A Broad Spectrum Catalytic System for Removal of Toxic Organics from Water by Deep Oxidation

Annual Progress Report
September 15, 1996 - September 14, 1997

AYUSMAN SEN
Department of Chemistry
The Pennsylvania State University
University Park, PA 16802
Phone: (814) 863-2460 FAX: (814) 863-8403
E-mail: asen@chem.psu.edu

September, 1997

U. S. Department of Energy
Contract No. DE-FG07-96ER14694
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.
ABSTRACT

During the first year, the palladium-catalyzed deep oxidation of toxic organics by dioxygen in aqueous solution was examined in some detail. The research performed has established the viability of the catalytic system to effect the deep (and complete) oxidation of a very wide range of organic substrates under mild conditions. One significant observation was that chemical warfare agent models containing phosphorus-carbon and sulfur-carbon bonds could be eliminated by using this procedure.
This report summarizes the work done in the first year. During this period we have worked on the palladium-catalyzed process for the deep oxidation of several classes of toxic organics compounds. The results to date are summarized below.

We had earlier described a catalytic system for the deep oxidation of toxic organics, such as benzene, phenol and substituted phenols, aliphatic and aromatic halogenated compounds, organophosphorus, and organosulfur compounds. In this system, metallic palladium was found to catalyze the oxidation of the substrate by dioxygen in aqueous medium at 80-100°C in the presence of carbon monoxide. For all the substrates examined, deep oxidation to carbon monoxide, carbon dioxide, and water occurred in high yields, resulting in up to several hundred turnovers over a 24 h period. Mechanistic studies indicated that the overall transformation encompassed three catalytic steps in tandem (Scheme 1). The first was the water-gas shift reaction involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involved the combination of dihydrogen with dioxygen to yield hydrogen peroxide. The third step
involved the metal catalyzed oxidation of the substrate by hydrogen peroxide.


Because of a pressing need for new procedures for the destruction of chemical warfare agents, we have examined in detail the deep oxidation of appropriate model compounds containing phosphorus-carbon and sulfur-carbon bonds using the same catalytic system. As described below, we have observed the first efficient catalytic oxidative cleavage of phosphorus-carbon and sulfur-carbon bonds under mild conditions, using dioxygen as the oxidant.

In water, metallic palladium was found to catalyze the deep oxidation of a number of organophosphorus and organosulphur...
compounds by dioxygen at 90°C in the presence of carbon monoxide. For example, starting with trimethylphosphine oxide, the phosphorus-containing products formed by sequential P-C cleavage were dimethylphosphinic acid, methylphosphonic acid, and phosphoric acid. A similar reaction sequence was also observed for triethylphosphine oxide, except that products formed by partial oxidation of the ethyl groups, such as phosphonoacetic acid, were also seen as intermediates. The deep oxidation of dimethyl and diethyl sulfides proceeded through the intermediacy of the corresponding sulfoxides. For the methyl derivatives, the ease of oxidation decreased in the order: \((\text{CH}_3)_2\text{S} > (\text{CH}_3)_2\text{SO} > (\text{CH}_3)_2\text{SO}_2\) and is consistent with the catalytic system acting as an electrophilic oxidant.

In addition to the achievements described above, we have unpublished results in several other areas. For example, we have investigated the possibility of using dihydrogen rather than carbon monoxide as a coreductant in the catalytic deep oxidation of substrates (cf., Scheme 1). Even more attractive from a practical standpoint is the possibility of using a mixture of carbon monoxide and dihydrogen (synthesis gas). Indeed, experiments indicated that it was possible to substitute carbon monoxide by dihydrogen or synthesis gas. Significantly, in the case of nitro compounds, the deep oxidation in fact proceeded faster when dihydrogen rather than carbon monoxide was the coreductant.

We are also investigating the eventual fate of the nitrogen functionality present in organic substrates when they underwent
deep oxidation. Interestingly, a significant amount of ammonia was formed from a wide range of nitrogen functionalities.

In conclusion, research performed in the first year has established the viability of the palladium-based catalytic system to effect the deep (and complete) oxidation of a very wide range of organic substrates under mild conditions using dioxygen as the oxidant.

Publications


PROPOSED RESEARCH

Toxic organics in water constitute a very serious and persistent environmental hazard. Many are difficult to remove efficiently either through bioremediation or by presently known catalytic systems. Over the course of next two years we plan to continue our research on new catalytic systems for the deep oxidation of toxic organics and polymers. As described in the original proposal, the research will encompass (a) the elucidation of the detailed mechanism of oxidation, including the identification of the active species and the nature of the bond-breaking and oxidation steps, and (b) the identification of the classes of organics and polymers that can be efficiently oxidized and thereby removed from water. The ultimate goal of the research is the design of one or more cleanup systems that would be useful from a practical standpoint. While the design of a procedure for removal of organics and polymers from water would be the first priority of research, the use of the same catalyst system for the deep oxidation of non-aqueous phase organics in either a mixed solvent system or in a two-phase (water/liquid organic substrate) system will also be investigated.