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A broad spectrum catalytic system for removal of toxic organics from water by deep oxidation using dioxygen as the oxidant

Terrence Hogan, Robert Simpson, Minren Lin and Ayusman Sen [1]

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

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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. Several classes of organic compounds were examined: benzene, phenol and substituted phenols, aliphatic and aromatic halogenated compounds, 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. Since the heterogeneous catalyst can be removed by simple filtration, simultaneous water purification and contaminant destruction becomes feasible. For those substrates that are insoluble in pure water, a mixture of water and perfluorobutyric acid was successfully employed as the solvent.

Keywords: palladium metal; oxidation; toxic organics

1. Introduction

Toxic organics in water constitute an important environmental hazard (for reviews see ref. [1]). 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 (for reviews see ref. [2]). 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 photooxidations (reviews in ref. [3] and recent representative examples in ref. [4]) and the "Fenton" systems involving H_2O_2 and a soluble transition metal catalyst (recent representative examples in ref. [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. The Fenton system suffers from the requirement of separately producing and transporting H_2O_2, an unstable and potentially explosive chemical. In the actual oxidation reactions, a portion of the H_2O_2 is also 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, potentially unstable, oxidants. Herein, we describe a new catalytic system for the deep oxidation of organics by dioxygen that does not share many of the disadvantages of the hitherto reported systems.

2. Experimental

General. The following chemicals were used as received: 5% Pd/carbon (Johnson Matthey); benzene, phenol, *p*-nitrophenol, *p*-chlorophenol, *p*-bromophenol, *p*-iodophenol, 2,4,6-trichlorophenol, 4,4′-bibromobiphenyl, triethylphosphine oxide, triethylphosphite, chloroacetic acid, 3-chloropropionic acid, nitromethane, diethylacetamide, ethane sulfonic acid sodium salt, propane sulfonic acid sodium salt, butane sulfonic acid sodium salt, heptafluorobutyric acid, 1,1,2,2-tetrachloroethane, and silver nitrate (Aldrich); ethane, carbon monoxide, oxygen, and nitrogen (Matheson);

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[1] To whom correspondence should be addressed.

deuterium oxide, 2-^{13}C-ethanol, chloroform-*d* (Isotech, Inc.). Reactions under pressure were carried out in Parr general purpose bombs using glass liners. Reaction products were identified by their ^{1}H-NMR spectra recorded on a Brucker 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 as an integration standard. The identity of specific NMR resonances was confirmed in some cases by rerunning the spectrum after the addition of authentic samples. In some substrates containing halogen atoms, the halides were determined gravimetrically by precipitation as the silver salt.

General procedure (reaction 1) [#1]. To a glass liner containing 3 μl of HCl acidified D_2O ($pH = 3$) was added 15 mg of 5% Pd/carbon (0.9 μmol surface Pd atoms [#2]) and 25 mg of substrate. The glass liner was then placed in a high pressure bomb which was then sealed. The bomb was purged with N_2 and pressurized to 100 psi with CO, to 1100 psi with N_2, and 1200 psi with O_2. The contents were stirred at 80–90°C for 1 d. After venting, the products were examined by ^{1}H-NMR spectroscopy. Unless noted below these conditions were used for the oxidation of all substrates.

Competition experiment between ethane and ethanol. In the presence of carbon monoxide. The reaction was conducted as described above (reaction 1) except that $^{13}CH_3CH_2OH$ (0.18 mmol, 10.8 μl), 100 psi CO, 500 psi C_2H_6, 500 psi N_2, and 100 psi O_2 were added to the bomb. *In the absence of carbon monoxide.* The reaction was conducted as described above (reaction 1) except that $^{13}CH_3CH_2OH$ (0.18 mmol, 10.8 μl), 500 psi C_2H_6, 600 psi N_2, and 100 psi O_2 were added to the bomb.

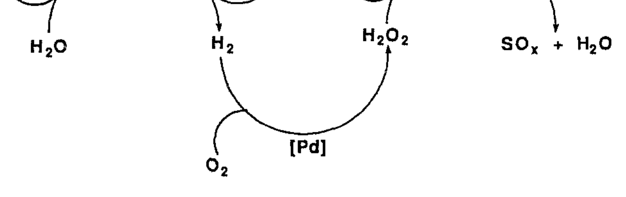
Oxidation of benzene. To a glass liner containing 5 ml of HCl acidified D_2O ($pH = 1$) was added 20 mg 5% Pd/carbon (1.2 μmol surface Pd atoms) and C_6H_6 (1.68 mmol, 150 μl). The glass liner was then placed in a high pressure bomb which was then sealed. The bomb was purged with N_2 and pressurized to 200 psi with CO, to 1000 psi with N_2, and 1200 psi with O_2. The contents were stirred at 80–90°C for 1 d. After venting, the products were examined by ^{1}H-NMR spectroscopy.

Oxidation of triethyl phosphine oxide and triethyl phosphite. The reactions were conducted as described above (reaction 1) except that twice the amount of substrate (50 mg) and twice the amount of Pd/carbon (1.8 μmol surface Pd atoms) were used.

Oxidation in perfluorobutyric acid/water. Oxidation of propane sulfonic acid sodium salt. The reaction was conducted as described above (reaction 1) except that five times the amount of substrate (125 mg, 0.76 mmol) and various ratios (v/v) of perfluorobutyric acid : D_2O ($pH = 3$) were used (fig. 2). *Oxidation of 1,1,2,2-tetrachloroethane.* The reaction was carried out as described above (reaction 1) except that 0.5 mmol (53 μl) of 1,1,2,2-tetrachloroethane and a 50% (v/v) perfluorobutyric acid : D_2O solvent mixture was used (total volume: 3 ml).

3. Results and discussion

We have previously described a catalytic system for the direct, low temperature, oxidation of methane and lower alkanes [7]. 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 were the initial products (and the reaction could be stopped at this stage by using a large amount of the starting alkane), the ultimate oxidation products were carbon monoxide and carbon dioxide. Using ethane as a test substrate, over 1000 turnovers (= mmol of substrate reacted/mmol of surface Pd atoms [#2]) were observed over a 24 h period at 90°C. Mechanistic studies previously reported indicated that the overall transformation encompassed three catalytic steps in tandem (scheme 1) [7]. 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 [8]. The third step involved the metal catalyzed oxidation of the substrate by hydrogen peroxide. 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 CO, only $^{13}CH_3{}^{12}CO_2H$ (0.03 mmol, 18 turnovers) was formed by the oxidation of $^{13}CH_3{}^{12}CH_2OH$. When CO was added, 40% of the products were derived from $^{12}CH_3{}^{12}CH_3$.



(S = substrate; SO_x = oxidized substrate)

Scheme 1.

[#1] Appropriate precautions should be taken while working with gases under high pressures. Particular attention should be paid to flammability limits of gas mixtures.

[#2] Amount of surface metal atoms in catalyst sample determined from dihydrogen chemisorption studies. We thank Professor M.A. Vannice for the determination.

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 CO. 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 (for reviews see ref. [9]).

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, aliphatic and aromatic halogenated compounds, organophosphorus, and organosulfur compounds. Typical reaction conditions (reaction 1) were as follows: 25 mg substrate in 3 ml of HCl acidified water (pH = 3), 15 mg 5% Pd/carbon (0.9μ mmol surface Pd atoms[#2]), 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 ($\sim$ 10%) was observed, presumably due to absorption). On the other hand, 5% Pd/Al_2O_3 was also found to be an active catalyst (optimum solution pH = 1); however, the turnover rate was somewhat lower than that for 5% Pd/carbon. Thus, under conditions similar to that for reaction 1 except with pH = 1, the conversions observed starting with 0.175 mmol of $CH_3CH_2CH_2SO_3Na$ were 74% for 15 mg of 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.

Table 1
Oxidation for para-substituted phenols. Reaction conditions: Pd/C (0.9 mmol of surface Pd atoms), phenol (25 mg), pH 3 D_2O (3 ml), CO (100 psi), N_2 (1000 psi), O_2 (100 psi), 24 h at 90°C

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

The deep oxidation of a number of para-substituted phenols was achieved under typical reaction conditions (reaction 1) (table 1). The products of the decomposition of *p*-bromophenol (25 mg, 0.145 mmol) were examined by ^1H-NMR spectroscopy and were found to include *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 fig. 1, the rate of conversion of 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 substituted phenol to the parent phenol. This is consistent with an initial electrophilic attack at the ring.

Perhalogenated aromatics were also examined. 2,4,6-trichlorophenol, a toxic byproduct from paper mills, was decomposed under conditions similar to reaction 1. 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 ^1H-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 acid were detected by ^1H-NMR spectroscopy, and bromide ions

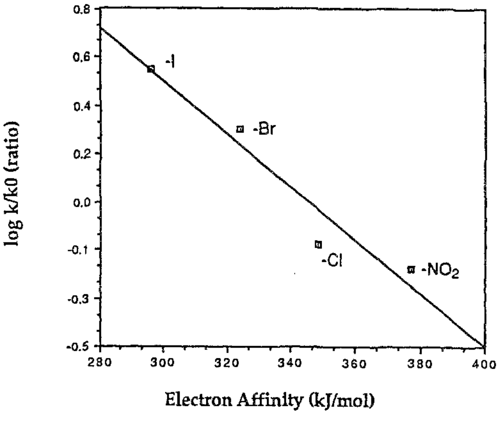


Fig. 1. Plot of the ratio of the log of the rate of oxidation of para-substituted phenol to the parent phenol versus electron affinity of the substituent. Reaction conditions: Pd/C (0.9 μmol of surface Pd atoms), C_6H_5OH (25 mg), *p*-X-C_6H_4OH (25 mg), pH 3 D_2O (3 ml), CO (100 psi), N_2 (1000 psi),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

Table 2
Effect of functional groups on degradation rate. Reaction conditions: 25 mg substrate in pH 3 D_2O (3 ml), 15–40 mg 5% Pd/carbon (0.9–2.4 μmol surface Pd atoms), 100 psi O_2, 100 psi CO, 1000 psi N_2, 80°C

Substrate	Time (h)	Temp. (°C)	Substrate (mmol)	Conversion (%)	Turnovers/ surface Pd	Products in solution (mmol)
$ClCH_2CO_2H$	25	95	0.53	67	197	HCO_2H (tr)
$ClCH_2CH_2CO_2H$	25	100	0.46	95	278	HCO_2H (tr)
CH_3NO_2	24	90	0.90	16	69	HCO_2H (tr) CDH_2NO_2 (tr) CH_3CO_2H (0.02)
Et_2NCOCH_3	22	120	0.40	6	13	CH_3CO_2H (0.05)
$CH_3CH_2SO_3Na$	20	80	0.38	100	210	$MeOSO_3H$ (0.47) CH_3CO_2H (0.07) HCO_2H (tr)

were quantitatively determined by precipitation with $AgNO_3$.

The catalytic system also demonstrates utility in decomposing compounds related to organophosphorus nerve agents [10]. Many nerve agents, e.g. Sarin, Soman, and VX, have phosphorus–alkyl and phosphorus–alkoxy bonds. Triethyl phosphine oxide and triethyl phosphite, were used as models for the oxidative degradation of the two kind of bonds. Under conditions akin to reaction 1 but with twice the amount of substrate (50 mg, 0.37 mmol) and catalyst (1.8 μmol surface Pd atoms), the former was oxidized with a 45% conversion (95 turnovers/surface Pd atoms). Acetic acid was the only significant organic species present in solution. With triethyl phosphite (100 μl, 0.58 mmol), an 87% conversion was observed. Hydrolysis was found to precede the oxidation step with a 35% selectivity to ethanol along with only a trace of acetic and formic acids detected by ^{1}H-NMR spectroscopy.

A variety of other functional organics were also studied (table 2). Aliphatic chlorocarboxylic acids and sulfonic acids were easily oxidized. Nitromethane mostly underwent H–D exchange under the reaction conditions. Amides appear to be particularly resistant to oxidation, with only 5% conversion observed for N,N-diethyformamide, acetic acid being the only organic product detected in solution.

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 (reaction 1). Consequently, we have briefly examined alternative solvent systems that are superior to water in dissolving organic compounds. One such solvent system 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 fig. 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 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 (reaction 1), 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.

4. Conclusion

In conclusion, we have discovered an unusually versatile catalytic system for the deep oxidation of toxic organics in water. This system possesses several attrac-

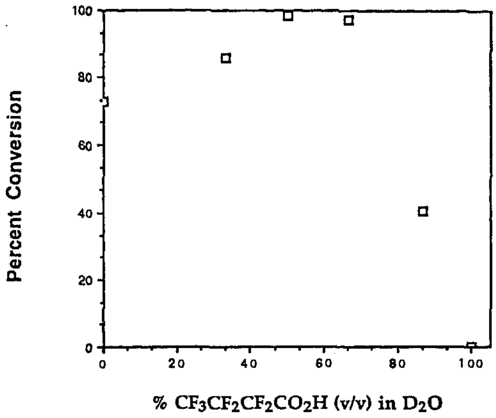


Fig. 2. Plot of the conversion of $CH_3CH_2CH_2SO_3Na$ versus %perfluorobutyric acid (v/v) in D_2O. Reaction conditions: Pd/C (1.5 μmol of surface Pd atoms), $CH_3CH_2CH_2SO_3Na$ (0.76 mmol), CO (100 psi), N_2 (1000 psi), O_2 (100 psi), solvent volume (3 ml), 90°C, 24 h.

tive features not found simultaneously in other reported systems. These are (a) the ability to directly utilize dioxygen as the oxidant, (b) the abilty 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.

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