The deep oxidation of chemical warfare agent models: facile catalytic oxidative cleavage of phosphorus–carbon and sulfur–carbon bonds using dioxygen

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In water, metallic palladium on carbon was found to catalyze the deep oxidation of organophosphorus and organosulfur compounds by dioxygen at 90°C in the presence of carbon monoxide. This system presents the first examples of catalytic cleavage of phosphorus–carbon bonds. 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: $(CH_3)_2S > (CH_3)_2SO > (CH_3)_2SO_2$ and is consistent with the system acting as an electrophilic oxidant.

Keywords: palladium metal, oxidation, organophosphorus compounds, organosulfur compounds

1. Introduction

It is estimated that there are 30,600 metric tons of chemical weapons stored in the continental US [1]. Since the Chemical Weapons Convention Treaty mandating the eradication of all chemical weapons by the year 2007 took effect in April 1997 [2] and Public Law 102-484 requiring the destruction of unitary chemical weapons by 31 December 2004 has already been enacted, there is significant pressure to develop novel methods for the decomposition of these chemicals [3,4]. Several methods for chemical weapons destruction have been employed, including incineration in a modified hydrazine furnace, hydrolysis of the agents with very concentrated NaOH solutions, and silver-mediated electrochemical oxidation [3–5]. These processes have certain disadvantages. The first requires high temperatures and a fuel to effect the complete oxidation of substrate, the second procedure produces large quantities of waste (the alkali salts), and the third suffers from AgCl precipitation with chloride-containing substrates. A number of alternate methods have been reviewed and rejected including open atmospheric dispersion and/or burning, ocean dumping, placing the chemicals in extraterrestrial orbit, destruction by underground nuclear weapons explosions, burial in volcanoes, and destruction of weapons in existing industrial facilities [4].

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 [6]) or sulfur–carbon (e. g., mustard gas [6]) bonds, and their neutralization requires the cleavage of these bonds. Herein, we report the *first* system for the efficient catalytic oxidative cleavage of phosphorus–carbon and sulfur–carbon bonds in model compounds under mild conditions, 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 [7]. 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 [8]. 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 [9]. To our knowledge, the present work provides the first detailed examples of catalytic cleavage of simple phosphorus–alkyl bonds.

2. Experimental

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

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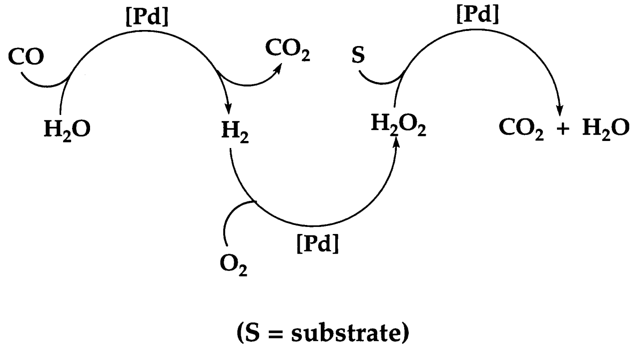

Scheme 1. Mechanism of Pd-catalyzed oxidation of organic substrates.

General procedures. To a glass liner containing 3 ml of HCl acidified D_2O (pH = 1) was added 15 mg of 5% Pd/carbon (0.9 μmol of surface Pd atoms, as determined from dihydrogen chemisorption studies) and varying amounts of substrate (see tables and text). The glass liner was then placed in a 125 ml stainless steel high pressure Parr reactor which was sealed. The reactor was purged with N_2 and pressurized to 100 psi with CO, to 1100 psi with N_2, and to 1200 psi with O_2. The contents were stirred at 80–90°C for 1 d. After venting, the products were examined by ^1H and/or ^{31}P NMR (referenced to H_3PO_4) spectroscopy. The products were identified by comparison to standard reference spectra and/or coinjection of standards.

3. Results and discussion

We had earlier described a catalytic system for the direct, low-temperature oxidation of methane and lower alkanes [10]. 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 an excess of the starting alkane), the ultimate oxidation products were carbon monoxide, carbon dioxide, and water. Mechanistic studies indicated that the overall transformation encompassed three catalytic steps in tandem (scheme 1) [10]. 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 [11]. The third step involved the metal-catalyzed oxidation of the substrate by hydrogen peroxide. It was possible to replace carbon monoxide and dioxygen by hydrogen peroxide; however, the amount of substrate oxidized relative to the hydrogen peroxide consumed was low due to the catalytic decomposition of hydrogen peroxide occurring in parallel with the oxidation. It was 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 was formed at a low steady rate through the first two catalytic reactions and was used more efficiently for substrate oxidation.

Two further control experiments are 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 was not a soluble palladium species and, indeed, the rapid reduction of K_2PdCl_4 to metallic palladium was observed under the reaction conditions. Presumably, the lower reaction rate observed starting with the former (compared to 5% Pd/carbon) was due to different aggregation of the metallic palladium formed in situ. Finally, a second control experiment indicated that the carbon support was not oxidized by the system.

Since the above catalytic system was able to effect the oxidation of molecules as unreactive as methane under unusually mild conditions, the deep oxidation of a number of hazardous organics was examined. These included benzene, phenol and substituted phenols, aliphatic and aromatic halogenated compounds, organophosphorus, and organosulfur compounds. In each case, deep oxidation to carbon monoxide, carbon dioxide,

Table 1
Oxidation of trimethylphosphine oxide. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 10 ml HCl acidified D_2O (pH = 1); 50 mg Pd/carbon (3 μmol surface Pd atoms); 500 mg $(CH_3)_3PO$ (5.43 mmol); 90°C

Time (h)	$(CH_3)_3PO$ (mmol)	$(CH_3)_2P(O)(OH)$ (mmol)	$(CH_3)P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	HCO_2H (mmol)	TON [a]
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] Turnover number defined as $\{[(CH_3)_2P(O)(OH)] + 2[(CH_3)P(O)(OH)_2] + 3[H_3PO_4]\}/[\text{surface Pd atoms}]$.

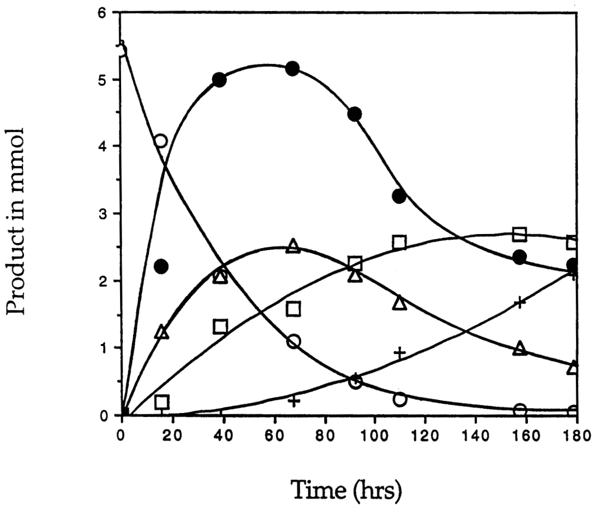

Figure 1. Plot of the products formed from $(CH_3)_3PO$ versus time. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 10 ml HCl acidified D_2O (pH = 1); 50 mg Pd/carbon (3 μmol surface Pd atoms); 500 mg $(CH_3)_3PO$ (5.43 mmol); 90°C. $(CH_3)_3PO$ (○); $(CH_3)_2P(O)(OH)$ (△); $CH_3P(O)(OH)_2$ (□); H_3PO_4 (+); HCO_2H (●).

and water occurred in high yields, resulting in up to several hundred turnovers over a 24 h period [12]. We now report a detailed study of the catalytic oxidative cleavage of phosphorus–carbon and sulfur–carbon bonds.

Oxidation of trimethylphosphine oxide produced three phosphorus-containing products: dimethylphosphinic acid, methylphosphonic acid, and phosphoric acid (table 1). 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 CO_2. From figure 1, it is evident that dimethylphosphinic acid and methylphosphonic acid are intermediates in the formation of phosphoric acid. After 179 h, only a trace of $(CH_3)_3PO$ remained. *In 179 h, over 4000 phosphorus–carbon bonds were cleaved by each Pd!* A ^{31}P NMR stack plot of the reaction is shown in figure 2. 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 little effect on the rate (tables 2 and 3). In order 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 ten 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-

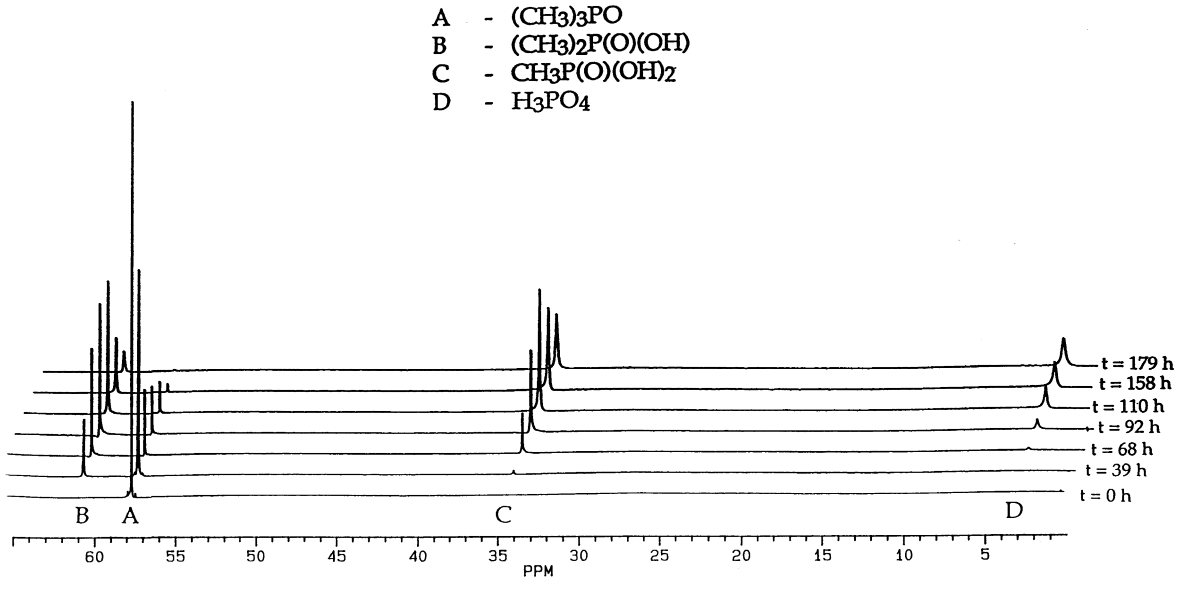

Figure 2. Stack plot of ^{31}P-NMR spectra obtained after the following reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 10 ml HCl acidified D_2O (pH = 1); 50 mg Pd/carbon (3 μmol surface Pd atoms); 500 mg $(CH_3)_3PO$ (5.43 mmol); 90°C.

Table 2
Oxidation of dimethylphosphinic acid. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 3 ml HCl acidified D_2O (pH = 1); 15 mg Pd/carbon (0.9 μmol surface Pd atoms); 94 mg $(CH_3)_2P(O)OH$ (1.00 mmol); 90°C

Time (h)	$(CH_3)_2P(O)OH$ (mmol)	$(CH_3)P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	HCO_2H (mmol)	TON [a]
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] Turnover number defined as $\{[CH_3P(O)(OH)_2] + 2[H_3PO_4]\}$/[surface Pd atoms].

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 4). 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 analogs 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 5). A 1 : 1 (v/v) mixture of water and perfluorobutyric acid was used in order 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 mmol, 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 is consistent with the earlier conclusion that the system acted as an electrophilic oxidant [12].

The ethyl analogs 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 analog and after 16.5 h of reaction the species present in 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).

Table 3
Oxidation of methylphosphonic acid. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 3 ml HCl acidified D_2O (pH = 1); 15 mg Pd/carbon (0.9 μmol surface Pd atoms); 96 mg $CH_3P(O)(OH)_2$ (1.00 mmol); 90°C

Time (h)	$(CH_3)P(O)(OH)_2$ (mmol)	H_3PO_4 (mmol)	HCO_2H (mmol)	TON [a]
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] Turnover number defined as $[H_3PO_4]$/[surface Pd atoms].

4. Conclusion

A palladium-based catalytic system for the oxidative cleavage of phosphorus–carbon and sulfur–carbon bonds under mild conditions has been developed that directly utilizes molecular oxygen as the oxidant. This system presents the first examples of catalytic cleavage of phosphorus–carbon bonds. It shows promise in the context of chemical weapons disposal, in particular as a low-cost procedure for the oxidation of the bulk of the chemical agent (although the use of gases at elevated

Table 4
Oxidation of ethylphosphonic acid. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 3 ml HCl acidified D_2O (pH = 1); 15 mg Pd/carbon (0.9 μmol surface Pd atoms); 110 mg $(C_2H_5)P(O)(OH)_2$ (1.00 mmol); 90°C

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 [a]
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] Turnover number defined as $\{[HO_2CCH_2P(O)(OH)_2] + [H_3PO_4]\}/[\text{surface Pd atoms}]$.

Table 5
Oxidation of methyl–sulfur compounds. Reaction conditions: 100 psi CO; 1000 psi N_2; 100 psi O_2; 3 ml HCl acidified D_2O (pH = 1); 15 mg Pd/carbon (0.9 μmol surface Pd atoms); 100°C

Substrate (mmol)	Time (h)	$(CH_3)_2S$ (mmol)	$(CH_3)_2SO$ (mmol)	$(CH_3)_2SO_2$ (mmol)	CH_3SO_3H (mmol)
$(CH_3)_2S$ [a,b] (1.00)	17.0	0.39	0.22	–	0.04
$(CH_3)_2SO$ [a] (0.50)	18.5	–	–	0.14	0.30
$(CH_3)_2SO_2$ (0.50)	18.5	–	–	0.47	0.03

[a] Deep oxidation to HCO_2H and CO_2 occurred.
[b] Solvent: 1.5 ml $CF_3CF_2CF_2CO_2H$ + 1.5 ml HCl acidified D_2O (pH = 1).

pressures may pose a safety problem). The remaining traces can then be removed using a more expensive procedure. The high efficiency, zero-order kinetics, and the ability to reuse the catalyst make this system especially attractive.

The general applicability of the system to a wide variety of substrates [12] increases its utility for concomitant destruction of a broad spectrum of chemicals used by the defence agencies, including chemical warfare agents, propellants, and explosives. In this context, we note that in addition to the legislations on chemical warfare agents discussed in the introduction, Public Law 99-145 encourages the swift destruction of M55 rockets because these particularly hazardous munitions have potential for self-ignition during storage.

Acknowledgement

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