isopropyl alcohol slush. The entire system was purged with nitrogen which was saturated with ether. A solution of 2.442 g (0.040 mol) of nitromethane in 150 ml of ether was placed in the reaction vessel. The solution was refluxed with stirring, and aliquots of Grignard solution were added. After each addition, the solution was allowed to continue refluxing for about 20 min. The cold trap was then warmed to room temperature and the gases were collected in a gas-measuring buret containing water. After measurement, the gases were analyzed using a 11 ft by $^1/_4$ in. column of 33% 2,4-dimethylsulfolane on 60–80 mesh Chromosorb P with an injection port temperature of 125°, column temperature of 50°, detector temperature of 270°, and a gas flow of 33 ml/min at 40 psi. Retention times follow: air, 1.7 min; butane, 3.55 min; 1-butene, 4.6 min; *cis*-2-butene, 5.2 min; and *trans*-2-butene, 5.8 min. A trace amount of unidentified material with a retention time of 2.5 min was also detected. The results are shown in Figures 2 and 3.

Neutral Products from the Reaction of *n*-Butylmagnesium Bromide with Nitromethane.—The ether used in this experiment was dried over sodium wire and distilled immediately before use. The *n*-butyl bromide was filtered through a 5 in. × 1 in. column of alumina to remove all traces of *n*-butyl alcohol. Its purity was assured by gas chromatographic analysis. All phases of the reaction were conducted under nitrogen which was purified by passage through two bottles of Fieser's solution, two bottles of concentrated sulfuric acid, solid sodium hydroxide, and solid calcium chloride.

A solution of *n*-butylmagnesium bromide was prepared from 19.4 g (0.80 mol) of magnesium and 80.5 ml (0.75 mol) of *n*-butyl bromide in 300 ml of ether. The Grignard flask was attached to a 1-l. three-necked flask equipped with mechanical stirrer, heating mantle, and reflux condenser. A solution of 13.5 g (0.25 mol) of nitromethane in 150 ml of ether was placed in the reaction vessel and the *n*-butylmagnesium bromide solution was added dropwise with stirring at a rate which maintained constant reflux. After addition was complete, the reaction mixture was refluxed with stirring for an additional 4 hr. The Grignard solution was decomposed by the dropwise addition of 125 ml of 6 *N* hydrochloric acid. After an additional 30 ml of concentrated hydrochloric acid was added to the solution, the ether was separated and the aqueous solution was extracted with three 100-ml portions of ether. The combined ether solutions were dried ($CaSO_4$) and distilled using a spinning band column. The fraction boiling from 80–118° weighed 6.78 g and by gas chromatographic analysis using a Carbowax column consisted of ether (0.60 g), *n*-octane (4.55 g), and *n*-butyl alcohol (1.63 g). Gas chromatographic analysis was carried out using a 6 ft by $^1/_8$ in. column of 15% Carbowax 4000 on 100–120 mesh Chromosorb P with an injection port temperature of 165°, column temperature of 100°, detector temperature of 225°, and a gas flow of 30 ml/min at 40 psi. The retention times follow: ether, 0.3 min; *n*-octane, 0.5 min; and *n*-butyl alcohol, 2.3–2.5 min, depending on sample size.

Registry No.—**4**, 40548-43-4; nitromethane, 75-52-5; ethyl bromide, 74-96-4; trimethylchlorosilane, 75-77-4; *N*-ethyl-*N*-methyl-*O*-trimethylsilylhydroxylamine, 40548-44-5; *N*-ethyl-*N*-methylhydroxylamine, 13429-36-2; *N*-ethyl-*N*-propyl-*O*-trimethylsilylhydroxylamine, 40548-46-7; *N*-ethyl-*N*-propylhydroxylamine, 40548-47-8; *n*-butyl bromide, 109-65-9; *N*-butylhydroxylamine, 5080-24-0; chloroplatinic acid, 17083-70-4.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. IX. The Hydration of Enol Acetates in Wet Acetic Acid[1]

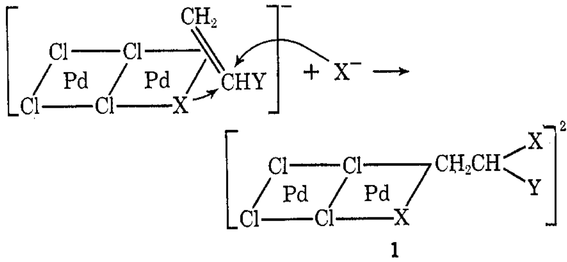
PATRICK M. HENRY[2]

Contribution No. 1603 from the Research Center, Hercules Incorporated, Wilmington, Delaware 19899

Received May 3, 1973

The rate expression for hydration of vinyl acetate to acetaldehyde was found to be rate = $k[Li_2Pd_2Cl_6][C_2H_3OAc][H_2O]^n/[LiCl]$ where n has a value of between 1 and 2. The rate expression is consistent with attack of external water on a dimeric palladium(II) vinyl acetate π complex to give a hydroxypalladation adduct which decomposes to acetaldehyde and $Li_2Pd_2Cl_6$. The decomposition of this adduct is not by simple acetate elimination to give vinyl alcohol since this mechanism would predict that 1-cyclopenten-1-yl acetate would not react. In fact this enol acetate is rapidly saponified. Formation of a palladium(II)-substituted acetaldehyde which then reacts with acetic acid solvent to give CH_3CHO seems to be the most likely mechanism. The determination of the rate expression is complicated by the fact that water is not only a reagent but affects the various equilibria present in the system. As with previous exchanges, substitution on vinyl carbon retards the rate of exchange. The nonintegral order in $[H_2O]$ is believed to be due to preferential solvation of the reactive metal ion species.

Previous papers of this series have considered exchange of vinyl[3] and allylic[4] ester with acetic acid, allylic esters with chloride,[5] and vinylic chlorides with radioactive chloride[6] and acetic acid.[7] A general feature of these exchanges is that they involve attack of acetate or chloride on a dimeric palladium(II) π complex to give a palladium(II) σ-bonded intermediate, **1**. For vinylic exchange the reaction scheme would be given by eq 1 (X and Y = Cl or OAc). Exchange is completed by elimination of Y to give back the olefin. When X is acetate, attack occurs only from outside the coordination sphere of the palladium(II); when X is chloride, attack can occur from either outside or inside the coordination sphere.



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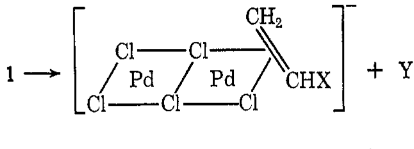
(1)



(2)

This paper will describe the palladium(II) chloride catalyzed reaction of vinyl acetate with a third and

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[1] Paper VIII: P. M. Henry, *J. Org. Chem.*, **38**, 1140 (1973).

[2] Address correspondence to author at Department of Chemistry, University of Guelph, Guelph, Ontario, N1G 2W1, Canada.

[3] P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

[4] P. M. Henry, *ibid.*, **94**, 1527, 5200 (1972).

[5] P. M. Henry, *Inorg. Chem.*, **11**, 1876 (1972).

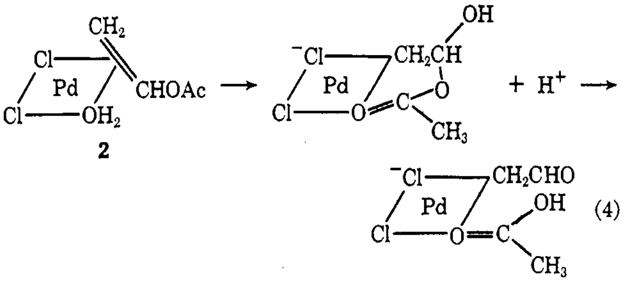
[6] P. M. Henry, *J. Org. Chem.*, **37**, 2443 (1972).

[7] P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7311 (1972).

unique reagent, water. Smidt and coworkers[8] reported that aqueous Pd(II) salts saponify vinyl ace-

$$CH_2{=}CHOAc \xrightarrow[H_2O]{Pd(II)} CH_3CHO \qquad (3)$$

tate. A kinetic study of this reaction in wet acetic acid led to the conclusion that the reaction was proceeding *via* eq 4 and 5.[9] However, because the various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3

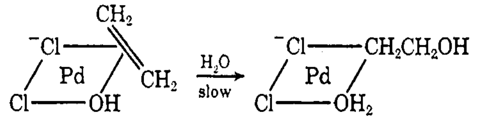
(4)

$$\mathbf{3} + H_2O + H^+ + C_2H_3OAc \longrightarrow \mathbf{2} + CH_3CHO \qquad (5)$$

equilibria in the system were not determined, the detailed reaction path could not be defined.

Water is different from most nucleophiles because not only can it act as a reactant but it can also change the nature of the solvent. Thus the various equilibria operative in a system containing metal salts would be affected. This shift in equilibria complicates the determination of the rate equation.

As a reagent, water is of special interest because it could react in the same mode as acetate in previous exchanges studied, or it could react in the manner found for olefin oxidation in water. Thus the slow step of this reaction is the addition of coordinated hydroxyl to coordinated ethylene to give the hydroxypalladation intermediate (eq 6), which decomposes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(6)

to acetaldehyde in a subsequent fast step of the reaction.[10-12] The hydroxypalladation step in acetic acid

$$\mathbf{4} \longrightarrow CH_3CHO + Pd(0) + 2Cl^- + 2H_2O \qquad (7)$$

may proceed by such an insertion or may involve attack of water from outside the coordination sphere in a manner found for the acetate exchanges studied previously.

Results

All studies were carried out at 25°. In order to properly interpret the kinetic results it is necessary to determine how the addition of water affects the equilibria represented by eq 8 and 9. In dry acetic acid

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \qquad (8)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \qquad (9)$$

the values of K_1 and K_D were previously found[13] to be 0.1 and 2.56 M^{-1}, respectively, at 25°.

The addition of water to Pd(II)–LiCl solutions with various ratios of total palladium(II), [Pd(II)], to total chloride, $[Cl]_t$, caused spectral changes. However, at constant $[Pd(II)]_t$ and $[Cl]_t$ the spectra at various water levels displayed three isosbestic points. This result would not be expected if Pd(II) species other than the two in eq 8 were being formed. In fact the addition of water caused the same spectral changes as the addition of LiCl. This result suggests that water is not directly involved in the spectral changes but is rather causing a shift in the equilibrium represented by eq 8 or, in other words, is changing the value of K_1. To confirm this, studies of the equilibrium were carried out at 1.0 and 10.0 M H_2O, using the nonlinear regression program employed previously in the study of the dry system.[13] At both water levels the data were consistent with eq 8 being the only equilibrium involving Pd(II). Values of K_1 were 0.48 and 5.6 M^{-1} at 1.0 and 10.0 M $[H_2O]$, respectively. Since the value of K_1 in dry acetic acid is 0.1 M^{-1}, the value of K_1 increases approximately linearly with water concentration. Values of K_1 at other water concentrations were calculated from this linear relationship.

When water was present in tenfold excess, kinetic plots, assuming a first-order dependence on [vinyl acetate], were linear for 4 half-lives. Furthermore, the initial vinyl acetate concentration was varied fivefold without an appreciable change in the first-order constant. Thus at $[Pd(II)_t]$ of 0.0224 M, $[Cl]_t$ of 0.1346 M, and $[H_2O]$ of 0.5 M, the first-order rate constant was found to be 2.8×10^{-5} sec^{-1} at an initial vinyl acetate concentration of 0.2 M and 2.66×10^{-5} sec^{-1} at an initial concentration of 1.0 M. In most runs the initial [vinyl acetate] was 0.2 M.

Lithium acetate was found to have no effect on the rate of hydration. Under one set of reaction conditions rates in the absence of acetate and at [LiAOc] = 0.1 M were within 5% of each other.

The order in dimer was determined using solutions of $Na_2Pd_2Cl_6$ which are saturated in NaCl. Since NaCl is sparingly soluble in acetic acid, the chloride is kept at a low but constant level and the Pd(II) should be entirely in the form of dimer. As shown in Figure 1 the reaction is first order in dimer at a water level of 0.5 M.

In Table I are listed the results of a series of runs at a water concentration of 0.5 M and constant $[Pd(II)]_t$ but varying $[Cl]_t$. The concentrations of the Pd(II) species were calculated using a value of K_1 of 0.3 M^{-1}. A problem arises at this point in treatment of data. The equilibria represented by eq 9 would be expected to be greatly affected by water but it is not easy to measure the magnitude of the effect. However, if K_D is assumed to be 2.6 M^{-1}, the value of the quotient in the last column of Table I was found to decrease systematically at the high $[Cl]_t$ at which dimerization becomes serious. However, if dimeriza-

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[8] J. Smidt, R. Jira, J. Sedlmeier, R. Sieber, R. Rüttinger, and H. Kojer, *Angew. Chem.*, **71**, 176 (1959).

[9] R. G. Schultz and P. R. Rony, *J. Catal.*, **16**, 133 (1970).

[10] I. I. Moiseev, M. N. Vargaftik, and Ya K. Sirkin, *Dokl. Akad. Nauk SSSR*, **153**, 140 (1963).

[11] R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693**, 99 (1966).

[12] P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964).

[13] P. M. Henry and O. Marks, *Inorg. Chem.*, **10**, 373 (1971).

TABLE I

EFFECT OF [LiCl] ON THE RATE OF HYDRATION[a]

$[Cl]_t$, M	$[Li_2Pd_2Cl_6]$,[b] M	$[Li_2PdCl_4]$,[b] M	[LiCl], M	k_{obsd}, $sec^{-1} \times 10^5$	$k_{obsd}[LiCl]/[Li_2Pd_2Cl_6]$, $sec^{-1} \times 10^4$
0.0852	0.01075	0.00090	0.0170	9.8	1.55
0.105	0.01033	0.00174	0.0366	5.15	1.82
0.1346	0.0098	0.038	0.065	2.8	1.85
0.184	0.00911	0.0042	0.113	1.87	2.32
0.2334	0.00855	0.0053	0.161	1.1	2.07
0.2852	0.00805	0.0063	0.212	1.05	2.78
0.4852	0.0067	0.0090	0.409	0.4	2.44
0.8852	0.0051	0.0122	0.810	0.13	2.06

[a] $[Pd(II)]_t = 0.0224\ M$, [LiOAc] = 0.1 M, and [vinyl acetate] = 0.2 M in all runs. [b] Calculated using $K_1 = 0.3\ M^{-1}$ in eq 8.

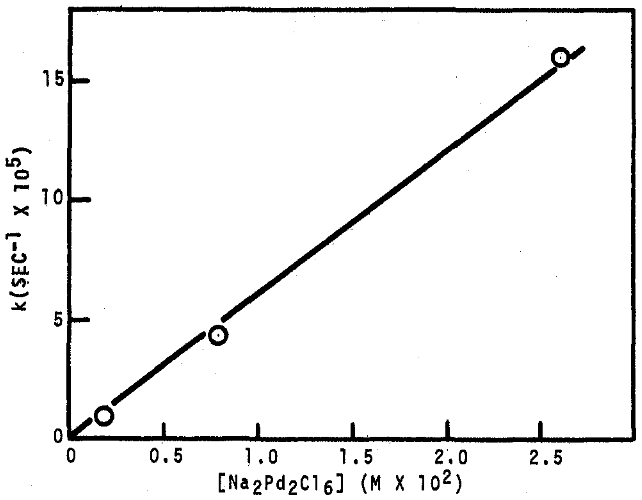


Figure 1.—Plot of k_{obsd} *vs.* $[Na_2Pd_2Cl_6]$ in saturated NaCl solutions; $[H_2O] = 0.5\ M$.

tion is assumed *not* to occur, then the values remain approximately constant. Thus dimerization of LiCl is ignored in the treatment of data in Table I.

The effect of water concentration on rate is shown in Table II. The increase in rate with H_2O is somewhat greater than expected for a first-order term in $[H_2O]$ but less than required for a $[H_2O]^2$ term. The complete rate expression is thus given by eq 10

$$\text{rate} = \frac{k[Li_2Pd_2Cl_6][C_2H_3OAc][H_2O]^n}{[LiCl]} \quad (10)$$

where

$$1 \leq n \leq 2 \quad (11)$$

The rates for three enol acetates under one set of reaction conditions are given in Table III.

Discussion

There seems little reason to doubt that the reaction proceeds *via* a hydroxypalladation analogous to that suggested previously[9] and there is considerable analogy for this type of reaction in the Hg(II)- and Tl(III)-catalyzed hydration of enol acetates.[14] However, the previous work was unable to define the kinetics because of lack of equilibrium data and the mechanism derived on the basis of kinetic data alone gave an erroneous view of the mode of hydroxypalladation.

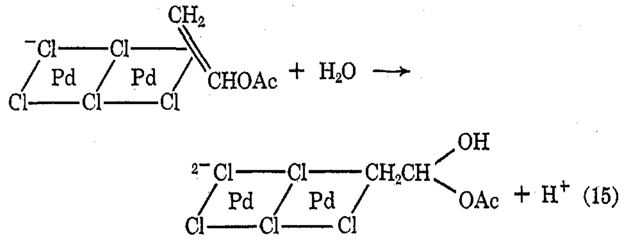
Since the reaction was found to be zero order in vinyl acetate,[15] complete formation of π complex according to eq 12 was assumed. Thus formation of π complex does not contribute a chloride inhibition term to the rate equation. The first-order inhibition term observed was attributed to replacement of chloride by water according to eq 13. The hydroxypalladation then occurs as shown in eq 4. The postulated mode of addition is analogous to the cis attack of hydroxyl which apparently takes place in the Wacker reaction.[17]

$$PdCl_4^{2-} + C_2H_3OAc \rightleftharpoons PdCl_3(C_2H_3OAc)^- + Cl^- \quad (12)$$

$$PdCl_3(C_2H_3OAc)^- + H_2O \rightleftharpoons PdCl_2(C_2H_3OAc)(H_2O) + Cl^- \quad (13)$$

The rate expression derived in the present study (eq 10) requires that the dimer be the reactive species. Furthermore, the interaction of the dimer with vinyl acetate to give π complex (eq 14) must be an equilibrium which is far to the left (*i. e.*, K_2 is small) since the reaction is first order in vinyl acetate concentration. The LiCl inhibition term in eq 10 must also result from the equilibrium. The lack of a second LiCl inhibition term indicates that water cannot be attacking from inside the coordination sphere of Pd(II). This suggests trans stereochemistry.[18] The most important result of this study, then, is the demonstration that hydroxypalladation can occur by more than one route. This result is in keeping with

$$Li_2Pd_2Cl_6 + C_2H_3OAc \overset{K_2}{\rightleftharpoons} LiPd_2Cl_5(C_2H_3OAc) + LiCl \quad (14)$$



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[14] P. Abley, J. E. Byrd, and J. Halpern, *J. Amer. Chem. Soc.*, **94**, 1985 (1972).

[15] In the present work the reaction was found to be definitely first order in vinyl acetate, in direct disagreement with the studies of Schultz and Rony.[9] However, in the same paper they report studies of the formation of acetaldehyde in dry acetic acid for which the reaction is zero order in vinyl acetate under some reaction conditions.[16] Perhaps because the order was zero in dry acetic acid they assumed it to be zero in wet acetic acid. *In any case they did not vary [vinyl acetate]* which is the best way of determining order.

[16] P. M. Henry, *J. Org. Chem.*, in press.

[17] The kinetics do not absolutely require cis attack of Pd(II)–OH. See P. M. Henry, *Advan. Chem. Ser.*, **No. 70**, 136 (1968).

[18] A referee has suggested that the kinetics do not eliminate attack of water from an axial position. This is true, but other exchange studies indicate that attack or elimination using axial coordination positions is not important in Pd(II) chemistry.[19]

[19] P. M. Henry, *Accounts Chem. Res.*, **6**, 16 (1973).

TABLE II

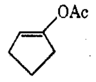
EFFECT OF WATER CONCENTRATION ON THE RATE OF HYDRATION[a]

$[Cl]_t$, M	K_1[b]	$[H_2O]$, M	$[Li_2Pd_2Cl_6]$, M	$[LiCl]$, M	k_{obsd}, $sec^{-1} \times 10^6$	$k_{obsd}[LiCl]_t/[Li_2Pd_2Cl_6]$, M
0.1346	0.3	0.5	0.0098	0.065	2.8	1.85
	0.48	1.0	0.0095	0.064	7.8	5.3
	1.34	2.5	0.00855	0.0625	20.3	14.8
	2.75	5.0	0.0077	0.0604	66.0	51.7
0.2334	0.3	0.5	0.00855	0.161	1.1	2.07
	2.75	5.0	0.0036	0.151	13.0	54.8

[a] $[Pd(II)]_t = 0.0224$ and [vinyl acetate] $= 0.2\ M$ in all runs. [b] This value of K_1 used in calculating $[Li_2Pd_2Cl_6]$ and [LiCl]; $[Li_2Pd_2Cl_4]$ can be calculated from $[Pd(II)]_t$ and $[Li_2Pd_2Cl_6]$.

TABLE III[a]

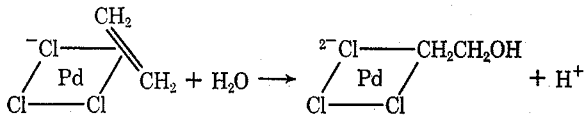
EFFECT OF ENOL ACETATE STRUCTURE ON RATE OF HYDRATION[a]

Registry no.	Enol acetate	k_{obsd}, $sec^{-1} \times 10^4$
108-05-4	$CH_2{=}CHOAc$	3.6
1528-10-5	*trans*-$CH_3CH{=}CHOAc$	0.023
933-06-2		0.021

[a] $[Na_2Pd_2Cl_6] = 0.0137$; $[H_2O] = 2.5\ M$; reaction mixture saturated with NaCl.

other studies,[19] which indicate that the mode of addition of Pd(II) and nucleophiles across double bonds is not unique but depends very much on the nucleophile and the reaction conditions.

The reason that the mode of hydroxypalladation is different from that in water most likely results from the equilibria present in the two systems. In acetic acid the predominant Pd(II) species is the reactive dimer $Li_2Pd_2Cl_6$, while in water containing greater than 0.1 M Cl^-, Pd(II) exists solely as $PdCl_4^{2-}$.[20] Thus in water the dimer route is not available to the Pd(II). The question then arises as to why the monomeric π complex does not decompose by attack of H_2O from outside the coordination rather than by


(16)

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internal attack of hydroxyl (eq 6). The answer may lie in the charge on the monomeric complex. In the study of allylic ester exchange[4] it was found that monomeric π complex was formed *via* eq 17 in

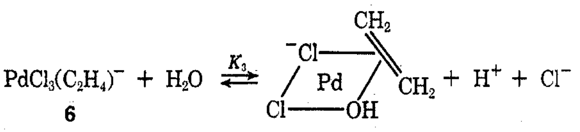
$$Li_2Pd_2Cl_6 + 2 \text{ allylic ester} \rightleftharpoons \underset{\mathbf{7}}{2LiPdCl_3 \text{ (allylic ester)}} \quad (17)$$

much larger quantities than reactive dimer π complex *via* eq 18. Yet the monomeric π complex was com-

$$Li_2Pd_2Cl_6 + \text{allylic ester} \rightleftharpoons \underset{\mathbf{8}}{LiPd_2Cl_5 \text{ (allylic ester)}} + LiCl \quad (18)$$

pletely unreactive. The reason postulated for lack of reactivity of **7** as compared with **8** was the higher negative charge of the Pd(II) containing the olefin in **7**. In the dimer the negative charge resides mainly on the Pd(II) not complexed to the olefin. This higher charge on the monomer π complex would cause the olefin to be less susceptible to nucleophilic attack. With negatively charged nucleophiles an additional factor would be the mutual repulsion of the negative charges.

Since attack of water from outside the coordination sphere is an unfavorable process, the monomeric π complex incorporates H_2O and releases a proton to give the more potent nucleophile hydroxyl, which attacks cis as shown in eq 6. The reason hydroxyl is formed


(19)

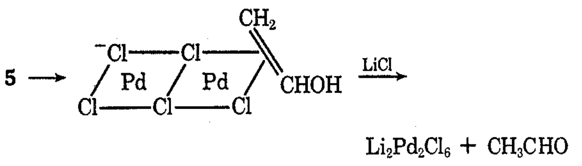
in the coordination sphere is that complexing greatly increases the acidity of water.[21] Thus complexed hydroxyl is much more readily than free hydroxyl. Another factor could be repulsion between the negative charges on the hydroxyl and the monomeric π complex **6** if attack were from outside the coordination sphere.

The final step in the reaction is the decomposition of **5** (eq 15) to product. Now formation of **5** must be rate-limiting step, for if eq 15 were an equilibrium

$$\mathbf{5} + LiCl \longrightarrow Li_2Pd_2Cl_6 + CH_3CHO + LiOAc \quad (20)$$

the reaction would have a dependence on LiOAc since proton is formed in this reaction. Acetate would shift the equilibrium to the right and increase the rate. Thus the kinetics tell us nothing about the decomposition reaction.

The most straightforward route would be simple elimination of OAc to give coordinated vinyl alcohol, which then rearranges to acetaldehyde. However,


(21)

the results with 1-cyclopenten-1-yl acetate are not consistent with this type of decomposition. Because water attacks from outside the coordination sphere of Pd(II), the stereochemistry of hydroxypalladation would be expected to be trans. The stereochemistry of acetoxypalladation, and thus deacetoxypalladation, by the principle of microscopic reversibility, has been shown to be trans.[22] As shown by eq 15, cyclic enol

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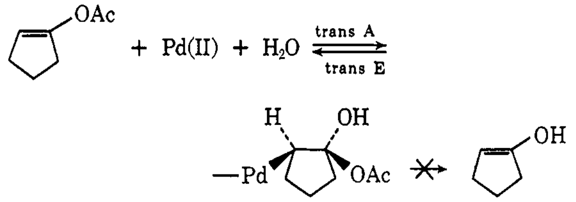
(20) A. Aguilo, *Advan. Organometal. Chem.*, **5**, 321 (1967).

(21) F. Basolo and R. G. Pearson in "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience, New York, N. Y., 1962.

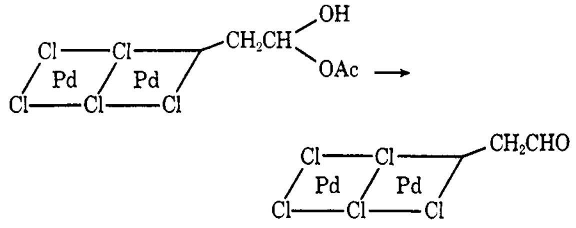
(22) P. M. Henry and G. A. Ward, *J. Amer. Chem. Soc.*, **93**, 1494 (1971).

acetates should not undergo hydration by this scheme if both addition and elimination have the same stereochemistry (A = addition, E = elimination).



(22)

A mode of decomposition which avoids this objection and which is consistent with the mechanism found for Hg(II)-catalyzed hydration of enol acetates[23] is given by eq 23–25. Other possible modes of decomposition are direct reaction of **9** with acid or disproportion of two of **9** to give **10** followed by reaction with acid. The important point is that decomposition need not occur in the case of hydration by the general route represented by eq 2, as was the case for the previous exchanges studied.[3-7]



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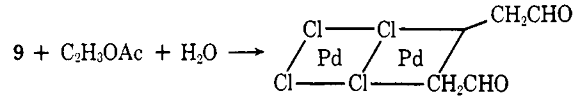
(23)



10

(24)

$$\mathbf{10} + \mathrm{HOAc} + \mathrm{Cl}^- \longrightarrow \mathbf{9} + \mathrm{CH_3CHO} + \mathrm{OAc}^- \qquad (25)$$

The fact that the order in water is not an integral value but between 1 and 2 is probably explicable in terms of solvation of the dimeric π complex by water. There would be a greater portion of water in the region around the polar catalytic species than in the bulk of the solution, giving an apparent order in water of greater than one. In this regard it was reported[9] that at higher [H_2O] (>25 *M*), the rate actually decreased with increasing [H_2O]. This range of water concentrations was not included in the present study but the decrease is understandable in terms of the effect of water on the equilibrium represented by eq 8. As K_1 is increased by increasing [H_2O], the amount of reactive dimer is decreased. At a certain water level this effect must become more important than catalysis by water. Another factor may be decreasing solubility of the vinyl acetate.

Another effect water apparently has is on the equilibrium represented by eq 9. The kinetics (Table I) are consistent with a much smaller value of K_D at 0.5 *M* [H_2O] than in anhydrous acetic acid. This result is not surprising, since increased solvent power would discourage dimerization.

The effect of structure on rate shown in Table III shows the expected trends with structure. The ratio of rates for vinyl acetate and *trans*-1-propen-1-yl acetate is about the same as that found for vinyl ester exchange[3] and indicates steric hindrance to addition of the elements of Pd(II) and acetate or water.

Experimental Section

Materials.—Sources of chemicals and preparation of stock solutions have been described previously.

Kinetic Runs.—Reaction mixtures were prepared by mixing known amounts of $Li_2Pd_2Cl_6$, LiCl, LiOAc, and H_2O stock solutions of known composition and diluting to a fixed volume, usually 5 ml. The reaction mixtures were placed in a 25° bath for about 1 hr and the run was started by adding a given amount of enol acetate. Samples were analyzed by gas chromatography using a 6-ft 20% Carbowax 20M on ABS (70–80 mesh) column programmed from 80 to 200° at 7.5°/min. Helium flow rate was 60 ml/min.

Ultraviolet Spectra Study.—Procedure was essentially the same as that used previously[18] except that in the present study the solutions contained a known amount of water. At 1.0 and 10.0 *M* [H_2O] the absorbancies of 16 solutions containing various amounts of Pd(II) and total chloride was measured at 245, 250, and 280 nm. At a given water level all the data were treated simultaneously in the nonlinear regression technique described earlier. The value of K_1 at 1.0 *M* [H_2O] was found to be 0.48 M^{-1} with a standard deviation of absorbance of 0.028. At 10.0 *M* [H_2O], K_1 was 5.6 M^{-1} with a standard deviation of 0.047. One problem in the treatment of data was that the program used a value for K_D of 2.6 M^{-1} while the actual value was probably much lower (see Results). However, this would have little effect on the calculated values of K_1, since most of the experimental points were at chloride concentrations at which the calculated amounts of dimerization would be small.

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Registry No.—LiCl, 7447-41-8; $Li_2Pd_2Cl_6$, 31183-05-8; $Li_2 \cdot PdCl_4$, 15525-45-8; $Na_2Pd_2Cl_6$, 16010-02-9.

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[23] J. E. Byrd and J. Halpern, *Chem. Commun.*, 1332 (1970).