same charge type are considered; only $[Os(bpy)_2(CO)NO_2]^+$ and $[Os(bpy)_2(CO)O_3SCF_3]^+$ are exceptions, in that both fall on the dication line.

Although the nonlinear form of the correlations can not be explained in detail, several qualitative observations are revealing. First, since $E_{1/2}(Ox)$ and E_{op} both reflect the amount of electron density at the Os(II) center, more specifically both measure the relative energy of the $d\pi$ orbitals, a decrease in $d\pi-\pi^*(CO)$ mixing is anticipated as $E_{1/2}(Ox)$ and E_{op} increase. Second, these correlations could be nonlinear from one or more of the following factors: (a) differing solvation energy contributions to $E_{1/2}(Ox)$ and stabilization of the transition dipole (for both E_{op} and ν_{CO}); (b) for the E_{op} correlation the π^*(bpy) levels slowly become more stable as E_{op} increases, as shown from the electrochemical results.

Acknowledgment is made to the Department of Energy under Grant No. DAAG29-82-KO111 for support of this research.

Registry No. $[Ru(bpy)_2(CO)Cl](PF_6)$, 79850-20-7; $[Os(bpy)_2(CO)Cl](PF_6)$, 80502-54-1; $[Ru(bpy)_2(CO)(O_2CH)](PF_6)$, 84117-41-9; $[Os(bpy)_2(CO)(O_2CH)](PF_6)$, 84117-43-1; *trans*-$[Os(phen)(PMe_3)_2(CO)Cl](PF_6)$, 89689-48-5; *trans*-$[Os(phen)(PPh_3)_2(CO)Cl](PF_6)$, 89689-50-9; *trans*-$[Os(phen)(PMePh_2)_2(CO)Cl](PF_6)$, 89689-52-1; $[Os(phen)(dppene)(CO)Cl](PF_6)$, 89689-54-3; $[Os(phen)(dppb)(CO)Cl](PF_6)$, 84117-39-5; $[Os(bpy)_2(CO)NO_2](PF_6)$, 89689-56-5; $[Os(phen)(dppene)(PMe_2Ph)Cl](PF_6)$, 89689-58-7; $[Os(bpy)_2(CO)H](PF_6)$, 84117-35-1; $[Os(phen)_2(CO)H](PF_6)$, 84117-33-9; $[Ru(bpy)_2(CO)H](PF_6)$, 82414-89-9; $[Ru(phen)_2(CO)H](PF_6)$, 89689-60-1; *cis*-$Ru(bpy)_2Cl_2$, 19542-80-4; $Os(bpy)_2Cl_2$, 15702-72-4; *trans*-$[Os(bpy)(PPh_3)_2(CO)H](PF_6)$, 84117-37-3; *trans*-$[Os(bpym)(PPh_3)_2(CO)H](PF_6)$, 89689-62-3; *trans*-$[Os(bpyz)(PPh_3)_2(CO)H](PF_6)$, 89689-64-5; *trans*-$[Os(3,4,7,8\text{-}Me_4phen)(PPh_3)_2(CO)H](PF_6)$, 89689-66-7; $[Os(phen)(dppb)(PPh_3)H](PF_6)$, 84117-29-3; $[Os(phen)(dppene)(PEt_3)H](PF_6)$, 84117-31-7; $[Os(phen)(dppene)(PPh_3)H](PF_6)$, 89689-68-9; $[Os(bpy)_2(CO)(O_2CCF_3)](PF_6)$, 89689-70-3; $[Os(bpy)_2(CO)(CF_3SO_3)](O_3SCF_3)$, 89689-72-5; $[Os(bpy)_2(CO)CF_3](PF_6)$, 89689-74-7; $[Os(bpy)_2(CO)(CH_3CN)](PF_6)$, 89689-76-9; $[Os(bpy)_2(CO)(C_7H_8)](PF_6)$, 89689-78-1; $[Os(bpy)_2(CO)py](PF_6)$, 89689-80-5; *trans*-$[Os(phen)(PMe_2Ph)_2(CO)Cl](PF_6)$, 89689-82-7; $Ru(bpy)_2CO_3$, 59460-48-9; $Os(bpy)_2CO_3$, 89689-83-8; $Os(phen)Cl_4$, 89689-84-9; *cis*-$Os(phen)(dppene)Cl_2$, 89689-85-0; $Os(bpy)Cl_4$, 57288-05-8; *mer*-$Os(PPh_3)_3(CO)HCl$, 36007-23-5; HCOOH, 64-18-6.

Supplementary Material Available: Table of elemental analysis for the hydride and carbonyl complexes (2 pages). Ordering information is given on any current masthead page.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. 12.[1] Isomerization and Water Exchange of Allyl Alcohol in Aqueous Solution Catalyzed by $PdCl_4^{2-}$

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The isomerization of allyl-*1,1*-d_2 alcohol (**5a**) into an equilibrium mixture of **5a** and allyl-*3,3*-d_2 alcohol (**5b**) in aqueous solution was studied by ^1H NMR at various palladium(II), proton, and chloride concentrations. The rate expression was found to be rate = $k_i[PdCl_4^{2-}][\mathbf{5a}]/[Cl^-]$. The exchange of nondeuterated allyl alcohol with oxygen-18 enriched water was studied by mass spectrum under one set of reaction conditions. The exchange rate was the same, within experimental error, as the isomerization rate. This result is consistent with both isomerization and exchange occurring by a hydroxypalladation–dehydroxypalladation route rather than by π-allyl intermediates. The rate expression for isomerization is consistent with exterior attack of water on a trichloropalladium(II)–allyl alcohol π complex to give trans stereochemistry. The isomerization rate equation is quite different from that for oxidation of allyl alcohol to carbonyl products, indicating that hydroxypalladation leading to oxidation is a different process from that leading to exchange. Furthermore, under the conditions (high chloride concentration in the presence of cupric chloride) that chloroethanol is produced from ethene, the hydroxypalladation leading to exchange is faster than that leading to oxidation to aldehydes and ketones. By analogy ethene would be expected to undergo the same type of nonoxidative hydroxypalladation as allyl alcohol with the same rate expression. All the evidence is consistent with the hydroxypalladation adduct *not* leading to aldehydes and ketones being the one captured by cupric chloride to give chloroethanol. Thus, the observed trans stereochemistry for the oxidation of ethene-*1,2*-d_2 to chloroethan-*1,2*-d_2-ol does not reflect the stereochemistry of the hydroxypalladation in the Wacker reaction.

Introduction

In recent years there has been considerable discussion concerning the stereochemistry of the hydroxypalladation step that is generally agreed to be operative in the palladium(II)-catalyzed oxidation of acyclic olefins to aldehydes and ketones.[3] The rate expression for eq 1 over a certain range of reaction conditions ([Pd(II)] = 0.005–0.04 M; $[Cl^-]$ = 0.1–1.0 M; $[H^+]$ = 0.04–1.0 M) is given by eq 2.[3]

$$PdCl_4^{2-} + C_nH_{2n} + H_2O \rightarrow Pd(O) + C_nH_{2n}O + 2HCl + 2Cl^- \quad (1)$$

$$\frac{-d[\text{olefin}]}{dt} = \frac{k_1[PdCl_4^{2-}][\text{olefin}]}{[H^+][Cl^-]^2} \quad (2)$$

With ethene as the simplest example the rate expression has been interpreted in terms of the two hydroxy-

(1) Part 11: Pandey, R. N.; Henry, P. M. *Can. J. Chem.* **1975**, *53*, 2223.
(2) (a) University of Guelph. (b) Loyola University of Chicago.
(3) For general discussion and references, see: Henry, P. M., "Palladium Catalyzed Oxidation of Hydrocarbons"; D. Reidel: Doordrecht, Holland, 1980; pp 41–84.

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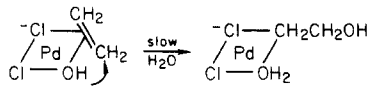
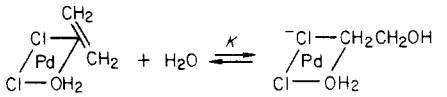
palladation paths shown in eq 3 and 4.[4] The first (eq 3),



(3)

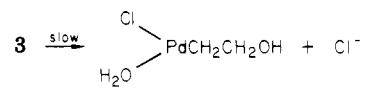
1 3



(4)

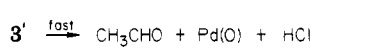
2 3

involving rate-determining formation of adduct **3**, was originally selected as most likely on the basis of isotope effects,[5] but the latter, involving equilibrium hydroxypalladation with adduct decomposition being rate determining, has more recently been proposed because of stereochemical studies that suggest hydroxypalladation occurs by attack of water from outside the coordination sphere of palladium(II).[6-8] The most convincing of these studies[7] involves the oxidation of ethene at high chloride (3.3 M) and high cupric chloride concentrations (2.7 M), conditions under which chloroethanol becomes the main product.[9] It was found that the configurations of the chloroethan-d_2-ol products from oxidation of (*Z*)- and (*E*)-ethene-d_2 were consistent with trans hydroxypalladation. With assumption that $CuCl_2$ was intercepting the intermediate **3**, a mechanism analogous to the second route (eq 4) was proposed.[7] However it was realized that one problem with this route is the fact that there is no kinetic isotope effect with ethene-d_4[5a] while there is a competitive deuterium isotope effect with ethene-*1,2*-d_2.[5b,c] These results suggest decomposition of **3** is not the rate-determining step. To overcome this difficulty they suggested that eq 5 is slow with decomposition of the tricoordinated intermediate **3'** being rapid.[7]



(5)

3'

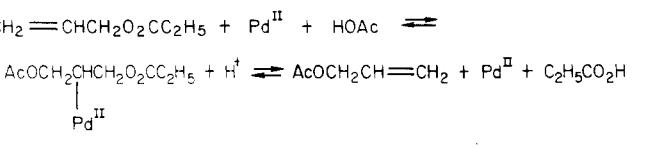


(6)

The basic assumption in all of these stereochemical studies is that there is only one mode of hydroxypalladation in Pd(II) chemistry. However, if any lesson is to be gained from studies of reactions in nonaqueous solvents, it is that the mode of oxypalladation is strongly dependent on ligands and solvent.[1,10-12]

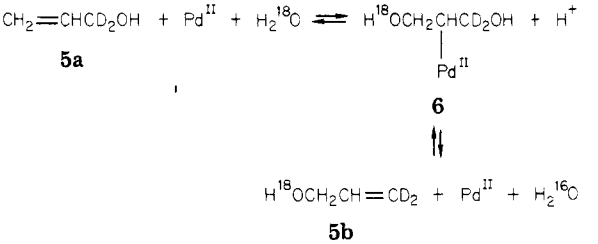
This paper will focus on detection of hydroxypalladation paths in aqueous solution other than those leading to **3**, the adduct which decomposes to acetaldehyde. Thus, as pointed out above the study with ethene-d_2 in aqueous solution was the most convincing and must be taken as a valid indication of the mode of hydroxypalladation leading to acetaldehyde unless it can be shown that there is another trans hydroxypalladation process leading to chloroethanol. There is, in fact, reason to believe another hydroxypalladation path is responsible for the chloroethanol product. In the original study of the $CuCl_2$-promoted reaction it was found necessary to have high chloride as well as high cupric chloride concentrations in order to obtain high chloroethanol yields.[9] If only cupric chloride is present, acetaldehyde is the predominant product.[13]

Scheme I



4

Scheme II



5a 6 5b

In order to detect hydroxypalladation paths other than those leading to carbonyl oxidation products, some nonoxidative reaction must be found that will give measurable chemical change if hydroxypalladation occurs. Such a reaction is exchange. Allylic ester exchanges with acetate (Scheme I) have been studied in acetic acid[14] and have been shown to proceed via the acetoxypalladation adduct **4**.[10,14b] The corresponding reaction in aqueous solution is the exchange of allyl alcohol with solvent water. As shown in Scheme II the exchange can be measured by either ^{18}O exchange or isomerization of deuterated allyl alcohol if the exchange proceeds via an intermediate such as **6**. It is, in fact, necessary to measure both ^{18}O exchange and isomerization. Thus, if the mechanism shown in Scheme II is operative, exchange occurs each time isomerization of **5a** to **5b** occurs. However, another possible mechanism, which has been observed in one case (acid-catalyzed exchange and isomerization of 3-cyclohexenyl esters in acetic acid[15]), involves Pd(IV) π-allylic species. As shown in Scheme III, this mechanism predicts ^{18}O exchange is twice as fast as isomerization. Thus, a combination of ^{18}O exchange and isomerization rate measurements will distinguish between the two mechanisms. A preliminary account of part of this work has appeared.[16]

Results

All kinetic measurements were carried out at 25 °C. Exchange and isomerization data are given in Table I. Although oxidation occurred in addition to isomerization

(4) In eq 4 both cis and trans isomers of **2** are present. Only the cis form is shown for simplicity.

(5) (a) Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246. (b) Henry, P. M. *Ibid.* **1973**, *38*, 2415. (c) Kosaki, M.; Isemura, M.; Kitaura, Y.; Shinoda, A.; Sarto, Y. *J. Mol. Catal.* **1977**, *2*, 351.

(6) Stille, J. K.; James, D. E. *J. Organomet. Chem.* **1976**, *108*, 401.

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

(8) Stille, J. K.; Divakarumi, R. *J. Organomet. Chem.* **1979**, *169*, 239.

(9) Stangl, R.; Jira, R. *Tetrahedron Lett.* **1970**, 3589.

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

(11) (a) Henry, P. M. *Adv. Organomet. Chem.* **1975**, *13*, 363. (b) Henry, P. M.; Pandey, R. N. *Adv. Chem. Ser.* **1974**, *No. 132*, 33.

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

(13) The need for high chloride has been postulated to involve the stabilization of the intermediate **3** to prevent its decomposition via eq 5. The problem with this suggestion is that, if eq 5 is the slow step and decomposition occurs every time **4** is formed, increasing the chloride concentration should not decrease the rate of decomposition of **3**. It is *possible* that at high chloride concentration eq 5 becomes an equilibrium and eq 6 becomes the slow step. The reaction would then display a third power chloride inhibition and further addition of chloride would inhibit decomposition of **3**.

(14) (a) Sabel, A.; Smidt, J.; Jira, A.; Prigg, H. *Chem. Ber.* **1969**, *102*, 2939. (b) Henry, P. M. *J. Am. Chem. Soc.* **1972**, *94*, 1527.

(15) Ng, F. T. T.; Henry, P. M. *J. Org. Chem.* **1973**, *38*, 3338.

(16) Gregor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681.

Scheme III

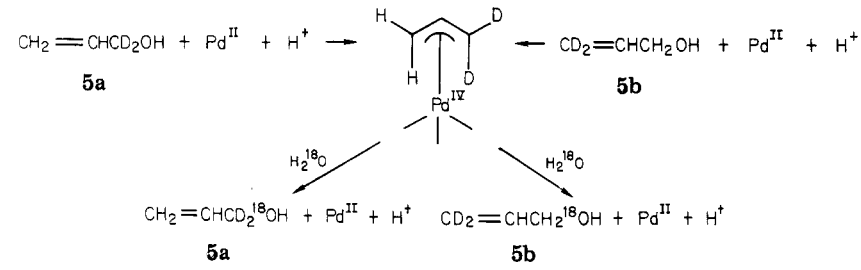


Table I. Rates of Isomerization and ^{18}O Exchange of Allyl Alcohol

run	$[PdCl_4^{2-}]$	$[H^+]^b$	$[Cl^-]^c$	$10^3 t_{1/2}$, s^{-1}	$10^5 k_{obsd}$, s^{-1}	$10^3(k_i$ or $k_{ex})$,[d] s^{-1}
			Isomerization			
1	0.01	1.0	0.2	5.4	6.4	1.3
2	0.05	1.0	1.0	5.6	6.1	1.2
3	0.01	1.0	1.0	27	1.3	1.3
4	0.01	0.2	1.0	25	1.4	1.4
5	0.025	1.0	1.0	9.1	3.8	1.5
6	0.01	1.0	0.5	8.7	4.0	2.0
7	0.10	1.0	1.0	2.0	19.0	1.9
8	0.10	1.0	1.5	3.5	10.0	1.5
9	0.02	0.5	0.5	11	3.3	1.8
10	0.02	0.5	3.3	40	0.87	1.4
			^{18}O Exchange			
11a	0.01	2.0	1.0	40	0.39	1.7
11b	0.01	2.0	1.0	47	0.31	1.5

[a] All runs are in aqueous solution at 25 °C; quinone (0.10 M) added to all runs to prevent precipitation of Pd(0). Allyl-d_2 alcohol was **5a** for all isomerization runs. In runs 1–9 initial [5a] = 0.1 M while for run 10 it was 0.25 M. For all runs in which $[H^+] + [Cl^-]$ was less than 2.0 M, $LiClO_4$ was added to bring ionic strength to 2.0. [b] Added as $HClO_4$. [c] Added as LiCl. [d] k_i (runs 1–9) and k_{ex} (run 11) were calculated by assuming rate expression given by eq 5 is operative and $[PdCl_4^{2-}]$ and $[Cl^-]$ are constant for each run.

and ^{18}O exchange, the rate measurements for the nonoxidative reactions are unaffected since **5a** and **5b** have equal probability of oxidation. The values of k_i were calculated by using the rate expression given in eq 7. The fact that the calculated k_i remains constant over a wide range of $[PdCl_4^{2-}]$, $[H^+]$, and $[Cl^-]$ indicates that eq 7 is in fact the correct rate expression with a value of 1.5×10^{-3} s^{-1} for k_i.

$$\text{rate} = k_i \frac{[PdCl_4^{2-}][C_3H_4D_2O]}{[Cl^-]} \qquad (7)$$

It is noteworthy that the rate expression holds up to a $[Cl^-]$ of 3.3 M, far above the ionic strength of 2.0 used for most of the runs (see run 10).

The ^{18}O exchange rate constant for one set of reaction conditions is also given in Table I. The value of k_{ex}, also calculated on the basis of eq 7, is the same as the value of k_i. This result requires that Scheme II rather than Scheme III is operative.

The values of k_i in the presence of cupric chloride are shown in Table II. The values of k_i are close to those in the absence of $CuCl_2$ (compare runs 10 and 14). The fact that the value of k_i is higher in the absence of added $HClO_4$ than in the presence of added acid probably reflects the effect of acid on the equilibria in the system rather than a proton term in the rate expression.

Discussion

The new and significant result of this study is the detection of an unexpected second mode of hydroxypalladation in aqueous solution. The two hydroxypalladations occur simultaneously but independently with one leading to oxidation and the second (at least in the absence of $CuCl_2$; see following discussion) leading only to isomerization and ^{18}O exchange of allylic alcohols.

Table II. Rates of Isomerization of Allyl Alcohols in the Presence of $CuCl_2$[a]

run	$[H^+]$	$10^5 k_{obsd}$, s^{-1}	$10^3 k_i$,[c] s^{-1}
12[b]		3.3	3.3
13	0.2	2.2	2.2
14	0.5	1.8	1.8

[a] For all runs $[PdCl_4^{2-}] = 0.033$ M, $[LiCl] = 3.3$ M, and $[CuCl_2] = 2.7$ M, no quinone in these runs. Initial **5a** was 0.25 M for run 12 and 0.1 M for runs 13 and 14. [b] No $HClO_4$ added. Actual value of $[H^+]$ unknown. [c] See footnote *d* of Table I.

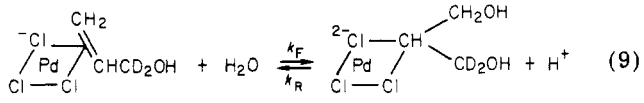
An interesting feature of the two hydroxypalladations is that they have quite different rate expressions. Thus, kinetic studies of the oxidation of allyl alcohol indicate its oxidation obeys eq 2, the same rate expression as was found for other acyclic olefins. The value of k_1 for allyl alcohol was 5.2×10^{-4} M^2 s^{-1}.[17] On the other hand isomerization obeys the rate expression given in eq 7 where k_i is 1.5×10^{-3} s^{-1}. Since the proton and chloride inhibitions are so different, under some conditions (low $[H^+]$ and $[Cl^-]$) oxidation is faster than isomerization, while, under other conditions (high $[H^+]$ and $[Cl^-]$), the reverse is true. Thus, in runs 1 and 2 in Table I oxidation is over twice as rapid as isomerization while in runs 8 and 10 isomerization is about 5 times faster than oxidation. These results require that the two hydroxypalladations are completely separate processes.[17]

If the nonoxidative path does not involve oxidation pathway intermediates such as **3**, what is the most likely pathway consistent with the kinetics? The simplest and most reasonable route involves the reaction pathway given

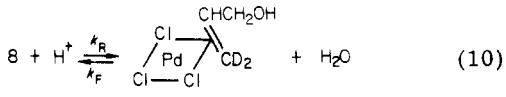
(17) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal*, **1982**, *16*, 81.

in eq 8–10. Since olefin activation by π complex formation is always a necessary step in palladium(II) catalysts, the first power chloride inhibition must result from the equilibrium shown in eq 8. The π complex is common to

$$\underset{\mathbf{5a}}{PdCl_4^{2-} + C_3H_4D_2O} \overset{K}{\rightleftharpoons} \underset{\mathbf{7a}}{PdCl_3(C_3H_4D_2O)^-} + Cl^- \quad (8)$$



7a **8** (9)



7b (10)

both pathways, but in the oxidation route it undergoes another chloride displacement to eventually given an intermediate analogous to **3**. However, in the isomerization reaction there is no second chloride inhibition so water must attack from outside the coordination sphere of Pd(II) as shown in eq 9. Thus, the predicted stereochemistry is trans.[18]

The reaction scheme given in eq 8–10 predicts a first-order chloride inhibition resulting from eq 8. The hydroxypalladation shown in eq 9 involves attack by solvent water, and, of course, solvent does not appear in the rate expression. Now both eq 9 and 10 have a proton in the equation. In spite of this, proton does not appear in the rate expression because half the time **8** is formed, it reverts to **7a**, and half the time to **7b**. Thus, although proton increases k_R and decreases the concentration of **8**, the rate-determining step in exchanges such as this is k_F (eq 9). In other words, the rate depends only on the rate of formation of **8**, not its equilibrium concentration. The rate thus depends on k_F[**7a**], and in turn, [**7a**] = K[$PdCl_4^{2-}$]-[**5a**]/[Cl^-] which gives a rate expression of the form of eq 7. Of course the detailed kinetic analysis is that of a reaction approaching an equilibrium (1:1) mixture of **5a** and **5b** since **5b** can revert to **5a** by the same process. (See Experimental Section.)

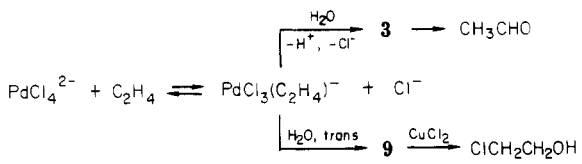
The possibility relationship of the nonoxidative isomerization to formation of chloro alcohol product will now be considered. Chloroglycols, the product analogous to chloroethanol from ethene, have not been reported. Although a detailed study of this reaction was not undertaken, preliminary results indicate chloroglycols are formed at high [Cl^-] and [$CuCl_2$] (>3.5 M each) although the rates, as might be expected, are appreciably slower than with ethene.[19] In Table II the value of the oxidation rate for run 12 cannot be calculated because [H^+] is unknown, but, for run 13, it is 7.8×10^{-6} s^{-1} and, for run 14, it is 3.2×10^{-6} s^{-1}. These rates are between $^1/_3$ and $^1/_6$ of the isomerization rates. Thus, under the conditions that the $CuCl_2$-promoted reaction first becomes the predominant reaction, the trans hydroxypalladation to give **8** is faster than oxidation to carboxyl compounds. The most logical conclusion is that **8** is the intermediate trapped by $CuCl_2$ to give chloroglycol products.

In extending the discussion to chloroethanol formation from ethene the assumption must be made that ethene undergoes a hydroxypalladation analogous to that shown in eq 9. However, if **8** is formed by trans attack of water

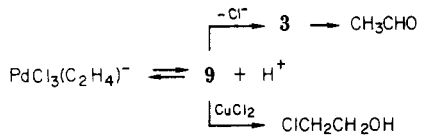
(18) Trans stereochemistry in nonaqueous solvents was predicted on the basis of similar kinetic arguments, and later the prediction was confirmed by stereochemical studies.[10]

(19) Zaw, K., unpublished results.

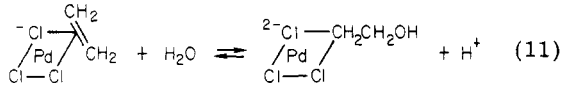
Scheme IV



Scheme V



on trichloropalladium–allyl alcohol π complex, the corresponding ethene π complex would certainly be expected to undergo the same reaction to give **9** as shown in eq 11.



9 (11)

Of course, in the case of ethene there would be no way to detect the intermediate **9** unless the adduct were intercepted by $CuCl_2$. The adduct **9** must therefore be considered as a possibility for the intermediate that is intercepted in the stereochemistry studies using ethene-d_2. Actually, as mentioned in the Introduction, the experimental facts favor **9** rather than **3** as the intermediate. In the original studies[9] both high [$CuCl_2$] and high [Cl^-] were required for chloroethanol formation.[13] Thus, at [$PdCl_4^{2-}$] = 0.0164 M and [$CuCl_2$] = 4 M but no added chloride, the mole ratio $CH_3CHO/ClCH_2CH_2OH$ was found to be 47. However, if the chloride is increased to 10 M, the ratio changes to 0.41. Clearly this is not the result expected if $CuCl_2$ is intercepting the same intermediate that decomposes to acetaldehyde. However, it is consistent with the need for high chloride concentration to inhibit the acetaldehyde forming reaction so the chloroethanol reaction becomes the predominant process. If this is the case, then the acetaldehyde route must have a higher chloride inhibition than the route producing chlorohydrin. This is exactly the case as the acetaldehyde route eq 2 has a chloride-squared inhibition while the isomerization route eq 7 has a first power chloride inhibition. Thus the data strongly favor **9** as the species intercepted by $CuCl_2$.

It is beyond the scope of the present discussion to consider the detailed mechanism of the Wacker reaction, but the combination of present and previously reported results are most consistent with the *general* reaction pathway shown in Scheme IV. The trans stereochemistry observed in the ethene-d_2 experiments is predicted on the basis of the kinetic studies described in this paper, but these studies bear no relationship to the stereochemistry of the hydroxypalladation leading to acetaldehyde if Scheme IV is correct.

Since Bäckwall, Åkermark, and Ljunggren[7] were unaware of the second mode of hydroxypalladation, they naturally proposed a mechanism consistent with trans hydroxypalladation. This involved the equilibrium hydroxypalladation mechanism shown in eq 3. A variation of this mechanism could, at first glance, explain the results in this paper. This reaction path, shown in Scheme V, involves **9** as a common intermediate in *both* oxidation and exchange.[20] In this scheme, trans hydroxypalladation

(20) This possibility was suggested by a reviewer.

would then apply for both processes. Returning to the model allyl alcohol system the intermediate **9** would be replaced by **8**. For Scheme V to be valid the hydroxypalladation shown in eq 7 *would always have to be faster than oxidation* and under all reaction conditions isomerization would have to be faster than oxidation. As has already been discussed, at lower $[Cl^-]$ and $[H^+]$ this is not the case for allyl alcohol and, by analogy, almost certainly not the case for ethene. Thus, Scheme V can be rejected as a viable alternative for Scheme IV.[21]

Two questions concerning the present results naturally arise. The first is: would attack by nucleophile water on a negatively charged olefin π complex be expected on the basis of other Pd(II)–olefin chemistry? It has been assumed in previous studies that this is not the first step in the kinetic studies, although, as mentioned above, reaction pathways such as Scheme V, which were consistent with the kinetics, could have been written. The reason expressed[7] is that attack of nucleophile water on a negatively charged π complex seems unlikely. However, in studies of exchange reactions of vinylic and allylic groups with acetic acid solvent a term that could only reasonably be interpreted as attack of acetic acid on a Pd(II) dimeric negatively charged olefin π complex appears in most exchange rate expressions.[10] In addition the kinetics of hydration of vinyl acetate to acetaldehyde in wet acetic acid indicate that a rather facile trans atack of water on an analogous dimeric olefin π complex must be taking place.[23] As might be expected from the fact that water is the better nucleophile, the attack of water occurs much more readily than acetic acid although the latter is present in large excess. Thus, it is perhaps not too surprising that the observed slow attack of solvent water on the $PdCl_3(olefin)^-$ complex is occurring.

The second question concerns the stability of **8** and **9** toward oxidative decomposition to carboxyl products. Certainly there is kinetic evidence that vacant or weakly coordinated sites are required for decomposition of oxypalladation adducts in nonaqueous solution,[12] and there is also evidence for the necessity of similar sites for decomposition of Pt(II) alkyls.[24] In fact stable oxypalladation adducts can be isolated when all sites are strongly coordinated. This is, no doubt, the reason stable oxypalladation adducts of (diolefin)palladium(II) complexes can be isolated,[25] and recently a stable methoxypalladation adduct of ethene has been isolated with the strongly complexing cyclopentadienyl and phosphine ligands.[26] The fact that the species **8** and **9** are stable to decomposition by hydride shift suggests chloride is a good ligand for Pd(II). This is consistent with the fact that in acetic acid containing chloride, although oxypalladation occurs readily, oxidation of oxypalladation adducts by hydride shift is almost nonexistent at 25 °C while for the weaker ligand acetate, oxidation is a reasonably fast process.[12] However, it must be pointed out that the stabilities of **8** and **9** depend on their lifetimes as well as the coordination environment. It is certainly possible that with some olefins the lifetime of the intermediate could be long enough for decomposition by hydride shift and oxidation to carboxyl products could occur through intermediates analogous to **8** and **9**. Thus cyclic olefins such as cyclohexene are oxidized by a rate expression different from eq 2 so presumably the mechanisms for cyclic and acylic olefins are different.[19,27-29] A possible route is via intermediates analogous to **8** and **9**.

Finally as mentioned in the Introduction, Bäckwall, Åkermark, and Ljunggren were not the only workers who found trans hydroxypalladation. However, in these other studies the conditions were even further removed from the acyclic olefin oxidation by Pd(II) in water and the trans stereochemistry observed was not surprising in light of previously published data. In one study the hydroxypalladation of the chelating diolefin 1,5-cyclooctadiene was examined.[6] The trans stereochemistry observed was not surprising, since in nonaqueous solvents, addition of nucleophiles to diolefin complexes Pt(II) and Pd(II) is almost always trans. The reason is simply that the nucleophile is prevented from coordinating to the metal, a requirement for cis addition. Also, as mentioned above, even the cyclic monoolefin cyclohexene has a different rate expression for oxidation that acyclic olefins and thus a different detailed mechanism. In a second study the stereochemistry of ethene-*1,2-d*$_2$ oxidation was studied in wet (ca. 2% H_2O) acetonitrile.[8,30] The trans stereochemistry observed was again not surprising since in a similar system, wet acetic acid, a kinetic study has indicated that hydroxypalladation is a trans process. However, the important point is that if with the same olefin allyl alcohol, in aqueous solution, two modes of hydroxypalladation can take place simultaneously, then how can stereochemical studies with different olefins or in different solvents possibly shed light on the mode of hydroxypalladation in the oxidation of acylic olefins in aqueous solution?

Experimental Section

Starting Materials. The palladous chloride was purchased from Engelhardt, Inc. The nondeuterated alcohol (Aldrich, Gold Label) was used as received. The allyl-*1,1-d*$_2$ alcohol was prepared by a literature procedure.[31] ^1H NMR indicated its isotopic purity was at least 98%. The water-^{18}O was purchased from MSD Isotopes. All other chemicals were of reagent grade.

Isomerization Kinetics. The isomerization of **5a** into **5b** was monitored by using ^1H NMR. The reaction was run on a 10-mL scale. Three experimental points were taken for each run. For the first two 3-mL aliquots of the mixture were extracted with 3–5-mL portions of ether. For the final sample, the remainder of the reaction mixture as used. After the mixture was dried with $MgSO_4$ and filtered, 0.15 mL of phenyl isocyanate was added to convert the allyl alcohol to the phenyl urethane derivative and the solution allowed to stand for 1 h. The ether was evaporated at room temperature, the residue extracted with $CDCl_3$, and this solution analyzed by ^1H NMR using a Bruker WP-60. For most samples 1000–2000 scans gave the required sensitivity. The % isomerization was obtained by dividing the area of the CD_2=C-HCH_2O–, which is a doublet at 4.7 ppm in the deuterated phenyl urethane derivative, by the areas of the 4.7 ppm peak *plus* the area of the CH_2=$CHCD_2O$–peak, which is multiplet centered at 5.3 ppm. Me_4Si was used as internal standard.

(21) In a recent review Bäckvall,[22] although citing ref 16 and 17 of this paper, again postulated the ethylene oxidation mechanism discussed in the Introduction (eq 4–6). Thus he apparently does not accept Scheme IV although he did not offer any rebuttal to this proposal. Rather he indicated that ref 16 and 17 were only concerned with the rate-determining step and not the basic mechanism. Actually as will be discussed in a forthcomming paper on the detailed mechanism, the rate-determining step is intimately linked with mechanism.

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(30) In this paper[8] two possible trans hydroxypalladation mechanisms are suggested for the Wacker process. One is effectively the same as eq 4 while the second is attack of external hydroxide on **2**. With use of the known rate and equilibrium constants, it can be calculated that the second route would have to be considerably faster than a diffusion-controlled process and thus clearly impossible.[5a]

The data were plotted as a reaction approaching equilibrium.[32] A plot of log (50% − % isomerized) vs time was made on semilog paper and the half-life read off at the 25% point. Since the value of the equilibrium constant for the isomerization is equal to 1, the rates of the forward and reverse reactions are identical and the value of the slope of ln (50% − % isomerized) = $-2k_{obsd}$. It is this corrected value of k_{obsd} that is given in Table I. The value of k_i was calculated by using the expression $k_{obsd} = k_i[PdCl_4^{2-}]/[Cl^-]$.

Although, because of the tedious nature of the experiment and the instrument time needed to obtain the desired accuracy, only three points were taken per run, there was little scatter in the kinetic plots and they all passed through the expected 50% intercept at zero time. Least-square treatment gave standard deviations of less than 5% in the slope in almost all runs. Duplicate runs were made in three cases: for run 6 the values of k_{obsd} were 4.18 and 3.73×10^{-5} s^{-1}, for run 7 they were 1.67 and 2.1×10^{-4} s^{-1}, and for run 14 they were 1.75 and 1.83×10^{-5} s^{-1}. Of course, these values were rounded off to two figures before calculating k_i.

Control experiments using all reagents but Pd(II) did not give any detectable isomerization over the period of the longest kinetic run.

^{18}O Exchange Kinetics. The experimental procedures were similar to those for the isomerization studies except nondeuterated allyl alcohol was used, and 1.6-mL aliquots were withdrawn to give a total of five experimental points. After suitable amounts of the $HClO_4$, Li_2PdCl_4, and LiCl stock solutions were mixed, the solution was diluted with a mixture of 1.5 atom % and 97.17 atom % water-^{18}O. The phenyl urethane samples were run on the hp 5985 GC/MS system of Northwestern University, Evanston, IL. The % ^{18}O in the allyl alcohol samples was determined by a comparison of the intensities of the M − 177 and M − 179 parent peaks of the ^{16}O and ^{18}O containing species. Control experiments in the absence of Pd(II) indicated there was a very slow acid-catalyzed exchange at the high acid concentrations employed.[33] No correction was made for this exchange that was less the 1% of the Pd(II)-catalyzed exchange under the reaction conditions employed.

The data were treated by the equation for isotopic exchange.[34] Control runs in the absence of $H_2{}^{18}O$ gave a correction for the small amount of M − 179 present in the absence of exchange, and this small correction was applied to the % ^{18}O values obtained during an actual run. From the known amount of $H_2{}^{18}O$, $H_2{}^{16}O$, and allyl alcohol the % ^{18}O at equilibrium could be calculated and the fraction of exchange F at each sampling time. Plots of log $(1 - F)$ vs. time on semilog paper were linear. From the value of the half-life the value of k_{obsd} (= R in ref 34) can be calculated from eq 12. The value of k_{ex} was then calculated from k_{obsd} by

$$k_{obsd} = \text{slope}\frac{([H_2{}^{18}O] + [H_2{}^{18}O])([\text{allyl alcohol}])}{([H_2{}^{18}O] + [H_2{}^{16}O]) + [\text{allyl alcohol}]} \quad (12)$$

using eq 13.

$$k_{ex} = k_{obsd}\frac{[Cl^-]}{[PdCl_4^{2-}][\text{allyl alcohol}]} \quad (13)$$

The values of the various quantities [allyl alcohol], $[H_2{}^{16}O]$, $[H_2{}^{18}O]$, and % ^{18}O equilibrium are as follows: run 11a, 0.2275, 47.739, 0.977, and 0.020 06; run 11b, 0.2103, 47.739, 0.976, and 0.020 04.

The plots showed more scatter that the isomerization runs, but the fact more points were taken improved the accuracy. Least-squares treatment of both runs gave standard deviations of less than 10%. Certainly the data are precise enough to show that the rate of exchange is about the same as the rate of isomerization rather than twice as high.

Conclusion

Allyl alcohol undergoes two modes of hydroxypalladation in aqueous solution: one leading to carbonyl oxidation products and one leading to isomerization and water-^{18}O exchange. Under conditions where saturated chloro alcohols are formed from ethene and allyl alcohol[29] (high $[Cl^-]$ in the presence of $CuCl_2$[9]) the hydroxypalladation leading to isomerization and exchange is faster than oxidation to carbonyl products. This and other experimental facts suggests that the hydroxypalladation adduct leading to isomerization and exchange is the one intercepted by $CuCl_2$ to give chloro alcohols. *By analogy* ethene would also be expected to undergo this second nonoxidation mode of hydroxypalladation and again the experimental facts strongly suggest that is is the adduct from this second mode of hydroxypalladation that is intercepted by $CuCl_2$ to give chloroethanol. The kinetics indicate the second hydroxypalladation has trans stereochemistry which is consistent with the results of a stereochemical study using (*Z*)- and (*E*)-ethene-*1,2*-d_2 to produce threo and erythro chloroethan-*1,2*-d_2-ol. However, the important point is that the results of these stereochemical studies do not shed light on the stereochemistry of the hydroxypalladation leading to carbonyl oxidation products. The present results indicate the great caution that must be exercised in interpreting stereochemical results in metal ion catalysts as reaction pathways can be very complicated.

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