Oxidation of Olefins by Palladium(II). 11.[1] Kinetics and Mechanism of the Oxidation of Allyl Alcohol by PdCl$_4^{2-}$ in Aqueous Solution

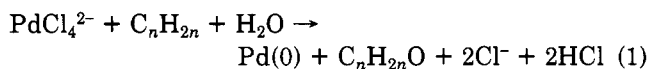W. K. Wan, K. Zaw,[2] and P. M. Henry*,[2]

Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1, and Department of Chemistry, Loyola University of Chicago, 6525 North Sheridan Road, Chicago, Illinois 60626

With use of a potentiometric procedure with quinone as reoxidant for Pd(0), the rate expression for allyl alcohol oxidation was determined to be rate = $k[\text{PdCl}_4^{2-}][\text{C}_6\text{H}_6\text{O}]/[\text{H}^+][\text{Cl}^-]^2$, an expression identical in form with that found previously for ethene and other acyclic olefin oxidations indicating similar mechanisms. The two trans attack mechanism suggested for acyclic olefin oxidation involve trans equilibrium hydroxypalladation and external hydroxide ion attack. In regard to the first, with most acyclic olefins the reversibility of the process cannot be determined. With allyl alcohol, however, the reversibility of hydroxypalladation can be tested by determining if allyl-$1,1$-d_2 alcohol (5a) isomerizes into an equilibrium mixture of 5a and allyl-$3,3$-d_2 alcohol (5b) during the course of the oxidation. It was found that isomerization of 5a did not occur during oxidation so hydroxypalladation is nonreversible and the equilibrium hydroxypalladation mechanism cannot be operative. Next the possibility of external hydroxide was tested. The equilibrium formation of the intermediate π-complex PdCl$_3$(C$_6$H$_6$O)$^-$ was studied by spectral means, and a value of 5 was found for the equilibrium constant, K_1. As with other acyclic olefins, the value of K_2 for formation of the second intermediate PdCl$_2$(C$_3$H$_6$O)(H$_2$O) was too small to be measured (<0.025). With use of the experimental values of k, K_1, and K_2, it could be calculated that hydroxide attack would have to be faster than a diffusion-controlled reaction and thus impossible. Thus both reasonable trans attack mechanisms can be eliminated for allyl alcohol.

Introduction

It is generally agreed that the oxidation of acyclic olefins by aqueous palladium(II) chloride salts to aldehydes and ketones (eq 1) proceeds by a mechanism involving con-

$$\text{PdCl}_4^{2-} + \text{C}_n\text{H}_{2n} + \text{H}_2\text{O} \rightarrow$$
$$\text{Pd}(0) + \text{C}_n\text{H}_{2n}\text{O} + 2\text{Cl}^- + 2\text{HCl} \quad (1)$$

version of an olefin π-bonded to a palladium(II) to a palladium(II) β-hydroxylalkyl species, a process called hydroxypalladation.[3] The rate expression (eq 2) can be

$$\frac{-d[\text{olefin}]}{dt} = \frac{k[\text{PdCl}_4^{2-}][\text{olefin}]}{[\text{H}^+][\text{Cl}^-]^2} \quad (2)$$

interpreted either in terms of a cis attack of coordinated hydroxide in the rate-limiting step (eq 3) or trans attack

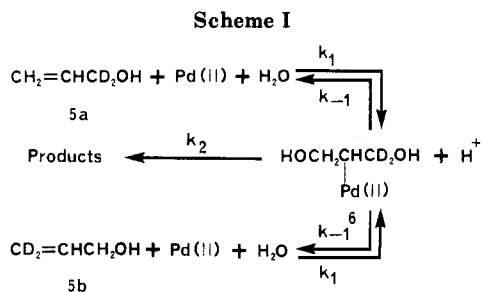of external water (eq 4)[4] in an equilibrium reaction. A

(3)

(4)
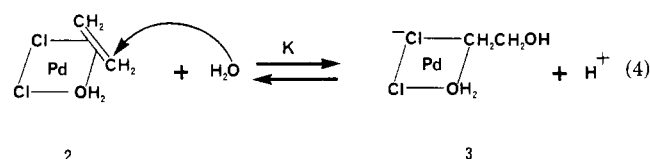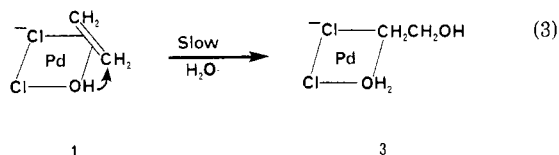
third mechanism involving trans attack of external hydroxide could be eliminated for other acyclic olefins by calculations that showed it would have to be faster than a diffusion-controlled process and thus impossible. The first was originally selected on the basis of isotope effects,[5,6]

(1) Part 10: Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* 1985, 4, 1286.

(2) Present address: Loyola University of Chicago.

(3) For general discussion and references, see: Henry, P. M. *Palladium Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, Holland, 1980; pp 41–84.
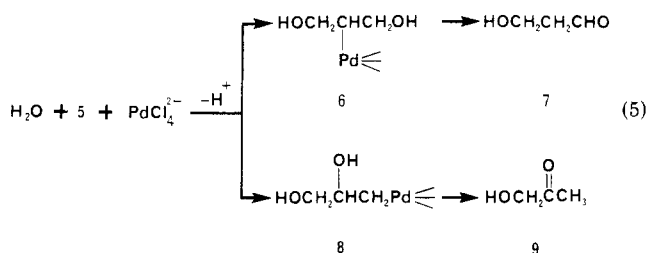
(4) In eq 4, 7, and 23 both cis and trans isomers of the π-complexes are present. Only the cis is shown for simplicity.

Scheme I

$$CH_2=CHCD_2OH + Pd(II) + H_2O \xrightleftharpoons[k_{-1}]{k_1}$$

5a

$$Products \xleftarrow{k_2} HOCH_2CHCD_2OH + H^+$$
$$\underset{Pd(II)}{|}$$

$$CD_2=CHCH_2OH + Pd(II) + H_2O \xrightleftharpoons[k_1]{k_{-1}}$$

5b

but more recent stereochemical studies indicate hydroxypalladation under certain reaction conditions occurs by trans attack of water from outside the coordination sphere of palladium(II).[7,8] The validity of extrapolating the results of these studies to the conditions of the aqueous olefin oxidation has been discussed.[9,10]

This paper is concerned with distinguishing between 3 and 4 by kinetic means. One possible way becomes apparent from examination of eq 3 and 4. To explain the deuterium isotope effects the cis hydroxypalladation was postulated to be the rate-determining step with decomposition of 3 to final products being fast. However, in the case of the trans hydroxypalladation shown in eq 4, the hydroxypalladation must be postulated to be an equilibrium reaction in order to explain the proton inhibition. If attack of water were the slow step of the sequence, no proton inhibition would be observed since proton release would occur after the rate-determining step. If an olefin which undergoes a measurable change every time hydroxypalladation–dehydroxypalladation occurs, there would be a way to determine the rate-determining step and thus decide between the routes shown in eq 3 and 4.

A good candidate for such an olefin is allyl alcohol (5). Thus, in analogy with other α-olefins, allyl alcohol would be expected to give products arising from the two possible modes of hyroxypalladation.[5b] As shown in eq 5 these two

$$H_2O + 5 + PdCl_4^{2-} \xrightarrow{-H^+}$$

$$\begin{array}{ll}
\to HOCH_2CHCH_2OH \underset{Pd\lessgtr}{|} \to HOCH_2CH_2CHO \\
\qquad\qquad 6 \qquad\qquad\qquad 7 \\
\\
\qquad\qquad OH \qquad\qquad\qquad O \\
\to HOCH_2\underset{|}{C}HCH_2Pd\lessgtr \to HOCH_2\overset{\|}{C}CH_3 \\
\qquad\qquad 8 \qquad\qquad\qquad 9
\end{array} \quad (5)$$

products would be β-hydroxypropanal (7), arising from 6, and α-hydroxyacetone (9), arising from 8. The hydroxypalladation adduct 6 is symmetrical and can thus eliminate hydroxide from either end of the adduct if hydroxypalladation is reversible. If a label such as deuterium is now put on the allyl alcohol, a reversible hydroxypalladation could be detected by isomerization of one deuteriated isomer into the other. Scheme I shows the reaction starting with either $CH_2=CHCD_2OH$ (**5a**) or $CD_2=CHCH_2OH$ (**5b**).

Thus, if $k_{-1} \gg k_2$, the hydroxypalladation is reversible, and **5a** or **5b** will be isomerized into an equilibrium mixture of the two before appreciable oxidation occurs. On the other hand, if $k_2 \gg k_{-1}$, hydroxypalladation is not reversible and the oxidation will occur with little or no isomerization.

Before this mechanistic test can be applied, it must be ascertained that allyl alcohol undergoes Wacker-type oxidation and that the oxidation obeys eq 2, the expression found for ethene and other acyclic olefins. In the previous paper of this series,[1] a study of the stoichiometric oxidation gave the following product distribution (% yields): 7 (40%), 9 (12–15%), acrolein (30%), propanal (15%), propene (7%), and acetone (2%). Since the main product was 7, 6 is a major intermediate and the test of mechanism discussed above is valid. This paper will be concerned with the rate expression for the oxidation as well as the determination of the extent of isomerization of the deuteriated allyl alcohols **5a** and **5b** during oxidation. A preliminary account of this work has appeared.[15]

Before the kinetic study is undertaken, it will first be necessary to carry out equilibrium studies to determine if allyl alcohol behaves in the same fashion as other acyclic olefins. With ethene, propene, and the butenes the first step in the reaction pathway was the formation of a olefin π-complex, and presumably this will also be the first step with allyl alcohol. The equilibrium is shown in eq 6 (R = H, CH_3, C_2H_5, or CH_2OH). With the gaseous olefins the equilibrium constant was measured by initial gas uptake using an efficient gas–liquid mixing reactor.[5]

$$PdCl_4^{2-} + CH_2=CHR \xrightleftharpoons{K_1}$$

$$\qquad\qquad\qquad (6)$$

10
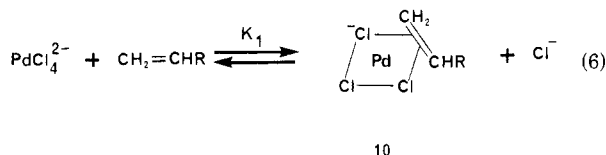
The next step in the reaction sequence is generally accepted to be the replacement of a second chloride by water as shown in eq 7.[4] Although it was originally claimed the

$$10(R=CH_2OH) + H_2O \xrightleftharpoons{K_2}$$

$$\qquad\qquad\qquad (7)$$

11a
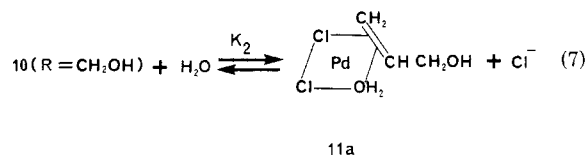
value of K_2 for ethene (R = H) was appreciable ($K_2 = 0.22$),[16] later extensive studies demonstrated K_2 to be much lower with a maximum value of less than 0.01.[17] In the case of allyl alcohol it is conceivable that coordination of the alcohol oxygen to give the chelate complex **11b** in eq 8 could occur.[18] Increased stability of **11b** could cause an increase in the value of K_2 for allyl alcohol and invalidate the kinetic arguments used to eliminate trans attack of hydroxide as a possible mechanism for the oxidation of

(5) (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246. (b) *Ibid.* **1966**, *88*, 1595.

(6) (a) Henry, P. M. *J. Org. Chem* **1973**, *38*, 2415. (b) Kosaki, M.; Isemura, M.; Kitaura, K.; Shinoda, S.; Saito, Y. *J. Mol. Catal.* **1977**, *2*, 351. (c) Saito, Y.; Shinoda, S. *J. Mol. Catal.* **1980**, *9*, 461.

(7) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

(8) (a) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401. (b) Stille, J. K.; Divakarumi, R. *J. Organomet. Chem.* **1979**, *169*, 239.

(9) Gregor, N.; Zaw, K.; Henry, P. M. *Organometallics* **1984**, *3*, 1251.

(10) In a very recent stereochemical study of hydroxypalladation of cyclohexadiene to give a (π-allyl)palladium(II) complex, trans addition was again observed.[11] In addition to the fact the reaction conditions were far removed from those of the aqueous oxidation, as was the case for earlier studies,[8] the observance of trans hydroxypalladation with this cyclic diolefin throws little light on the mode of hydroxypalladation of acyclic olefins in aqueous solution since cyclic olefins react differently from acyclic olefins. Thus for the oxidation of cyclohexene[12,13] and 2-cyclohexenol[14] in aqueous solution, the rate expression is much simpler than eq 2, indicating these cyclohexenes react by a different mechanism than the acyclic olefins.

(11) Åkermark, B.; Söderberg, B. C.; Hall, S. S. *Organometallics* **1987**, *6*, 2608.

(12) Vargaftik, M. N.; Moiseev, I. I.; Syrkin, Y. K. *Dokl. Akad. Nauk USSR* **1961**, *139*, 3196.

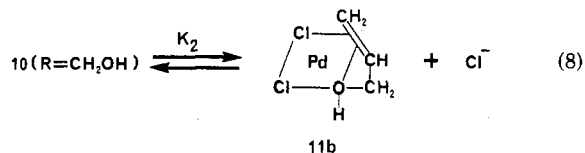(13) Bratz, E.; Prauser, G.; Dialer, K. *Chem-Ing.-Tech.* **1974**, *46*, 161.

(14) Wan, W. K.; Zaw, K., unpublished results.

(15) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81.

(16) Levanda, D. A.; Moiseev, I. I. *Kinet. Katal.* **1971**, *12*, 354.

(17) Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1979**, *57*, 982.

(18) This possibility was suggested by a reviewer.

$$10(R=CH_2OH) \underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} \quad \text{[structure 11b]} \quad + \quad Cl^- \qquad (8)$$

11b

other acyclic olefins.[5] Thus it is important to determine K_1 and, if possible, K_2 for allyl alcohol.

Results

Equilibrium Studies. These studies were carried out at 25 °C by using 430 nm, the wavelength at which the π-complex has a maximum in absorbance. The treatment of data is similar to that used in previous spectral studies in these laboratories.[19] First assume only eq 6 is operative $(K_1 \gg K_2)$, $P_1 = [PdCl_4{}^{2-}]$, and $P_2 = [10]$; ϵ_1 and ϵ_2 are the corresponding extinction coefficients; D_0 is the initial optical density, and D_i is the optical density at a given allyl alcohol concentration (= P_3). All runs were made with a 1.0-cm cell so the path length will not be included in the equations. Since all runs are made at constant $[Cl^-]$, we can define an equilibrium constant, K', as shown in eq 9.

$$K' = K_1/[Cl^-] = P_2/P_1P_3 \qquad (9)$$

The following equations can be written for change in optical density as the allyl alcohol concentration is increased for each run (P_0 = total $[Pd(II)]$).

$$D_0 = \epsilon_1 P_0 \qquad (10)$$

$$\Delta D = D_i - D_0 = \epsilon_1 P_1 + \epsilon_2 P_2 - \epsilon_1 P_1 - \epsilon_1 P_2 \qquad (11)$$

Collecting terms we get eq 12.

$$\Delta D = (\epsilon_2 - \epsilon_1)P_2 = \Delta\epsilon P_2 \qquad (12)$$

Substituting into eq 9 we obtain eq 13

$$K' = \frac{P_2}{P_1P_3} = \frac{\Delta D}{\Delta\epsilon(P_0 - \Delta D/\Delta\epsilon)P_3} \qquad (13)$$

which can be rearranged to give eq 14.

$$\frac{P_0}{\Delta D} = \frac{1}{\Delta\epsilon} + \frac{1}{K'\Delta\epsilon P_3} \qquad (14)$$

Thus a plot of $P_0/\Delta D$ vs $1/P_3$ for a given run should give a straight line within a slope of $1/K'\Delta\epsilon$ and an intercept of $1/\Delta\epsilon$. As expected, straight lines were obtained for all runs.

If eq 6 is the only equilibrium operative, then, according to eq 9, a plot of K' vs $1/[Cl^-]$ should give a straight line with slope of K_1, or, more simply, the product $K'[Cl^-] = K_1$ should remain constant.

Now let us consider eq 7 and assume $K_2 \gg K_1$. K_β is defined by eq 15.

$$K_1K_2 = K_\beta = [11][Cl^-]^2/[PdCl_4{}^{2-}][\text{allyl alcohol}] \qquad (15)$$

Letting P_4 now be equal to $[11]$ we can now define K'' at constant $[Cl^-]$ by eq 16.

$$K_\beta/[Cl^-]^2 = K'' = P_4/P_1P_3 \qquad (16)$$

Equation 17 can now be derived in a manner analogous to that for eq 14.

$$\frac{P_0}{\Delta D} = \frac{1}{\Delta\epsilon} + \frac{1}{K''\Delta\epsilon P_3} \qquad (17)$$

According to eq 16 a plot of K'' vs $1/[Cl^-]^2$ should give a straight line with a slope of K_β or the product $K''[Cl^-]^2$ should remain constant. An equation analogous to eq 14 and 17 can also be derived for the case where the values

(19) Lee, H.-B.; Henry, P. M. *Can. J. Chem.* **1976**, *54*, 1726.

Table I. Summary of Equilibrium Studies[a]

$[Cl^-]$,[b] M	$[H^+]$,[c] M	$10^2(1/\Delta\epsilon)$	slope[d] × 10^4	K' or K'', M^{-1}	K_1	K_β, M
0.1	0.25	3.9	8.1	48	4.8	0.48
0.1	0.5	5.0	12	43	4.3	0.43
0.1	1.0	4.0	6.3	64	6.4	0.64
0.17	0.25	4.2	6.3	25	4.3	0.73
0.25	0.10	4.5	14	21	5.3	1.3
0.25	0.25	3.8	21	18	4.6	1.1
0.50	0.25	4.0	40	10	5.0	2.5

[a] Measurements made at 430 nm. Path length was 1 cm for all runs. Ionic strength adjusted to 2.0 with $LiClO_4$. Total $[Pd(II)]$ = 5×10^{-3} M for all runs. Solutions were also 0.01 M in quinone to prevent precipitation of Pd(0). [b] Added as LiCl. [c] Added as HClO$_4$. [d] Slope = $1/\Delta\epsilon K'$ or $1/\Delta\epsilon K''$ in eq 14 and 17, respectively.
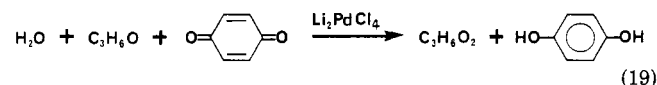
of K_1 and K_2 are of the same order of magnitude, but, in this case, an apparent equilibrium constant, K_{ap}, is obtained for each run. The relationship of these K_{ap}'s to K_1 and K_2 is given by eq 18. Thus a plot of $K_{ap}[Cl^-]$ vs $1/[Cl^-]$

$$K_{ap}[Cl^-] = K_1 + K_1K_2/[Cl^-] \qquad (18)$$

will give a straight line with a slope of K_1K_2 and an intercept of K_1.

The data are summarized in Table I. In the next to last column is the value of K_1 calculated assuming the only equilibrium operative is that given by eq 6, and in the last column is the value of K_β calculated assuming eq 15 is the correct equilibrium expression. Note that K_1 does not vary systematically while K_β increases steadily as the chloride ion increases. Some idea of the level of detection of K_2 can be obtained by using eq 18. With the exception of the run at lowest $[Cl^-]$ (0.1 M) and highest acid (1.0 M) concentrations the spread in K_1 is 1.0 unit or 15%. *If this had been a systematic variation* from $[Cl^-]$ = 0.1–0.5 M, the value of K_2 *would be* 0.025 M. The values of K_1 do not vary with acid concentration, indicating that no detectable acid–base equilibrium. Of course if **10** is the only species formed in appreciable amounts, none would be expected.

Kinetic Studies. All kinetic runs were carried out at 25 °C in the presence of quinone so the reaction was catalytic in Pd(II). The reaction is shown in eq 19 for

$$H_2O + C_3H_6O + O\text{—}\langle\text{—}\rangle\text{—}O \xrightarrow{Li_2PdCl_4} C_3H_6O_2 + HO\text{—}\langle\bigcirc\rangle\text{—}OH \qquad (19)$$

formation of the Wacker products **7** and **9**. The kinetics were studied by using a potentiometric procedure based on the quinone–hydroquinone redox couple. Lithium salts were used for the kinetic runs, and the ionic strength was maintained at 2.0 by using lithium perchlorate as an inert electrolyte.

In treating the kinetic data, correction was made for the decrease in free $PdCl_4{}^{2-}$ and olefin concentrations due to the preequilibrium π-complex formation shown in eq 6. Another correction that was *not* made was for the hydrolysis equilbrium shown in eq 20. The value found for

$$PdCl_4{}^{2-} + H_2O \underset{\longleftarrow}{\overset{K_H}{\longrightarrow}} PdCl_3(H_2O)^- + Cl^- \qquad (20)$$

2 M NaClO$_4$ is 0.012, and it is probably lower in 2 M LiClO$_4$ since it is 0.006 in 3 M LiClO$_4$.[17] Although this correction could be made, it would be insignificant compared to the experimental error and was thus ignored.

The data are listed in Table II. The initial allyl alcohol concentration was 0.005 M in all runs, and good first-order plots were obtained for all runs. In runs 1–4 the effect of chloride concentration is tested and in runs 5–8 the acid dependence. Runs 8–12 test mainly the $[PdCl_4{}^{2-}]$ dependence.

Table II. Rates of Oxidation of Allyl Alcohol[a]

run	$[Pd(II)]_t$,[b] M	$[H^+]$,[c] M	$[Cl^-]$,[d] M	$10^4 k_{obsd}$, s^{-1}	$10^4 k$, M^2 s^{-1}[e]
1	0.002	0.2	0.1	4.3	6.1
2	0.002	0.2	0.2	0.90	4.1
3	0.002	0.2	0.5	0.24	6.4
4	0.002	.2	1.0	0.10	10
5	0.002	0.1	0.3	1.1	5.6
6	0.002	0.5	0.3	0.25	6.3
7	0.002	1.0	0.3	0.13	6.6
8	0.002	0.2	0.3	0.57	5.8
9	0.005	0.2	0.3	1.8	7.6
10	0.01	0.2	0.3	3.3	7.5
11	0.02	0.2	0.7	0.73	4.2
12	0.05	0.2	0.7	2.4	5.6

[a] All runs in aqueous solution at 25 °C. LiClO$_4$ was added to bring the ionic sttrength to 2.0. Initial allyl alcohol and quinone concentrations are 0.005 M. Data are treated as a first-order reaction in allyl alcohol. [b] Total palladium(II) concentration; it equals $[PdCl_4^{2-}]$ + [10]. [c] Added as HClO$_4$. [d] Added as LiClO$_4$. [e] Calculated assuming the rate expression given by eq 2 is operative. Corrections are made for the amounts of palladium(II) and allyl alcohol existing as π-complex 10.

The exchange experiments outlined in Scheme I were carried out under the following reaction conditions: $[PdCl_4^{2-}]$ = 0.01 M, $[Cl^-]$ = 0.4 M, $[H^+]$ = 0.04 M, [quinone] = 0.1 M, and $[C_3H_4D_2O]$ = 0.01 M. ^{1}H NMR was used to monitor the appearance of **5b**. At 1 half-life for oxidation (ca. 15 min) the amount of **5b** was less than 3% of the total **5** remaining. The experiment was repeated two more times with the same result.

The small amount of isomerization did not occur because of acid-catalyzed exchange since, under the same conditions, in the absence of Li$_2$PdCl$_4$, no isomerization occurred for several hours. It can be calculated to be due to the nonoxidative palladium(II)-catalyzed isomerization which is the main reaction at high chloride concentration.[9]

Product Distribution. A short study of the product distribution and yields in relationship to quinone reduced was undertaken under catalytic conditions for two sets of Pd(II), proton, and chloride concentrations. For the concentrations [Pd(II)] = 0.05 M, $[Cl^-]$ = 0.7 M, and $[H^+]$ = 0.2 M, the total yields of carbonyl products in terms of quinone reduced was 98.6%. The product distribution was found to be the following (percent yields based on quinone reduced): **7** (46–49%), **9** (13–16%), acrolein (29–30%), and propanal (8–9%). No acetone or propene was detected in this run. For the concentrations [Pd(II)] = 0.02 M, $[Cl^-]$ = 0.2 M, and $[H^+]$ = 1.0 M, the total yield of carbonyl products based on quinone was 99.2%. The product distribution was the following: **7** (39%), **9** (12%), acrolein (40%), and propanal (9%). Acetone was also not detected in this run, and no attempt was made to analyze for propene.

Discussion

The product distribution study indicates a fairly complicated system for a kinetic study, but fortunately it was much simpler than the stoichiometric reaction.[1] Also the material balance of carbonyl product based on quinone reduced was very good; ~99%. Since about 8% of the carbonyl product was propanal, which is not a net oxidation product, the total oxidation yield is about 92%. As might be expected, propene, which would arise from π-allylic species,[1] was not a product, and acetone, which would arise from oxidation of the propene, was also not found.

The present results are in general agreement with more extensive studies of product distribution under stoichiometric conditions. The ratio of Wacker products to acrolein does vary somewhat with changes in reactant concentrations but not enough to indicate different kinetic dependencies. Thus all oxidation products must be formed by the rate expression given by eq 2. It is interesting that the material balance taking into account all carbonyl products is almost 100% based on quinone reduced. This suggests the propanal may be formed by reduction of acrolein by some reducing species other than Pd(II) hydride or during workup. However, control experiments indicate acrolein is not being reduced during the removal of Pd(II) by Zn dust.

The data in Table II leave no doubt that the rate expression for oxidation of allyl alcohol by PdCl$_4^{2-}$ in aqueous solutions obeys the rate expression given by eq 2. With one exception (run 4) over a range of 25 in $[PdCl_4^{2-}]$, 10 in $[H^+]$, and 10 in $[Cl^-]$ the rate constant varies by less than a factor of 2. This is certainly acceptable variation for such a complicated rate expression. The average value of k (excluding run 4) is 6.0×10^{-4} M^2 s^{-1}. The fact that the value of k remains constant over such a wide range of conditions is further evidence that all oxidation products, **7, 9**, and acrolein, obey the rate expression given by eq 2. Since the Wacker products **7** and **9** amount to about two-thirds of the total oxidation products, the rate constant for their formation is ~4×10^{-4} M^2 s^{-1}.

The isomerization results with the deuteriated allyl alcohols **5a** and **5b** confirm the earlier product distribution studies that indicate **5a** and **5b** were not isomerized into an equilibrium mixture before oxidation[1] and definitely establish that hydroxypalladation of **5** is not an equilibrium process. This result eliminates equilibrium trans hydroxypalladation routes analogous to that shown in eq 4 for ethene.

Another mechanism consistent with the kinetics for trans hydroxypalladation is attack of hydroxide from outside the coordination sphere of Pd(II) in the rate-limiting step as shown in eq 21. The analogous mechanism

$$\textbf{11a or 11b} + OH^- \xrightarrow[k_3]{slow} \textbf{6 or 8} \xrightarrow{fast} \text{products} \quad (21)$$
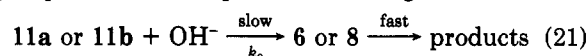
for ethene and other acyclic olefins could be eliminated on the basis of rate considerations.[5] As mentioned in the Introduction, it has been suggested that the equilibrium shown in eq 8 may be far to the side of **11b** so hydroxide ion attack may be a much more likely process in the present case. The equilibrium studies demonstrate that this is, in fact, not the case since the upper limit for K_2 is 0.025. The measurements of the value of K_1 and an upper limit for K_2 allow the calculation of the lower limit of k_3 for allyl alcohol. The rate for the reacton shown in eq 21 is k_3[11][OH$^-$]. Since [11] = K_1K_2-$[PdCl_4^{2-}][C_3H_6O]/[Cl^-]$ and [OH$^-$] = $K_w/[H^+]$, the rate equation for eq 21 can be equated to the experimental rate equation as shown in eq 22.

$$k_3[11][OH^-] = \frac{k_3 K_1 K_2 K_w [PdCl_4^{2-}][C_3H_6O]}{[H^+][Cl^-]^2} =$$
$$\frac{k[PdCl_4^{2-}][C_3H_6O]}{[H^+][Cl^-]^2} \quad (22)$$

Substituting in a value of 5 for K_1, a maximum value of 0.025 for K_2, and the value of 10^{-14} for K_w, it can be calculated that $k_3 = 8 \times 10^{14}k$. Since k is 4×10^{-4} M^2 s^{-1}, the value of k_3 is at least 3×10^{11} M^{-1} s^{-1} or about 10^2 times higher than the rate constant for a diffusion-controlled process in aqueous solution.[20] Thus external attack of

(20) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanism*, 3rd ed.; Wiley: New York, 1981; Chapter 7.

hydroxide is clearly impossible for allyl alcohol oxidation.

The elimination of the equilibrium hydroxypalladation and external hydroxide attack severely limits the possible trans hydroxypalladation routes which are consistent with the kinetics, and, in fact, they were the only two routes suggested up to this point.[7,8] In order to explain the proton inhibition, an acid–base equilibrium step must be postulated. The two most likely ones are shown in eq 23 and 24.[4]

(23)

12a

(24)

12b
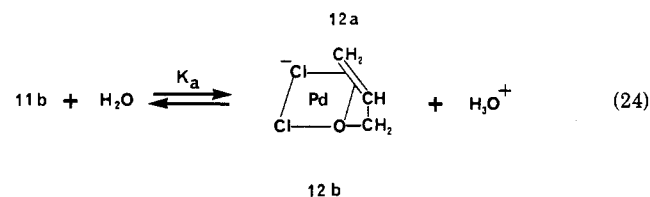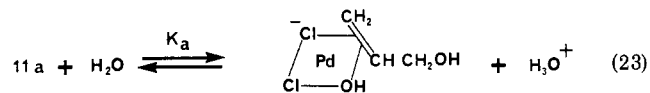
The trans attack of water would then have to occur on **12a** or **12b**.[21] However, unless there is some special activating effect of hydroxide, on electronic grounds **11a** or **11b** should be much more susceptible to attack by nucleophile water than would **12a** or **12b** because of the lower negative charge of the former species. A special activating effect for hydroxide seems unlikely since its trans effect is about the same as water and lower than chloride.[22]

Actually there is precedent which suggests that **12a** or **12b** will undergo a *slow* trans hydroxypalladation. However, this type of addition would not lead to oxidation and only dehydroxypalladation can occur. Thus at high acid and chloride concentrations (>1.0 M), conditions under which the oxidation is very slow, the palladium(II)-catalyzed isomerization of **5a** or **5b** into the other isomer was observed.[9] The kinetics, which are quite different from those for oxidation, are consistent with attack of water on a allyl alcohol–trichloropalladium(II) π-complex as shown in eq 25.[23] The intermediate **13** does not decompose

(25)

13
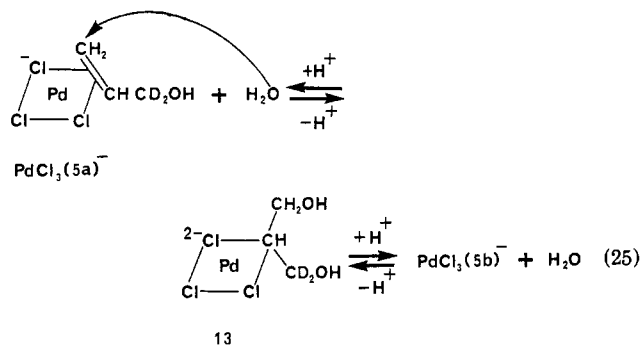
oxidatively to carbonyl products, but the authors believe it is the intermediate intercepted by CuCl₂ to give 2-chloroethanol. The reason that **13** does not decompose

(21) It is true that **12b** has been suggested as a possible *kinetic* intermediate in acrolein formation.[1] However, the decomposition route postulated was quite different from external attack of water. This route was hydride transfer from the alcoholic carbon to the Pd(II).

(22) Basolo, F. *Adv. Chem. Ser.* **1965**, *No. 49*, 81.

(23) Note that no proton inhibition would be expected for the process shown in eq 25 or for external water attack on **11a** or **11b**. As discussed in the Introduction, this prediction follows from the fact proton release ocurs after the slow step in external water attack. In the isomerization and ¹⁸O exchange of deuteriated allyl alcohol the kinetics were consistent with the hydroxypalladation occuring by external water attack in a manner analogous to that shown in eq 25.[9] In this case, as expected, no proton inhibition was observed.

Scheme II
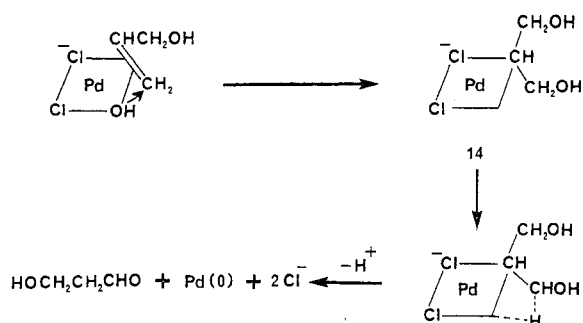
oxidatively in the absence of CuCl₂ is believed to be related to the fact all its coordination positions are filled by strongly complexing chloride ions. Stable oxypalladation adducts can be isolated when strongly complexing ligands such as chelating diolefins,[8a,24] phosphines, or η⁵-C₅H₅ are used.[25]

The above considerations point to a reason why allyl alcohol may be oxidized by an *irreversible* cis insertion mechanism. The cis addition would necessarily lead to a vacant coordination site that could be used for cis hydride elimination which is generally accepted as the first step in decomposition of the intermediate to carbonyl products.[26] The reaction pathway is shown in Scheme II.

The vacant coordination site would make **14** much more reactive than **13**. Certainly there is kinetic evidence that vacant or weakly coordinated sites are required for decomposition of oxypalladation intermediates in nonaqueous solution,[27] and there is also evidence that such sites are required for decomposition of Pt(II) alkyls.[28]

Whatever the reason for the cis addition the kinetic evidence would seem to preclude a reasonable trans attack mechanism for allyl alcohol. The final question is, of course, if these results can be validly extrapolated to other acyclic olefins for which such a test of reversibility is not available. Certainly, in terms of kinetics and equilibria, allyl alcohol behaves in a manner similar to other acyclic olefins. The value of K_1 of **5** compares well with values of 14.5 and 11.2 for propene and 1-butene, respectively, while the value of 4×10^{-4} M² s⁻¹ for k compares well with the corresponding values of 9.5×10^{-4} and 4.0×10^{-4} M² s⁻¹ for propene and 1-butene, respectively.[5b] In particular equilibrium such as that shown in eq 8 does not occur to any measurable extent. In light of these facts there appears to be no reason to propose that allyl alcohol is being oxidized by a mechanism different from that for other acyclic olefins.

There are several other recent studies that are germane to the present study. A very interesting study by Bryndza involves the reaction of a methylplatinum compound containing both a coordinated methoxide and methyl with tetrafluoroethylene shown in eq 26 (DPPE =

(26)
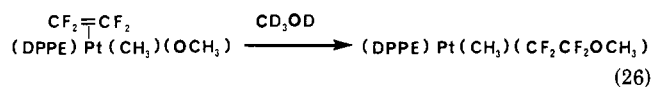
$(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$.[29] This is a very significant

(24) (a) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496, 3413. (b) White, D. A. *J. Chem. Soc. A* **1971**, 145. (c) Reference 3, pp 224–234.

(25) Majima, T.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1977**, 610.

(26) Reference 3, pp 75–77.

(27) Winstein, S. W.; McCaskie, J.; Lee, H.-B.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 6913.

(28) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258.

result since Pt(II) and Pd(II) chemistries are analogous, and the more stable Pt(II) organometallics are often used as models for Pd(II) catalytic chemistry. By use of CD_3OD in the solvent Bryndza was able to demonstrate the methoxide originated in the coordination sphere of the Pt(II) and that the methoxide insertion was at least 3 orders of magnitude faster than methyl insertion. This result is important in the present context because it demonstrates the ease of methoxide insertion in a d^8 complex, and, in fact, it goes much more readily than carbon insertion. This facility could explain the reason Pd(II) might prefer the mechanism given by eq 3. In another study Bäckvall and co-workers have published calculations suggesting hydroxide ligands will always migrate more slowly to coordinated olefins than alkyl ligand on four-coordinate Pd(II) complexes.[30] The writers are not in a position to judge the validity of these approximate calculations, but the results of Bryndza and the present study certainly appear inconsistent with them.

Secondary isotope effects with $CH_2=CD_2$ have also been used to imply the mechanism of hydroxypalladation.[6b,c] The product ratio of $CH_2DCDO/CHD_2CHO = 0.89$ has been interpreted in terms of rate-determining hydroxypalladation but not equilibrium hydroxypalladation, an interpretation compatible with the present results.

The data are in general agreement with previous studies carried out by somewhat different techniques. Thus, in one study the oxidation was run in the absence of quinone and the rate of appearance of π-$C_3H_5PdCl_2^-$ formed from the reaction of Pd(0) with allyl alcohol was measured.[31] A rate expression of the same form as eq 2 was found with rate constants of the same magnitude as those in the present work. The second study was carried out in basic solution by using potassium hexacyanoferrate(III) as a reoxidant for Pd(0).[32] α-Hydroxyacetone was reported to be the product, but yields were not given. A rate expression similar to eq 2 was reported, but in place of the proton inhibition term a catalytic term in hydroxide ion is present. The hydroxide term can, of course, be converted to an inhibition term in proton by using the K_w of water. However, if this is done, the value of k calculated is much lower than that found in this work so it is doubtful that the reactions in acidic and basic solutions proceed by exactly the same route.

Although acrolein and propanal are side products in the present work, there is a question as to their mode of formation. The fact that the rate expression for acrolein formation obeys eq 2 is consistent with the species **12b** in eq 24 being the one which decomposes by hydride shift to Pd(II) to give acrolein. A possible detailed pathway for the decomposition has been given.[1] The propanal is most likely formed by reduction of acrolein by the palladium(II) hydride in the reaction mixture, and possible detailed pathways for the reduction have also been discussed previously.[1] However, as mentioned previously, the very good mass balance between quinone reduced and *total* carbonyls suggests the reduction may be carried out by another species that does not regenerate Pd(II).

Experimental Section

Materials. The palladous chloride was purchased from Engelhardt, Inc. The allyl alcohol (Aldrich) was distilled before use. The deuteriated allyl alcohol $CH_2=CHCD_2OH$ was prepared by

a literature procedure.[33] ^1H NMR indicated its isotopic purity was at least 98%. All other chemicals were of reagent grade.

Physical Measurements. The ^1H NMR spectra were recorded on either a Bruker WP-60 or a Varian VXR-300 spectrometer. Visible spectra were recorded on a Perkin-Elmer 330 spectrophotometer.

Equilibrium Studies. All spectral measurements were made by using a cell of 1-cm path length. Preliminary experiments indicated that the tetrachloropalladate absorbance, which is at 470 nm in the absence of allyl alcohol, shifts to 430 nm due to π-complex formation when allyl alcohol is added. An isosbestic point appears at 450 nm. Since oxidation is occurring, the measurements had to be made quickly. Reference and sample solutions were made up in 10-mL volumetrics and thermostated at 25 °C for an hour. The reference solution, which contained all ingredients but Pd(II) and allyl alcohol, was diluted to 10 mL while the sample solution contained about 9.5 mL and no allyl alcohol. After the reference solution was put in the reference cell, allyl alcohol was added to the sample solution and its volume made up to 10 mL. After thorough shaking the spectrum was taken immediately at a scan rate of 400 nm/min. The spectrum was completed in less than a minute after the alcohol was added. At the lowest [Cl⁻] (0.1 M) and [H⁺] (0.25 M) calculations show that less than 10% of the olefin was oxidized. At higher [Cl⁻] and [H⁺] the error is much less. The range of chloride concentrations that could be studied was severely limited. At chloride concentrations much below 0.1 M the values of K_1 drifted and were different at different hydrogen ion concentrations. The phenomena has been reported previously for other acyclic olefins,[5b] and it has also been reported that eq 2 does not hold at low [Cl⁻] and [H⁺].[34] At chloride concentrations higher than 0.5 M the π-complex formation was too small for accurate measurements.

Kinetic Studies. The reactions were run in the presence of p-benzoquinone (Q) which oxidized the Pd(0) formed in the oxidation back to Pd(II) forming hydroquinone (QH_2). The extent of reacton was determined by measuring the emf of the cell: Pt/Q, QH_2, Pd(II), HCl, LiClO₄, olefin/Pd(II), HCl, LiClO₄, Q, QH_2/Pt. The two compartments of the cell are separated by a medium-porosity glass frit. The emf was measured with a Fisher Accumet Model 520 Digital pH meter. The output was recorded on a Heath Model 205 strip chart recorder moving at a known chart speed. This system is the same as that used by Moiseev and co-workers.[35,36] The procedure for treatment of data is given in ref 36.

The procedure for determining the degree of isomerization of deuteriated allyl alcohol has been described.[9] The sensitivity for detection of **5b** was less than 1%.

Product Distribution. The product distribution under catalytic conditions was determined by analyzing two kinetic reaction mixtures whose extent of oxidation was accurately known. A reaction mixture of 50-mL volume containing known concentrations of [Pd(II)], [Cl⁻], and [H⁺] along the following initial concentrations of reactants [allyl alcohol] = 0.075 M; [H⁺] = 0.2 M, [Q] = 0.075 M, and [QH_2] = 0.005 M was placed in the working cell of the electrochemical apparatus. In the reference cell was placed a solution containing the same concentrations of [Pd(II)], [Cl⁻], and [H⁺] but without allyl alcohol and [Q] = [QH_2] = 0.005 M. The initial emf was 30.6 mV. When the reaction was terminated by addition of zinc dust to precipitate the Pd(0), the emf was -53.7 mV for both reactions, which corresponds to a quinone concentration of 0.012 M. Thus the amount of quinone reduced = (0.075 M - 0.0012 M) × 50 mL = 3.69 mmol.

The chemical analysis used for product determination has been described.[1] Since control experiments indicated that quinone formed a monooxime under the conditions of the oximation procedure for total carbonyls, a correction had to be made for the small amount (0.06 mmol) of unreacted quinone. One portion of the reaction mixture was analyzed for total carbonyls by the

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oximation procedure. After extraction with ether to remove acrolein, propanal, acetone, and quinone, another portion of the aqueous phase was again analyzed to give β-hydroxypropanal plus acetol. The other carbonyls extracted by ether were then calculated by difference. The Fehling's solution analysis on another portion of the ether extracted aqueous phase gave total acetol. Since some Cu_2O is lost during filtration, the actual yield of acetol is believed to be slightly higher than that given by this analysis. By difference, the β-hydroxypropanal yield is then determined.

Next, the (2,4-dinitriphenyl)hydrazone derivatives of the reaction mixture were prepared and chromatographed as previously described to separate the acrolein, propanal, and acetone derivatives.[1] The composition of these lower molecular weight products was determined by ¹H NMR. No acetone was detected. The ratios of the other two products were found by comparing the integrations of the CH_2=CH— and CH_3CH_2— protons or the CH_2=CHCH= and CH_3CH_2CH= protons. Chemical shifts are given in ref 1. To ensure that propanal was not formed by re-

duction of acrolein during removal of Pd(II) with Zn dust, the hydrazones were prepared from a portion of one reaction mixture that had not been treated with Zn dust. The propanal yield was unaffected.

The reaction was also run in a closed system attached to gas burets. No gaseous products, such as propene, were formed.

NaBH₄ Reduction of CO in the Cationic Iron Carbonyl Complexes [C₅Me₅Fe(CO)₂L]⁺PF₆⁻ (L = CO or Phosphine)

Claude Lapinte,*,† Daniel Catheline,† and Didier Astruc*,‡

Laboratoire de Chimie des Organométalliques, UA CNRS 415, Université de Rennes I, 35042 Rennes Cedex, France, and Laboratoire de Chimie Organique et Organométallique, UA CNRS 45, Université de Bordeaux I, 33405 Talence Cedex, France

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The complex [Fp*CO]⁺PF₆⁻ (1; Fp* = Cp*Fe(CO)₂, Cp* = (η⁵-C₅(CH₃)₅) reacts with NaBH₄ at −80 °C in THF to give specifically Fp*CHO (2); warming the reaction mixture to −60 °C yields Fp*CH₂OH (3); further warming to 0 °C gives Fp*CH₃ (4; 91% yield). In the presence of H₂O, the same reaction gives only Fp*H (5). Compound 3 is best synthesized by using CH₂Cl₂ as the reaction solvent (72% yield). It slowly decomposes to Fp*₂ (6) in C₆D₆ at 40 °C and rapidly gives 4 in CD₃NO₂ or CD₃OD. Protonation of 3 using aqueous HBr yields 30% MeOH and Fp*Br (13) whereas CH₄ and C₂H₆ are obtained by using H⁺BF₄⁻ in Et₂O. Methane and 14 are obtained by protonation of 4. The long-known hydride reduction of [FpPPh₃]⁺PF₆⁻ (Fp = (η⁵-C₅H₅)Fe(CO)₂) to (η⁴-C₅H₆)Fe(CO)₂PPh₃ at −80 °C proceeds via the formyl intermediate CpFe(CO)(PPh₃)CHO. The complexes [Fp*PR₃]⁺PF₆⁻ (R = n-Bu (9a), CH₃ (9b), or Ph (9c)) react with NaBH₄ only at −30 °C in THF giving mixtures of Cp*Fe(CO)(PR₃)CHO (10) and Cp*Fe-(CO)(PR₃)(CHO·BH₃) (11) detected by ¹H NMR. Warming the reaction mixtures to −20 °C leads to the direct observation of Cp*Fe(CO)(PR₃)CH₃ (12) that can be extracted in 46–82% yields. However, direct reaction of 9 and NaBH₄ at 20 °C only gives 5. The reaction between 2 and BH₃ (1 equiv) yields a mixture of 1 and 4 while that between 10 and BH₃ gives 9 and 12. In contrast, reactions of 2·BH₃ with H₂O or 10·BH₃ (11) with PPh₃ only lead to 5. Three equivalents of NaBH₄ are necessary to reduce 1 and 9, and the use of NaBH₄/NaBD₄ mixture confirms that the reduction is intermolecular. Complex 1 is also reduced by the transition-metal hydrides 5 and H₄Mo(dppe)₂. Free carbon monoxide is reduced to 240% yield (vs [Fp*THF]⁺PF₆⁻ (7)) by using excess 5.

Introduction

"The recognition that petroleum reserves are finite has resulted in renewed interest in coal as an alternative source for petrochemical feedstock and fuels. Many of the promising processes for coal conversion such as Fischer–Tropsch reactions involve hydrogenation of carbon monoxide in the presence of transition-metal catalysts".[1] This motive is found at the start of a great many papers on hydride reduction of transition metal carbonyls since the late 1970s.[1-8] Whether it will remain valid in the future is speculative, but is has promoted immense research efforts in the area of reductive CO polymerization by homogeneous[9-15] and heterogeneous[16-20] catalysts and its

mimicking in organometallic chemistry of model complexes.

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†Université de Rennes I.
‡Université de Bordeaux I.