A New Superoxo-complex of Palladium that Oxidizes Alkenes to Epoxides

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A new palladium superoxo-complex, which can oxidize linear alkenes to epoxides, has been synthesized.

A peroxo-complex of palladium, AcOPd–O–O–R, prepared from palladium acetate and t-butyl hydroperoxide, is known to react with hex-1-ene producing a mixture of hexan-2-one and 2-acetoxyhex-1-ene.[1] The formation of these products and the absence of epoxide may be accounted for by assuming oxygen transfer into the alkene occurs *via* insertion of the alkene molecule into the Pd–OOR or Pd–OAc bond, followed by decomposition of the product of peroxy- or acetoxy-palladation *via* β-hydride shift or β-H elimination. The high reactivity of the Pd^{II} ion in oxypalladation and β-H elimination seems to explain the fact that the electrophilic attack of the oxygen atom of the peroxide group on the alkene does not contribute to the total rate of the oxidation, and also that epoxides are not formed.[2] We now report that we have found a palladium superoxo-complex which can oxidize linear alkenes, such as ethylene and propene, to epoxides.

The palladium superoxo-complex was prepared by agitating a solution of palladium acetate in chloroform [3 ml, $Pd(OAc)_2$ concentration 0.2 mol/l] with 30% hydrogen peroxide (1 ml) for 3—5 min. Prior to e.s.r. analysis, the brown chloroform layer was separated. The e.s.r. signal from the $O_2^{\cdot-}$ radical anion had a hyperfine structure indicating coupling to one ^{105}Pd nucleus with I 5/2 (g_1 2.108, g_2 2.011, g_3 2.001; A_1^{Pd} 6.7; A_2^{Pd} 3.5; A_3^{Pd} 5.4 G, see Figure 1). The concentration of $O_2^{\cdot-}$ co-ordinated to the palladium ion was about 10^{-2} mol/l ($CuCl_2 \cdot 2H_2O$ single crystal as reference).

The palladium superoxo-complex of proposed composition $AcOPdO_2^{\cdot}$ thus synthesized was quite stable. When dissolved in chloroform, 10% of the complex was decomposed at 300 K during 1 h, and when separated in the solid state together with palladium acetate [1% relative to $Pd(OAc)_2$] from chloroform, the complex could be stored at room temperature for several months. Furthermore, the complex showed high reactivity towards alkenes.

Addition of alkenes to a solution of the superoxo-complex in chloroform resulted in a rapid decrease in its concentration, reflected by the decrease in the e.s.r. signal intensity. The rate of the disappearance of the signal showed a first-order dependence on alkene concentration. With excess of alkene, the disappearance obeyed pseudo-first-order kinetics with respect to $AcOPdO_2^{\cdot}$, the conversion being 90%. The first-order rate constants determined for various alkenes at 300 K (initial concentration of superoxo-complex 5 mmol/l and of alkene 0.3 mol/l) are as follows: ($10^3\,k$/s^{-1}) $CH_2{=}CH_2$, 3.3; $MeCH{=}CH_2$, 5.1; $Me_2C{=}CH_2$, 5.1; and $Me_2C{=}CMe_2$, 1.2.

^1H N.m.r. data show that the reaction of the alkenes with the superoxo-complex produced epoxides, oxirane being the only product from ethylene. Propene yielded acetone, along with the epoxide (2 : 1). The total yield of oxidation products after the reaction was 1 mol per 1 mol of the superoxo-complex.

Many superoxo-complexes of transition metals are now known (Ni^{II}, Zn^{II}, Co^{II}–Co^{III}, Ce^{III}, Cr^{III}, Th^{IV}, Ti^{IV}, Zr^{IV}, Sn^{IV}, Hf^{IV}, V^{V}, Nb^{V}, and Mo^{VI}).[4—7] However, either these complexes are unreactive, or data on their reactivity in the oxidation of alkenes are not available, with the sole exception

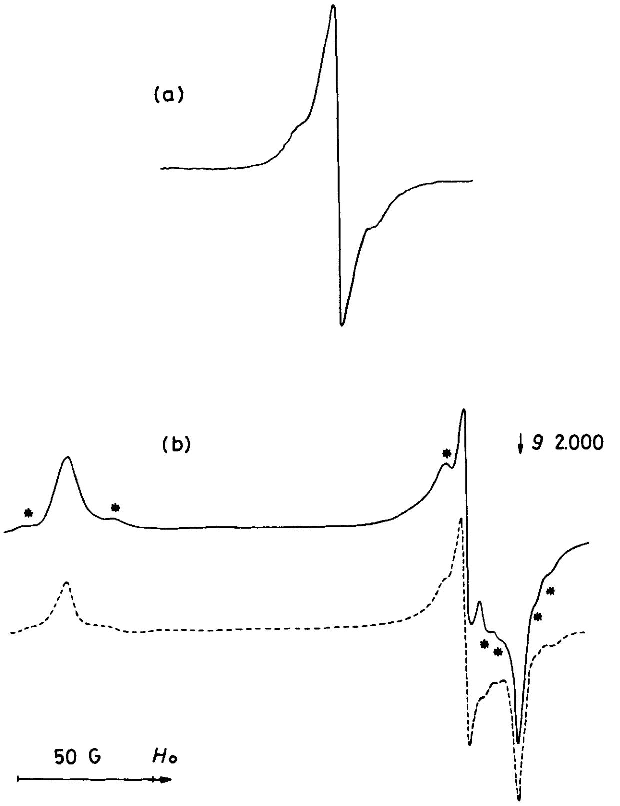

Figure 1. E.s.r. spectra of the palladium superoxo-complex (10^{-2} mol/l) in $CHCl_3$ at (a) 300 K and (b) 77 K. The components of the hyperfine structure due to the ^{105}Pd nucleus are denoted by asterisks, and the simulated[3] spectrum (BESM-6 computer) by a broken line. 1 G = 10^{-4} T.

of the cobalt superoxo-complex $LCo^{III}–O_2^{\cdot}$ (L = tetra-*p*-tolylporphyrin), which oxidizes cyclohexene to the epoxide in 13% yield.[8] In the present work, not only has the formation of a palladium superoxo-complex been observed for the first time, but its high reactivity for the oxidation of linear alkenes to epoxides has also been demonstrated.

There are two unusual features of this alkene oxidation by the palladium superoxo-complex. A comparison of the superoxo-complex, which may be regarded as containing electrophilic oxygen, with similar agents, such as peroxy-acids,[9] shows that the rate of formation of oxirane during the oxidation of ethylene by the superoxo-complex is ~10^3 times greater than the rate of oxidation by peroxy-acids. Furthermore, whereas the rate of oxidation by peroxy-acids increases markedly upon increasing the number of methyl substituents near the double bond,[9] the rates of oxidation of the four alkenes studied here are similar. These features require further investigation.

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