The dried extracts were rotovaporated to yield 65 mg of a residue, which was shown by vpc to be a mixture of 1-pleiadene (41%), pleiadane (21%), and pleiadiene (38%). Preparative vpc gave a sample of 1-pleiadene, mp 47–47.5°.

6,9-Di-*tert*-butyl-1-pleiadene (11a) was prepared as in the unsubstituted case. Treatment of **9a** with diimide for 5 days gave the following mixture (vpc): 6,9-di-*tert*-butylpleiadane (10%), 6,9-di-*tert*-butyl-1-pleiadene (43%), and 6,9-di-*tert*-butylpleiadiene (47%). Preparative tlc (silica gel, PF_{254} 12.5% $AgNO_3$, benzene, 2×, R_f 0.4) gave 28 mg of product, which was sublimed: mp 99–100.5°; nmr ($CDCl_3$) δ 13.8 (s, 18 H), 2.55 (m, 2 H), 3.20 (m, 2 H), 5.90–6.82 (m, 2 H), 7.2 (d, J = 2 Hz, 1 H), 7.33 (d, J = 2 Hz, 1 H), 7.58 (d, J = 2 Hz, 2 H); ir ($CHCl_3$) 3.48, 6.22, 6.30, 6.81, 7.39, 11.41 μ; uv λ_{max} (log ϵ) 238 (4.65), 256 (4.26), 299 (sh) (3.91), 3.08 (4.00), 321 (sh) (3.89); exact mass 292.2207 (calcd for $C_{22}H_{28}$, 292.2191).

The compounds **10a** and **10b** were never prepared, although esr spectra, observed upon allowing reducing mixtures of **8a** and **8b** to warm, were recorded. The esr spectra were recorded on a Varian E.15 spectrometer, and sample preparation was as previously described.[8a,b]

6b,10b-Dihydrobenzo[3,4]cyclobut[1,2-*a*]acenaphthylene (14).—A refluxing methylene chloride solution (30 ml) of 1.25 g of acenaphthylene was treated with 1.25 g of solid benzenediazonium 2-carboxylate[19] in small portions over a period of 4 hr. The black solution was concentrated, and preparative tlc (silica gel PF_{254}, 12.5% $AgNO_3$, benzene, R_f 0.5) gave 100 mg (5%) of **14**, mp 129–130° (lit.[10a] mp 133–134°).

Acknowledgment.—We thank the National Science Foundation, the Sloan Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work, and the National Science Foundation's major instrument program for funds used in purchase of the nmr, esr, and mass spectral equipment used.

Registry No.—**8**·⁻, 40782-39-6; **8a**·⁻, 40782-69-2; **8b**·⁻, 40782-70-5; **9**, 208-20-8; **9a**, 40949-40-4; **10**, 40949-41-5; **10**·⁻, 40949-42-6; **10a**·⁻ 40949-43-7; **10b**·⁻, 40949-44-8; **11**, 40949-45-9; **11a**, 40949-46-0; **13**·⁻, 40949-47-1; **14**·⁻, 40949-48-2; **17**·⁻, 40949-49-3; **18**·⁻, 40949-50-6.

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[19] M. Stiles, R. G. Miller, and U. Burkhart, *J. Amer. Chem. Soc.*, **85**, 1792 (1963).

Palladium(II) Chloride Catalyzed Decomposition of Vinyl Acetate in Dry Acetic Acid[1]

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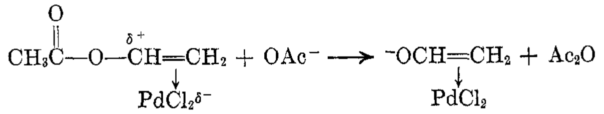
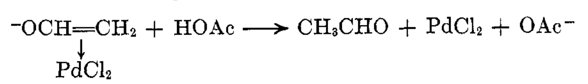
The decomposition of vinyl acetate to give acetaldehyde and acetic anhydride was found to have two regions of kinetic behavior. In one, which occurs at low chloride, high Pd(II), and high vinyl acetate concentrations, the reaction rate had little dependence on these variables and addition of acetic anhydride depressed the rate only slightly. In the second region, which occurs at high chloride, low Pd(II), and low vinyl acetate concentrations, the kinetic behavior becomes conventional and follows the rate expression $-d[C_2H_3OAc]/dt = k[Li_2Pd_2Cl_6]\cdot[C_2H_3OAc]/[LiCl]$. In this range the reaction is strongly inhibited by acetic anhydride. The mechanism which best fits all the data involves the slow formation of water and acetic anhydride in a reaction not involving Pd(II) catalysis. The water then reacts with vinyl acetate in a Pd(II)-catalyzed reaction to give acetaldehyde and acetic acid. The two regions of kinetic behavior arise from the fact that either water formation or the reaction of water with vinyl acetate can be the rate-limiting step.

The palladium(II)-catalyzed decomposition of vinyl acetate, first reported in 1959,[3] has been the subject of at least two mechanistic studies.[4,5] Noting that both palladium(II) chloride and sodium acetate were required for the decomposition, Clement and Selwitz proposed a mechanism involving attack of acetate on a Pd(II)-olefin complex (eq 1 and 2).



$$CH_3\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{PdCl_2{}^{\delta-}}{\downarrow}}{\overset{\delta+}{C}H}{=}CH_2 + OAc^- \longrightarrow {}^-O\underset{\underset{PdCl_2}{\downarrow}}{CH}{=}CH_2 + Ac_2O \quad (1)$$



$$ {}^-O\underset{\underset{PdCl_2}{\downarrow}}{CH}{=}CH_2 + HOAc \longrightarrow CH_3CHO + PdCl_2 + OAc^- \quad (2)$$

Schultz and Rony,[5] on the other hand, found that sodium acetate was not required for the decomposition and, in fact, was a mild inhibitor. Furthermore, they found the reaction to be zero order in vinyl acetate and inhibited by LiCl. They also found that addition of Ac_2O had no effect on the rate. They explained these observations by first proposing that the predominant species in solution is either $Cl_2PdCl(CH_2{=}CHOAc)^-$ or the dimeric species $Cl_2PdCl_2PdCl(CH_2{=}CHOAc)^-$, which was found to be the active species in vinyl ester exchange.[6] Further steps in the sequence are given by eq 3–6.

$$>PdCl(CH_2{=}CHOAc) + HOAc \rightleftarrows \underset{\mathbf{1}}{>Pd(HOAc)(CH_2{=}CHOAc)} + Cl^- \quad (3)$$

$$\mathbf{1} \longrightarrow \underset{\mathbf{2}}{>PdCH_2CH(OAc)_2} + H^+ \quad (4)$$

$$\mathbf{2} \longrightarrow \underset{\mathbf{3}}{>PdCH_2CHO(Ac_2O)} \quad (5)$$

$$\mathbf{3} + HOAc + CH_2{=}CHOAc + H^+ \longrightarrow \mathbf{1} + Ac_2O + CH_3CHO \quad (6)$$

There is one serious objection to this reaction scheme. Vinyl ester exchange, which almost certainly proceeds by way of an intermediate such as **2**, exhibits quite different kinetics from decomposition. Exchange is first order in both vinyl acetate and acetate ion. This

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[1] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969; *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (2), B15 (1969).

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

[3] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttinger, and H. Kojer, *Angew. Chem.*, **71**, 176 (1959).

[4] W. H. Clement and C. M. Selwitz, *Tetrahedron Lett.*, 1081 (1962).

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

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

difference in kinetic behavior would not be expected if 2 is a common intermediate for both reactions. A further problem is that Schultz and Rony[5] did not measure the order in Pd(II). A first-order dependence would have been expected on the basis of the mechanism represented by eq 3–6.

This paper will describe the author's own studies of the decomposition reaction which indicate that the reaction is considerably more complex than suggested by previous workers.

Results

All runs were carried out at 25° in dry acetic acid using palladium(II) chloride as catalyst in the presence of either NaCl or LiCl. In acetic acid saturated with NaCl (0.013 *M*), the Pd(II) is known to exist almost exclusively as the dimeric species $Na_2Pd_2Cl_6$.[7] When the chloride is introduced in the form of LiCl, the following two equilibria must be considered, where K_1 has a value of 0.1 M^{-1} and K_D a value of 2.6 M^{-1}

$$Li_2Pd_2Cl_6 + 2LiCl \overset{K_1}{\rightleftharpoons} 2Li_2PdCl_4 \qquad (7)$$

$$2LiCl \overset{K_D}{\rightleftharpoons} Li_2Cl_2 \qquad (8)$$

at 25°. The concentrations of all species can be calculated from a knowledge of total palladium(II), $[Pd(II)]_t$, and total chloride, $[Cl]_t$, concentrations.

Kinetic Dependence on Vinyl Acetate Concentration.—In any given run it was difficult to determine the kinetic order in vinyl acetate since the runs could not be carried out for much over one half-life because of precipitation of solids. Therefore, the order in vinyl acetate was studied by varying the initial vinyl acetate concentration.

The order in vinyl actate was found to be neither zero order nor first order, but rather somewhere between the two. If plotted as first-order reactions, reasonably good plots were obtained which usually varied with initial vinyl acetate concentration. On the other hand, the zero-order rate constants also varied with initial vinyl acetate concentration. Only at higher chloride and lower vinyl acetate concentrations did the reaction appear to be first order in vinyl acetate. Some representative data are given in Table I. The rate data in this paper will be reported in terms of psuedo-first-order rate constants obtained from the first-order plots of the data, since they offer a reasonable measure of rate.

Effect of Lithium Acetate Concentration.—Above a concentration of about 0.1 *M*, the rate was independent of [LiOAc]. A plot of k_{obsd} *vs.* [LiOAc] under one set of reaction conditions is shown in Figure 1. Except where indicated otherwise all runs in this paper were carried out at [LiOAc] = 0.1 *M*.

Dependence of Rate on Palladium(II) Concentration.—The order in palladium(II) was also not simple. At low chloride the dependence was less than one-half order. Table II shows some results in solutions saturated with NaCl to maintain a low but constant [NaCl] (0.013 *M*). The palladium(II) concentration varies by a factor of 32 while the rate varies by a factor of only 3. Even a half-order dependence would have predicted a change by a factor of 5.6.

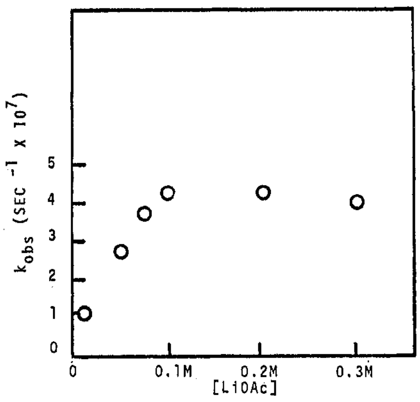

Figure 1.—Plot of k_{obsd} *vs.* [LiOAc]: $[Pd(II)]_t$, 0.02 *M;* $[Cl]_t$, 0.27 *M;* initial [vinyl acetate], 0.2 *M*.

TABLE I

REACTION ORDER IN VINYL ACETATE UNDER SEVERAL REACTION CONDITIONS[a]

$[Pd(II)]_t$	$[Cl]_t$	Initial [vinyl acetate]	First-order plot, k_{obsd}, sec^{-1} × 10^6	Zero-order plot, *M*/hr × 10^4
0.02644	0.0994[b]	0.19	1.08	1.8
0.02644	0.0994[b]	0.48	0.43	5.6
0.0224	0.0852[c]	0.10	0.8	1.9
0.0224	0.0852	0.825	0.46	14
0.02540	0.2908[d]	0.082	0.80	1.05
0.02540	0.2908[d]	0.18	0.71	2.1
0.02540	0.2908[d]	0.47	0.31	3.5
0.02540	0.2908[d]	0.98	0.16	5.2

[a] [LiOAc] = 0.1 *M;* [Ac_2O] = 0.3 *M*. [b] Chloride added as NaCl; free NaCl was 0.013 *M* (saturated solution). [c] Chloride added as LiCl; free LiCl was 0.017 *M*. [d] Chloride added as LiCl; free LiCl was *ca.* 0.15 *M*.

TABLE II

DEPENDENCE OF RATE ON $Na_2Pd_2Cl_6$ CONCENTRATION IN SOLUTIONS SATURATED WITH NaCl[a]

[$Na_2Pd_2Cl_6$], *M* × 10^2	k_{obsd}, sec^{-1} × 10^6
2.68	1.51
1.34	1.17
0.67	0.96
0.335	0.77
0.0167	0.64
0.0835	0.48

[a] [NaCl] = 0.013 *M;* [LiOAc] = 0.1 *M;* [Ac_2O] = 0.3 *M;* initial [vinyl acetate] = 0.2 *M*.

However, at higher chloride concentrations the dependence becomes much more pronounced. A plot of k_{obsd} *vs.* $[Pd(II)]_t$ at [LiCl] = *ca.* 0.2 *M* is shown in Figure 2. At lower $[Pd(II)]_t$ there is a first-order dependence on $[Pd(II)]_t$. If [$Li_2Pd_2Cl_6$] is used in place of $[Pd(II)]_t$, the plot is somewhat more curved at higher values of [$Li_2Pd_2Cl_6$], but a linear dependence is still observed at low values.

Effect of [LiCl] on Rate.—A plot of k_{obsd} *vs.* 1/[LiCl] is shown in Figure 3.[8] At high [LiCl] the reaction displays a first-order inhibition by LiCl while, at lower [LiCl], the reaction becomes independent of lithium chloride concentration. A plot of k_{obsd}/[$Li_2Pd_2Cl_6$] *vs.* 1/[LiCl], which would correct for removal of dimer

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

[8] Schultz and Rony plotted 1/k_{obsd} *vs.* [LiCl] and obtained a straight line with a positive intercept. The data used for Figure 3 would have given a similar plot. However, we feel the type of plot shown in Figure 3 is more indicative of mechanism.

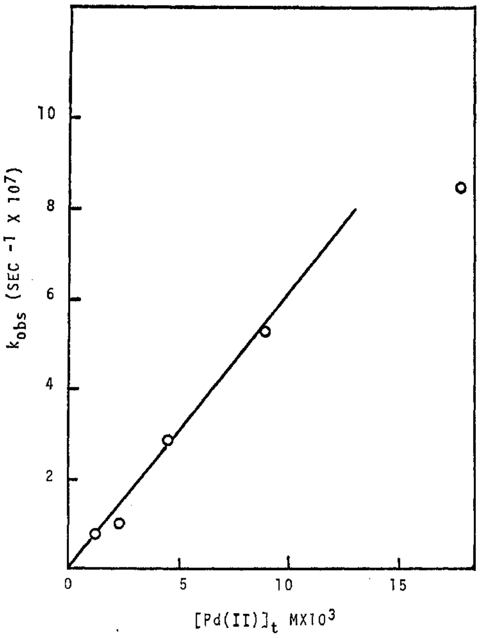

Figure 2.—Plot of k_{obsd} *vs.* $[Pd(II)]_t$ in the LiCl system: [LiCl], 0.2 ± 0.02 *M*; [LiOAc], 0.1 *M*; initial [vinyl acetate], 0.2 *M*.

because of the equilibrium shown in eq 7, is very similar to the plot shown in Figure 3.[9]

Effect of Acetic Anhydride Concentration.—Most of the runs in this study were made at acetic anhydride concentrations of 0.3 *M*. However in several runs the concentration was varied to determine the effect on rate (see Table III). At the low chloride concentrations of the $Na_2Pd_2Cl_6$ system, increasing the Ac_2O concentration by a factor of 10 decreased the rate by a factor of about 2. On the other hand, at higher chloride concentration the addition of AcO_2 strongly depressed the rate. For runs at 0.3 and 0.6 *M* $[Ac_2O]$ the rate was proportional to $1/[Ac_2O]$.

TABLE III

EFFECT OF ACETIC ANHYDRIDE ON RATE AT TWO DIFFERENT REACTION CONDITIONS[a]

$[Pd(II)]_t$, *M*	$[Cl]_t$, *M*	$[Ac_2O]$, *M*	k_{obsd}, sec^{-1} × 10^6
0.05288	0.186[b]	0.1	1.15
0.05288	0.186[b]	1.0	0.51
0.02540	0.2908[c]	0.3	0.71
0.02540	0.2908[c]	0.6	0.34
0.02540	0.2908[c]	2.0	Very slow[d]

[a] [LiOAc] = 1.0 *M*; initial [vinyl acetate] = 0.2 *M*. [b] Chloride added as NaCl; free NaCl was 0.013 *M* (saturated solution). [c] Chloride added on LiCl; free LiCl was *ca.* 0.15 *M*. [d] No change in vinyl acetate concentration in 600 hr.

Effect of Enol Acetate Structure on Rate.—As the rates of decomposition were already too slow for convenient measurement and substituents on the vinylic carbon would be expected to decrease the rates even further, no quantitative study of the effect of enol ester structure was undertaken. Qualitative observations, however, indicated that substituents on the double bond depressed rates of decomposition much less than rates of vinyl ester exchange. Thus 1-cyclopenten-1-yl acetate, which does not undergo exchange, decomposes at an appreciable rate. Isopropenyl propionate exchanges with acetic acid at low [LiOAc] (~0.01 *M*) about 200 times slower than vinyl propionate.[11] However, its rate of decomposition under these conditions is about equal to its rate of exchange, while vinyl propionate under these conditions still exchanges much faster than it decomposes.

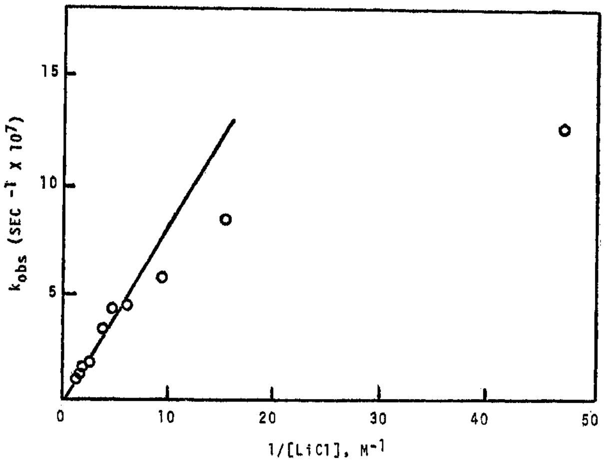

Figure 3.—Plot of k_{obsd} *vs.* 1/[LiCl]: $[Pd(II)]_t$, 0.02 *M*; [LiOAc], 0.02 *M*; initial [vinyl acetate], 0.2 *M*.

Discussion

The results clearly indicate two kinetic domains. One is that, at low [vinyl acetate], low $[Pd(II)]_t$, and high $[Cl]_t$, the reactions follow conventional kinetics. In this range the kinetic expression appears to have the form given by eq 9. The dimeric species is used

$$\text{rate} = [Li_2Pd_2Cl_6][\text{vinyl acetate}][4]/[LiCl] \qquad (9)$$

in the rate expression because the rate shows no correlation with Li_2PdCl_4, the only other Pd(II) species present in these reaction mixtures. **4** in the reaction sequence represents some unknown species which must react with vinyl acetate to give the products.

The other domain consists of ill-defined kinetics in which the dependencies on [vinyl acetate], $[Pd(II)]_t$, and [LiCl] rapidly fade as the first two increase and the last decreases. This overall behavior suggests the following reaction sequence

$$\text{reaction mixture} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 4 + \text{other products } (Ac_2O?) \qquad (10)$$

$$CH_2{=}CHOAc + 4 \xrightarrow[k_2]{Pd(II)} CH_3CHO + \text{other products } (Ac_2O?) \qquad (11)$$

Under conditions such as low [chloride], high $[Pd(II)]_t$, and high [vinyl acetate], the second reaction becomes the faster of the two, and k_1 becomes rate determining. Alternatively, under conditions of high [chloride], low $[Pd(II)]_t$, and low [vinyl acetate], the rate of the second reaction becomes slower than the first and thus rate determining. The concentration of **4** must, under these conditions, build up to a steady-state concentration.

Several results suggest that water is the reactive species, **4**. First is the inhibition of rate by acetic anhydride. At high [chloride] this inhibition is very

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[9] A plot of $k_{obsd}/[Li_2Pd_2Cl_6]$ *vs.* 1/[LiCl] is, of course, based on the assumption that the dimer is the reactive species. This assumption is very reasonable since the dimer has been found to be the reactive species in most Pd(II)-catalyzed reactions in acetic acid containing lithium chloride.[10]

(10) P. M. Henry, *Accounts Chem. Res.*, **6**, 16 (1973).

(11) P. M. Henry, *J. Amer. Chem. Soc.*, **94**, 7316 (1972).

marked, while at low [chloride] it is not so pronounced. This is exactly what is expected according to the reaction scheme represented by eq 10 and 11. Consider the reaction sequence given by eq 12 and 13.

$$2HOAc \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_2O + Ac_2O \quad (12)$$

$$CH_2{=}CHOAc + H_2O \xrightarrow[Pd(II)]{k_2} CH_3CHO + HOAc \quad (13)$$

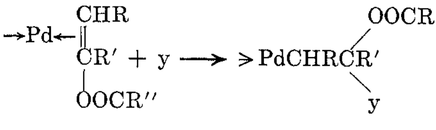
When k_1 is rate determining, the addition of Ac_2O would be expected to have little effect on the rate of the overall reaction. In fact at low [chloride] when k_1 is rate determining, a change in $[Ac_2O]$ by a factor of 10 decreases the rate by a factor of only 2. However, at high [chloride] when eq 12 must reach equilibrium and eq 13 becomes rate determining, addition of Ac_2O strongly inhibits the rate. The failure to observe Ac_2O inhibition in a previous study[5] can also be explained on the basis of this scheme. These studies of the effect of $[Ac_2O]$ were at very low chloride concentrations where k_1 was almost certainly rate determining. Under these conditions inhibition by Ac_2O would not be expected to be observed.

The next reason to believe that water is the reactive species is the rate expression in the Pd(II)-catalyzed region (eq 9). A recent study[12] by the author of the Pd(II)-catalyzed saponification of vinyl acetates in wet acetic acid indicated that the following rate expression was operative where the exponent n is about 1.4.

$$\text{rate} = k_H[Li_2Pd_2Cl_6][C_2H_3OAc][H_2O]^n/[LiCl] \quad (14)$$

This rate expression is of the same form as eq 9 if **4** is H_2O. From a knowledge of the value of k_H at higher $[H_2O]$ and the rate of decomposition in this study, an estimate of the equilibrium water concentration when eq 13 is the rate-determining reaction at 0.3 M $[Ac_2O]$ indicates that this concentration is in the range of 0.01–0.05 M $[H_2O]$. Of course, there is considerable uncertainty in the extrapolation from the range of water concentrations in the hydration study (0.5–5.0 M $[H_2O]$) to the conditions of the present study.

The final piece of evidence in favor of water being the reactive species is provided by the qualitative observations on the effect of enol acetate structure on rate. The hydration of enol acetates also does not have a strong retardation of rate by substitution on vinylic carbons while in other exchange reactions, such as vinylic ester exchange, substitution does strongly retard rate. The rate-determining step for both reactions is the oxypalladation reaction ($y = OAc^-$, H_2O) shown in eq 15. The reason for the different substituent effects is believed to be the lower steric requirements of H_2O as compared to acetate.



$$\rightarrow Pd \leftarrow \begin{matrix} CHR \\ \| \\ CR' \\ | \\ OOCR'' \end{matrix} + y \longrightarrow \;\geq PdCHRCR'\begin{matrix} OOCR'' \\ \\ y \end{matrix} \quad (15)$$

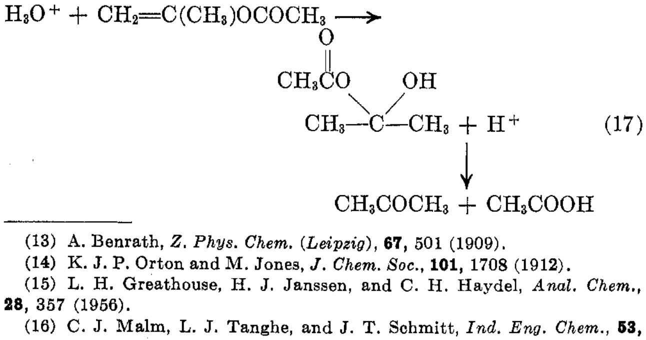
The formation of water in acetic acid in the presence of acetic anhydride would not be expected on the basis of previous experience and the possibility of its formation in the systems used in the present studies should be examined. The hydrolysis of Ac_2O in wet acetic acid has been studied by several workers,[13–16] but the author is aware of only one study of the reverse reaction and equilibirum. This study[17] was carried out in the gas phase at over 400° so is of little use for present purposes. The reaction of Ac_2O with water is slow in the absence of catalysts but is accelerated considerably by addition of protonic acids such as $HClO_4$. The reaction of Ac_2O with equimolar quantities of water catalyzed by small amounts of $HClO_4$ (0.001 M) is rapid and complete and is used to prepare essentially anhydrous acetic acid with water contents of less than 0.01%.[18]

Two questions must be answered. (1) Are the water contents required to explain the rate data in this study too large to be reasonable? (2) Is it reasonable that these amount of water are formed under the reaction conditions *via* eq 12 when in pure acetic acid the equilibria is well to the left? In answer to the first question a water content of 0.01% for "essentially anhydrous" is equivalent to 0.006 M which is slightly less than the range of 0.01 to 0.05 M obtained by the extrapolation of rate data from wet acetic acid. Thus the water contents required are only a little above that found in what is usually considered to be dry acetic acid.

In regard to the second question, although the equilibrium represented by eq 12 is far to the left in pure acetic acid, it might be expected to be shifted to the right by protons or metal salts because of solvation of the water. These reaction energies, of course, are significant. In water the hydration energy of the proton is 263 kcal while that of Li^+ is 125 kcal and that of Na^+ is 100 kcal.[19] The author knows of no studies on the effect of metal salts on this equilibrium. It has been reported that 0.5 M $HClO_4$ solutions with initial water contents of 0.005% will gradualy increase in water content to several hundredths of 1% over a period of a month or more.[18] This could be due to water pickup from the glassware but could also result from eq 12. A reaction which could proceed by a mechanism analogous to eq 12 and 13 is the acid-catalyzed decomposition of isopropenyl acetate to give acetone and Ac_2O.[20] Water could be

$$CH_2{=}C(CH_3)OCOH_3 + H^+ \longrightarrow CH_3COCH_3 + Ac_2O \quad (16)$$

formed by eq 12 and then used to hydrate the ester in an acid-catalyzed addition.



$$H_3O^+ + CH_2{=}C(CH_3)OCOCH_3 \longrightarrow \begin{matrix} CH_3\overset{\overset{O}{\|}}{C}O \quad OH \\ \diagdown \;\; \diagup \\ CH_3{-}C{-}CH_3 \end{matrix} + H^+ \quad (17)$$
$$\downarrow$$
$$CH_3COCH_3 + CH_3COOH$$

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[12] P. M. Henry, *J. Org. Chem.*, **38**, 2766 (1973).

[13] A. Benrath, *Z. Phys. Chem. (Leipzig)*, **67**, 501 (1909).

[14] K. J. P. Orton and M. Jones, *J. Chem. Soc.*, **101**, 1708 (1912).

[15] L. H. Greathouse, H. J. Janssen, and C. H. Haydel, *Anal. Chem.*, **28**, 357 (1956).

[16] C. J. Malm, L. J. Tanghe, and J. T. Schmitt, *Ind. Eng. Chem.*, **53**, 363 (1961).

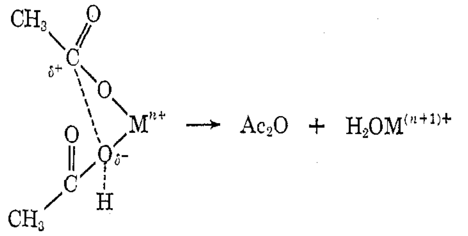
[17] W. Mühlhaüsser and M. Trautz, *Z. Phys. Chem. Bodenstein-Festband*, 319 (1931); *Chem. Abstr.*, **25**, 5337¹ (1931).

[18] H. J. Keily and D. N. Hume, *Anal. Chem.*, **36**, 543 (1964).

[19] L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, "Chemistry and Metallurgy of Miscellaneous Materials," L. L. Quill, Ed., McGraw-Hill, New York, N. Y., 1950, p 165 ff.

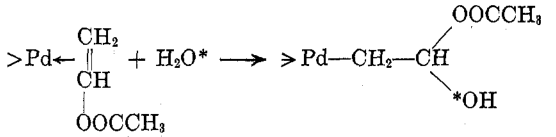
[20] E. A. Jeffrey and D. P. N. Satchell, *Chem. Ind. (London)*, 1444 (1960).

The present work does not give much evidence as to possible catalysis of the formation of water. The kinetics require the order in Pd(II) be less than one. A possible route involves reaction on a positive metal ion center. The thermal decomposition of $Cu(OAc)_2$ has been reported to give acetic anhydride.[21]

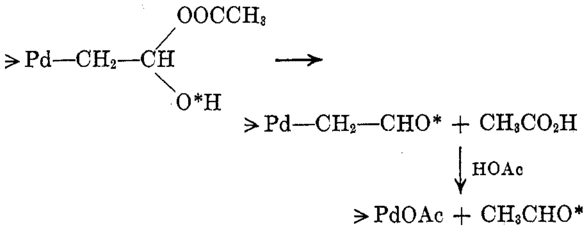

(18)

One test of this mechanism would be to run the reaction using an ^{18}O label. As shown below, the ^{18}O label in the acetic acid should end up in the acetaldehyde.

$$2CH_3CO_2{}^*H \longrightarrow (CH_3CO^*)_2O^* + H_2O^* \qquad (19)$$



$$>\mathrm{Pd}\leftarrow\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ OOCCH_3\end{array} + H_2O^* \longrightarrow >\mathrm{Pd}{-}CH_2{-}\overset{\displaystyle OOCCH_3}{\underset{\displaystyle {}^*OH}{CH}} \qquad (20)$$



$$>\mathrm{Pd}{-}CH_2{-}\overset{\displaystyle OOCCH_3}{\underset{\displaystyle O^*H}{CH}} \longrightarrow >\mathrm{Pd}{-}CH_2{-}CHO^* + CH_3CO_2H \qquad (21)$$
$$\big\downarrow \mathrm{HOAc}$$
$$>\mathrm{PdOAc} + CH_3CHO^*$$

Other mechanisms such as those given by eq 1 and 2 and 3–6 would predict different distributions. This experiment was tried several times, but two experimental difficulties prevented the obtaining of useful results. First, the exchange of vinyl acetate with labeled solvent[6] (eq 22) is much faster than decomposition, and second, the exchange of acetaldehyde product with the solvent is also fast (eq 23). Perhaps a system could be found which would permit this experiment to give definitive results.

$$CH_2{=}CHO_2CCH_3 + CH_3CO_2{}^*H \longrightarrow CH_2{=}CHO_2{}^*CCH_3 + CH_3CO_2H \qquad (22)$$

$$CH_3CO_2{}^*H + CH_3CHO \longrightarrow CH_3COO^*H + CH_3CHO^* \qquad (23)$$

Finally, the dependence on [LiOAc] (Figure 1) cannot be explained on the basis of present results nor can the disagreement with earlier workers[5] who found NaOAc was a mild inhibitor at low [NaOAc]. However, the reaction condition for the two sets of runs were quite different. In the present work the concentration of [LiCl] was about 0.15 *M* while in the previous work there was no added chloride. Thus not too much significance can be attached to these differences.

Experimental Section

Materials.—Sources of most chemicals and preparation of stock solutions have been described previously.[6,7]

Kinetic Runs.—Vpc analysis was used for all runs. A 6-ft Carbowax 20M column programmed from 80 to 200° at 7.5°/min with a helium flow rate of 60 ml/min was used for all runs. *m*-Xylene was used as internal standard. Runs were made on 1-, 2-, and 10-ml scales in tubes sealed with serum caps or pop bottle tops. In a given run, all the ingredients except vinyl acetate were added and the reaction mixture was heated on a steam bath for an hour. The run was cooled to room temperature, put in a 25° bath, and the run started by addition of vinyl acetate. In some runs the heating period was eliminated without an effect on the rates.

The reproducibility of the data was poorer than, for instance, the vinyl ester exchange. Rates of decomposition were reproducible to only about 20%.

Runs were usually only followed for 600 hr as after that period solids began to precipitate.

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Registry No.—Palladium(II) chloride, 7647-10-1; vinyl acetate, 108-05-4; acetic anhydride, 108-24-7.

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(21) T. Chang and P. Kao, *J. Chem. Eng. (China)*, **4**, 160 (1937); *Chem. Abstr.*, **31**, 6614¹ (1937).