Broad Spectrum Catalytic System for the Deep Oxidation of Toxic Organics in Aqueous Medium Using Dioxygen as the Oxidant

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Abstract: In water, metallic palladium was found to catalyze the deep oxidation of a wide variety of functional organics by dioxygen at 80−90 °C in the presence of carbon monoxide or dihydrogen. Several classes of organic compounds were examined: benzene, phenol and substituted phenols, nitro and halo organics, organophosphorus, and organosulfur compounds. In every case, 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. For substrates susceptible to hydrogenation, the conversions were generally higher with dihydrogen than with carbon monoxide. For organophosphorus compounds, the system presents the first examples of catalytic cleavage of phosphorus−alkyl bonds.

This paper encompasses the description of a catalytic system for the deep oxidation of toxic organics to carbon monoxide, carbon dioxide, and water in aqueous medium using dioxygen as the oxidant.[1] Two broad classes of organic compounds have been examined: those that model the organic pollutants found in water and those that model the common chemical warfare agents.

Toxic organics in water constitute an important environmental hazard.[2] Many are byproducts of industrial production. Several are introduced into aqueous systems through their usage, e.g., as biocides. Additionally, chlorinated organics often result from the conversion of organic impurities during chlorination of municipal water. Any procedure for the removal of toxic organics from water must meet the following criteria. First, the process must be economical, i.e., only inexpensive reagents and catalysts may be used. Second, the procedure should be applicable to a broad spectrum of toxic organics with a variety of functional groups. Finally, the procedure should not result in the introduction of anything to the water that needs to be removed subsequently, i.e., simultaneous water purification and contaminant destruction should be feasible.

One obvious solution to the problem is bioremediation.[3] However, many of the toxic organics are xenobiotic in character. In addition, when enzymes with low substrate specificity encounter foreign molecules, products that are xenobiotic often result. Among the catalytic oxidation systems, two that have been studied most extensively are the TiO_2-catalyzed photo-

oxidations[4] and the "Fenton" systems involving H_2O_2 and a soluble transition metal catalyst.[5] Again, although they have the advantages of broad substrate applicability and cleanliness, these systems are not optimal in many situations. For example, photons are relatively expensive, and the photooxidation systems cannot be employed where there is a dearth of sunlight or where large volumes of contaminated water are involved. In Fenton oxidations, a portion of the H_2O_2 is wasted because of a parallel (metal-catalyzed) decomposition pathway. Additionally, soluble catalysts that are usually used are difficult to remove following decontamination. Very recently, metal complexes of macrocyclic ligands have been used as catalysts in conjunction with the persulfate ion as the oxidant.[6] Again, the systems suffer from one or more drawbacks: (a) incomplete oxidation of the substrate, (b) use of expensive ligands and their eventual oxidative degradation, and (c) the use of expensive, oxidants.

With respect to chemical warfare agents, it is estimated that there are 30 000 metric tons of chemical weapons stored in the continental U.S.[7] Since the Chemical Weapons Convention Treaty mandating the eradication of all chemical weapons by the year 2007 took effect in April, 1997,[8] and Public Law 102-484 requiring the destruction of unitary chemical weapons by

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(2) Reviews: (a) *Drinking Water and Health*; National Academy of Sciences: Washington, DC, 1977; Chapter VI. (b) *Organic Contaminants in Waste Water, Sludge and Sediment*; Quaghebeur, D.; Temmerman, I., Angeletti, G., Eds.; Elsevier: New York, 1989. (c) *Organic Contaminants in the Environment*; Jones, K. C., Ed.; Elsevier: New York, 1991.

(3) Reviews: (a) Gottschalk, G.; Knackmuss, H.-J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1398. (b) *Bioremediation of Chlorinated and Polycyclic Aromatic Hydrocarbon Compounds*; Hinchee, R. E., Leeson, A., Semprini, L., Ong, S. K., Eds.; Lewis: Boca Raton, FL, 1994. (c) Abramowicz, D. A.; Olson, D. R. CHEMTECH **1995**, 36.

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(5) Recent representative examples: (a) Koyama, O.; Kamagata, Y.; Nakamura, K. *Water Res.* **1994**, *28*, 895. (b) Kiwi, J.; Pulgarin, C.; Peringer, P. *Appl. Catal., B* **1994**, *3*, 335. (c) Sorokin A.; Meunier, B. *J. Chem. Soc., Chem. Commun.* **1994**, 1799. (d) Fortuny, A.; Ferrer, C.; Bengoa, C.; Font J.; Fabregat, A. *Catal. Today* **1995**, *24*, 79. (e) Li, Z. M.; Comfort, S. D.; Shea, P. J. *J. Environ. Qual.* **1997**, *26*, 480.

(6) (a) Sorokin, A.; Seris, J.-L.; Meunier, B. *Science* **1995**, *268*, 1163. (b) Sorokin, A.; Seris, J.-L.; Meunier, B. *Chim. Ind.* **1995**, 151.

(7) *U.S. Chemical Weapons Stockpile Information; Declassified News Release*; Office of Assistant Secretary of Defense (Public Affairs): Washington, DC; January 22, 1996.

(8) Ember, L. *Chem. Eng. News* **1996**, *74*, 9.

December 31, 2004, has already been enacted, there is significant pressure to develop novel methods for the decomposition of these chemicals.[9,10] The optimal method for the destruction of chemical weapon stockpiles requires an efficient system which involves minimum exposure of the operators to the toxins. As such, a closed system that converts these compounds into benign products is required. Particularly desirable would be a mild catalytic procedure for deep oxidation using dioxygen. Most chemical warfare agents contain phosphorus−carbon (e.g., Tabun, Sarin, Soman, and VX) or sulfur−carbon (e.g., mustard gas) bonds,[12] and their neutralization requires the cleavage of these bonds. Herein, we report a novel system for the efficient catalytic oxidative cleavage of phosphorus−alkyl and sulfur−alkyl bonds in model compounds under mild conditions, by using dioxygen as the oxidant. Previous work has shown that certain metal−phosphine complexes of Fe, Co, Ni, and Rh undergo stoichiometric phosphorus−carbon cleavage.[13] However, the phosphorus−carbon bonds in question were generally phosphorus−aryl bonds and the ease of phosphorus−carbon bond rupture follows the order $P-C_{sp} > P-C_{sp}^{2} > P-C_{sp}^{3}$, with $P-C_{sp}^{3}$ bond cleavage observed very rarely.[14] In one such report, the activation of the $P-C_{sp}^{3}$ bond by using electron-withdrawing CF_3 groups was required to effect attack by hydroxide.[15] To our knowledge, the present work provides the first detailed examples of catalytic cleavage of simple phosphorus−alkyl bonds.

Results and Discussion

A. Catalytic System. We have previously described a catalytic system for the direct, low temperature, oxidation of methane and lower alkanes.[16] In this system, metallic palladium was found to catalyze the oxidation of alkanes, including methane, by dioxygen in aqueous medium at 70−100 °C in the presence of carbon monoxide. While carboxylic acids are the initial products (and the reaction can be stopped at this stage by using a large amount of the starting alkane), the ultimate oxidation products are carbon monoxide and carbon dioxide. Using ethane as a test substrate, over 1000 turnovers (= mmol of substrate reacted/mmol of surface Pd atoms) were observed over a 24 h period at 90 °C. Mechanistic studies previously reported indicate that the overall transformation encompasses three catalytic steps in tandem (Scheme 1).[16a] The first is the water−gas shift reaction (WGSR) involving the oxidation of carbon monoxide to carbon dioxide with the simultaneous formation of dihydrogen. The second catalytic step involves the combination of dihydrogen with dioxygen to yield hydrogen peroxide (or its equivalent, M-OOH).[17] The formation of hydrogen peroxide through palladium-catalyzed reaction between carbon monoxide, water, and dioxygen has also been the subject of several patent applications.[18]

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(10) *National Research Council, Alternative Technologies for the Destruction of Chemical Agents and Munitions*; National Academy Press: Washington, DC, 1993.

(11) Flamm, K. J.; Kwan, Q.; McNulty, W. B. *Chemical Agent and Munitions Disposal: Summary of the U.S. Army's Experience*; Report SAEPEO-CDE-IS-87005, 1987.

(12) *Chemical Warfare Agents*; Somani, S. M., Ed.; Academic: San Diego, 1992.

(13) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171 and references therein.

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(16) (a) Lin M.; Sen, A. *J. Am. Chem. Soc.* **1992**, *114*, 7307. (b) Lin, M.; Hogan, T. E.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 6048.

(17) Gosser, L. W. U.S. Patent 4,681,751, 1987.

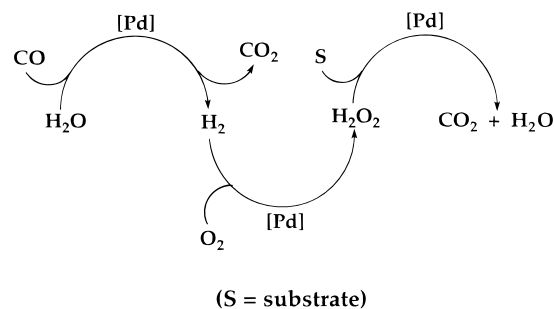**Scheme 1.** Mechanism of Pd-Catalyzed Oxidation of Organic Substrates

(S = substrate)

Table 1. Oxidation for para-Substituted Phenols[a]

substrate	substrate (mmol)	conversion (%)	turnovers/surface Pd
p-nitrophenol	0.18	10	20
p-chlorophenol	0.20	17	37
p-bromophenol	0.15	78	125
p-iodophenol	0.11	94	119
phenol	0.27	46	137

[a] Reaction conditions: 25 mg of phenol, 15 mg of 5% Pd/C (0.9 μmol of surface Pd atoms), 3 mL of D_2O/DCl (pH = 3), 100 psi CO, 1000 psi N_2, 100 psi O_2, 90 °C, 24 h.

The third step in the oxidation process involves the metal-catalyzed oxidation of the substrate by the hydrogen peroxide equivalent. It is possible to replace carbon monoxide and dioxygen by hydrogen peroxide; however, unless the latter is added slowly (see below) the amount of substrate oxidized relative to the hydrogen peroxide consumed is low due to the catalytic decomposition of hydrogen peroxide occurring in parallel with the oxidation. It is this latter undesirable reaction that made the combination of carbon monoxide and dioxygen more effective than hydrogen peroxide. Starting with carbon monoxide and dioxygen, hydrogen peroxide is formed at a low steady rate through the first two catalytic reactions and is used more efficiently for substrate oxidation. This was verified by carrying out the oxidation of phenol under conditions similar to that shown in Table 1, except that the gas mixture was replaced by 50% hydrogen peroxide added slowly over a period of 24 h through a syringe pump. A 40% conversion of phenol was obtained which is only slightly lower than that observed with a carbon monoxide−dioxygen mixture.

Several control experiments are also of relevance to the above catalytic system. First, significantly lower oxidation rates were observed when a soluble palladium(II) salt, such as K_2PdCl_4, was employed instead of supported metallic palladium. This suggests that the active catalyst is not a soluble palladium species, and indeed, the rapid reduction of K_2PdCl_4 to metallic palladium is observed under the reaction conditions. Presumably, the lower reaction rate observed starting with the former (compared to 5% Pd/carbon) is due to different aggregation of the metallic palladium formed in situ. A second control experiment indicated that the carbon support is not oxidized by the system. The essential role of carbon monoxide in achieving "difficult" oxidations is shown by the following competition experiment between $^{12}CH_3^{12}CH_3$ (500 psi, 0.03 M solution concentration) and $^{13}CH_3^{12}CH_2OH$ (0.18 mmol, 0.06 M solution concentration), both in the presence and absence of 100 psi of CO. The reaction conditions were similar to those described below. In the absence of added carbon monoxide, only

(18) (a) Rossella, B.; D'Aloisio, R.; Bianchi, D. Eur. Pat. Appl. EP 788,-998, 1997. (b) Bianchi, D.; Rossella, B.; D'Aloisio, R.; Ricci, M.; Soattini, S. Eur. Pat. Appl. EP 808,796 A1, 1997.

$^{13}CH_3{}^{12}CO_2H$ (0.03 mmol, 18 turnovers) was formed by the oxidation of $^{13}CH_3{}^{12}CH_2OH$. When carbon monoxide was added, 40% of the products were derived from $^{12}CH_3{}^{12}CH_3$. The products from this reaction were: $^{12}CH_3{}^{12}CH_2OH$ (0.008 mmol, 4 turnovers), $^{12}CH_3{}^{12}CO_2H$ (0.012 mmol, 7 turnovers), and $^{13}CH_3{}^{12}CO_2H$ (0.030 mmol, 16 turnovers). Thus, the more inert ethane was oxidized only in the presence of added carbon monoxide. The requirement of a coreductant (carbon monoxide) makes the overall reaction formally analogous to the monooxygenases in which only one of the two oxygen atoms in the dioxygen molecule is used for substrate oxidation.[19]

Finally, it was of some interest to find out whether the overall stoichiometry in the oxidation was close to what is shown in Scheme 1; the system would obviously be less useful if many equivalents of carbon monoxide were oxidized for every mole of substrate that was converted. Accordingly, the oxidation of phenol was carried out to 54% conversion under conditions similar to that shown in Table 1. A total of 0.14 mmol of phenol was oxidized, and 1.58 mmol of carbon dioxide was formed. Assuming 1:1 stoichiometry for conversion of the substrate and carbon monoxide to carbon dioxide, the formation of 1.68 mmol of carbon dioxide was expected. While the agreement with experimental results is gratifying, it raises another interesting issue given that there are six carbons and five hydrogens in phenol that have to be oxidized. It suggests that the coreductant is only required for the most difficult oxidations. Indeed, as discussed above, carbon monoxide is required as a coreductant in the oxidation of an alkane to the alcohol but is *not* required for the subsequent oxidation of the alcohol.

B. Oxidation of Aromatics, Nitro and Halo Organics. 1. Scope. Since the above catalytic system was able to effect the deep oxidation of molecules as unreactive as methane under unusually mild conditions, we have explored the ability of the system to catalyze the deep oxidation of hazardous organics. Several classes of organic compounds were examined: benzene, phenol and substituted phenols, nitro and halo organics, organophosphorus, and organosulfur compounds. Typical reaction conditions were as follows: substrate dissolved in 3 mL of DCl acidified D_2O, 5% Pd/carbon (60 μmol surface Pd atoms/g catalyst, as determined by dihydrogen chemisorption studies) as catalyst, 100 psi O_2, 100 psi CO, 1000 psi N_2, 80−90 °C. *In every case, 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.* No catalysis was observed when carbon alone was employed (although a small loss of reactants (~10%) was observed, presumably due to absorption). On the other hand, 5% Pd/Al_2O_3 was also found to be an active catalyst; however, the turnover rate was somewhat lower than that for 5% Pd/carbon. Thus, under similar reaction conditions, the conversions observed starting with 0.175 mmol of $CH_3CH_2CH_2SO_3Na$ were 74% for 5% Pd/Al_2O_3 and 95% for 5% Pd/carbon.

Phenol was found to be the initial oxidation product of benzene. *p*-Benzoquinone, glycolic, and formic acids were formed subsequently. That these products arose from benzene (and not by the hydrogenation of carbon monoxide) was verified by starting with $^{13}C_6H_6$ which lead to the formation of the corresponding ^{13}C-labeled products. Because of the poor solubility of benzene in water, as described later, quantitative studies of benzene oxidation were carried out in a mixture of perfluorobutyric acid and water.
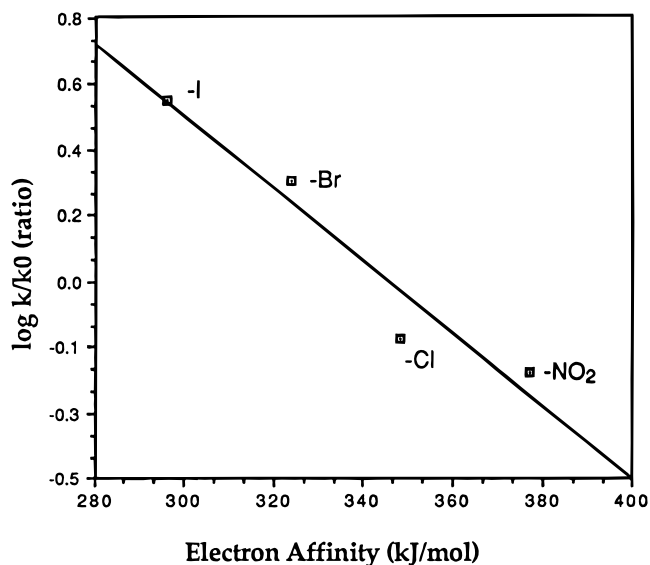
(19) Recent reviews on monooxygenases and their synthetic analogues: (a) *Metalloporphyrins in Catalytic Oxidations*; Sheldon, R. A., Ed.; Marcel Dekker: New York, 1994. (b) *Metalloporphyrins Catalyzed Oxidations*; Montanari, F.; Casella, L., Eds.; Kluwer: Dordrecht, 1994.

Figure 1. Plot of the ratio of the log of the rate of oxidation of para-substituted phenol to the parent phenol versus electron affinity of the substituent. Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 3 mL of D_2O/DCl (pH = 3), 15 mg of 5% Pd/C (0.9 μmol of surface Pd atoms), 25 mg of C_6H_5OH, 25 mg of p-X-C_6H_4OH, 24 h at 90 °C.

The deep oxidation of a number of para-substituted phenols was achieved under typical reaction conditions (Table 1). The products of the decomposition of *p*-bromophenol (25 mg, 0.145 mmol) were examined by ^{1}H NMR spectroscopy and were found to included *p*-benzoquinone (0.08 mmol) and formic acid (0.28 mmol). Trace amounts of acetic and glycolic acids were also detected. The remainder of the *p*-bromophenol was converted to CO_x, H_2O, and Br^-. At longer reaction times, no organics were observed in solution from any of the substrates. A series of competition experiments were performed and, as can be seen in Figure 1, the rate of conversion of the substrate decreased with increasing electronegativity of the para-substituent, with an approximately linear correlation between the electron affinity of the substituent and the ratio of the log of the rate of oxidation of the substituted phenol to the parent phenol. This is consistent with an initial electrophilic attack at the ring. While the exact nature of the electrophile remains to be elucidated, one possibility in analogy with monoxygenases is a metal−oxo species generated on the metal surface (see Conclusion).

Perhalogenated aromatics were also examined. 2,4,6-Trichlorophenol, a toxic byproduct from paper mills, was decomposed under similar reaction conditions. Of note is that trichlorophenol is poorly soluble in water and yet oxidation occurred. Starting with 25 mg (0.13 mmol) of 2,4,6-trichlorophenol, 94% conversion was noted after 1 d (100 turnovers/surface Pd atoms). The analysis was performed by examining the ^{1}H NMR spectra of both the aqueous layer and the $CDCl_3$ extract. Trace amounts of acetic and formic acids were the only carbon-containing products found. The chloride ions formed in solution were determined gravimetrically by precipitation with $AgNO_3$. The results indicated that the chlorine atoms present in the substrate were quantitatively converted to chloride ions.

In a similar manner 4,4′-bibromobiphenyl (25 mg, 0.08 mmol) was oxidized with an 40% conversion to CO_x, H_2O, and Br^- (35 turnovers/surface Pd atoms). Again, only traces of acetic and formic acids were detected by ^{1}H NMR spectroscopy, and bromide ions were quantitatively determined by precipitation with $AgNO_3$.

Table 2. Oxidation of Nitro, and Halo Aromatics[a]

substrate	conversion with H_2/O_2 (%)	conversion with CO/O_2 (%)	side products with H_2/O_2 (mmol)	side products with CO/O_2 (mmol)
nitromethane	94	86	ammonium (0.01) nitrate (>0.04) formic acid (0.06)	ammonium (0.01) nitrate (>0.04) formic acid (0.02)
p-nitrophenol	+99	+99	ammonium (0.10) nitrate (<0.04) formic acid (tr)	ammonium (0.06) nitrate (>0.08) formic acid (0.21)
m-nitrophenol	+99	+99	ammonium (0.06) nitrate (<0.04) formic acid (tr)	ammonium (0.06) nitrate (>0.08) formic acid (0.07)
nitrobenzene	+99	98	ammonium (0.07) nitrate (<0.04) formic acid (tr)	ammonium (0.04) nitrate (>0.08) formic acid (0.08)
nitrosobenzene	+99	+99	ammonium (0.02) nitrate (>0.08) formic acid (0.06)	ammonium (0.09) nitrate (<0.04) formic acid (tr) aminophenol (0.04) aniline (0.01) hydroquinone (tr)
azobenzene	96	85	ammonium (0.04) nitrate (<0.04) aniline (0.02)	ammonium (0.03) nitrate (<0.04) formic adid (0.01) aniline (0.02) hydroquinone (tr)
aniline	62	87	ammonium (0.05) nitrate (<0.04) formic acid (tr)	ammopnium (0.07) nitrate (<0.04) formic acid (0.08)
1,2-dinitrobenzene	98	99	ammonium (0.10) nitrate (<0.04)	ammonium (0.05) nitrate (>0.04) formic acid (0.04)
1,4-dinitrobenzene	99	88	ammonium (0.14) nitrate (>0.08) formic acid (tr)	ammonium (tr) nitrate (<0.04) formic acid (tr)
1,3-dinitrobenzene	73	77	ammonium (0.10) nitrate (<0.04)	ammonium (0.01) nitrate (<0.04) formic acid (0.05)
1-chloro-3-nitrobenzene	+99	86	ammonium (0.08) nitrate (<0.04) formic acid (0.04) aniline (0.06)	ammonium (0.02) nitrate (>0.08) formic acid (0.03)
1-chloro-4-nitrobenzene	80	85	ammonium (0.03) nitrate (>0.08) formic acid (0.06)	ammonium (0.02) nitrate (>0.04) formic acid (0.03)
p-chlorophenol	96	92	formic acid (0.01)	formic acid (0.09) hydroquinone (0.06)
m-chlorophenol	+99	89	formic acid (0.02)	formic acid (0.09)
p-bromophenol	+99	99	formic acid (0.08)	formic acid (0.08) hydroquinone (0.03) p-hydroxybenzoic acid (0.04)
m-bromophenol	+99	+99	formic acid (0.09) hydroquinone (tr)	formic acid (0.04) m-hydroxybenzoic acid (0.08)

[a] Reaction conditions: 0.25 mmol substrate, 30 mg of 5% Pd/C, 3 mL of H_2O/HCl (pH = 1), 100 psi H_2 or CO, 1000 psi N_2, 100 psi O_2, 130 °C, 16 h.

Table 3. Comparison of CO/O_2 vs H_2/O_2 at Lower Conversions[a]

substrate	conversion with H_2/O_2 (%)	conversion with CO/O_2 (%)	side products with H_2/O_2 (mmol)	side products with CO/O_2 (mmol)
p-nitrophenol	79	31	ammonium (0.04) formic acid (0.06) hydroquinone (0.07)	ammonium (tr) formic acid (0.03) hydroquinone (0.04)
p-chlorophenol	89	57	formic acid (0.09) phenol (0.17)	formic acid (0.03) hydroquinone (0.10)
aniline	38	16	unidentified	unidentified
nitrobenzene	92	67	ammonium (0.11) aniline (0.28) hydroquinone (0.01)	ammonium (0.03) formic acid (0.13)

[a] Reaction conditions: 1 mmol substrate, 15 mg of 5% Pd/C, 3 mL of H_2O/HCl (pH = 1), 100 psi H_2 or CO, 1000 psi N_2, 100 psi O_2, 90 °C, 16 h.

Although the catalytic system described above exhibits many attractive features, one potential problem is that many toxic organics are insoluble in water and therefore are likely to be oxidized very slowly under typical reaction conditions. Consequently, we have briefly examined alternative solvent systems that are superior to water in dissolving organic compounds. One such solvent system (which is not, however, useful from a practical standpoint) consists of a mixture of water and perfluorobutyric acid, and $CH_3CH_2CH_2SO_3Na$ was used as the test substrate (125 mg, 0.76 mmol). As shown in Figure 2, a slight enhancement in oxidation rate was observed initially with increasing perfluorobutyric acid concentration in the solvent mixture. The maximum rate was achieved at 50% (v/v) perfluorobutyric acid:water mixture with a 98% conversion of the substrate (500 turnovers/surface Pd atoms). Beyond 60% (v/v) perfluorobutyric acid, the reaction rate decreased sharply

Table 4. Oxidation of Nitro Aromatics in CF_3CO_2H/H_2O^a

substrate	conversion with H_2/O_2 (%)	side products with H_2/O_2 (mmol)
1,4-dinitrobenzene	+99	ammonium (0.35) nitrate (>0.08)
1,2-dinitrobenzene	+99	ammonium (0.32) nitrate (<0.04) formic acid (0.03)
1,3-dinitrobenzene	+99	ammonium (0.20) nitrate (<0.04) formic acid (tr)

^{a} Reaction conditions: 0.25 mmol substrate, 30 mg of 5% Pd/C, 1.5 mL of H_2O, 1.5 mL of CF_3CO_2H, 100 psi H_2, 1000 psi N_2, 100 psi O_2, 150 °C, 16 h.
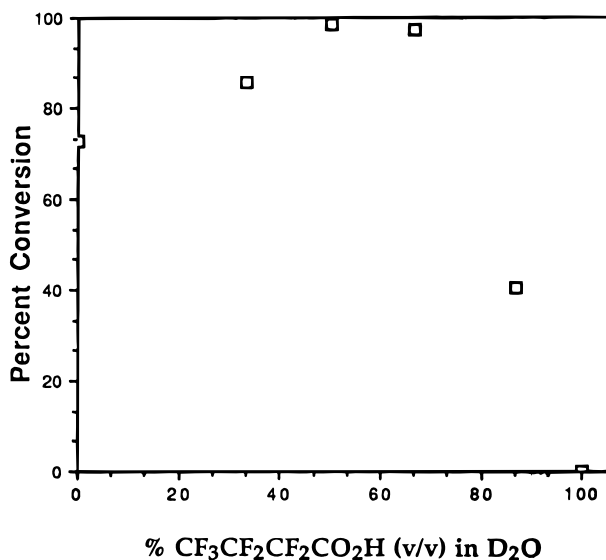

Figure 2. Plot of the conversion of $CH_3CH_2CH_2SO_3Na$ versus %perfluorobutyric acid (v/v) in D_2O. Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 25 mg of 5% Pd/C (1.5 μmol of surface Pd atoms), 0.76 mmol $CH_3CH_2CH_2SO_3Na$, 3 mL of solvent, 90 °C, 24 h.

presumably because water was necessary for the generation of H_2O_2 (Scheme 1).

The 50% (v/v) perfluorobutyric acid:water mixture was used as the solvent to carry out the deep oxidation of two substrates that are poorly soluble in water alone: benzene and 1,1,2,2-tetrachloroethane. Under typical reaction conditions, starting with 0.5 mmol of benzene in 3 mL of solvent mixture, 435 turnovers/surface Pd atoms to CO_x and H_2O were observed in a 24 h period. Traces of formic and glycolic acids were the only organic products observed in solution. In the case of 1,1,2,2-tetrachloroethane, 35 turnovers/surface Pd atoms were observed as determined by gravimetric chloride analysis.

2. Use of Carbon Monoxide−Dioxygen Mixture versus Dihydrogen−Dioxygen Mixture. Since the function of the added carbon monoxide in the above system is to generate dihydrogen (Scheme 1), an interesting issue involves the comparison of oxidation rates starting with dioxygen and dihydrogen versus dioxygen and carbon monoxide. Clearly, the rate in the first case should be equal to or higher than that observed with the latter combination. The issue is further complicated by the question of whether in the case of aromatic substrates a prereduction step facilitates the subsequent deep oxidation. Accordingly, we have examined the effect of added dihydrogen versus that of carbon monoxide in the deep oxidation of nitro and halo aromatics. Nitro aromatics are a major class of groundwater and soil contaminants because of their use as pesticides (e.g., 2-*sec*-butyl-4,6-dinitrophenol, trade name: di-

noseb) and explosives (e.g., di- and trinitrotoluene).[20] These compounds persist in the soil for many years.[21] Halo organic contaminants stem from their use as degreasing solvents, pesticides, herbicides, and heat transfer fluids. Again, the bioremediation of these compounds is an extremely slow process.[3]

As can be seen from Table 2, efficient oxidative degradation of substrates occurred when either dihydrogen or carbon monoxide was used as the coreductant. However, where there is a difference, lower substrate decomposition was almost invariably observed using carbon monoxide as the coreductant. This trend became more obvious when the reactions were carried out at lower conversion (Table 3). Note that no reaction occurred when the coreductant was absent. There was no reaction either when carbon monoxide but not dioxygen was present. On the other hand, near quantitative reduction to cyclohexane derivatives occurred when dihydrogen but not dioxygen was present in the reaction mixture. Additionally, for nitrogen-containing substrates, the formation of ammonium ion was observed. It is clear from these experiments that while the prior reduction of the substrate is *not* a requirement for its oxidative degradation, such a step *may* enhance the decomposition rate, as is evident from the comparison of the reactions involving dihydrogen and carbon monoxide as coreductants. Interestingly, however, aniline was slower to react than either nitro or nitroso benzene and is, therefore, not an intermediate in the oxidation of the latter substrates (see Tables 2 and 3). Presumably, aniline is protonated in the reaction medium, and the resultant electron-withdrawing anilinium group deactivates the ring toward electrophilic attack.

In all of the oxidations involving nitrogen-containing substrates, the ammonium ion was detected by ^{1}H NMR spectroscopy,[22] and in many cases the nitrate was also detected (Table 2). However, the combined amount of these two products was significantly lower than that of the total nitrogen in the substrate, thereby indicating that other nitrogen-containing species were also generated in the reactions (for example, NH_4NO_3 is known to decompose thermally to N_2O and water). No ammonia gas was detected by GC analysis in the headspace of the reactor after the reaction of *p*-nitrophenol under standard conditions in the presence of 100 psi of dihydrogen. To determine if partial decomposition of the ammonium ion was occurring following its formation, a control reaction using NH_4Cl (1 mmol) as the substrate was conducted in 1:1 H_2O/CF_3CO_2H. Some decomposition (approximately 20%) of the ammonium ion was observed by ^{1}H NMR spectroscopy. Approximately half of this decomposition was to the nitrate ion. The use of $NaNO_3$ (1 mmol) as the substrate under standard conditions afforded no ammonium ion, thereby indicating that the ammonium was not produced from an intermediate nitrate ion. Additionally, when starting with $NaNO_3$, neither ammonia nor the ammonium ion was detected by GC analysis and ^{1}H NMR spectroscopy, respectively, when an organic hydrogen source, phenol (1 mmol), was added or when dioxygen was removed from the reaction mixture.

The pH and the composition of the solvent appears to have a significant effect on the oxidative degradation of the above substrates. For example, using the dihydrogen/dioxygen mixture, substituting H_2SO_4 for HCl but maintaining a pH = 1 resulted

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Table 5. Oxidation of Phosphorus and Sulfur Compounds[a]

substrate	conversion with H₂/O₂ (%)	conversion with CO/O₂ (%)	side products with H₂/O₂ (mmol)	side products with CO/O₂ (mmol)
trimethylphosphine oxide	15	40	dimethylphosphinic acid (0.14) methylphosphonic acid (tr) formic acid (tr)	dimethylphosphinic acid (0.34) methylphosphonic acid (0.06) formic acid (tr)
dimethylphosphinic acid	16	11	methylphosphonic acid (0.15) formic acid (tr)	methylphosphonic acid (0.11) formic acid (0.27)
methylphosphonic acid	5	10	formic acid (tr)	formic acid (0.15)
dimethylsulfide	66	61	dimethylsulfoxide (0.02) formic acid (tr)	dimethylsulfoxide (0.22) dimethylsulfone (0.04) formic acid (tr)
dimethylsulfone[b]	9	6	dimethylsulfoxide (0.03)	methylsulfoxide (0.05)

[a] Reaction conditions: 1 mmol substrate, 15 mg of 5% Pd/C, 3 mL of H₂O/HCl (pH = 1), 100 psi H₂ or CO, 1000 psi N₂, 100 psi O₂, 90 °C, 20 h. [b] 0.5 mmol substrate.

Table 6. Oxidation of Trimethylphosphine Oxide[a]

time (h)	(CH₃)₃PO (mmol)	(CH₃)₂P(O)(OH) (mmol)	(CH₃)P(O)(OH)₂ (mmol)	H₃PO₄ (mmol)	HCO₂H (mmol)	TON[b]
0.00	5.43	0.00	0.00	0.00	0.00	0
15.75	4.07	1.25	0.19	0.00	2.21	543
39.0	2.06	2.06	1.31	0.00	5.00	1560
68.0	1.11	2.51	1.58	0.22	5.16	2110
92.0	0.51	2.09	2.26	0.56	4.48	2763
109.5	0.25	1.67	2.57	0.93	3.27	3200
157.5	0.07	1.00	2.68	1.68	2.35	3800
179.0	0.04	0.72	2.57	2.10	2.22	4053

[a] Reaction conditions: 100 psi CO, 1000 psi N₂, 100 psi O₂, 10 mL of D₂O/DCl (pH = 1), 50 mg Pd/carbon (3 μmol surface Pd atoms), 500 mg of (CH₃)₃PO (5.43 mmol), 90 °C. [b] Turnover number defined as {[(CH₃)₂P(O)(OH)] + 2[(CH₃)P(O)(OH)₂] + 3[H₃PO₄]}/[surface Pd atoms].

in a similar oxidation rate for 1,3-dinitrobenzene. On the other hand, a significantly lower conversion rate was observed in neutral water. The use of pure CF₃CO₂H resulted in reduced oxidation and formation of cyclohexane derivatives and ammonium ion from 1,3-dinitrobenzene by hydrogenation/hydrogenolysis. On the other hand, the use of a 1:1 (v/v) mixture of CF₃CO₂H and water resulted in efficient substrate oxidation that was generally comparable to HCl-acidified water (Table 4). The former solvent system was, however, significantly superior for substrates that are poorly soluble in water, such as 1,3-dinitrobenzene.

Finally, an alternative explanation for the increase in substrate oxidation rate with dihydrogen/dioxygen mixture over carbon monoxide/dioxygen mixture may be that hydrogen simply produces a higher concentration of hydrogen peroxide (see Scheme 1). However, a comparison of the two systems for substrates for which hydrogenation is unlikely appears to rule out this possibility. Thus, for a series of organic phosphorus and sulfur compounds similar (or lower) oxidation rates were observed for the dihydrogen/dioxygen mixture (Table 5).

The most likely explanation for the superiority of the dihydrogen/dioxygen mixture over carbon monoxide/dioxygen mixture for the deep oxidation of aromatics is that the observed prereduction by dihydrogen converts the stronger sp² C–H bonds to weaker sp³ C–H bonds (e.g., the C–H bond energy is ~15 kcal lower in cyclohexane compared to that in benzene), thereby facilitating their subsequent activation and oxidation.

C. Oxidation of Organophosphorus and Sulfur Compounds. Oxidation of trimethylphosphine oxide produced three phosphorus-containing products: dimethylphosphinic acid, methylphosphonic acid, and phosphoric acid (Table 6). These resulted from the cleavage of one, two, and three phosphorus–carbon bonds, respectively. The methyl groups were oxidized to form formic acid and ultimately CO₂. From Figure 3, it is evident that dimethylphosphinic acid and methylphosphonic acid are intermediates in the formation of phosphoric acid. After 179
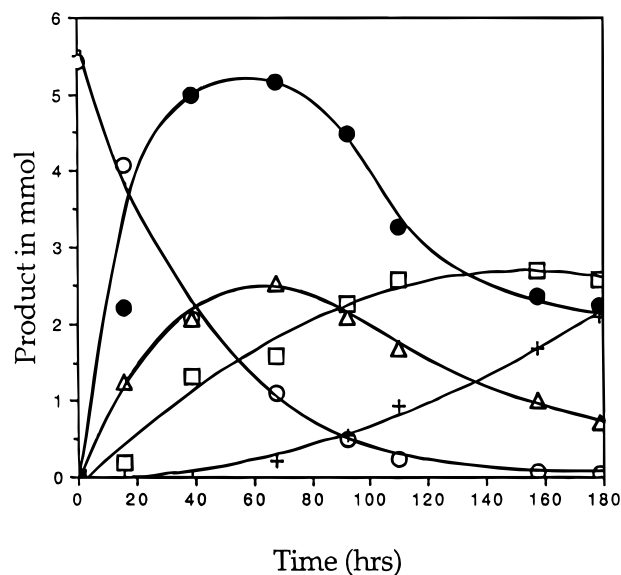

Figure 3. Plot of the products formed from (CH₃)₃PO versus time. Reaction conditions: 100 psi CO, 1000 psi N₂, 100 psi O₂, 10 mL of D₂O/DCl (pH = 1), 50 mg of 5% Pd/carbon (3 μmol surface Pd atoms), 500 mg of (CH₃)₃PO (5.43 mmol), 90 °C. (CH₃)₃PO, (○); (CH₃)₂P-(O)(OH), (△); CH₃P(O)(OH)₂, (□); H₃PO₄, (+); HCO₂H, (●).

h, only a trace of (CH₃)₃PO remained. *In 179 h, over 4000 phosphorus–carbon bonds were cleaved by each Pd!* A ³¹P NMR stack plot of the reaction is shown in Figure 4. Again, it is apparent that only traces of starting material remain. A study of the kinetics of both dimethylphosphinic acid and methylphosphonic acid oxidation indicated a zero-order relationship between reaction rate and substrate concentration. Such a relationship is ideal in the context of efficient oxidation of substrates down to low concentrations. More significantly, both substrates appear to be oxidized at similar rates thereby indicating that other substituents present on the phosphorus had
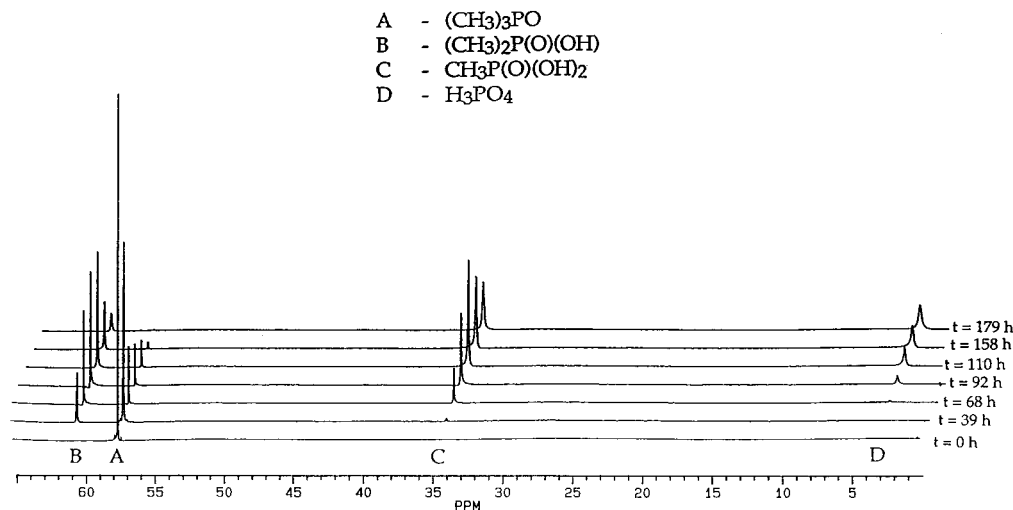
A - $(CH_3)_3PO$
B - $(CH_3)_2P(O)(OH)$
C - $CH_3P(O)(OH)_2$
D - H_3PO_4

Figure 4. Stack plot of ^{31}P NMR spectra obtained after the following reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 10 mL of D2O/DCl (pH = 1), 50 mg of 5% Pd/carbon (3 μmol surface Pd atoms), 500 mg of $(CH_3)_3PO$ (5.43 mmol), 90 °C.

Table 7. Oxidation of Dimethylphosphinic Acid[a]

time (h)	$(CH_3)_2P(O)OH$ (mmol)	$(CH_3)P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	HCO_2H (mmol)	TON[b]
0	1.00	0.00	0.00	0.00	0
18	0.89	0.11	0.00	0.27	122
38	0.81	0.18	0.01	0.21	222
59.5	0.73	0.25	0.02	0.66	322

[a] Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 3 mL of D2O/DCl (pH = 1), 15 mg of Pd/carbon (0.9 μmol surface Pd atoms), 94 mg of $(CH_3)_2P(O)OH$ (1.00 mmol), 90 °C. [b] Turnover number defined as $\{[CH_3P(O)(OH)_2] + 2[H_3PO_4]\}/[\text{surface Pd atoms}]$.

Table 8. Oxidation of Methylphosphonic Acid[a]

time (h)	$(CH_3)P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	HCO_2H (mmol)	TON[b]
0	1.00	0.00	0.00	0
18	0.90	0.10	0.15	111
38	0.80	0.20	0.28	222
59.5	0.71	0.29	0.23	322

[a] Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 3 mL of D2O/DCl (pH = 1), 15 m of Pd/carbon (0.9 μmol surface Pd atoms), 96 mg of $CH_3P(O)(OH)_2$ (1.00 mmol), 90 °C. [b] Turnover number defined as $[H_3PO_4]/[\text{surface Pd atoms}]$.

little effect on the rate (Tables 7 and 8). To ascertain whether the final product, orthophosphate, inhibited the oxidation, the oxidation of 1 mmol of trimethylphosphine oxide was carried out under identical conditions with and without the addition of 1 mmol of NaH_2PO_4. A 25% reduction in rate was observed in the presence of the phosphate.

The oxidation of triethylphosphine oxide led to 10 phosphorus-containing products. Partial oxidation of the ethyl groups competed with phosphorus–carbon cleavage. The phosphorus-containing products derived from phosphorus–carbon cleavage that were identified were diethylphosphinic acid, ethylphosphonic acid, and phosphoric acid. In addition phosphonoacetic acid was identified as a product derived from the partial oxidation of an ethyl group. Other organic products derived from the oxidation of the ethyl group that were present in solution were acetic and formic acids. After 128.5 h, no starting material remained, and the major phosphorus-containing products were phosphonoacetic acid, ethylphosphonic acid, and phosphoric acid. A separate study of ethylphosphonic acid oxidation showed that phosphorus–carbon cleavage was significantly favored over carbon–hydrogen cleavage and oxidation (Table 9). From the ratio of H_3PO_4 to $HO_2CCH_2P(O)(OH)_2$, it can be estimated that the relative phosphorus–carbon to carbon–hydrogen cleavage

was 5.6 on a per bond basis. However, this number is subject to error since phosphonoacetic acid itself was efficiently oxidized to phosphoric acid. For example, when phosphonoacetic acid (0.71 mmol) was oxidized under standard conditions for 16 h, a 46% conversion to phosphoric acid resulted.

By simple filtration, the catalyst could be retrieved and reused with no significant loss in activity. For example, 85.3% of $(CH_3)_3PO$ (0.54 mmol) was oxidized in 20 h. Removal of the catalyst by filtration and subsequent reuse resulted in the oxidation of 78.6% of $(CH_3)_3PO$ (0.54 mmol) in 20 h. The small loss in activity was most likely due to loss of catalyst during filtration.

The deep oxidation of sulfur-containing analogues to mustard gas, $(ClCH_2CH_2)_2S$, occurred readily with the bulk of the substrate being converted to carbon monoxide, carbon dioxide, and water (Table 10). A 1:1 (v/v) mixture of water and perfluorobutyric acid was used to enhance the solubility of the substrate. Starting with dimethylsulfide (1.00 mmol), the species observed in solution after 17 h of reaction were dimethylsulfoxide (0.22 mmol), methanesulfonic acid (0.04 mmol), and formic acid (0.26 mmol). Dimethylsulfoxide (0.5 mmol) itself was converted to methanesulfonic acid (0.14 mmol), and dimethylsulfone (0.30 mmol) after 18 h. To determine if dimethylsulfone was an intermediate in the oxidation of dimethylsulfoxide to methanesulfonic acid, the products from oxidation of dimethylsulfoxide (2 mmol) and the oxidation of a mixture of dimethylsulfoxide (1 mmol) and dimethylsulfone (1 mmol) was analyzed. Since the yield of methanesulfonic acid was similar in both reactions (0.59, 0.53 mmols, respectively), it is evident that dimethylsulfone was *not* an intermediate in the oxidation of dimethylsulfoxide to methanesulfonic acid. Unlike dimethylsulfide and dimethylsulfoxide, dimethylsulfone and methanesulfonic acid were particularly resistant to oxidation. Starting with 0.5 mmol of substrate, over 90% of the substrate remained unreacted in each case after 18 h. The ease of oxidation decreased in the order: $(CH_3)_2S > (CH_3)_2SO > (CH_3)_2SO_2$ and further supports the conclusion that the system acts as an electrophilic oxidant.

The ethyl analogues showed a similar reactivity pattern. Starting with diethyl sulfide (1.00 mmol), the species observed in solution after 28 h of reaction were: diethylsulfoxide (0.13 mmol) and unreacted diethyl sulfide (0.42 mmol). Diethyl sulfone (0.82 mmol) was much more reactive than its methyl analogue, and after 16.5 h of reaction the species present in

Table 9. Oxidation of Ethylphosphonic Acid[a]

time (h)	$(C_2H_5)P(O)(OH)_2$ (mmol)	$HO_2CCH_2P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	CH_3CO_2H (mmol)	HCO_2H (mmol)	TON[b]
0	1.00	0.00	0.00	0.00	0.00	0
18	0.71	0.10	0.19	0.05	0.24	322
38	0.43	0.20	0.36	0.09	0.46	622
59.5	0.14	0.30	0.56	0.13	0.45	956

[a] Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 3 mL of D_2O/DCl (pH = 1), 15 mg of Pd/carbon (0.9 μmol surface Pd atoms), 110 mg of $(C_2H_5)P(O)(OH)_2$ (1.00 mmol), 90 °C. [b] Turnover number defined as $\{[HO_2CCH_2P(O)(OH)_2] + [H_3PO_4]\}$/[surface Pd atoms].

Table 10. Oxidation of Methyl−Sulfur Compounds[a]

| substrate (mmol)	time (h)	$(CH_3)_2S$ (mmol)	$(CH_3)_2SO$ (mmol)	$(CH_3)_2SO_2$ (mmol)	CH_3SO_3H (mmol)
$(CH_3)_2S^{b,c}$ (1.00)	17.0	0.39	0.22		0.04
$(CH_3)_2SO^b$ (0.50)	18.5			0.14	0.30
$(CH_3)_2SO_2$ (0.50)	18.5			0.47	0.03

[a] Reaction conditions: 100 psi CO, 1000 psi N_2, 100 psi O_2, 3 mL of D_2O/DCl (pH = 1), 15 mg of Pd/carbon (0.9 μmol surface Pd atoms), 100 °C. [b] Deep oxidation to HCO_2H and CO_2 occurred. [c] Solvent: 1.5 mL of $CF_3CF_2CF_2CO_2H$ + 1.5 mL of D_2O/DCl (pH = 1).

solution were: ethanesulfonic acid (0.15 mmol), acetic acid (0.08 mmol), formic acid (0.13 mmol), along with unreacted sulfone (0.60 mmol). After 20.5 h of reaction time the following species were observed in solution starting with ethane sulfonic acid (0.2 mmol): methylsulfate (0.03 mmol), acetic acid (0.06 mmol), formic acid (0.12 mmol), along with unreacted starting material (0.03 mmol).

Conclusion

In conclusion, we have discovered an unusually versatile catalytic system for the deep oxidation of toxic organics in water. This system possesses several attractive features not found simultaneously in other reported systems. These are (a) the ability to directly utilize dioxygen as the oxidant, (b) the ability to carry out the deep oxidation of a particularly wide range of functional organics, and (c) the ease of recovery of the catalyst by simple filtration.

While our understanding of the mechanistic steps involved in the overall oxidation is far from complete, it is clear that a powerful electrophilic oxidant is generated in situ. One possibility is a metal−oxo species generated on the metal surface through the sequence of steps outlined in eq 1. An initial metal−hydride is expected to form through the water−gas shift reaction or by direct reaction with dihydrogen. Such a species is known to react with dioxygen to form a metal−hydroperoxide,[23] which can be subsequently protonated to release water and form the metal−oxo species (hence the requirement of an acid). The sequence of

(1)
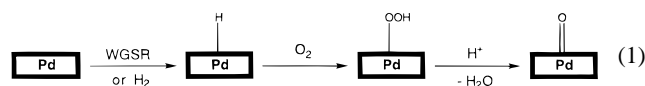
steps is precedented and bears resemblance to that occurring in monoxygenases.[19]

(23) (a) Specific example: Hosokawa, T.; Nakahira, T.; Takano, M.; Murahashi, S. *J Mol. Catal.* **1992**, *74*, 489. (b) Review: *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*; Strukul, G., Ed.; Kluwer Academic: Dordrecht, 1992.

Experimental Section

Appropriate precautions should be taken while working with gases under high pressures. Particular attention should be paid to flammability limits of gas mixtures. In our experiments, a 1000 psi of dinitrogen was routinely used as a diluent.

A. Materials and Equipment. Reagent grade chemicals were used as received. Reactions under pressure were carried out in Parr general purpose bombs using glass liners. Reaction products were identified by their ^{1}H NMR and/or ^{31}P NMR spectra recorded on a Brüker AM 300 FT-NMR spectrometer using solvent resonance at appropriate frequency or an external standard consisting of a capillary tube containing 1 μL of DMSO in 60 μL of D_2O for lock, reference, and integration standard (for ^{1}H NMR spectra) or H_3PO_4 (for ^{31}P NMR spectra). The identity of specific NMR resonances was confirmed by comparison to standard reference spectra and/or co-injection of standards. The ammonium ion was quantified by ^{1}H NMR spectroscopy.[22] The procedure for detection of nitrate ion in solution was adapted from a colorimetric method used for low concentrations of nitrate in groundwater samples.[24] A brucine−sulfanilic acid reagent was prepared, and when added, along with NaCl(aq) and H_2SO_4, to a reaction solution containing nitrate, the solution turned bright pink. The gaseous products in several reactions were identified via gas-phase injection GC conducted on a HP 5890 GC equipped with a Supelco 15 ft × $^1/_8$ in. column with 60/80 Caroxen 1000 support. Reaction chromatograms were compared with standards for positive identification of products.

B. Catalyst. Commercial (Aldrich or Alfa Aesar) 5% palladium on carbon (60 μmol surface Pd atoms/g catalyst, as determined by dihydrogen chemisorption studies) was employed. A scanning electron micrograph of the catalyst revealed the presence of particles ranging from 10 to 140 Å in size. An X-ray dot map analysis showed the palladium to be evenly dispersed throughout the carbon support with domain sizes smaller than detection limits.

C. General Procedure. Specific reaction conditions are given as footnotes to the tables. In a typical reaction, the substrate was added to 3 mL of DCl acidified D_2O (pH = 1) and placed in a glass liner containing an appropriate amount of 5% palladium on carbon. The liner was placed in a high-pressure Parr reactor that was subsequently charged to 100 psi with dihydrogen or carbon monoxide, to 1100 psi with dinitrogen, and finally to 1200 psi with dioxygen, and heated for a specific time period. At the end of this period, the gases were vented and the contents of the liner were analyzed. To test the reproducibility of the reactions, the key experiments were repeated and the results were found to be within 10% of each other.

(24) Skougstad, M. W.; Fishman, M. J.; Friedman, L. C.; Erdmann, D. E.; Duncan, S. S. *Techniques of Water-Resources Investigations of the United States Geological Survey*; US Department of Interior: Washington, DC; Book 5, Chapter A1, p 429.