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PRODUCTION OF PEROXIDIC COMPOUNDS FROM PHENOLS BY AQUEOUS TITANIUM(IV) - HYDROGEN PEROXIDE OXIDANT SYSTEMS

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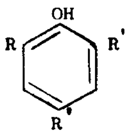
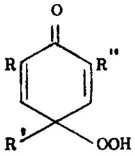
By using titanium(IV) compounds as catalysts for reactions of phenols with hydrogen peroxide in partly aqueous media, we observe oxidative effects which have both preparative and mechanistic interest. In numerous related investigations of titanium catalysis[1,2,3] attention has been focussed on applications of e.s.r. spectroscopy to aqueous Ti(III)-H_2O_2 systems, under fast-flow conditions, both in the absence and presence of organic substrates. Transient radicals have thus been identified, but comparatively little information has become available concerning the nature and yields of end products of the resulting oxidations of substrates.

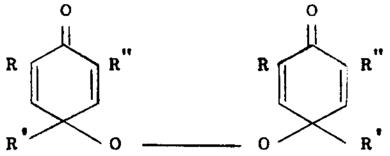
We find that titanium, introduced as a Ti(IV) species, effectively catalyses oxidation by hydrogen peroxide, and, when a 2,4,6-trialkylphenol (1) is the substrate, the 4-hydroperoxycyclohexa-2,5-dienone (2) is the major product of the reactions. Six such phenols (2,4,6-trimethyl-, 2,4-dimethyl-6-t-butyl-, 2,6-dimethyl-4-t-butyl-, 2-methyl-4,6-di-t-butyl-, 4-methyl-2,6-di-t-butyl- and 2,4,6-tri-t-butyl-phenol) gave the corresponding hydroperoxides in yields of ~ 10% to ~ 90% when the oxidations were carried out in aqueous t-butanol at 40° for 5-25 hr. The most responsive was 2,6-di-t-butyl-4-methylphenol, which gave the hydroperoxide (2; R,R" = Bu^t, R' = Me) (60-90%), previously reported as a product from autoxidation of the phenol in the presence of bases[4] or of a cobalt complex.[5]



(1)



(2)



(3)

Titanium(IV) was introduced into reaction mixtures as the aqueous tetrachloride or as the crystalline biscyclopentadienyl complex, $TiCl_2(C_5H_5)_2$.[6] Oxidation of the phenols was accompanied by decomposition of some of the hydrogen peroxide to oxygen, and excess of the reagent was therefore employed. Typically, the chosen molar ratio, phenol : H_2O_2 : Ti(IV), was 1 : 4 : 0.04-0.08. The composition of resulting mixtures of products varied with the concentration of reagents and with other factors. Among the minor constituents (commonly ~ 1-10% each) were products in which coupling had occurred through a para-methyl group (i.e., bibenzyls or stilbenequinones) and others in which CH_3 had undergone oxygenation to CH_2OH, CHO, or CO_2H; quinones and hydroxydienones (2; with OH in place of OOH) also appeared. Peroxidic products also included derivatives in which the OOH group of (2) was modified to $OOBu^t$; one phenol yielded a peroxo-bridged dimer (3; R, R', R" = Bu^t); certain products from other phenols appear to be 2-hydroperoxycyclohexa-3,5-dienones, or to have transannular peroxidic structures.

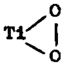
In the previous e.s.r. studies,[1] signals observed in the absence of substrates were attributed to hydroxyl radicals, arising from a Fenton-type redox reaction:

$$Ti^{3+} + H_2O_2 \longrightarrow Ti^{4+} + HO^- + HO\cdot$$

This assignment was later revised and the signals were attributed to species formed by interaction of hydroxyl radicals with titanium(IV) peroxide complexes.[2,3,7] Specifically, the Ti(IV) species $Ti\text{-}O\text{-}O\cdot^{3+}$ was suggested.[3] On the other hand, it has been argued that hydroxyl radicals, and not metal complexes, are responsible (by adduct formation or hydrogen abstraction) for the transient radicals which are given by organic substrates and are detected in the fast-flow systems.[1,7]

Under the conditions we employed the titanium catalyst functions mainly as a carrier for pairs of peroxidic oxygen atoms, and an outline reaction scheme of the following type may be appropriate:

$$\begin{tikzcd}
\text{Ti(IV)} \arrow[r, "(H_2O_2)"] & \begin{array}{l}\text{peroxidic}\\ \text{Ti(IV) complexes}\end{array} \arrow[r, "\text{(phenol)}"] \arrow[d, "(4)"] & \begin{array}{l}\text{Ti(IV) species with}\\ \text{peroxidic and phenolic}\\ \text{ligands}\end{array} \arrow[d] \\
 & O_2 + \text{Ti species} & \begin{array}{l}\text{phenolic oxidation}\\ \text{products + Ti species}\end{array}
\end{tikzcd}$$

The peroxidic titanium(IV) complexes (4) may begin as structures of the type Ti(IV)-OOH, but complicated reaction sequences lead to mono- and poly-nuclear species, which include Ti-O-O-Ti and  linkages.[8] An intermediate step in the production of oxygen and of peroxidic phenol derivatives may be the conversion of Ti(IV)-OOH (or other peroxidic complexes) into Ti(III)-OO· (*i.e.*, electron-transfer may occur, giving a complexed $^{-}$OO· radical-ion). Conversion of Ti(IV) into lower oxidation states is a feature of Ziegler-Natta polymerisation catalysis[9] and of van Tamelen's deoxygenative coupling reaction,[10] but in these cases powerful reductants are present.

The intermediacy of HOO· radicals has been postulated to account for production of the hydroperoxide (2; R,R" = Bu^t, R' = Me) in oxidations of 2,6-di-t-butyl-4-methylphenol by hydrogen peroxide in the presence of iron, copper, or cobalt ions.[11] Testing these metal ions under similar experimental conditions to those employed for titanium, we find them relatively ineffective catalysts for production of the hydroperoxide. On the other hand, we observe similar effectiveness to that of titanium if we employ some metals which are closer to it in the periodic table and which likewise readily form peroxidic complexes; molybdenum(VI), in the form of molybdate ion, is a particularly good catalyst for hydroperoxide formation.

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