New Routes to Hydrogen Peroxide: Alternatives for Established Processes?

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Hydrogen peroxide is produced industrially on a megaton scale. Aqueous solutions (3–85 weight% of H_2O_2) are of technical importance in a series of industrial processes. Most of the hydrogen peroxide is used for ecological reasons to replace chlorine and chlorine oxides in paper production. Further important applications are in the synthesis of fine chemicals, treatment of drinking and waste water, etching and purification in the electronic industry, bleaching of fabrics, and metallurgic processes. The cosmetic and pharmaceutical industries also makes use of its disinfecting properties.[1] While hydrogen peroxide has been known for more than 180 years, these applications have only been set up during the last few decades.

From 1818, when it was discovered by Thénard,[2] up to the beginning of the 20th century, solutions containing about 3% of hydrogen peroxide could only be obtained by the hydrolysis of barium peroxide with sulfuric acid (world production in 1900 was about 2000 t). Investigations on the electrolysis of sulfuric acid, carried out at the Consortium für Elektrochemische Industrie, proved the formation of peroxomono- and peroxodisulfuric acid and finally resulted in a new and economically favorable process for the production of more highly concentrated solutions of hydrogen peroxide with increased purity and stability.[3] On the basis of the work of Manchot,[4] Riedel and Pfleiderer (BASF) developed the anthraquinone process between 1935–45.[5] This process, which is used at the moment in most of the technical hydrogen peroxide plants worldwide, allows the production of ultrapure and highly concentrated solutions of hydrogen peroxide under economically beneficial conditions. In addition, a series of alternative ideas for the generation of hydrogen peroxide has been worked out: autoxidation of isopropanol, direct reaction of hydrogen and dioxygen in the presence of silent discharges or in the presence of transition metal catalysts, or cathodic reduction of dioxygen. However, there is no alternative to the established anthraquinone process. Although still far from a technical breakthrough, two new routes to hydrogen peroxide have recently begun to attract attention.

Beside its technical potential, hydrogen peroxide also plays an important role in the biosphere. It is formed in small amounts in living organisms as a by-product of autoxidation reactions or during the one-electron reduction of dioxygen. The superoxide and hydroperoxo radicals created in the latter process undergo conproportionation either spontaneously or enzyme catalyzed (superoxide dismutase) to give hydrogen peroxide and dioxygen. As a consequence of its high toxicity, efficient mechanisms for the decomposition of hydrogen peroxide had to be developed by all organisms. But hydrogen peroxide is also used as an oxidizing agent in the metabolism of the cell. For this purpose it is synthesized enzymatically, often using dioxygen for the oxidation of organic substrates. Recently, two groups succeeded independently in modeling the biological features and function of galactose oxidase by mono- and dinuclear copper complexes.[6, 7] Since the biochemical importance of these results has already been a matter of discussion here in this journal,[8] these publications will only be cited in terms of their potential for the biomimetic synthesis of hydrogen peroxide. The broad spectrum of substrates accepted by galactose oxidase not only allows the oxidation of the primary OH group of galctose to give the corresponding aldehyde, but also enables the conversion of a series of simple primary alcohols. This observation is a common feature of the enzyme and the model complexes: oxidation of an alcohol in the presence of dioxygen generates the carbonyl compound and one equivalent of hydrogen peroxide. Primary alcohols are converted with higher rates than secondary alcohols. Only minor amounts of side products (from C-C coupling and over-oxidation) are detected. These biomimetic processes may finally result in a technical application, not only for the selective formation of aldehydes and ketones but also for the generation of hydrogen peroxide, when further ligand optimization leads to catalysts of improved stability and activity.

Ligand optimization had a decisive influence on the success of Bianchi, Ricci, and co-workers.[9] The idea of using palladium for the synthesis of hydroygen peroxide in a two phase system can be traced back to 1979 with the results of Ermakof et al., who obtained the compound by reacting dioxygen, carbon monoxide, and water in the presence of palladium acetate and triphenylphosphane.[10] As a result of a rapid oxidation of the phosphane ligands, the turnover numbers of this system were too low for a technical application. A good reason for a reinvestigation of these results may be found in the thermodynamics of Equation (1).

$$O_2 + CO + H_2O \rightarrow H_2O_2 + CO_2;\ \Delta G^0 = -134\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

In the new two-phase procedure (1,2,4-trichlorobenzene or toluene, 2-methyl-2-butanol/water) of EniChem, aromatic N,N-chelate ligands such as 1,10-phenanthroline, which are quite inert to oxidation relative to phosphanes, are used to stabilize the palladium catalyst. High pressure (6500–7500 kPa O_2 and 600 kPa CO), a reaction temperature of about 70 °C, and the addition of an excess of acids that form weakly coordinating anions such as CF_3COOH, $C_7F_{15}COOH$, or $CH_3C_6H_4SO_3H$ ([Pd]:[acid] = 1:40) are obligatory for high yields. Optimized conditions give solutions of hydrogen peroxide up to 8%. Additionally the chemical structure of the chelate ligand ([Pd]:[ligand] = 1:4–1:8) was found to be crucial for the efficiency of the catalytic system. The best results were obtained using 2,9-dimethyl-4,7-diphenyl-1,10-

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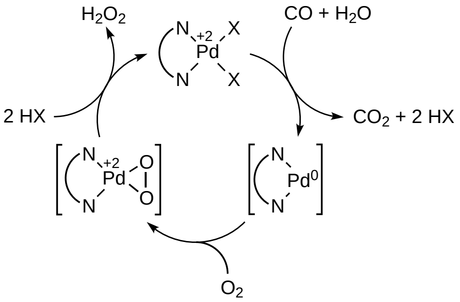
phenanthroline. It seems that the methyl substituents in the 2- and 9-positions prevent the formation of dinuclear, catalytically inactive palladium complexes. It has been found, that electron-withdrawing (Cl) or bulky substituents (n-C_4H_9, C_6H_5) in these positions lead to a decreased activity. The pronounced steric effects are quite surprising, since only small reactants (CO, O_2, H_2O) are converted at the palladium center. The palladium complex of 2,9-dimethyl-1,10-phenanthroline is too soluble in the aqueous solution, which leads to a complete loss of activity and further proves that the conversion should take place in the organic phase. This lack of reactivity can either be overcome by the application of the long-chain perfluorooctanoic acid as the co-reagent or by introducing phenyl substituents in the 4- and 7-positions of the chelate ligand.

The formation of palladium peroxo complexes, starting from Pd^{II} precursors, is proposed by the authors as a basis of a mechanistic discussion (Scheme 1). Such complexes, stabilized by phosphane ligands, have been known for a long time.[11] However, analogous systems bearing nitrogen donors have not yet been reported. The reduction of Pd^{II} to Pd^0 with carbon monoxide in aqueous systems is known to give CO_2. This reaction is fast in the presence of weakly coordinating anions.[12]



Scheme 1. Proposed reaction mechanism for the Pd-catalyzed reduction of dioxygen to H_2O_2. $X = CF_3CO_2$, $C_7H_{15}CO_2$, $CH_3C_6H_4SO_3$.

Unfortunately, the authors do not discuss the selectivity of their process. Carbon monoxide[13] as well as carbon dioxide[14] undergoes an insertion reaction in the O-O bond of $[(PPh_3)_2Pd(\eta^2\text{-}O_2)]$ and in both cases $[(PPh_3)_2Pd(\eta^2\text{-}CO_3)]$ is formed. Insertion of CO_2 probably first leads to the percarbonato complex $[(PPh_3)_2Pd(\eta^2\text{-}CO_4)]$, which gives $[(PPh_3)_2Pd(\eta^2\text{-}CO_3)]$ by oxidation of PPh_3. In principle, both insertions may be possible for the corresponding N,N-chelate complexes of palladium (CO may be used for the reduction of the percarbonato complex) and would not produce any hydrogen peroxide but only consume carbon monoxide and dioxygen ($2CO + O_2 \rightarrow 2CO_2$). The answering of such questions, in combination with a further ligand optimization and mechanistic investigations, are of high importance for a possible technical application of the new hydrogen peroxide process.

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