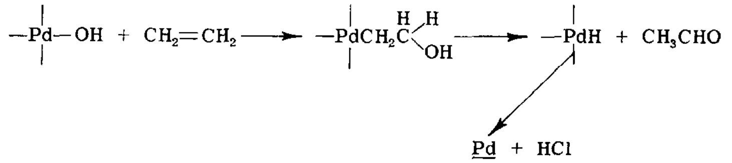


(35)

This hydrolytic reaction can also be written using water or other protonic ligands. It is similar to that proposed by Pestrikov (*12*) in his discussion of ethylene oxidation by palladium chloride.

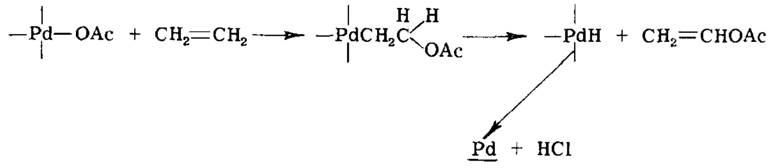
The role of water in this reaction scheme is not certain. It could take the place of acetic acid in II, in which case the intermediate equivalent to VII would be X, which could spontaneously decompose to IX [Eq. (33)]. Alternately, it could take the place of acetic acid in IX to give a hydrolytic reaction [Eq. (34)]. In either case, the rate determining step in the reaction would occur after the water is in the coordination sphere.

Mechanisms of palladium(II)-catalyzed reactions. Equations (30)–(34) contain the elements of an essential unity of mechanism for the Wacker process, vinyl acetate synthesis [Eq. (5)], vinyl ester interchange [Eq. (7)], catalytic vinylations [Eqs. (8) and (12)], as well as vinyl acetate decomposition [Eq. (1)]. This common mechanism, proposed below is based upon both our work and that of many other authors [*13*, *14*]. In the case of the Wacker process, X = OH and Y = H, and the general mechanism can be written as



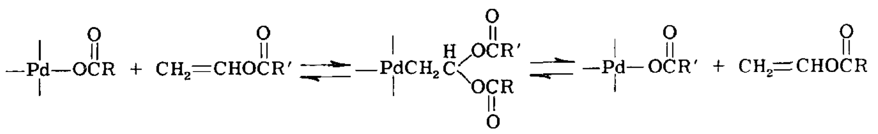
$$-\overset{|}{\underset{|}{Pd}}-OH + CH_2{=}CH_2 \longrightarrow -\overset{|}{\underset{|}{Pd}}CH_2C{<}^{H\ H}_{OH} \longrightarrow -\overset{|}{\underset{|}{Pd}}H + CH_3CHO;\quad -\overset{|}{\underset{|}{Pd}}H \longrightarrow \underline{Pd} + HCl \qquad (36)$$

For vinyl acetate synthesis, X = OAc and Y = H, and the reaction becomes



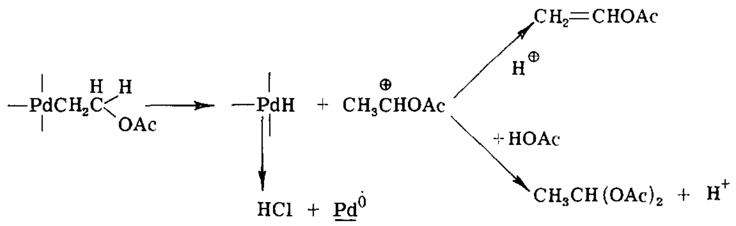
$$-\overset{|}{\underset{|}{Pd}}-OAc + CH_2{=}CH_2 \longrightarrow -\overset{|}{\underset{|}{Pd}}CH_2C{<}^{H\ H}_{OAc} \longrightarrow -\overset{|}{\underset{|}{Pd}}H + CH_2{=}CHOAc;\quad -\overset{|}{\underset{|}{Pd}}H \longrightarrow \underline{Pd} + HCl \qquad (37)$$

For vinyl ester interchange, X = $\overset{\overset{O}{\|}}{O C}R$, and Y = $\overset{\overset{O}{\|}}{O C}R'$,



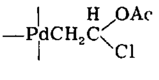
$$-\overset{|}{\underset{|}{Pd}}-O\overset{\overset{O}{\|}}{C}R + CH_2{=}CHO\overset{\overset{O}{\|}}{C}R' \rightleftharpoons -\overset{|}{\underset{|}{Pd}}CH_2C{<}^{H\ O\overset{\overset{O}{\|}}{C}R'}_{O\underset{\underset{O}{\|}}{C}R} \rightleftharpoons -\overset{|}{\underset{|}{Pd}}-O\overset{\overset{O}{\|}}{C}R' + CH_2{=}CHO\overset{\overset{O}{\|}}{C}R \qquad (38)$$

In the case of vinyl ester decomposition, the disubstituted intermediate (VII) can decompose according to the route shown in Eqs. (31) and (32). Hydrolytic reactions of the vinyl acetate intermediate [where X = H and Y = OAc] can account for the formation of ethylidene diacetate from ethylene,



$$-\overset{|}{\underset{|}{Pd}}CH_2C{<}^{H\ H}_{OAc} \longrightarrow -\overset{|}{Pd}H + CH_3\overset{\oplus}{C}HOAc;\quad CH_3\overset{\oplus}{C}HOAc \xrightarrow{-H^{\oplus}} CH_2{=}CHOAc;\quad CH_3\overset{\oplus}{C}HOAc \xrightarrow{+HOAc} CH_3CH(OAc)_2 + H^+;\quad -PdH \longrightarrow HCl + \underline{Pd}^0 \qquad (39)$$

Catalytic vinylations can be similarly explained by the existence of the disubstituted intermediate,



$$-\overset{|}{\underset{|}{Pd}}CH_2C{<}^{H\ OAc}_{Cl}$$

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