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Review

Allylic oxidation of alkenes with palladium catalysts

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Contents

Abstract

Studies of the Pd-catalysed alkene oxidation to allylic, vinylic, and homoallylic esters are summarized. The regioselectivity and mechanism of stoichiometric reactions between alkenes and Pd^{II} through the π- and σ-complexes are discussed, with particular emphasis on the ligand and solvent effects. Two different pathways of the Pd-catalysed oxidative esterification of alkenes are considered: (i) stepwise Pd^{II}/Pd^0 reactions, (ii) reactions mediated by low-valence Pd giant clusters modeling the active component of hetreogeneous Pd catalysts.

Keywords: Palladium; Alkenes; π-Complex; σ-Complex; Oxidative esterification; Regioselectivity; Carbocations; Reaction mechanism

1. Introduction

As far back as 1934, Anderson observed [1] that upon refluxing an aqueous solution of Zeise's salt $K[PtCl_3{\cdot}C_2H_4]$ [2] acetaldehyde and platinum metal were produced (Eq. (1)):

$$K[PtCl_3 \cdot C_2H_4] + H_2O = CH_3CHO + Pt^0 + KCl + 2HCl. \quad (1)$$

Examination of the scope of reaction (1) over platinum group metals showed that the palladium(II) complex $[\pi\text{-}C_2H_4{\cdot}PdCl_2]_2$ (Kharash's complex [3]) is readily decomposed in water to produce acetaldehyde and Pd metal [4a] (Eq. (2)):

$$[\pi\text{-}C_2H_4 \cdot PdCl_2]_2 + 2H_2O = 2CH_3CHO + 2Pd^0 + 4HCl. \quad (2)$$

The same reaction products are formed when ethylene reacts with an aqueous solution of a Pd^{II} salt, and the palladium(0) that forms can be re-oxidized to Pd^{II}, thus providing the basis for a homogeneous catalytic system for ethylene oxidation to acetaldehyde [4–7] (Eq. (3)):

$$C_2H_4 + Pd^{II} \rightarrow [[\pi\text{-}C_2H_4 \cdot Pd^{II}] \xrightarrow{H_2O} CH_3CHO + Pd^0 \xrightarrow{Ox} Pd^{II}, \quad (3)$$

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where Ox is an oxidizing agent like H_2O_2, O_2, Cu^{II}, *p*-benzoquinone, etc. The homogeneous Pd catalyst with the $O_2 + CuCl_2$ oxidant is used in the industrial Wacker process for producing acetaldehyde from ethylene [5–7]. Higher alkenes transform to ketones in this catalytic system [4a,5–7].

Palladium(II) alkene π-complexes have also been found [4b] to undergo analogous redox decomposition in other hydroxylic solvents. Both alkenes and the corresponding palladium alkene π-complexes are converted in alcohol solutions to acetals or ketals instead of carbonyl compounds.

$$C_2H_4 + PdCl_2 \rightarrow [\pi\text{-}C_2H_4 \cdot Pd^{II}] \xrightarrow{2ROH} CH_3CH(OR)_2 + Pd^0 + 2HCl,$$

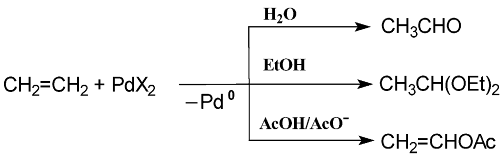
$$C_3H_6 + PdCl_2 \rightarrow [\pi\text{-}C_3H_6 \cdot Pd^{II}] \xrightarrow{2ROH} CH_3CH(OR)_2CH_3 + Pd^0 + 2HCl.$$

The palladium ethylene π-complex has been found to be inert toward acetic acid [5], unlike water and alcohols, until a nucleophilic agent like alkaline acetate is added [4b]. When ethylene is passed through acetic acid containing $PdCl_2$, the π-complex formed undergoes no redox transformation [5]. However, after addition of sodium or potassium acetate, ethylene is rapidly converted to vinyl acetate, along with traces of ethylidene diacetate (Eq. (4)) [4b,7]:

$$C_2H_4 + PdCl_2 \rightarrow [\pi\text{-}C_2H_4Pd^{II}] \xrightarrow{2AcONa} \left\{\begin{matrix} CH_2{=}CHOAc_{\sim 99\%} \\ CH_3{=}CH(OAc)_{2\sim 1\%} \end{matrix}\right\} + Pd^0 + 2NaCl + AcOH \qquad (4)$$

Similar to the Wacker process, reaction (Eq. (4)) can be supplemented with recovery of Pd^{II} from Pd^0 by oxidizing agents like $O_2 + Cu^{II}$, *p*-benzoquinone, or benzoyl peroxide, giving rise to a Pd-mediated catalytic cycle performing the oxidative ethylene acetoxylation to vinyl acetate [4b,7].

On the basis of early mechanistic studies, including reaction kinetics [8–10], H/D isotopic exchange [11,12], and independent synthesis of the suggested σ-palladium organyls [13], all the Pd^{II}-mediated alkene oxidations in different media (Scheme 1) have been rationalized as occurring *via* a common key stage, viz., isomerization of the palladium π-alkene complex to σ-organopalladium compound $XPd\text{-}CH_2CH_2OR$ (**1**), R = H (in water), alkyl (in alcohol), and Ac (in acetic acid) [7,13,14].



Scheme 1.

Palladium σ-organyl **1** was suggested [7,8,10,13] to undergo fast redox decomposition including the heterolytic cleavage of the σ-Pd–C bond to give rise to the reaction products, viz., Pd^0 and aldehyde or ketone (in aqueous solution), acetal or ketal (in alcohol solution), and vinyl ester or ethylidene diacetate (in $AcOH/AcO^-$ solution).

Another mechanistic viewpoint [14a,b] includes elimination of the Pd–H species from intermediate **1** followed by Pd–H addition across the C=C double bond of the coordinated vinyl alcohol or its derivative (Scheme 2).

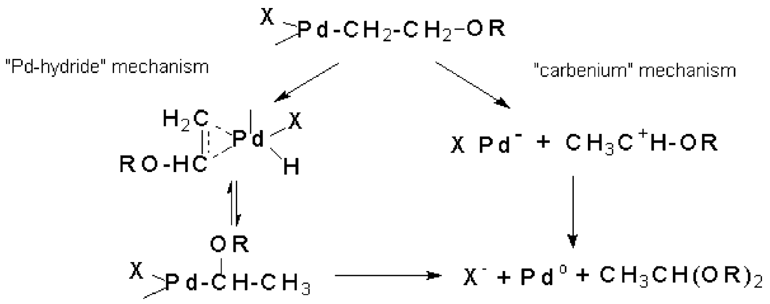
Both mechanistic approaches give a satisfactory account for reactions of ethylene with palladium(II) in all three media (water, alcohol, and acetic acid). Moreover, these schemes can be applied to rationalize the reactions of higher alkenes in aqueous and alcohol solutions. However, none of these mechanisms can explain the reactions of the latter substrates in acetic acid and, especially, the formation of new reaction products, viz., allylic and homoallylic esters in this medium.

To understand the reasons behind distinctions between the reactions in acetic acid and other solvents, it was necessary to study the vinylic/allylic/homoallylic regioselectivity over a wide range of alkenes as a function of the solvent composition, Pd^{II} complex nuclearity, and palladium oxidation state. This paper presents an account of these studies.

2. Homogeneous oxidative esterification of alkenes with Pd^{II} complexes

2.1. Regioselectivity of reaction

The reaction shown in Eq. (4) is of general occurrence. Higher alkenes and carboxylic acids can be involved in the

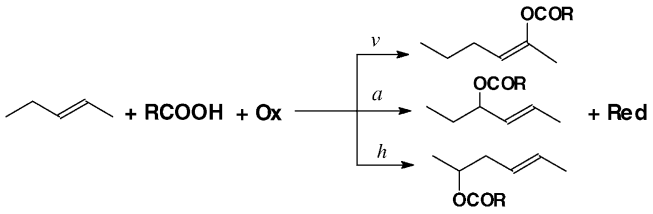


R = H (in water), alkyl (in alcohol), and OAc− (in acetic acid).

Scheme 2.

Pd-catalysed oxidative esterification as a direct synthetic way from alkenes to alkenyl esters. By analogy with alkene oxidations in aqueous and alcohol solutions, the reaction was expected to produce mainly α-alkenyl esters according to the Markovnikov rule. The first observation [4b] seemingly confirmed this expectation: the oxidation of propylene with Pd^{II} in an AcOH solution containing AcONa was found to produce mainly isopropenyl acetate both in the presence and absence of an additional oxidant (*p*-benzoquinone). The product mixture of propylene oxidation also contains *cis*- and *trans*-1-propenyl acetates along with 2-propenyl acetate [15,16]. The yield of allylic esters is remarkably higher in the case of higher propylene homologues. For instance, 1-hexene and 1-heptene were unexpectedly found [17] to produce 2-hexenyl and 2-heptenyl acetates, respectively, under the same conditions.

Generally, the alkene molecule is expected to undergo replacement of an H atom by the RCOO group in the vinylic (v), allylic (a), or homoallylic (h) positions according to Eq. (5):



(5)

(Ox = O_2, Cu^{II}, *p*-benzoquinone, MnO_2, or benzoyl peroxide, Red = H_2O, Cu^{I}, hydroquinone, MnO, or benzoic acid, respectively).

Comprehensive studies [18–24] showed that the regioselectivity of the Pd^{II}-mediated oxidative esterification of higher alkenes depends on the reaction conditions (viz., solvent, temperature, water content, the nature of the alkene, carboxylate anions, oxidizing agent, and the nuclearity of the palladium(II) complexes).

2.1.1. *Effects of Pd^{II} complex nuclearity and solvent nature*

All structurally characterized palladium(II) binary carboxylates are cyclic trinuclear complexes $Pd_3(\mu^2\text{-OCOR})_6$ (R=CH_3 [25a], CF_3 [25b], C_2H_5 [25c], $(CH_3)_3C$ [25c], S(+)-2-MeC*HCH_2CH_2 [25d]). Alkene oxidations with the trinuclear Pd^{II} carboxylates occur rather slowly but are greatly accelerated when $RCOO^-$ anions are added in the form of the alkaline, tetraalkylammonium, or $[(Ph_3P)_2N]^+$ (PNP) salts, which convert the trimers to the more reactive di- and mononuclear Pd^{II} anionic complexes **1** and **2** [22–24,26]:

$$2Pd_3(OCOR)_6 + 6RCOO^- \rightleftharpoons 3\underset{\mathbf{1}}{[Pd_2(OCOR)_6]^{2-}}\,, \qquad (6)$$

$$[Pd_2(OCOR)_6]^2 + 2RCOO^- \rightleftharpoons 2\underset{\mathbf{2}}{[Pd(OCOR)_4]^{2-}}\,. \qquad (7)$$

The PNP carboxylates, unlike alkaline salts, are very soluble both in carboxylic acids and in aprotic low-polarity solvents, providing homogeneous conditions for alkene oxidative acetoxylation with Pd^{II} complexes in these media [22–24]. The reaction solutions were prepared from $(PNP)^+OAc^-$ and a three-fold excess of $Pd_3(OAc)_6$ and preliminarily equilibrated according to Eqs. (6) and (7) for 12–20 h at 20 °C. Under these experimental conditions, practically all the AcO^- anions which were added, entered the composition of the anionic Pd^{II} complexes (^1H NMR monitoring), and the concentration of “free” (i.e., unbound to Pd^{II}) AcO^- anions in the equilibrated solutions was negligible (<1% of its initial concentration). This prevents a possible outersphere attack of the intermediate π-complex by free AcO^- anions.

Oxidation of higher alkenes with the di- and mononuclear Pd^{II} complexes in $AcOH/OAc^-$ is highly sensitive to the water admixture (either formed by the reaction or added). In a water-free medium the reaction normally produces mixtures of vinylic, allylic, and sometimes homoallylic esters [7,18–21]. However, when ≥1% of water is present in the solution, acetaldehyde and acetone are formed instead of vinyl and isopropenyl acetate from ethylene and propylene, respectively [7].

When alkene oxidation is conducted in an aprotic medium without additional oxidant, the Pd^{II} complexes are converted to colloidal low-valent Pd clusters or small Pd metal species (so-called Pd black). These species are efficient catalysts for alkene dehydrogenation, isomerization, and redox disproportionation [27]. For instance, benzene was found as main reaction product (yield ∼95% based on Pd^{II} consumed) in the stoichiometric cyclohexene oxidation with Pd^{II} carboxylates in chloroform [23]. The addition of *p*-benzoquinone (Q), which is capable of Pd^0 reoxidation [4], can preclude the undesired side reactions. However, the reaction

$$Pd^0 + Q + 2\,RCOOH = Pd(OCOR)_2 + QH,$$

needs protons and cannot occur in an aprotic medium. Instead, *p*-benzoquinone (Q) and the alkene molecule (Un) bind the Pd^0 species *in statu nascendi*

$$Pd^0 + BQ + Un = BQ \cdot Pd \cdot Un,$$

to form the π-complex BQ·Pd·Un which is rather stable in aprotic media [28,29], thus preventing the formation of the dispersed palladium phase and the side reactions. Another way to avoid the negative effect of the Pd^0 species is the use of benzoyl peroxide as oxidizing agent.

Studies [22–24] showed that alkene oxidation in aprotic low-polarity solvents (viz., THF, chloroform, dichloromethane, dichloroethane, and liquid/fluid CO_2) with the anionic Pd^{II} carboxylates **1** and **2** produce predominantly allylic esters and only traces of vinylic esters. For instance, both the stoichiometric (with respect to Pd^{II}) and catalytic (in the presence of extra oxidants such as *p*-benzoquinone, nitrosobenzene, or benzoyl peroxide)

Table 1
Propylene oxidative acetoxylation with Pd^{II} acetato complexes in different solvents at 25 °C [22]

Solvent	Reaction products/molar composition				Allyl to vinyl ratio
	Allyl acetate	2-Propenyl acetate	*cis* + *trans* 1-Propenyl acetates	Aceton + propanal	
$CHCl_3$	∼0.99	≤0.01	≤0.01	≤0.01	>1000
CH_2Cl_2	∼0.99	≤0.01	–	–	>1000
$CHCl_2CH_2Cl$	∼0.99	≤0.01	–	–	>1000
CH_2Cl_2[a]	∼0.99	≤0.01	–	–	>1000
CH_2Cl_2[b]	∼0.99	≤0.01	–	–	>1000
$CHCl_2CH_2Cl$ + 5% AcOH	0.92	0.058	–	0.023	11
AcOH[c]	0.009	0.986	0.005	–	<0.01
AcOH + 0.9 M NaOAc[d]	0.94	0.06 (total vinyl products)			16
AcOH + 0.9 M NaOAc + 1% H_2O[e]	0.49	0.51 (total vinyl products)			∼1
CO_2 liquid + 1% H_2O[f]	0.62	0.38 (total vinylic products)			1.6
CO_2 fluid + 1% H_2O[g]	0.76	0.24 (total vinylic products)			3.1
CO_2 fluid + 10% AcOH[h]	0.72	0.28 (total vinylic products)			2.6

[a] Benzoyl peroxide 1 mol/mol Pd added.
[b] Nitrosobenzene 1.2 mol/mol Pd added.
[c] Data from [8], oxidant $Pd_3(OAc)_6$, no alkaline acetate added.
[d] Data from [19].
[e] Data from [21].
[f] 25 °C, $p(CO_2) = 90$ atm, $p(C_3H_6) = 12$ atm.
[g] 42 °C, $p_{CO_2} = 190$ atm, $p_{C_3H_6} = 12$ atm.
[h] 46 °C, $p_{CO_2} = 190$ atm, $p_{C_3H_6} = 12$ atm.

propylene oxidations in chloroform, dichloromethane, and 1,1,2-trichloroethane afforded allyl acetate in the yield of at least 99% and only traces of the sum of vinylic esters, acetone, and propanal (latter two were formed by hydrolysis of the vinylic esters with the residual water in the solvent) (see Table 1).

However, when 5% (v/v) of acetic acid was added to the reaction solution, noticeable amounts of isopropenyl and *n*-propenyl acetates, along with acetone and propanal (total yield about 10%) were formed, attesting to a sharp decrease in the reaction selectivity with respect to allyl acetate [22]. The same product distribution was found in liquid/supercritical CO_2.

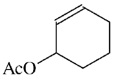
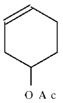
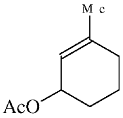
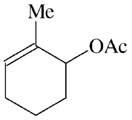
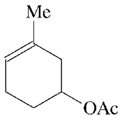
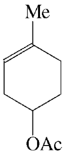
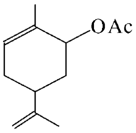
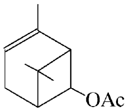
The predominance of the allylic pathway on going from carboxylic acid to the low-polarity aprotic solvents was also found in the oxidation of propylene, 1-hexene, cyclohexene, 1-methylcyclohexene, and α-pinene with the Pd^{II} acido complexes **1** and **2** containing achiral [CH_3COO and $(CH_3)_2CHCH_2COO$], chiral [S(+)-MeC*H(Et)COO and (+)-$CF_3CF_2CF_2OC^*F(CF_3)COO$], and racemic [(±)-$CF_3CF_2CF_2OC^*F(CF_3)$] carboxylate ligands (see Table 2 for cyclohexene oxidation) [23,24].

Table 2
Cyclohexene oxidative esterification with Pd^{II} carboxylates in aprotic solvents (Ar atm, concentration of reoxidants added 1 mol/mol Pd)

Solvent	Carboxylate ligand	Reoxidant	Reaction products (%)			
			Allyl: cyclohe-xene-2-ol ester	Homo-allyl: cyclohe-xene-3-ol ester	Allyl/Homo-allyl ratio	Other products
$CHCl_3$	OAc^-	–	≤1	≤1	∼**1**	C_6H_6 ≥98%
$CHCl_3$	OAc^-	Q[a]	61.3	38.7	**1.6**	C_6H_6 <1%
$CHCl_3$	OAc^-	$(PhCO)_2O_2$	52.9	44.1	**1.2**	C_6H_6 3.0%
i-C_5H_{11}OMe	OAc^-	Q[a]	65.36	34.64	**1. 9**	C_6H_6 <1%
Cyclohexene	$R_fCO_2{}^{-b}$ (racemic)	Q[a]	No reaction			
$CHCl_3$	$R_fCO_2{}^{-b}$ (racemic)$^{)}$	–	–	–		C_6H_6 62% C_6H_6 59%
$CHCl_3$	$R_fCO_2{}^{-b}$ (racemic)$^{)}$	Q[a]	70.59	29.41	**2.4**	C_6H_6 <1%
$CHCl_3$	$R_fCO_2{}^{-b}$ (chiral)	Q[a]	85.63	14.37	**5.9**	C_6H_6 <1%
$CHCl_3$	3-Methylbutyrate (achiral)	Q[a]	84.3	15.7	**5.4**	C_6H_6 <1%
$CHCl_3$	2-(±)-Methyl-butyrate	Q[a]	86.7	13.3	**6.5**	C_6H_6 <1%
$CHCl_3$	2-(+)-Methyl-butyrate	Q[a]	98.5	1.53	**64.4**	C_6H_6 <1%
THF	2-(±)-Methyl-butyrate	Q[a]	84.02	15.98	**5.3**	C_6H_6 <1%
THF	2-(+)-Methyl-butyrate	Q[a]	68.22	31.78	**2.2**	C_6H_6 <1%

[a] Q = *p*-benzoquinone.
[b] $R_fCO_2{}^- = CF_3CF_2CF_2OC^*F(CF_3)COO^-$.

Table 3
Oxidative acetoxylation of alkenes with Pd^{II} acetato complexes in chloroform at 20 °C

Alkene	Allylic acetates (%)[a]	Homoallylic acetates (%)[a]
1-Hexene[b]	*cis* + *trans*-Hex-2-en-1-ol (59) *cis* + *trans*-Hex-4-en-3-ol (33)	*cis* + *trans*-Hex-3-en-1-ol (8)
Cyclohexene	 (61)	 (39)
1-Methyl-cyclohexene	 (40)  (49)	 (3)  (8)
α-Pinene	 (10)	 (90)

[a] Yield based on the total esters formed.

It seems that the solvent and Pd nuclearity effects can overlap. For instance, the allylic pathway was found to predominate in the oxidation of cyclohexene with the trinuclear complex $Pd_3(OAc)_6$ in acetic acid with no extra OAc^- ion added [26,28].

2.1.2. Substrate effect

Both allylic and homoallylic esters can be produced by the oxidative esterification of higher alkenes with Pd^{II}. The most pronounced homoallylic esterification was found when cyclohexene was oxidized in the strongly acidic Pd^{II}—CH_3SO_3H—*p*-benzoquinone [20b,30] and Pd^{II}—HNO_3 [31] systems in acetic acid. Meanwhile, the composition and nuclearity of the Pd^{II} complexes operating in such complicated systems are unclear, which hampers interpretation of these results.

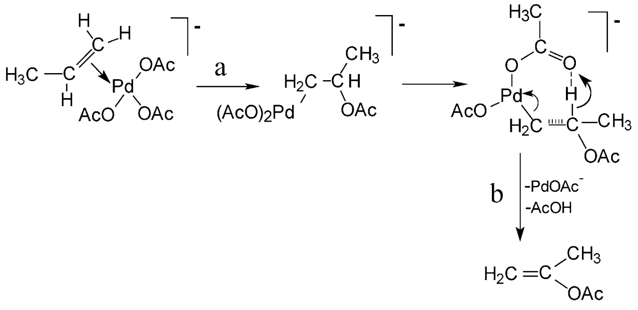
The substrate effect was studied in more detail [24] in the oxidation of 1-hexene, cyclohexene, 1-methylcyclohexene, and α-pinene in chloroform solutions containing the *in situ* prepared equilibrium mixture of $Pd_3(OAc)_6$, $(PNP)^+{}_2[Pd_2(OAc)_6]^{2-}$, and $(PNP)^+{}_2[Pd(OAc)_4]^{2-}$ complexes (see above). The oxidation of 1-hexene, cyclohexene, 1-methylcyclohexene, and α-pinene under these conditions was found to produce practically no vinylic esters. As can be seen in Table 3, allylic and homoallylic esters are the main reaction products in the oxidation of all the alkenes under study.[1]

2.2. Mechanistic speculations

On the basis of the above observations, some mechanistic conclusions can be drawn. A sharp increase in the selectivity to allylic oxidation of propylene on going from acetic acid to low polar aprotic solvents (Table 1) can hardly be understood within the framework of the conventional 1,2-oxypalladation mechanism (Scheme 3), which had been proposed in early studies [4,7,16].

According to this scheme, propylene oxidation should afford isopropenyl acetate when the stage "a" in Scheme 2 occurs as the Markovnikov-addition followed by the Pd–C bond heterolysis (stage "b"). When 1,2-oxypalladation occurs *via* the anti-Markovnikov-route, the second observable reaction product, *n*-propenyl acetate should be expected as shown in Scheme 4.

Meanwhile, the formation of the third reaction product, allyl acetate, requires not only anti-Markovnikov addition but also splitting of the H atom from the methyl group during Pd–H elimination.



Scheme 3.

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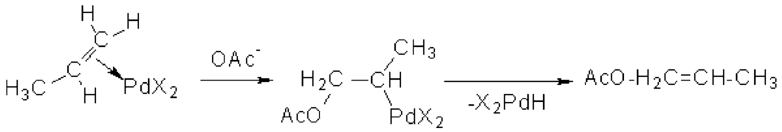
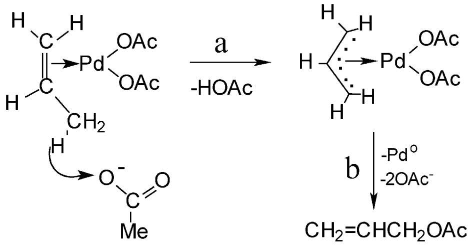
[1] Virtually, the same results were obtained in experiments with the use of tetraethylammonium acetate, $(NEt_4)^+OAc^-$, instead of $(PNP)^+OAc^-$.



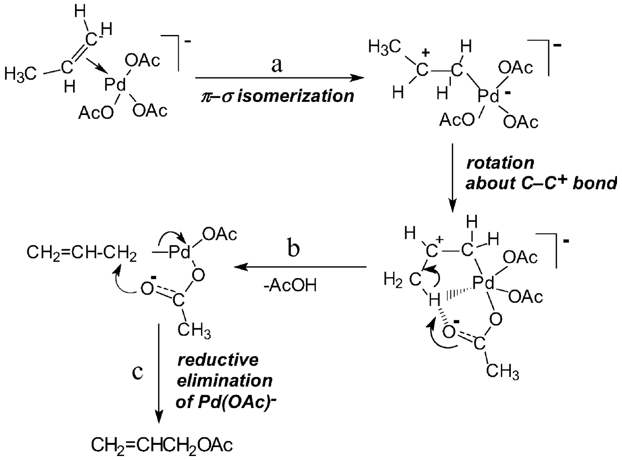
Scheme 4.

An alternative mechanistic viewpoint proposed by Kitching et al. [16] suggested the reaction to occur through an intermediate π-allyl complex (Scheme 5).

At first glance, this mechanism looks fairly attractive, especially because the palladium π-allyl complexes are well known since 1959, when the first stable complex $[\pi\text{-}C_3H_5\cdot PdCl]_2$ was synthesized by the reactions of $PdCl_2$ with allyl alcohol (Moiseev et al. [32]) or allyl chloride (Smidt and Hafner [33]). Involvement of π-allyl complexes in the mechanism like that shown in Scheme 6 seems to be quite plausible for alkene oxidations in an AcOH solution with high concentration of OAc^- anion, which is necessary for the transformation of the palladium η^2-alkene to η^3-allyl complex (stage "a" in Scheme 5). A study by Grennberg and Bäckvall [20b] gave evidence for the formation of the π-allylpalladium intermediate in the reaction between $Pd_3(OAc)_6$ and 1,2-dideuterocyclohexene in an AcOH solution. However, the way in which the π-allyl complex undergoes redox disproportionation into allyl acetate and Pd^0 (Scheme 3, stage "b") is still not clear. Studies of the reactivity of Pd^{II} π-allyl complexes toward nucleophilic and electrophilic reagents [34] showed that such a disproportionation occurs but in fact it is a side reaction accompanied by other transformations of the π-allyl complex not producing allylic esters.



Scheme 5.



Scheme 6.

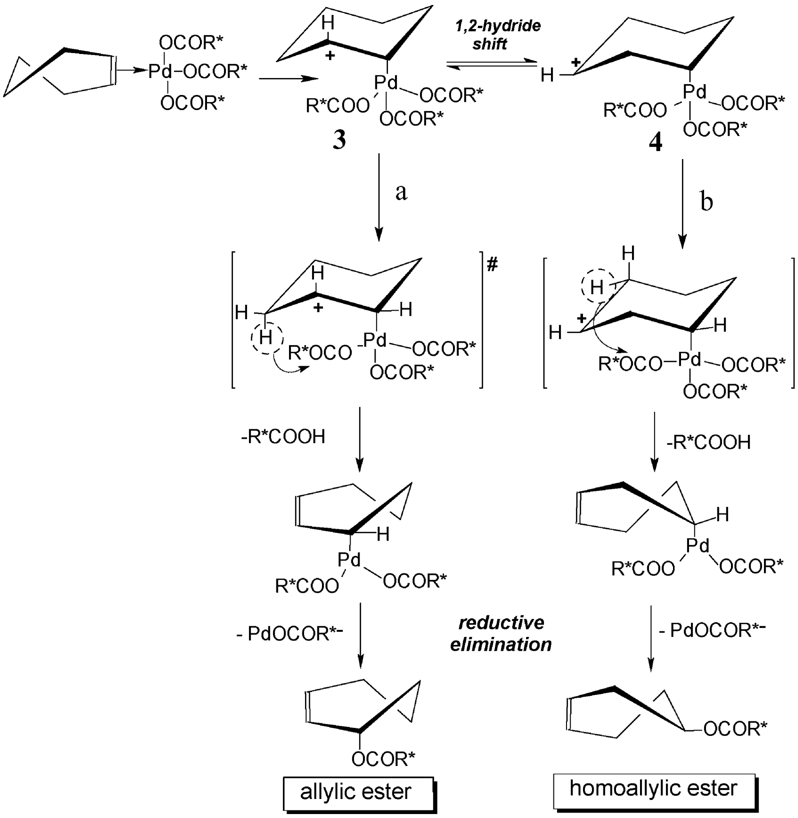
In the experiments under discussion [22–24], the "free" OAc^- anions were in negligible concentration ($[OAc^-] \leq 10^{-3}$ mol/l), being mostly bound into the composition of the complexes $[Pd_2(OCOR)_6]^{2-}$ and $[Pd(OAc)_4]^{2-}$. Minor amounts of OAc^- anions that remain unbound to palladium(II) should seem to exist as tight ion pairs with the bulky PNP cations, being barely accessible for attacking the η^2-alkene complex in a low polar organic medium ($CHCl_3$, CH_2Cl_2, THF).

The data obtained in aprotic media can be realized within the framework of the mechanism, whose key stage is an intramolecular electrophilic attack of the Pd^{II} atom on the coordinated alkene molecule without the OAc^- nucleophilic attack as shown in Scheme 6.

With a deficiency of free OAc^- anions, the electrophilic attack by the Pd^{II} atom to η^2-alkene ligand cannot be assisted with simultaneous attack of the outer-sphere OAc^- anion (so-called nucleophilic assistance). Under these conditions, the palladium σ-complex with a carbenium moiety is most likely to form (see Scheme 6, stage "a") and the coordinated carbenium group $CH_3CH^+CH_2$-Pd is expected to react intramolecularly, through proton elimination from the CH_3 group, possibly assisted by an additional Pd···H weak interaction (stage "b").

The observations [23] for cyclohexene oxidation in low-polarity aprotic media (Table 2) agree well with this mechanism. Noteworthy is the observation that homoallylic esters are always formed along with allylic esters. Within the framework of the "allylic" mechanism, this fact needs an additional assumption that reaction under question is accompanied by positional isomerization of the double bond in the allylic esters the first formed. However, such an isomerization is known to be catalysed by Pd metal and low-valent Pd complexes and is efficiently inhibited by *p*-benzoquinone and other oxidants capable of reoxidation of Pd^0 compounds [7,35,36]. Our observations showed that the oxidants in fact terminate the oxidative dehydrogenation and disproportionation of cyclohexene, which are also catalysed by Pd^0, but have no effect on the formation of homoallylic esters. Moreover, the assumed isomerization should produce vinylic esters, which in fact were not found in aprotic media.

All these data seem to support the mechanism shown in Scheme 7, which is similar to that in Scheme 6 and includes an inner-sphere attack of the coordinated carboxylate an-



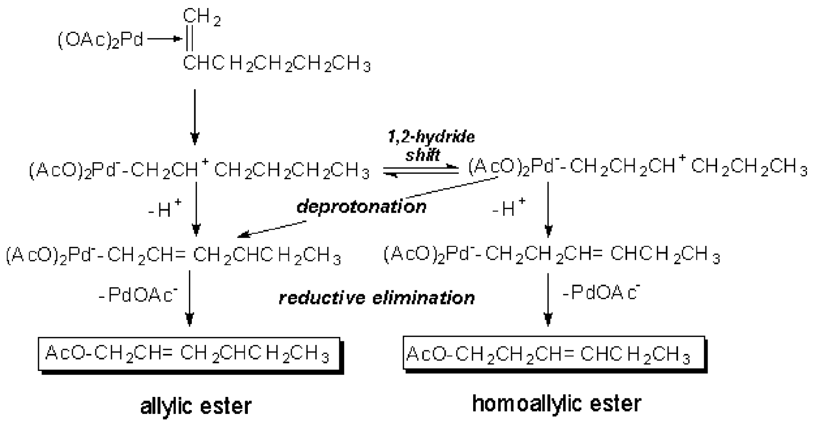
Scheme 7.

ion $RCOO^-$ to the CH_2 group of the σ-bound carbenium ligand.

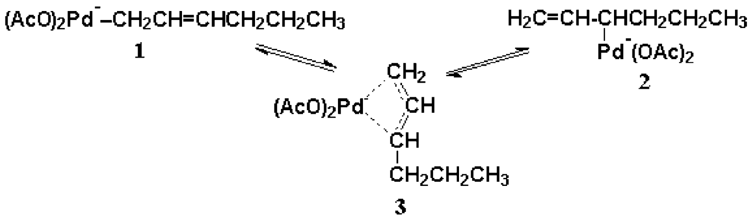
The mechanism in Scheme 7 assumes that the lifetime of σ-complex **3** is long enough to undergo a 1,2-hydride shift and displacement of the carbenium center to an adjacent C atom of the cyclohexane ring before redox decomposition of the original σ-complex **3**. The inner-sphere attack of the OAc^- ligand to the CH_2 group of the original σ-complex results in the formation of allylic ester (path "a"), whereas a similar process involving the isomerized σ-complex **4** affords homoallylic ester (path "b").

The data on the regioselectivity of oxidative esterification of 1-hexene in a chloroform solution [24] are also consistent with the "carbenium" mechanism (see Scheme 8).

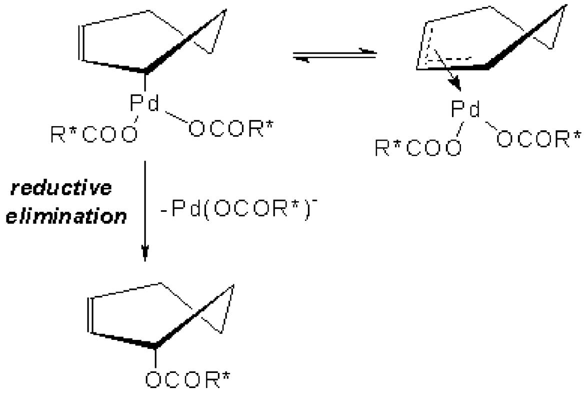
The "carbenium" mechanism of alkene oxidation (Schemes 7 and 8) is in fact closely related to the "allylic" mechanism mentioned above and shown in Scheme 6. According to numerous NMR observations (see, for instance, [34–36]), η^3-allylic complexes rapidly and reversibly isomerize in solution to σ-allylic complexes. Hence, Schemes 7 and 8 can be generalized by supplementing with the reversible π–σ-isomerization (Schemes 9 and 10), thus re-



Scheme 8.



Scheme 10.



Scheme 9.

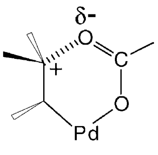
flecting the totality of the data on the allylic pathway of alkene oxidation with Pd^{II}.

The homoallyl pathway of alkene esterification, unlike the allylic one, has attracted less attention in the literature. The observation in the studies [20b,30,31] that the addition of strong acids like $MeSO_3H$ noticeably favors the homoallylic oxidation of cyclohexene, seems to agree with the Schemes 8 and 10, because strong acids should prevent both 1,2-oxypalladation and the transformation of η^2-alkene to η^3-allylic complex, favoring the formation of the σ-bound carbenium ligand.

Several points still remain to be clarified in these mechanisms.

(i) What is the driving force for the formation of the carbenium ion Pd–CH_2 C^+HR and factors facilitating its generation?
(ii) Why does the carbenium ion have sufficient time for its isomerization?
(iii) Why does the primary carbenium ion isomerize to the secondary ion? and, eventually,
(iv) What is the actual reason for distinctions between the reactions in RCOOH, H_2O, and ROH?

It seems that stabilization of the carbenium ion can be due somewhat to a Coulomb interaction $RHC^+\cdots O{=}C{-}O$ resulting in the formation of an intermediate cyclic structure of the type:



Such a hypothesis could give a reasonable account for distinctions between the reactions in different solvents. In the case of cyclohexene and its derivatives, the geometry of the above cycle can also determine the pathway of the carbenium ion isomerization and RCOOH elimination to produce either allylic or homoallylic ester.

3. Heterogeneous catalysis on nanoscale level

At first sight, the outcome of the catalytic Pd^{II}/Pd^0 cycle should be independent of the starting oxidation state of the palladium catalyst because the catalytic cycle could start from either Pd^{II} or Pd^0. Meanwhile, experiments showed that the selectivity of alkene oxidative esterification (Eq. (5)) depends to a great extent on the nature of and primarily on the oxidation state of the initial Pd species [37,38].

When the Pd^{II} complexes (e.g., $Pd_3(OAc)_6$, $Pd_2(OAc)_6{}^{2-}$, or $Pd(OAc)_4{}^{2-}$) are used as starting material for ethylene oxidative acetoxylation, a small (1–3%) quantity of water added to the NaOAc/AcOH solvent changes sharply the reaction route to produce mainly acetaldehyde instead of vinyl acetate. Unlike this, the Pd metal catalysts (e.g., Pd-black prepared by H_2 or N_2H_4 reduction of Pd^{II} complexes in combination with NaOAc or KOAc) provide the formation of vinyl acetate from ethylene and AcOH with high selectivity, regardless of the water content up to 10% [37a].

In propylene oxidation, the allylic pathway predominates in both the liquid- [37b,38] and vapor-phase [39,40] processes with the Pd metal catalyst and O_2 oxidizing agent, and the allylic versus vinylic selectivity is barely sensitive to the temperature and water content up to 10% of the latter. Analogously, the supported Pd metal catalysts produce vinyl acetate from ethylene and AcOH with high selectivity, regardless of the 0.2–10% water added [39,40].

These facts suggest two different routes of alkene activation to exist: (1) through palladium(II) and (2) through palladium metal or low-valent Pd clusters formed in the Pd^{II}/Pd^0 reaction system. In this connection, the question arises: what is the nature of the catalytically active Pd^0 species?

Experiments with different Pd metal samples (viz., finely ground bulk palladium metal and different Pd blacks prepared by reduction of K_2PdCl_4 and $Pd_3(OAc)_6$ with H_2, HCOONa, CO, N_2H_4, ethylene, and propylene in water, acetic acid, and ethanol) showed that none of these samples catalysed oxidative acetoxylation of ethylene and propylene, even when sodium or potassium acetate was added to the as-prepared Pd sample. Unlike this, when the Pd^{II} salts were reduced in a solution containing a base (NaOAc, 1,10-phenanthroline (phen), 4,4′-bipyridine (bpy), etc.), the Pd black formed exhibited high catalytic activity in the reaction [37a,b,38]. We can therefore conclude that the catalytically active Pd^0 (or low-valent Pd) species should contain an inherent base.

4. Pd cluster-catalysed alkene oxidation

4.1. Palladium cluster catalyst

Rather stable, catalytically active Pd species named the Pd-561 giant clusters [41] were synthesized by successive treatment of $Pd(OAc)_2$ with H_2 and O_2 in an AcOH solution containing 1/2 mole of an N-base (L = phen or bpy) per Pd atom [27,38,42]. Studies with TEM, HREM, electron diffraction, STM, NMR, EXAFS, elemental analysis, and the measurements of molecular mass and magnetic susceptibility revealed the empirical formula of the substance to be $Pd_{570\pm30}L_{63\pm3}(OAc)_{190\pm10}$. [38,42]. Within the framework of the Chini cluster model [43] this can be approximated by the idealized formula $[Pd_{561}L_{60}](OAc)_{180}$. The molecule of Pd-561 cluster consist of a positively charged metal core ~25 Å in diameter containing 570 ± 30 dense-packed Pd atoms (or 561 atoms in an idealized five-shall icosahedron or cuboctahedron-shaped core), ~60 neutral L ligands, which are bound to the surface of the metal core, and ~180 outer-sphere OAc^- anions; the latter counterbalancing the positive charge of the metal core [42] (Fig. 1).

The outer-sphere OAc^- anions can be replaced by other anions. For instance, the O^{2-} and $PF_6{}^-$ anions readily substitute OAc^- anions in an aqueous solution containing KPF_6, affording the giant cluster with the idealized formula $[Pd_{561}L_{60}O_{60}](PF_6)_{60}$ [38,42]. The Pd-561 giant clusters exhibit high catalytic activity in liquid-phase alkene acetoxylation under mild conditions (20–60 °C, 1 atm O_2), providing conversion of ethylene to vinyl acetate and propylene to allyl acetate in AcOH solutions and allylic (but not vinylic!) esterification of higher acyclic alkenes in solutions of carboxylic acids [27,38]. However, in the case of cyclic alkenes (e.g., cyclohexene and 1-methylcyclohexene) the main reaction route is redox disproportionation to the corresponding arene and cycloalkane (Zelinsky reaction):

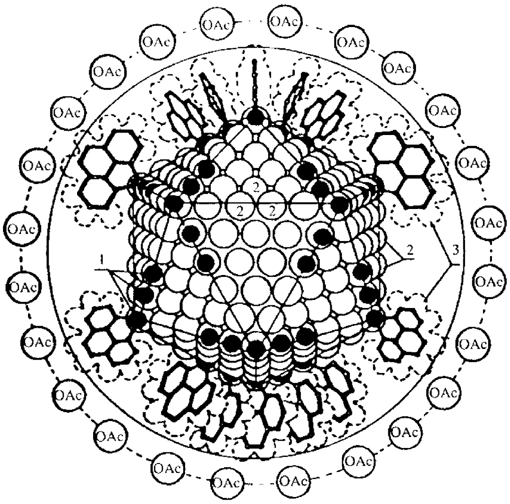


Fig. 1. Idealized structure of the Pd-561 cluster: (1) Pd atoms coordinated to phen ligands; (2) Pd atoms accessible for coordination of the anions or solvent molecules; (3) van der Waals' contours of the coordinated phen ligands.

$$3\,\textit{cyclo}\text{-}C_6H_{10} = C_6H_6 + 2\,\textit{cyclo}\text{-}C_6H_{12}$$

Meanwhile, the oxidative esterification of acyclic alkenes (viz., ethylene, propylene, and 1-hexene) by O_2 in the presence of the Pd-561 giant clusters produces at least 95–98% of allylic esters. No decrease in the selectivity was found even in solutions containing up to 10% of water. The only side reaction with the Pd-561 catalysts is the subsequent oxidation of alkenyl esters to form ethylidene and allylidene diacetates, respectively. The soluble Pd-561 giant clusters provide no homoallylic oxidation and to a lesser extent promote side reactions compared to the commercial Pd metal catalysts, which are active at much higher temperatures.

4.2. Mechanism of reaction

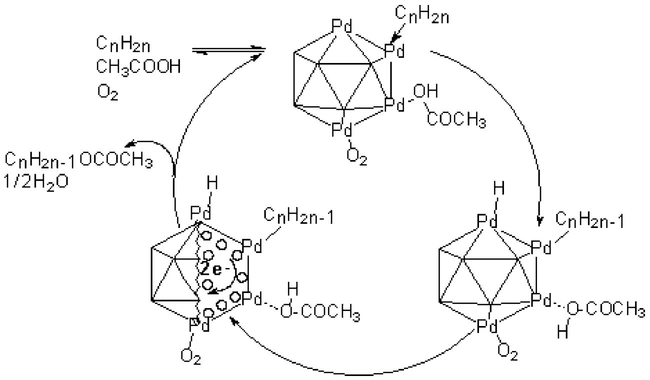
The reaction kinetics for the Pd-561-catalysed oxidation of ethylene and propylene obeys the following equation [38,42]:

$$r_0 = k[\text{Pd-561}]\frac{[C_2H_4][O_2][\text{AcOH}]}{(K_{\text{I}} + [C_2H_4])(K_{\text{II}} + [O_2])(K_{\text{III}} + [\text{AcOH}])}$$

The Michaelis–Menten character of the kinetics suggests that the formation of the reaction product is preceded by reversible coordination of the alkene, O_2, and AcOH molecules by the cluster.

The kinetic isotope effects provide evidence that the mechanisms of oxidative acetoxylation catalysed with Pd^{II} and low-valence Pd clusters are different. On the basis of kinetic data, including the H/D kinetic isotope effects, the following reaction mechanism has been proposed for the Pd-561 cluster-catalysed reaction [38] (Scheme 11).

The surface of the metal core of giant clusters is substantially screened by phen or bpy ligands that retard an access of the reactant and solvent molecules to the cluster metal core (Fig. 1). A study of the extra ligand effect on the kinetics of the Pd-561 cluster-catalysed oxidative acetoxylation of C_2H_4 and C_3H_6 in solutions of the giant cluster [27,38] showed that bulky extra ligands, which are capable of strong binding to Pd atoms (viz., PPh_3 and phen) exert only negligible effects on the rate of alkene oxidation. This is due to the fact that these ligands cannot reach the sites suitable for the coordination of the smaller molecules, C_2H_4, O_2 or AcOH. Smaller ligands, such as C_2H_5SH and SCN^-, effectively slow down oxidation. About 50 "poisonous" ligand



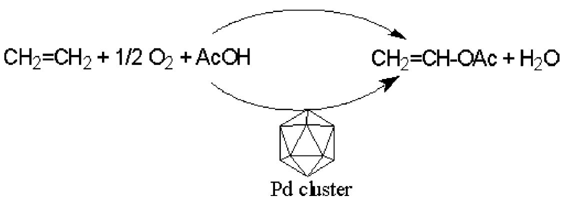
Scheme 11.

molecules per the Pd cluster are necessary to stop the oxidation of C_2H_4. Meanwhile, only ∼15 poison molecules per Pd-561 cluster are sufficient for complete inhibition of the C_3H_6 oxidation. This is in line with the estimation of the number of accessible surface centers on the surface of the cluster metal core based on the idealized model of the giant cluster molecule. Among 252 metal atoms in the outer layer of the Pd metal core, ∼20% (50 of 252) of this amount can participate in the catalytic oxidation of ethylene and ∼6% (15 of 252) are implicated in the reaction with the more bulky C_3H_6 molecule.

5. Conclusion

Hence, the Pd-catalysed oxidative esterification of alkenes can occur through two different pathways: either *via* the stepwise Pd^{II}/Pd^0 mechanism or through the route mediated by the low-valence Pd giant clusters as shown in Scheme 12.

Cluster-catalysed oxidative esterification of alkenes drastically differs from the Pd^{II}-catalysed reaction. First, the oxidation of alkenes by Pd^{II} is suppressed by donor ligands, even bulky ones such as PPh_3 and phen, due to strong complexation with Pd^{II}. In contrast, the rate of reaction catalysed by giant Pd clusters is unaffected by these ligands. Second, the rate of alkene oxidation by Pd^{II} in aqueous solution is inversely proportional to the H^+ concentration, and adding 1–2 M mineral acid quenches the reaction. But, alkene oxidation does not occur in neutral aqueous solutions of the Pd-561 clusters. The cluster-catalysed ethylene oxidation reaction starts only after addition of strong acids ($HClO_4$ or H_2SO_4), and its rate increase with increasing acid concentration and is maximal at the acid concentration, which is sufficient to stop the reaction of alkenes with Pd^{II}. Finally, the products of alkene oxidation mediated by Pd^{II} and Pd-561 clusters are different. In a 10% aqueous solution of H_2SO_4 containing the Pd-561 cluster, ethylene is oxidized successively to acetaldehyde and acetic acid at 323 K and 0.1 MPa [44]:



Scheme 12.

$$C_2H_4 + O_2 \rightarrow CH_3CHO \rightarrow CH_3COOH$$

Meanwhile, acetaldehyde is scarcely oxidized by Pd^{II} to acetic acid under these conditions. A more pronounced difference was observed for propylene: in acidic aqueous solution of Pd-561 cluster propylene is converted successively to allyl alcohol, acrolein, and acrylic acid [44]:

$$C_3H_6 + O_2 \rightarrow CH_2CHCH_2OH \rightarrow CH_2{=}CHCHO$$
$$\rightarrow CH_2{=}CHCOOH$$

Only traces of acetone were found in the reaction products, in contrast to the reaction mediated by Pd^{II}, in which acetone was almost a sole product.

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