Palladium Acetate as a Catalyst in the Oxidation of n-Hexenes and a Direct Preparation of tri-*hapto*-Hexenylpalladium Complexes

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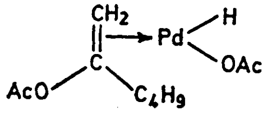
Summary Palladium acetate reacts with hex-1-ene and hex-*cis*-2-ene to form trinuclear and dinuclear *trihapto*-hexenylpalladium complexes with acetato-bridges and it acts as a catalyst in oxidation reactions of the olefins, some of which are of a free radical type.

The catalytic action of palladium acetate in the oxidation of olefins is well known[1] although the only mechanistic information concerns the "oxypalladation step".[2] We have elucidated the problem of selectivity between the various possible reactions of n-hexenes in the presence of palladium acetate.

Hex-1-ene (I) reacts with palladium acetate in acetic acid *in vacuo* at 25° to yield tetra-μ-acetato-bis-(1,2,3-tri-*hapto*-hexenyl)tripalladium, (II). Concurrently there is a rapid conversion of part (20%) of the palladium(II) into metal with consequent oxidation of the olefin to hexenyl acetates of which hex-1-en-2-yl acetate (III) is the major product (60 mol %). Also, (I) is isomerised selectively to *cis*-hex-2-ene (IV) and *trans*-hex-2-ene in the constant ratio of 1:5·0 with no hex-3-enes. After *ca.* 4 h the oxidation and isomerisation reactions become very slow but conversion of (II) into di-μ-acetato-bis-(1,2,3-tri-*hapto*-hexenyl)dipalladium (V) then proceeds. Similar trinuclear and dinuclear

2,3,4-tri-*hapto*-hexenyl complexes are formed from (IV) but its oxidation by palladium acetate is sluggish yielding mainly allylic esters (4%) before formation of the trinuclear complex is complete. The hexenylpalladium complexes are stable in acetic acid with respect to solvolysis or reduction and therefore the dinuclear series are the end-products of the reactions of palladium acetate *in vacuo*. This contrasts with the unstable nature of tri-*hapto*-cyclohexenylpalladium complexes.[3]

In the presence of oxygen (*ca.* 1 atm) (I) and (IV) undergo Pd catalysed oxidation.† In the case of (I) the initial rate is relatively fast while the palladium(II) remains in solution as palladium acetate but becomes slower after 4 h when conversion into the hexenylpalladium complex (II) is complete. The formation of (V) is inhibited by oxygen and in the presence of (II) the catalytic reaction proceeds through many cycles at a constant rate which is independent of the olefin concentration but dependent on both oxygen and palladium(II) concentrations. The essential features of the product distribution remained constant during both the fast and the slow stages, mole fractions being, typically (g.l.c.): hex-1-en-2-yl acetate, 0·71; hex-*cis*-2-en-2-yl acetate, 0·10; hex-2-en-1-yl acetate, 0·10; hex-1-en-3-yl acetate, 0·02; a mixture of *trans*-hex-2-en-2-yl acetate, hex-3-en-2-yl acetate, and hex-4-en-3-yl acetate 0·03; hexan-2-one, (VI), 0·01; mixed hexen-2-ols and hexen-2-ones, 0·02. Subsequently some allylic isomerisation[4] took place. Under conditions of catalytic reaction when water is present, palladium acetate catalyses the decomposition of (III) to (VI), but together (III) and (VI) comprise a time-invariant mole fraction of the oxidation products (*ca.* 0·65). The unsaturated alcohols and ketones were not present after stoicheiometric oxidation and their formation in catalytic reactions was suppressed by quinol (<1% of catalyst concentration). The inhibitor had little effect upon the rate or product distribution amongst the esters. Sodium acetate has no effect upon the rate but it enhances the mole fraction of hex-2-en-1-yl acetate amongst the products and promotes the isomerisation of other esters.



(VII)

In the catalytic oxidation of (IV) the mole fractions of products were: hex-1-en-3-yl acetate, 0·24; hex-2-en-1-yl acetate, 0·05; hex-3-en-1-yl acetate, 0·04; a mixture of hex-3-en-2-yl acetate, hex-4-en-2-yl acetate, and hex-2-en-3-yl acetate, 0·30; hexanones, 0·05; mixed hexanols and hexenones, 0·34. The kinetics of reaction were strikingly different from those of (I). There was an induction period of 2—4 h after which the rate of uptake of oxygen increased to a constant value. The reaction orders in (IV), oxygen, and palladium acetate were about 1·0, 0·7, and 0·3, respectively. Quinol (4×10^{-5} M) inhibits the oxidation totally.

We believe that oxidation of (I) proceeds by oxypalladation followed by elimination of PdH(OAc) to give (VI). Since the product distribution is the same in both the slow and fast stages of reaction it is likely that monomeric palladium acetate is the active catalytic species, being derived from $Pd_3(C_6H_{11})_2(OAc)_4$ in the slow stage. Successive addition and re-elimination of PdH(OAc) would lead to the isomerised esters while displacement of hex-1-en-2-yl acetate from (VI) by (I) would transfer the active catalyst for isomerisation onto the hydrocarbon. By contrast, the catalytic oxidation of (IV) has the characteristics of a free radical chain reaction.

The complexes $Pd_3(C_6H_{11})_2(OAc)_4$ undergo chemical exchange processes in solution since the ^1H n.m.r. spectra ($-60°$ to $+65°$) are similar to those of the dinuclear tri-*hapto*-allylic complexes.[5] Presumably the three palladium atoms are connected by acetato-bridges. Trinuclear complexes may be prepared from the dinuclear complexes and palladium acetate, equation (1). The reaction proceeds to the right but the reverse reaction may well be a source of free palladium acetate which is then catalytically active. The dinuclear complexes are catalytically inactive.

$$Pd_2(C_6H_{11})_2(OAc)_2 + \tfrac{1}{3}Pd_3(OAc)_6 \rightleftharpoons Pd_3(C_6H_{11})_2(OAc)_4 \qquad (1)$$

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† Solutions contained 0·04—0·004 M-palladium(II) and 0·26—0·07 M-hexenes. Rates were measured by uptake of oxygen. Hexenylpalladium complexes had satisfactory elemental analyses and molecular weights in chloroform and benzene.

[1] For a review see P. M. Maitlis 'The Organic Chemistry of Palladium, vols. 1 and 2, Academic Press, London, 1971.

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[4] P. M. Henry, *Chem. Comm.*, 1971, 328.

[5] J. Powell, *J. Chem. Soc. (A)*, 1971, 2239.