

## Research paper

# Diethyl phosphite production from phosphorothioate degradation with molybdenum peroxides and hydrogen peroxide in ethanol

Louis Y. Kuo\*, Qianli Miao, Emily Bright, Kei Inoue, Owen Phillips, Joe Seaman, Megan Ng, Lauren Kang

Department of Chemistry, Lewis & Clark College, Portland Oregon, United States of America



## A B S T R A C T

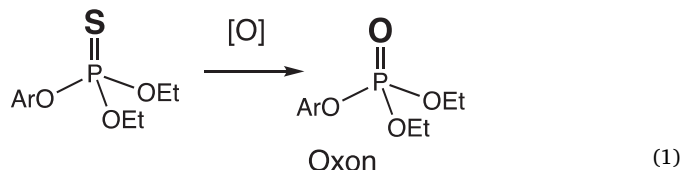
A polystyrene-supported molybdate-peroxide polymer (Mo-Y(s)) destroys phosphorothioate pesticides of the form  $(\text{ArO})\text{P}(=\text{S})(\text{OEt})_2$  in EtOH under mild oxidative ( $\text{H}_2\text{O}_2$ ) conditions and produces a commodity organophosphate. This is the first report of a metal-based system that successfully degrades the “live” pesticides parathion, diazinon and coumaphos. In addition to the operational advantages of heterogeneous reaction chemistry, the Mo-Y(s) support degrades multiple equivalents of the pesticide in  $\text{H}_2\text{O}_2(\text{aq})$ . Of particular importance is the predominant production of diethyl phosphite, a commodity chemical, from diazinon degradation over Mo-Y(s) in EtOH; no toxic oxon is found. Coumaphos and parathion produce the corresponding oxon which have  $\Delta H^\ddagger$  (kcal/mol) of 15.4 (0.5) and 21.7 (0.8), respectively; these activation parameters are consistent with key observations found in the relative amount of coumoxon and paraoxon produced. Finally, a discrete molybdate-peroxide complex is presented as a possible solution model for this heterogeneous reaction.

## 1. Introduction

Phosphorothioates of the form  $(\text{RO})_3\text{P}(=\text{S})$  [1] are commonly used as agricultural and residential pesticides. Common phosphorothioate pesticides take the form  $(\text{ArO})\text{P}(=\text{S})(\text{OEt})_2$  that include parathion, coumaphos, and diazinon (Fig. 1); they all act as neurotoxin acetylcholine esterase inhibitors [2].

Given the prevalence of organophosphate neurotoxins found in stream waters, [3] there is a need for safe and effective means to degrade these pesticides in the environment. Hydrolysis is the common method for degrading phosphorothioate neurotoxins, [4–6] and in some cases heterogeneous supports and matrices have been used [7–9]. Solid supports are operationally advantageous because of the convenience associated with product separation. Indeed, clay has been found to degrade some organophosphate pesticides albeit very slowly [10,11]. To that end, a variety of active metal complexes have been supported on silica [12], and on MOF [13] that accelerate the degradation. In this connection, this report presents the first case of a metal-peroxo polymer that accelerates the degradation of phosphorothioate pesticides in an alcohol solvent. Alcoholysis of organophosphate neurotoxins [14] by metal complexes has been reported even for supported systems [15]. An alcohol matrix is advantageous because of the poor water solubility of most phosphorothioates and in some systems, the rates were faster in an alcohol media [16] than in water solution. While peroxide [17–19] and ozone [20] -promoted degradation of phosphorothioates are known, they inevitably form the toxic oxon [21]  $(\text{ArO})\text{P}(=\text{O})(\text{OEt})_2$  in a

desulfurization reaction (Eq. (1)).



This report reveals conditions for phosphorothioate pesticide degradation that does not yield oxon formation with the operational advantages of heterogeneous catalysis. Moreover, for the pesticide diazinon, the commodity chemical diethyl phosphite is the main product which represents a form of phosphorus recovery from an organophosphate neurotoxin [22].

## 2. Materials and methods

## 2.1. Equipment and materials

All  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker Avance-300 spectrometer at 121.495, 300.130 and 75.468 MHz, respectively. IR spectra of the molybdenum compounds were obtained with a Nicolet 380 FT-IR spectrometer as nujol mull. Reactions for Arrhenius plots were run in either a Fischer Scientific Isotemp Refrigerated Circulator (Model 9000) or on an IKA RCT hot plate/stirrer. All UV-Vis spectra were obtained with an Agilent 8453 UV-Vis spectrometer. Molybdenum compounds such as bis(acetylacetonato)

\* Corresponding author.

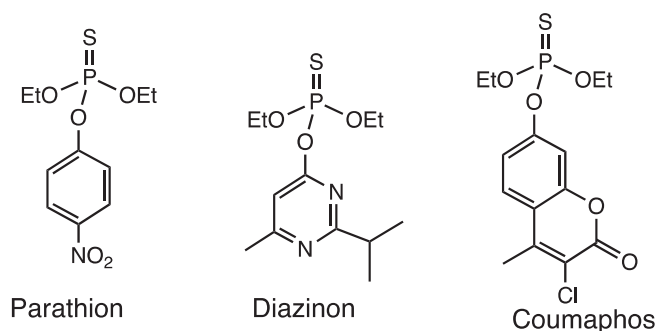
E-mail address: [kuo@lclark.edu](mailto:kuo@lclark.edu) (L.Y. Kuo).

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**Fig. 1.** Structure of phosphorothioate pesticides parathion, diazinon and coumaphos that shows the conserved diethylphosphorothioate ((EtO)<sub>2</sub>P(=S)) group.

dioxomolybdenum(VI), MoO<sub>3</sub> and molybdenum powder (99.999%) were from Alpha Aesar, and aqueous H<sub>2</sub>O<sub>2</sub> (27–30%) was from Sigma Aldrich. All phosphorothioate pesticides were purchased from Sigma-Aldrich or ChemService and used as is. The corresponding oxons (i.e. paraoxon and coumoxon) were purchased from Chemical Services, and the Diaion CR20 polystyrene beads were a gift from Mitsubishi Chemical Co. Elemental analyses were conducted by ALS Environmental (Tucson AZ), and energy dispersive X-ray (EDX) spectroscopy were carried out at the Center for Electron Microscopy and Nanofabrication facility at Portland State University (USA). Gas chromatography-mass spectral analyses were done at the Pankow Mass Spectrometry Facility (Portland State University, USA).

The solution analog dioxo-2,6-bis[hydroxyl(methyl)amino]-4-morpholino-1,3,5-triazine molybdate(VI) (**1**) [23] was made from cyanuric acid, morpholine, *N*-methylhydroxylamine-HCl (TCI America) and bis(acetylacetonato)dioxomolybdenum(VI). The analog oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) (**2**) [24] was made according to prior literature reports from pyridine-2-carboxylic acid (TCI America) molybdenum trioxide.

The supported molybdenum-peroxo catalyst, abbreviated as Mo-Y(s), was synthesized according to a modified procedure [25]. Specifically, molybdenum powder (0.75 g, 7.8 mmole) was added in small portions to 10 mL of aqueous 30% hydrogen peroxide (327 mmole) over the course of ~2 min at room temperature without excessive foaming. The solution initially became opaque with a dark green hue but transitioned to translucent (bright) yellow over the course of the molybdenum addition. Diaion CR20 polymeric beads (2.15 g) were slowly added to the stirring yellow suspension over the course of 20 min. The suspension was stirred slowly (magnetically) to avoid damaging the beads. After ~18 h of gentle stirring, the bright yellow beads were filtered on a fritted funnel and washed with DI water (100 mL) followed by diethyl ether and dried overnight under vacuum at room temperature. Elemental analysis for Mo-Y(s): C, 56.66; H 5.80; N 3.67; Mo 11.68. Elemental analysis for CR20 (No Mo added): C 72.70; H 8.95; N 8.35

## 2.2. Kinetic runs

The title reaction was carried out in 1 dram vials with 50 mg of the Mo-Y(s) support (0.09 mmole molybdenum); the Mo content was based on elemental analyses of the Mo-Y(s) beads. The ethanol solvent (2.0 mL) was added to the Mo-Y(s) followed by addition of 60 μL of aqueous 30% H<sub>2</sub>O<sub>2</sub> (0.60 mmole); this suspension was allowed to sit for 20–30 min. Kinetic runs commenced with the addition of 0.01 mmole of the phosphorothioate pesticide (2.3 μL for parathion, 2.2 μL for diazinon and 3.6 mg for coumaphos), and all kinetic runs were unstirred unless otherwise specified. At specific time intervals, the solution above the Mo-Y(s) beads/support was transferred from the vial into a 5 mm NMR tube without collecting any of the 0.5 mm beads. Following a <sup>31</sup>P

NMR spectrum, this solution was pipetted back to the 1 dram reaction vial containing the Mo-Y(s) beads/support. This process was repeated at various time points for kinetic runs wherein NMR acquisitions were done at the same temperature as the kinetic runs.

For kinetic runs monitored with UV/Vis spectroscopy, the reactions were done in 1.0 mL EtOH (40 °C) with 30 μL of aqueous H<sub>2</sub>O<sub>2</sub> (0.30 mmole). After the addition of 0.01 mmole of either parathion or coumaphos, 10 μL-aliquots of the EtOH reaction were taken at 5–20 min intervals and quenched in 1.5 mL 0.10 M NaOH. Product formation (i.e. *p*-nitrophenolate or chlorferon) was recorded at 400 nm and 374 nm for parathion and coumaphos, respectively.

Rate constants for the oxidative degradation of the phosphorothioate were obtained with both <sup>31</sup>P NMR and UV/Vis where the signals fit well to Eq. (2) where C is a constant:

$$P_t = C(1 - e^{-kt}) \quad (2)$$

In the case of UV/Vis,  $P_t$  is the absorbance at either 400 nm (parathion) or 374 nm (coumaphos) at time  $t$ . For NMR kinetic runs, the integrals from all signals (67 ppm starting material, 12 ppm diethyl phosphite, –4 to –6 ppm oxon and 2 ppm triethylphosphate) were combined, and  $P_t$  is ratio of the product integral (i.e. either diethyl phosphite or oxon) to the aforementioned total combined signals at time  $t$ . All kinetic plots obtained by either <sup>31</sup>P NMR or UV/Vis were fitted to Eq. (2) with Solver (Excel) to obtain rate constant  $k$ .

Solution (homogeneous) kinetic runs used 56.4 mg (0.103 mmole) of **2** in 1.5 mL of EtOH with the addition of 15 μL (0.15 mmole) of 30% H<sub>2</sub>O<sub>2</sub>(aq). Following dissolution of **2** in a 1 dram vial at 60 °C (~5 min), the ethanolic solution of **2** was transferred into a NMR tube, set to the desired temperature and <sup>31</sup>P NMR accumulation commenced after addition of 0.01 mmole of the pesticide. All <sup>31</sup>P NMR collection (both heterogeneous and homogeneous) used 64 scans with a 3 s delay. Prior studies with a similar protocol found that changing the pulse delay did not affect the rate constant [26]. Appearance of products were fitted to Eq. (2) to attain pseudo-first order rate constants for the homogeneous degradation by **2**.

## 3. Results and discussion

### 3.1. Mo-Y(s) material and peroxide activation

The oxidation of Mo(s) powder with H<sub>2</sub>O<sub>2</sub> (aq) generates a canary-yellow solution referred to as Mo-Y(l). This yellow solution was postulated [27,28] to be a polyoxomolybdate consisting of a chain of Mo–O–Mo (μ-oxo) linkages that carried out homogeneous alkene oxidation chemistry with H<sub>2</sub>O<sub>2</sub> addition. This polyoxomolybdate (Mo-Y(l)) was immobilized on the CR20 poly(ethyleneamine) support (0.5 mm beads), and will now be referred to as Mo-Y(s); as a modified polystyrene polymer (see table of contents Figure), CR20 has been used as a metal ion chelator.[29] The original protocol [25] was used to support the molybdenum peroxide functionality (Mo-Y(l)) on the CR20 polymer. The Mo-Y(s) support was exhaustively washed with water and ether after loading with the molybdenum peroxide; the washes initially were dull yellow and ended up colorless. IR spectroscopy of crushed Mo-Y(s) beads revealed a prominent Mo = O 943 cm<sup>-1</sup> stretch with weaker peroxy stretches at 870 and 580 cm<sup>-1</sup> (SI Fig S1). There is a strong 909 cm<sup>-1</sup> stretch, and a prior report of dried Mo-Y(l) attributed this stretch to a μ-oxo functional group [27,28]. Furthermore, energy dispersive X-ray spectroscopy (EDX) on Mo-Y(s) showed modification of the CR20 beads resulted in the surface attachment of molybdenum that was previously absent (SI Fig. S2A). To this end, Mo elemental analysis gave 11.68% which is close to the 10% reported previously [25], and subsequent Mo loading is based on this percentage of molybdenum content. The oxygen atoms on the Mo-Y(s) are a combination of Mo = O, Mo(OO) peroxy, and Mo–O–Mo functionalities that originate from the added H<sub>2</sub>O<sub>2</sub> (aq). Both elemental analysis and EDX yield (calculations in SI Fig. S2B) ratios of oxygens to molybdenum of 5.3:1

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