Oxidation of Olefins by Palladium(II). 9.[1] Mechanism of the Oxidation of Olefins by the Dimeric Species, $Na_2Pd_2(OAc)_6$, in Acetic Acid

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Abstract: The rate of oxidation of ethylene by palladium(II) ocetate in acetic acid first rises with increasing sodium acetate concentration, reaches a maximum at 0.2 M [NaOAc], and then decreases with further increase in [NaOAc]. With the aid of previous equilibria studies it can be shown that the initial increase in rate results from conversion of less reactive trimer, $Pd_3(OAc)_6$, to a more reactive dimer, $Na_2Pd_2(OAc)_6$, by sodium ocetate. Above 0.2 M [NaOAc] the dimer is the only reactive species; a monomeric species, $Na_2Pd(OAc)_4$, formed to some extent, is unreactive. The oxidation of ethylene by dimer has the rate expression: $-d[C_2H_4]/dt = k_EK_{22}[Na_2Pd_2(OAc)_6][C_2H_4]/[NaOAc]$ where K_{22} is the equilibrium constant for formation of the dimeric π-complex, $NaPd_2(OAc)_5(C_2H_4)$. The rate of oxidation of 3,3-dimethyl-1-butene is slower than ethylene but displays the same kinetic behavior. One difference is that increasing olefin concentration decreases the rate. The value of K_{21} for the following equilibrium was determined: $Na_2Pd_2(OAc)_6 + 2(CH_3)_3CCH{=}CH_2 \rightleftharpoons 2NaPd(OAc)_3[(CH_3)_3CCH{=}CH_2]$. It could be shown that the rate retardation results from formation of unreactive monomeric π-complexes via this equilibrium. 3,3-Dimethyl-1-butene and propylene give both secondary enol acetates and primary enol and allylic acetates. The secondary acetates predominate at low [NaOAc] and the primary acetates at high [NaOAc]. A mechanism which is consistent with the rate expression and explains the change in product distribution with [NaOAc] is proposed. An important feature of this mechanism is the need for a vacant coordination site on Pd(II) before palladium(II) hydride elimination can occur from the acetoxypalladation intermediate.

Because of its commercial importance the oxidation of olefins by palladium(II) salts in acetic acid has received considerable attention.[3] In the catalytic oxidation system, which contains oxidants such as $CuCl_2$ to prevent the precipitation of palladium metal, a variety of products are produced. thus ethylene gives β-chloroethyl acetate, ethylene glycol mono- and diacetates, 1,1-diacetoxyethane, acetaldehyde, and vinyl acetate. The mechanistic picture was clarified somewhat when it was noted that the 1,2-disubstituted ethanes and possibly 1,1-diacetoxyethane arose from a reaction involving both Pd(II) and oxidant[4] and acetaldehyde arose from a secondary reaction involving a Pd(II) catalyzed saponification of vinyl acetate.[5,6] Thus in the absence of oxidants the primary product is vinyl cetate with perhops some 1,1-diacetoxyethane ot higher temperatures[7,8] (eq 1, X = Cl^- or OAc^-). Mechanisms of

$$PdX_2 + C_2H_4 + 2OAc^- \xrightarrow{HOAc} Pd(0) + 2X^- + C_2H_3OAc + HOAc \quad (1)$$

Pd(II) catalyzed reactions in the chloride containing system have been studied to a considerable extent and are now fairly well understood.[9] This paper will describe a study of the olefin oxidation reaction in the chloride-free system.

The oxidation of olefins by palladium(II) acetate in acetic acid containing sodium acetate has been studied by several workers.[10-18] However, there are two rather unusual observations which have yet to be explained. The first is a peculiar dependence of the rate of ethylene oxidation on sodium acetate concentration.[11,12] Thus the rate first increases with increasing [NaOAc], reaches a maximum at about 0.2 M [NaOAc], and then decreases markedly with further increase in [NaOAc]. Moiseev and co-workers attributed the original increase in rate to the dissociation of polymeric palladium acetate species to give $Na_2Pd(OAc)_4$.

$$[Pd(OAc)_2]_n + 2nNaOAc \rightleftharpoons nNa_2Pd(OAc)_4 \quad (2)$$

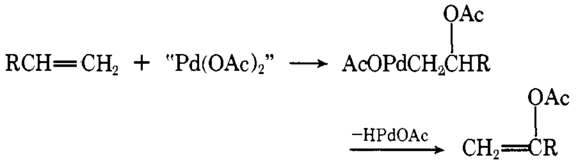
The interaction of ethylene with the palladium(II) acetates species present at [NaOAc] > 0.2 M was also studied and the important equilibrium was proposed to be given by eq 3 where K has the value 0.3 M at 35 °C. Finally the rate expression at

$$C_2H_4 + Na_2Pd(OAc)_4 \overset{K}{\rightleftharpoons} (C_2H_4)Pd(OAc)_2 + 2NaOAc \quad (3)$$

sodium acetate concentrations above 0.2 M was proposed to be given by eq 4, where k has a value of $1.3 \times 10^{-3}\ s^{-1}$ at 35 °C.

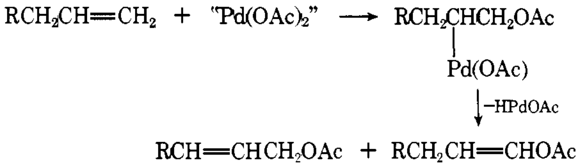
$$\text{rate} = \frac{kK[Na_2Pd(OAc)_4][C_2H_4]}{[NaOAc]^2} \quad (4)$$

The second unusual observation in this system is a change in product ratios with change in sodium acetate concentration.[16-18] Thus at low acetate concentrations the main products are secondary enol acetates which most likely arise from Markovnikov acetoxypalladation followed by palladium hydride elimination.[10] At higher [NaOAc] the main product



$$RCH{=}CH_2 + \text{"}Pd(OAc)_2\text{"} \longrightarrow AcOPdCH_2\overset{\overset{OAc}{|}}{C}HR \xrightarrow{-HPdOAc} CH_2{=}\overset{\overset{OAc}{|}}{C}R \quad (5)$$

changes to primary enol and allylic acetates which would arise from non-Markovnikov addition followed by palladium hydride elimination.



$$RCH_2CH{=}CH_2 + \text{"}Pd(OAc)_2\text{"} \longrightarrow RCH_2\underset{\underset{Pd(OAc)}{|}}{C}HCH_2OAc \xrightarrow{-HPdOAc} RCH{=}CHCH_2OAc + RCH_2CH{=}CHOAc \quad (6)$$

Two recent publications might shed some light on the rate dependence of sodium acetate concentration. In a study of the equilibrium between palladium(II) acetate and sodium acetate in acetic acid it was found that the following two equilibria are operative.[19] At 25°C the value of K_t is $7.77 \times 10^4\ M^{-5}$ and K_d is $7.6 \times 10^{-4}\ M^{-1}$. These values are such at 25 °C that at

$$2Pd_3(OAc)_6 + 6NaOAc \overset{K_t}{\rightleftharpoons} 3Na_2Pd_2(OAc)_6 \quad (7)$$

$$Na_2Pd_2(OAc)_6 + 2NaOAc \overset{K_d}{\rightleftharpoons} 2Na_2Pd(OAc)_4 \quad (8)$$

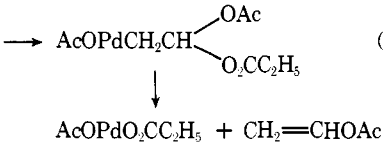
[NaOAc] = 0.2 M the only species present in any appreciable amount is the dimer, $Na_2Pd_2(OAc)_6$. An unexpected feature of these equilibria is that they take hours to come to equilibrium. Thus in kinetic stuides of catalytic reactions of olefins in this system, in order to obtain meaningful data, it is necessary to allow sufficient time for complete equilibration between palladium(II) acetate and sodium acetate.

The second publication described a study of the palladium(II) catalyzed exchange of vinyl propionates with acetic acid.[20] This reaction should be mechanistically similar to olefin

$$CH_2{=}CHO_2CC_2H_5 + HOAc \xrightarrow{\text{"Pd(OAc)}_2\text{"}} CH_2{=}CHOAc + C_2H_5CO_2H \quad (9)$$

oxidation to give unsaturated esters (eq 5 and 6), since it must also involve addition of the elements of Pd(II) and acetate across the double bond. However, in this case the elements of

$CH_2{=}CHO_2CC_2H_5$ + "$Pd(OAc)_2$"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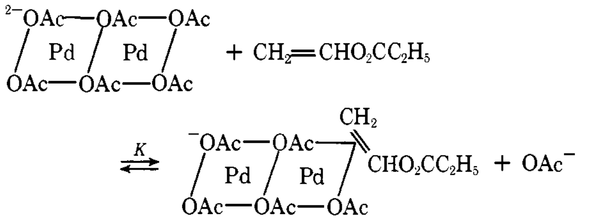
Pd(II) and propionate are eliminated in a nonoxidative reaction rather than palladium(II) hydride in an oxidative reaction.

The rate of the exchange reaction also increased with initial increase in sodium acetate concentration until a maximum in rate at [NaOAc] = 0.2 M is reached. The rate then decreases slightly with further increase in [NaOAc]. Using the values of K_t ond K_d in eq 7 and 8, it can be shown that the rate expression for exchange is given by eq 11 (VP = vinyl propionate) where k_d is greater than k_t. Thus the initial increase in rate

$$\text{rate} = (k_t[Pd_3(OAc)_6] + k_d[Na_2Pd_2(OAc)_6])\,[VP] \quad (11)$$

results from the transformation of a relatively unreactive trimer to a more reactive dimer. Another point to note is that the rate expression does not contain a term in [NaOAc]. All the sodium acetate is doing is converting one palladium(II) acetate species to another. The slight decrease in rate at higher sodium acetate concentrntions results from conversion of reactive dimer, $Na_2Pd_2(OAc)_6$, to unreactive monomer, $Na_2Pd(OAc)_4$. The lack of a sodium acetate inhibition term for vinyl ester exchange is somewhat surprising since on the basis of previous exchange studies in chloride containing acetic acid one would expect π-complex formation between $Na_2Pd_2(OAc)_6$ and vinyl propionate to be the first step in the reaction. This π-complex formation would be inhibited by sodium acetate. The only convincing reason for the lack of a [NaOAc] term is that the inhibition term in eq 12 is cancelled by a catalytic term which arises from eq 13. Equation 13 must be the slow step in the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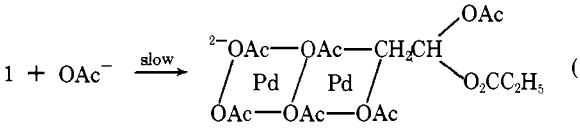
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reaction since acetate and propionate, being very similar in reactions, must have about equal tendencies to eliminate from **2**. Thus once **2** is reached exchange must occur half of the time.

Finally another publication which is related to the present study describes the equilibrium between $Na_2Pd_2(OAc)_6$ and olefins.[21] The two equilibria operative in this system are given by eq 14 and 15 (ol = olefin).

$$\text{ol} + Na_2Pd_2(OAc)_6 \overset{K_{22}}{\rightleftharpoons} \underset{\mathbf{3}}{NaPd_2(OAc)_5(\text{ol})} + NaOAc \quad (14)$$

$$2\text{ol} + Na_2Pd_2(AcO)_6 \overset{K_{21}}{\rightleftharpoons} \underset{\mathbf{4}}{2NaPd(OAc)_3(\text{ol})} \quad (15)$$

Another dimension of complexity to Pd(II) catalysis in this system is provided by the fact dimeric π-complex, **3**, is formed rapidly while monomeric π-complex, **4**, takes several hours to come to completion. Now in analogy with the chloride containing system, **3** would be expected to be the reactive species with **4** unreactive. This has actually been shown to be the case. Thus depending on the rate of the particular reaction, formation of **4** by eq 15 may or may not have to be taken into account. In the case of vinyl ester exchange the reaction was complete before appreciable amounts of **4** were formed. However, allyl propionate exchange is much slower and the rate decreases with time because of formation of unreactive **4**.[22]

At 25 °C the value of K_{22} for ethylene was found to be 8.23 while for 3,3-dimethyl-1-butene the value is 0.44.[21] For these two olefins the value of K_{21} was not determined because the attainment of equilibrium could not be achieved before the precipitation of palladium resulting from the oxidative reaction discussed in this paper.

The exchange and equilibrium data discussed above suggest that eq 4 may not be the exact rate expression for ethylene oxidation. Thus, the dimer, $Na_2Pd_2(OAc)_6$, is the predominant reactive species at [NaOAc] = 0.2 M and the second-order inhibition by sodium acetate may result from inaccurate equilibrium assumptions.

It is the purpose of this study to determine the exact rate expression in the region of [NaOAc] that $Na_2Pd_2(OAc)_6$ is the reactive species. It is hoped a mechanism consistent with this rate expression and previous exchange and equilibria studies can be reduced. In addition this paper will describe studies of the change in product distribution with [NaOAc].

Results

All kinetic runs, equilibria determinations, and product distribution studies were carried out at 25 °C. The olefinic substrates used for the kinetic studies were ethylene and 3,3-dimethyl-1-butene while product distributions were determined for 3,3-dimethyl-1-butene and propylene.

Before the start of a run by addition of olefin the palladium(II) acetate and sodium acetate are allowed to come to equilibrium. The concentrations of the various Pd(II) species are calculated from the known values of K_t and K_d in eq 7 and 8.

Ethylene. The major product was vinyl acetate with smaller amounts of acetaldehyde. No 1,1-diacetoxyethane was observed. A plot of rate vs. [NaOAc] at atmosphere ethylene pressure is shown in Figure 1 and an analysis of data in the range [NaOAc] = 0.2–1.0 M is given in Table I. Although the rate of oxidation decreases by only a factor of 2.5 for a fivefold change in [NaOAc], it can be shown that the rate is proportional to dimeric π-complex concentration (**3**,ol = C_2H_4). Thus in the next to last column is given the concentration of $NaPd_2(OAc)_5(C_2H_4)$ calculated from the previously determined value of K_{22} in eq 14. The value for ethylene is 8.23 M. The value of the first-order rate constant calculated from these π-complex concentrations is given in the last column. They are

Table I. Effect of NaOAc Concentration on Rates of Ethylene Oxidation at 25 °C

$[NaOAc]_0$, M	$[Na_2Pd_2(OAc)_6]_0$,[a] 10^2M	k_{obsd}, 10^6M s^{-1}	$[C_2H_4]$, M	$[NaPd_2(OAc)_5(C_2H_4)]$, 10^3M	$k_{obsd}/[NaPd_2(OAc)_5(C_2H_4)]$, $10^4 s^{-1}$
Total [Pd(II)] = 0.0278 M					
0.20	1.25	6.41	0.0741	9.75	6.57
0.30	1.35	5.97	0.0725	9.27	6.44
0.40	1.33	5.21	0.0702	8.09	6.44
0.50	1.315	4.63	0.0687	7.17	6.46
0.60	1.30	4.30	0.0675	6.40	6.72
0.80	1.27	3.41	0.0657	5.23	6.52
1.0	1.24	2.75	0.0605	4.20	6.55
Total [Pd(II)] = 0.0125 M					
0.20	0.605	2.99	0.0741	4.63	6.46
0.30	0.595	2.43	0.0725	4.02	6.04
0.40	0.584	2.25	0.0702	3.50	6.43
0.50	0.574	2.00	0.0687	3.08	6.51
0.60	0.564	1.80	0.0675	2.74	6.57
0.80	0.545	1.53	0.0657	2.22	6.88
1.00	0.527	1.18	0.0605	1.77	6.68

[a] Dimer concentration before addition of ethylene. If all Pd(II) is in form of $Na_2Pd_2(OAc)_6$ then $[Na_2Pd_2(OAc)_6]_0$ should equal total [Pd(II)]/2. Difference between this value at $[Na_2Pd_2(OAc)_6]_0$ at 0.2 M[NaOAc] results from incomplete conversion of $Pd_3(OAc)_6$ to $Na_2Pd_2(OAc)_6$ (eq 7). At higher values of [NaOAc] difference results from conversion of $Na_2Pd_2(OAc)_6$ to $Na_2Pd(OAc)_4$ (eq 8).

Table II. Calculation of K_{21} at 25 °C for 3,3-Dimethyl-1-butene[a]

$[Olefin]_0$, M	Absorbance at 300 mμ	$[ol]_{eq}$, M	$[NaPd(OAc)_3(ol)]$,[b] 10^2M	$[Na_2Pd_2(OAc)_6]$,[b] 10^2M	K_{21},[b] 10^2M^{-1}
0	0.031	–	–	0.695	–
0.010	0.043	0.00986	0.0137	0.688	2.78
0.050	0.081	0.0493	0.0675	0.661	2.83
0.10	0.123	0.0987	0.127	0.632	2.62
0.25	0.241	0.247	0.294	0.548	2.59
0.50	0.389	0.495	0.504	0.443	2.34
0.75	0.543	0.743	0.722	0.334	2.83
1.00	0.650	0.991	0.873	0.258	3.01

[a] [NaOAc] = 0.8 M, time = 12 h. [b] Calculated using the values; $\epsilon_\pi = 730$, $\epsilon_{Pd_2} = 45$.

constant within experimental error indicating the correct rate expression is given by eq 16 where k has a value of 6.5×10^{-4} s^{-1} at 25 °C. This rate expression can also be written as eq 17

$$-d[C_2H_4]/dt = k[NaPd_2(OAc)_5(C_2H_4)] \quad (16)$$

or eq 18 where $[Na_2Pd_2(OAc)_6]_0$ is the dimer concentration before addition of ethylene.

$$-d[C_2H_4]/dt = kK_{22}[Na_2Pd_2(OAc)_6][C_2H_4]/[NaOAc] \quad (17)$$

$$-d[C_2H_4]/dt = \frac{kK_{22}[Na_2Pd_2(OAc)_6]_0[C_2H_4]}{[NaOAc] + K_{22}[C_2H_4]} \quad (18)$$

In this treatment of the kinetic data no account is taken of the formation of unreactive monomeric π-complexes according to eq 15. In the previous study of π-complex formation the value of K_{21} could not be determined because precipitation of palladium metal resulting from ethylene oxidation was too rapid. However, this equilibrium need not be considered in this study because the rates of ethylene oxidation were so fast that the rates could easily be measured before appreciable amounts of monomeric π-complex (**4**,ol = C_2H_4) are formed. Of course if one were to measure reaction rates over a period of many hours this equilibrium would have to be taken into account.

3,3-Dimethyl-1-butene. The rates of oxidation of this olefin are much slower than those of ethylene so inhibition by formation of unreactive monomeric π-complexes via eq 15 must be considered. In the previous study on π-complex formation the value of K_{21} for this olefin was not determined because of olefin oxidation as discussed in the previous section. However, because of the importance of this equilibrium in interpreting the kinetics of this olefin oxidation another attempt was made to define this equilibrium.

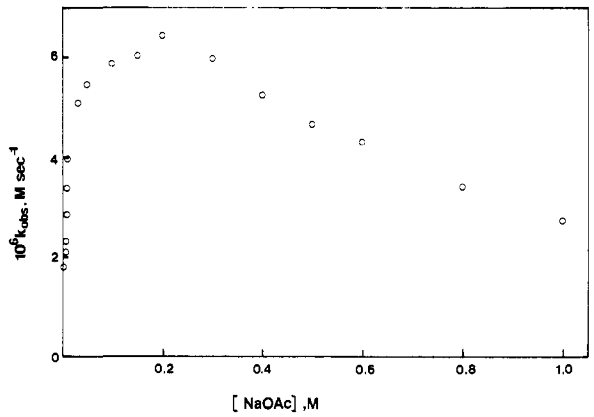


Figure 1. Plot of k_{obsd} vs. [NaOAc] for oxidation of ethylene at 25 °C; $[Pd(II)]_t$ = 0.0278 M.

Since the results with ethylene suggested that olefin oxidation was retarded by sodium acetate, the equilibrium studies were carried out at a high sodium acetate concentration of 0.8 M. Under these conditions equilibrium between $Na_2Pd_2(OAc)_6$ and olefin could be achieved in about 12 h without precipitation of palladium metal. A distinct isosbestic point at 370 nm was observed. Since at high olefin concentrations the conversion to monomeric π-complex, $NaPd(OAc)_3(ol)$, was almost complete, the calculation of K_{21} was straightforward. An example of the data used to calculate K_{21} is given in Table II. The average value is 2.7×10^{-2} M^{-1} at 25 °C.

Table III. Effect of Olefin Concentration on k_{obsd} of Oxidation of 3,3-Dimethyl-1-butene (ol)[a]

[Olefin], M	$[NaPd_2(OAc)_5(ol)]$,[b] 10^3M	$[NaPd(OAc)_3(ol)]$,[b] 10^3M	k_{obsd}, $10^6 s^{-1}$	$k_{obsd}[ol]/[NaPd_2(OAc)_5(ol)]$, $10^5 s^{-1}$
0.020	0.520	0.341	1.50	5.77
0.030	0.758	0.505	1.58	6.25
0.075	1.69	1.19	1.60	7.11
0.10	2.12	1.54	1.48	7.00
0.20	3.40	2.76	1.07	6.30
0.40	4.67	5.07	0.786	6.74
0.50	5.14	5.37	0.702	6.83
0.80	5.69	7.14	0.496	6.97
1.0	5.82	8.07	0.384	6.60

[a] [NaOAc] = 0.20 M, $[Pd(II)]_t = 0.0278$ M. [b] Calculated from the values: $K_{22} = 0.44$ and $K_{21} = 0.027$.

The formation of monomeric π-complex is appreciable at higher olefin concentrations so retardation of rate by olefin might be expected. As shown in Table III this is, in fact, observed. However, when the rate is corrected for this inhibition using the experimental value of K_{21}, the rate constant, k, does not vary over a wide range of olefin concentrations.

The treatment of data in this table requires some comments. At low olefin concentrations $NaPd_2(OAc)_5(ol)$ is small compared to initial $Na_2Pd_2(OAc)_6$ concentration and is directly proportional to olefin concentration. Under these conditions the reaction is first order in olefin and the data can be treated as such. At high olefin concentrations both $NaPd_2(OAc)_5(ol)$ and $NaPd(OAc)_3(ol)$ are large compared with $Na_2Pd_2(OAc)_6$ so under these conditions the reactions are not strictly first order but rather between zero and first order in olefin. Under these conditions initial zero-order rates of reaction were obtained and divided by initial olefin concentration to obtain an apparent first-order rate constant, k_1, for comparison with the data at low olefin. Finally all values of k_1 are converted to zero-order rates by multiplying by olefin concentration and then divided by $[NaPd_2(OAc)_5(ol)]$ to obtain the first-order rate constants in dimeric π-complex. As shown in the last column of the table, the values of this rate constant are the same within experimental error even when appreciable amounts of unreactive monomeric π-complex, $NaPd(OAc)_3(ol)$, are present.

Since at 3,3-dimethyl-1-butene concentrations of less than about 0.1 M, the inhibition by formation of monomeric π-complex is small and the reaction is close to first order in olefin, the effect of sodium acetate concentration was tested at 0.1 M 3,3-dimethyl-1-butene. As shown in Figure 2, a plot of $k_1/[Na_2Pd_2(OAc)_6]$ vs. 1/[NaOAc] is linear indicating a first-order sodium acetate inhibition. The rate expression for 3,3-dimethyl-1-butene oxidation is thus given by eq 19 (ol = 3,3-dimethyl-1-butene) where k' have a value of 6.6×10^{-5} s^{-1} where at low [ol] the equilibrium concentration of $Na_2Pd_2(OAc)_6$ can be replaced by the initial concentration because both are the same within experimental error. Alternately the

$$\text{rate} = k'K_{22}'[Na_2Pd_2(OAc)_6][ol]/[NaOAc] \quad (19)$$

rate expression can be written in forms corresponding to eq 16 and 18.

The product distribution at various sodium acetate concentrations was determined. Results are listed in Table IV.

Propylene The product distribution for propylene oxidation was also determined at four sodium acetate concentrations. Results are listed in Table V. In addition to the unsaturated acetates some acetone was detected. No isomerization between allylic and enol acetates was observed.

Table IV. Distribution of 3,3-Dimethyl-1-butene Oxidation Products at Various [NaOAc][a]

[NaOAc], M	% $(CH_3)_3CC(OAc)=CH_2$	% *trans*-$(CH_3)_3CCH=CH(OAc)$
Nil	96	4
0.10	87	13
0.20	80	20
0.30	65	35
0.40	54	46
0.50	48	52
0.60	43	57
0.80	38	62
1.0	35	65

[a] $Pd(II)]_t = 0.0278$ M, [olefin] = 0.1 M, [quinone] = 0.1 M.

Table V. Distribution of Propylene Oxidation Products at Various [NaOAc] and 25 °C[a]

[NaOAc], M	% $CH_2=CH-CH_2OAc$	% $CH_3CH=CHOAc$	% $CH_3C(OAc)=CH_2$
Nil	2	2	96
0.098	13	0.5	86.5
0.49	71	3	26
0.90	94	<0.5	6

[a] [Pd(II)] = 0.0033 M, reaction time was 45–65 min.

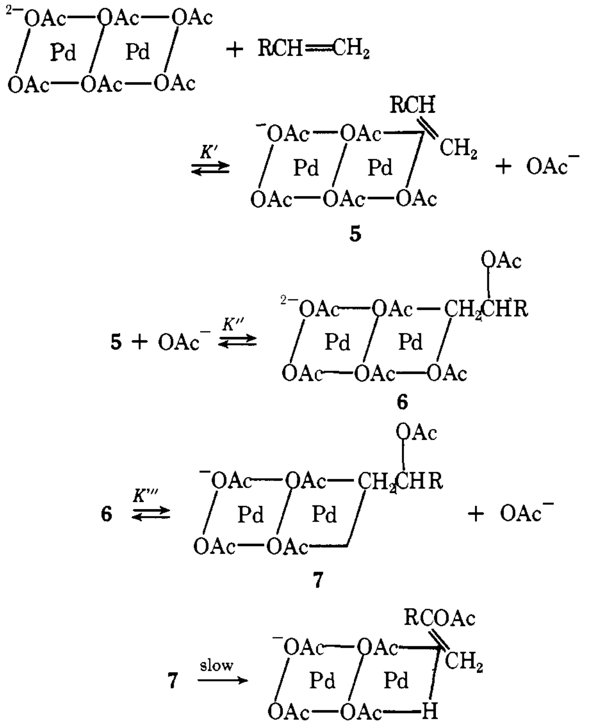
Discussion

The kinetic results of this study clearly indicate a first-order inhibition by sodium acetate in the rate expression for olefin oxidation rather than the second-order dependence proposed previously.[11,12]

In devising a mechanism consistent with the rate expression, the earlier kinetic results for vinyl propionate exchange must be kept in mind since both reactions are mechanistically similar. In this case there is no [NaOAc] term in this rate expression because an inhibition term in eq 12 is cancelled by a catalytic term in eq 13. The acetate inhibition in the olefin oxidation indicates a different series of steps. A mechanism consistent with all the data is given by eq 20–23.

This path differs from exchange mainly in that the acetoxypalladation step for oxidation (eq 21) is an equilibrium rather than the slow step. The difference is reasonable since acetate and hydride are quite different groups so their tendencies to eliminate could vary considerably while in exchange chemically very similar groups are being added and eliminated.

The main new feature of this mechanism is the need for a vacant site on Pd(II) before hydride elimination can occur. Although not previously proposed for hydride elimination, in the exchange of vinyl chloride with acetic acid to give vinyl



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(21)

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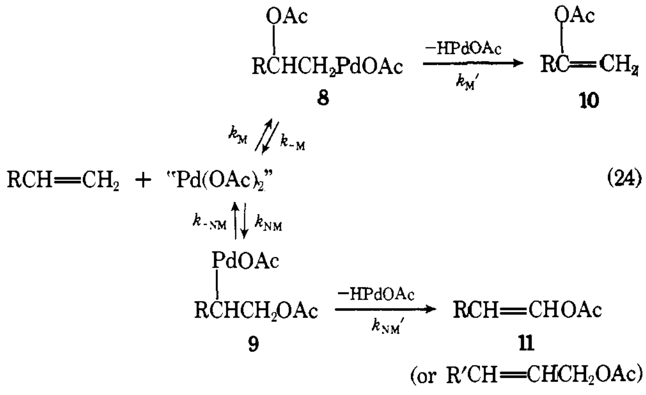
acetate the kinetics again strongly suggested that a vacant coordination site on Pd(II) was necessary before chloride could be transferred from the organopalladium(II) intermediate to the coordination sphere of Pd(II) to complete exchange.[23] There is also evidence that decomposition of Pt(II) allyls by platinum(II)-hydride elimination requires a vacant coordination site on Pt(II).[24]

The reaction scheme proposed above can also explain the change in product distribution with sodium acetate concentration observed for propylene and 3,3-dimethyl-1-butene.



(24)

Consider the scheme given below where M stands for Markovnikov and NM for non-Markovnikov addition. If the reaction scheme given by eq 24 is treated according to the steady state approximation, keeping in mind that hydride elimination is inhibited by sodium acetate, eq 25 is readily derived.

$$\frac{d\mathbf{10}/dt}{d\mathbf{11}/dt} = \frac{(k_M'/[\mathrm{NaOAc}])k_M/(k_{-M} + k_M'/[\mathrm{NaOAc}])}{(k_{NM}'/[\mathrm{NaOAc}])k_{NM}/(k_{-NM} + k_{NM}'/[\mathrm{NaOAc}])} \quad (25)$$

If at low [NaOAc], $k_M'/[\mathrm{NaOAc}]$ and $k_{NM}'/[\mathrm{NaOAc}]$ are large compared with k_{-M} and k_{-NM}, respectively, the ratio of **10**/**11** is the same as the ratio of the rates of formation of **8**/**9** or k_M/k_{NM}. However, if at high [NaOAc] the rates of hydride elimination are slowed sufficiently so $k_{-M} \gg k_M'$ [NaOAc] and $k_{-NM} \gg k_{NM}'/[\mathrm{NaOAc}]$ then the ratio of **10** to **11** becomes $k_M k_M'/k_{-M}:k_{NM}k_{NM}'/k_{-NM}$. Between these two extremes a gradual change from one product distribution to another would be expected. In other words at low [NaOAc] the product distribution is *kinetically* controlled while at high [NaOAc] the distribution is *equilibrium* controlled.

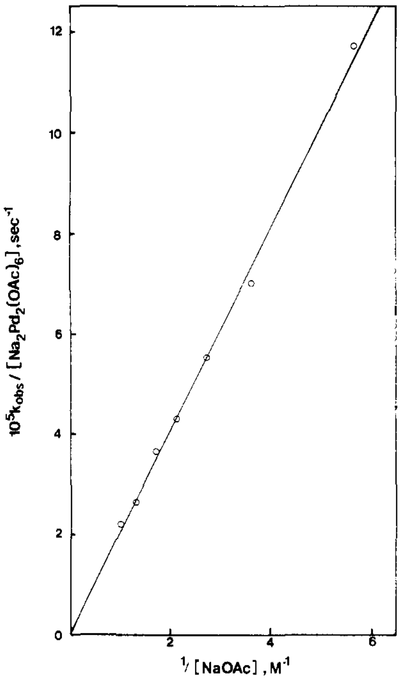


Figure 2. Plot of $k_{obsd}/[Na_2Pd_2(OAc)_6]$ vs. 1/[NaOAc] at 25 °C for the neohexene oxidation; $[Pd(II)]_t$ = 0.0278 M and $[(CH_3)_3CCH{=}CH_2]$ = 0.1 M.

The decrease of rate with increasing [NaOAc] above 0.2 M [NaOAc] is somewhat more gradual than that reported earlier by Moiseev and co-workers.[11,12] This difference can be explained by the variation in reaction conditions. Moiseev et al. used low ethylene concentrations such that $[Pd(II)] \gg [C_2H_4]$. Under these conditions the $K_{22}[C_2H_4]$ term in eq 17 is much less than [NaOAc] so the decrease in rate with increasing [NaOAc] is proportional to 1/[NaOAc]. In the present study atmospheric ethylene pressure was used and under these conditions of higher olefin solubility the $K_{22}[C_2H_4]$ and [NaOAc] terms are comparable. Under these conditions the decrease in rate with 1/[NaOAc] is less than first order. In the case of 3,3-dimethyl-1-butene the decrease in rate is again proportional to 1/[NaOAc] (Figure 2) at olefin concentrations less than 0.1 M. This of course results from the lower value of K_{22}' for 3,3-dimethyl-1-butene as compared with ethylene. At concentrations of less than 0.1 M, K_{22}'[3,3-dimethyl-1-butene] is much less than [NaOAc].

The slower rate of oxidation of 3,3-dimethyl-1-butene as compared with ethylene results from a lower value of both $k'(6.6 \times 10^{-5}\ s^{-1})$ and $K_{22}'(0.44)$. Corresponding values for ethylene are $k = 6.5 \times 10^{-4}\ s^{-1}$ and $K_{22} = 8.23$.

The earlier incorrect assumptions[12] as to reactive Pd(II) species and order in [NaOAc] arose from inadequate equilibrium data. This demonstrates the peril in analyzing kinetic data in metal salt catalyzed reactions without a complete knowledge of the equilibrium involved.

Certainly the palladium(II) acetate system in acetic acid is an example of a particularly complicated system. Not only are the equilibria more complicated than the previously studied palladium(II) chloride system in acetic acid but also some equilibria are slow. Thus in the chloride containing system inhibition by formation of unreactive monomeric π-complexes was observed in allylic ester exchange, but the equilibria were attained instantaneously so the inhibition was observed for all olefins which formed appreciable amounts of monomeric π-complexes. In the acetate system inhibition is observed only with olefins which react slowly enough to allow monomeric

π-complexes to be formed via eq 15. Thus inhibition is not observed with ethylene but is observed with 3,3-dimethyl-1-butene (Table III) which is oxidized much more slowly than ethylene.

In this study the oxidation of olefins by the trimeric species $Pd_3(OAc)_6$ was not investigated in detail. Such an investigation would be difficult since it would be necessary to separate the reaction of $Na_2Pd_2(OAc)_6$ which is important even at low values of [NaOAc]. Another complicating factor is the fact that the reaction of trimer with olefin to form the reactive species is a slow reaction. One detailed study in the absence of any added acetate but in the presence of O_2 as reoxidizing agent has elucidated many of the mechanistic features of oxidation by the trimer.[13]

Almost the only product observed in all oxidations is the unsaturated esters with some carbonyl products which must have arisen from a secondary saponification reaction of the unsaturated esters. Thus 1,1-disubstituted alkanes are not primary products under these reaction conditions.

The value of 2.7×10^{-2} M^{-1} for K_{21} of 3,3-dimethyl-1-butene is quite low considering its value of 0.44 for K_{22}. For instance vinyl acetate has a value of 0.51 M^{-1} for K_{21} and a value of 0.07 for K_{22}. Thus different steric and electronic factors must be operative in the two equilibria.

One result which deserves brief comment is the small and variable yield of *n*-propenyl acetate shown in Table V. The actual numbers cannot be taken too seriously since only trace amounts were found and the analysis was thus of low accuracy. However, it does again demonstrate the reluctance of Pd(II) in the intermediate organometallic species to eliminate a hydride from the carbon containing the acetate group. The *n*-propenyl acetate must have arisen from the same adduct, the allyl acetate (**9**; R = CH_3), but the yield of allyl acetate at high [NaOAc] is over a hundred times greater. This tendency of allylic acetates to form in preference to enol acetates has been previously observed in the oxidation of 2-butene[10] and cyclohexene.[25]

Experimental Section

Materials. Palladium acetate (purchased from Engelhard Chemicals and Catalysts, N.J.) was purified by the method of Stephenson et al.[26] The acetic acid (Baker Chemical Co.) was dried by refluxing over triacetylborate, $B(OAc)_3$, and distilled.[27] Sodium acetate (Baker Chemical Co.) was reagent grade. 3,3-Dimethyl-1-butene (Aldrich Chemical Co.), ethylene, and propylene (both C.P. grade from Matheson Co.) were used without further purification.

Kinetic Runs. The oxidation of ethylene was followed by the uptake of ethylene measured in gas burets at 25.0 ± 0.1 °C as previously described.[28] All runs were carried out in the presence of quinone and at a constant ethylene pressure of 1 atm.

Gas-liquid chromatography (GLC) analysis was used for kinetic runs with 3,3-dimethyl-1-butene. The 6-ft Carbowax 20M column programmed from 50 to 200 °C at 15°/min with a helium flow rate of 50 ml/min was used to analyze the olefin concentration. The latter was calibrated by means of an inert internal standard (CH_2Cl_2). A plot of log [olefin] vs. time gave straight lines for several half-lives at initial olefin concentrations of 0.1 M or less.

Equilibrium Measurements. The formation of π-complexes between Pd(II) species and 3,3-dimethyl-1-butene was followed spectrally in the range 400–250 nm.[4] Spectra were recorded on a Cary 118 spectrophotometer. Solutions of palladium(II) acetate and sodium acetate were equilibrated at 25 °C for at least 24 h prior to the addition of 3,3-dimethyl-1-butene. Addition of the olefin caused an instantaneous change in the spectra followed by a much slower change. The slower reaction took ca. 12 h to come to equilibrium.

Product Distributions. All products were analyzed using the GLC conditions described previously for the kinetic studies with 3,3-dimethyl-1-butene.

The products of oxidation of 3,3-dimethyl-1-butene were identified by their NMR spectra. Thus the 3,3-dimethyl-1-butene-2-yl acetate, $(CH_3)CC(OAc){=}CH_2$, gave resonance at δ 1.10 (s,$(CH_3)_3C$–), 2.17 (s, –$OCOCH_3$), 4.70 (d, J = 2.0 Hz, $=CH_2$) and 4.93 (d, J = 2.0 Hz, $=CH_2$). The –1-yl acetate, $(CH_3)_3CH{=}CHOAc$, was assigned as the trans isomer by virtue of the coupling constant of its olefinic protons. δ 1.07 (s, $(CH_3)_3C$–), 2.12 (s, –$OCOCH_3$), 5.52 (d, J 12.5 Hz, $(CH_3)_3CC\mathit{H}{=}$), and 7.12 (d, J = 12.5 Hz, $=C\mathit{H}OAc$).

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