Homogeneous Autoxidation Catalysis by Palladium(0) Complexes

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Summary Autoxidation catalysis by arylphosphinepalladium(0) complexes depends on the particular arylphosphine ligands employed.

HOMOGENEOUS catalysis of hydrocarbon autoxidation by several diamagnetic oxygen complexes has been reported.[1] Recent investigations indicate that these reactions have the characteristics of radical chain processes initiated by hydroperoxide decomposition.[2] These results do not exclude the possibility of direct chain initiation. However, such a process would be masked rapidly by hydroperoxide decomposition.

Less equivocal results have been obtained in the autoxidation of peroxide-free cumene. In the presence of catalytic amounts (*ca.* 0·17 mmole/l) of certain triarylphosphinepalladium(0) complexes, reaction occurred readily at 35° under 1 atm. O_2. Under these conditions, no hydroperoxide decomposition was found and no reaction was noted in the absence of the catalysts. Initial oxygen absorption rates were influenced by the nature of triarylphosphine ligands in the Pd^0 complexes employed. Thus, in the presence of tris(tri-*p*-tolylphosphine)palladium(0) (I), these were consistently 2—5 times greater than those observed with tetrakis(triphenylphosphine)palladium(0)(II). Tetrakis(tri-*p*-chlorophenylphosphine)palladium(0) (III) was inactive. Similar observations have been made in the case of the previously reported[3] autoxidation of triarylphosphines. In benzene solution at 40° and 1 atm. O_2, absorption rates in the presence of (I) were 3—6 times those observed with (II). Compound (III) reacted with oxygen to yield phosphine oxide, but lost catalytic activity rapidly. Corresponding Pd^{II} complexes, such as bis(tri-*p*-tolylphosphine) palladium(II) chloride, although soluble, did not catalyse the above reactions.

Other materials capable of oxygen-complex formation such as tetrakis(triphenylphosphine)platinum(0) (IV) and bis(triphenylphosphine)carbonyliridium(I) chloride (V) displayed some catalytic activity in cumene autoxidation. However, in these cases, long induction periods were observed which could be eliminated by addition of cumene hydroperoxide. Complex (V) reacted rapidly with cumene hydroperoxide under anaerobic conditions with evolution of CO_2. It appears, therefore, that (IV) and (V) catalyse hydroperoxide decomposition rather than formation.

The results obtained with Pd^0 complexes in peroxide-free systems can be interpreted along the lines suggested for initiation by cobalt(II)[4] and copper(I)[5] complexes, *i.e.*, by formation of superoxidic oxygen complexes capable of hydrogen abstraction (eqs. 1—4). Hydride abstraction is also compatible with suggestions concerning analogies between complexed and singlet oxygen[6] and would seem to be more consistent with the diamagnetism of the complexes in question.

$$(Ar_3P)_4Pd + 2O_2 \rightarrow (Ar_3P)_2PdO_2\cdot + 2Ar_3PO \qquad (1)$$

$$(Ar_3P)_2PdO_2\cdot + RH \rightarrow (Ar_3P)_2PdO_2H + R\cdot \qquad (2)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (3)$$

$$RO_2\cdot + RH \rightarrow RO_2H + R\cdot \qquad (4)$$

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