Heterogeneous Catalysis

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Simple and Compelling Biomimetic Metal–Organic Framework Catalyst for the Degradation of Nerve Agent Simulants**

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Abstract: *Inspired by biology, in which a bimetallic hydroxide-bridged zinc(II)-containing enzyme is utilized to catalytically hydrolyze phosphate ester bonds, the utility of a zirconium(IV)-cluster-containing metal–organic framework as a catalyst for the methanolysis and hydrolysis of phosphate-based nerve agent simulants was examined. The combination of the strong Lewis-acidic Zr^{IV} and bridging hydroxide anions led to ultrafast half-lives for these solvolysis reactions. This is especially remarkable considering that the actual catalyst loading was a mere 0.045 % as a result of the surface-only catalysis observed.*

The catalytic decomposition of phosphate ester bonds is an important challenge for the destruction of chemical warfare agents,[1,2] as well as for the hydrolytic cleavage of biologically relevant molecules such as DNA and RNA.[3,4] Nerve agents based on phosphate esters inhibit the degradation of acetylcholine (an excitatory neurotransmitter that initiates muscular response), which ultimately leads to asphyxiation.[5] In nature, the phosphotriesterase (PTE) enzyme, found in *Pseudomonas diminuta*, *Flavobacterium*, *Agrobacterium radiobacter*, and *Chryseobacterium balustinum* bacteria, is known to be highly active in the hydrolysis of phosphate ester bonds.[5,6] From a catalytic design perspective, the active site of PTE is composed of a pair of Zn^{II} ions, bridged by a hydroxo ligand, that operate cooperatively to perform the cleavage of P–O bonds (Figure 1 a); one Zn^{II} center binds and activates the P=O bond while the other transfers an OH^- to induce the cleavage of an –OR group from the substrate.

Enzyme mimics capable of catalytically decomposing phosphate esters in homogeneous solution have been investigated, including many coordination complexes. There have been several reports regarding the catalytic degradation of organophosphates using bimetallic Zn^{II} systems in which the active sites commonly comprise alkoxide-bridged Zn^{II} centers surrounded by 2–3 nitrogen-based donors.[7–10] Additionally, complexes containing highly Lewis-acidic cations such as, but not limited to, Ln^{III},[11–14] Al^{III},[15,16] and Ce^{IV} have been explored.[3,17] While these studies have provided valuable mechanistic information, in the context of chemical-threat protection (i.e. the filtering and catalytic destruction of toxic chemicals), the field implementation of these solution-phase catalysts would likely be cumbersome.[18–20]

There has thus been interest in utilizing solid heterogeneous catalysts for the hydrolysis of phosphate ester (and other) bonds within known chemical warfare agents. For example, we recently demonstrated that amorphous, metal-ion-functionalized, porous organic polymers (POPs) show catalytic activity for the solvolysis of phosphotriesters. Specifically, we found that aluminum(III)-porphyrin-containing[21] and lanthanum(III)-catechol-containing POPs[21,22] are capable of catalyzing the methanolysis of methyl paraoxon (Scheme 1 a). Metal oxides have also been extensively studied;[1] an impressive recent study from Peterson and co-

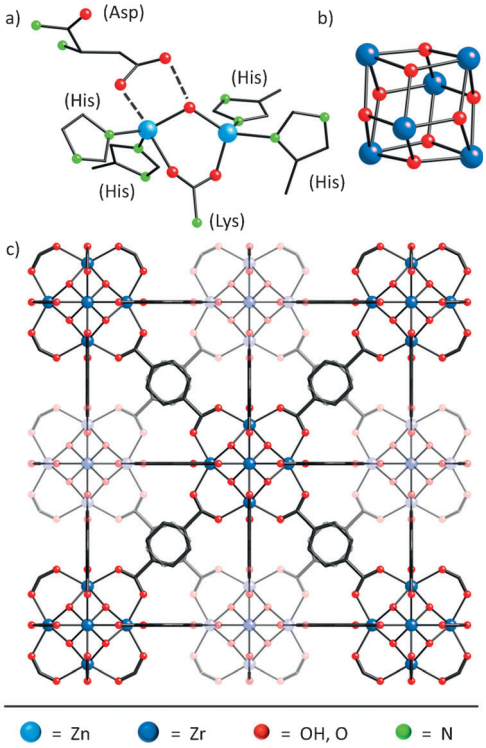

Figure 1. a) A schematic drawing of the structure of the active site of phosphotriesterase.[6] b) The $[Zr_6O_4(OH)_4]$ cluster. c) The 3D structure of UiO-66.

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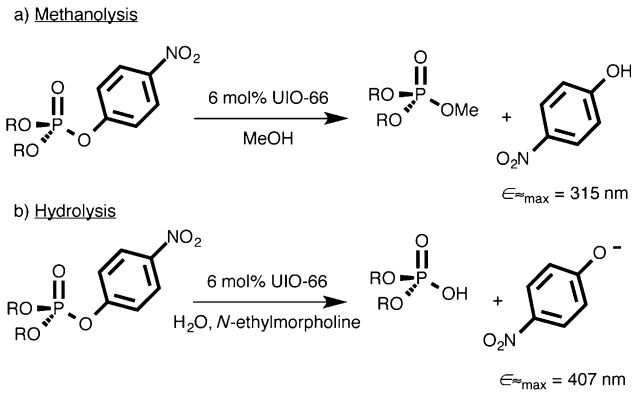

Scheme 1. a) Methanolysis of both methyl paraoxon (R = CH_3) and PNPDPP (R = phenyl). b) Hydrolysis of methyl paraoxon (R = CH_3).

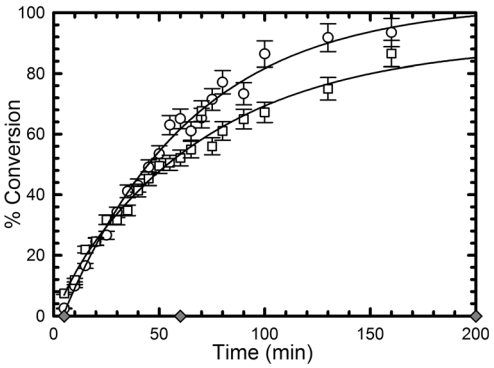

Figure 2. Conversion profiles for the methanolysis of methyl paraoxon (○) and PNPDPP (□) in the presence of UiO-66 as functions of time. Gray ◆ represent the conversion profile for the uncatalyzed reactions.

workers noted the efficacy of zirconium hydroxide for the decomposition of the nerve agents VX, Soman (GD), and distilled mustard (HD).[23]

Intrigued by the observation that metal oxides/hydroxides are quite reactive toward nerve agents based on phosphate esters,[1,23] we turned to an alternative class of materials, metal–organic frameworks (MOFs).[24–26] Owing to their porosity and broad compositional tunability, MOFs have attracted significant attention as potential catalysts for a wide range of chemical reactions.[24,27,28] Furthermore, given their crystallographically resolved structures, MOFs are highly amenable to mechanistic and computational studies (by contrast, such studies are much more difficult at the surface of bulk metal oxides/hydroxides and inside POPs).[29]

Herein, we report the use of the MOF UiO-66 (Figure 1 c)[30] as a compelling biomimetic catalyst for the methanolysis and hydrolysis of two organophosphate nerve agent simulants.[31] The node of UiO-66 is a $[Zr_6O_4(OH)_4]$ cluster that contains several Zr−OH−Zr bonds, reminiscent of the bimetallic Zn−OH−Zn active site found in phosphotriesterase enzymes (Figure 1 a,b). UiO-66 is also particularly attractive as a solid catalyst because: 1) it is readily synthesized in high yield, and 2) it is among the most chemically, hydrothermally, and mechanically stable MOFs known.[32–39]

Given the toxicity of phosphate nerve agents and the concomitant risk in handling them, especially in the vapour phase, we investigated the catalytic activity of UiO-66 using the less toxic simulants methyl paraoxon (dimethyl 4-nitrophenyl phosphate) and *p*-nitrophenyl diphenyl phosphate (PNPDPP) in solution (Scheme 1). The formation of UV/blue-absorbing nitrophenol/nitrophenoxide makes for straightforward monitoring of the reaction progress by using UV/Vis spectroscopy (Scheme 1).

The UiO-66-catalyzed methanolysis of methyl paraoxon and PNPDPP were carried out at 333 K by stirring a 6 mol% slurry of UiO-66 powder (based on formula weight) in methanol (Figure S1 in the Supporting Information). Although the methanolysis of methyl paraoxon necessarily stops at trimethylphosphate, in the case of PNPDPP the first methanolysis product, methyl diphenyl phosphate (Scheme 1a), can undergo further methanolysis. Indeed, the $^{31}P\{^1H\}$ NMR spectrum of the PNPDPP product recorded after 5 h (Figure S3 in the Supporting Information) exhibits a resonance at $\delta = -4.4$ ppm (15% relative intensity) that can be attributed to dimethyl phenyl phosphate, the second methanolysis product of PNPDPP.

The conversion profiles for both methyl paraoxon and PNPDPP methanolyses are shown in Figure 2. Interestingly, the reaction half-lives are independent of the substrate ($t_{1/2}$ = 45–50 min for both phosphate triesters). We postulate that under our reaction conditions, the rate of methanolysis is limited by the formation of methoxide. Initial rates of 5×10^{-6} M s^{-1} and 4×10^{-6} M s^{-1} were observed for methyl paraoxon and PNPDPP, respectively; no appreciable background reaction was observed over the course of 24 h. In comparison to several catalysts reported for the methanolysis of methyl paraoxon and PNPDPP, UiO-66 is among the fastest.[8,15,21] For example, the half-life of methyl paraoxon methanolysis by UiO-66 is 2–3 times shorter than that observed for the analogous reaction catalyzed by our aluminum(III)-porphyrin-containing POPs,[21] and more than ten-fold shorter than the half-life observed for the homogeneous, supramolecular aluminum(III)-porphyrin-based catalyst.[15] Relative to catalysis by a dimeric Zn^{II} coordination complex structurally akin to the PTE active site, the half-life with UiO-66 is four times shorter.[8]

Encouraged by the excellent activity of UiO-66 in phosphate ester methanolysis, we decided to test the activity of UiO-66 for catalytic hydrolysis. From the perspective of human protection, as opposed to simple agent destruction, hydrolysis is much more practical than methanolysis. Hydrolysis of methyl paraoxon was carried out in the presence of a 6 mol% slurry of UiO-66 in an aqueous solution containing 0.45 M *N*-ethylmorpholine (as a buffer at pH 10 and also presumably as a proximal base). As in the case of methanolysis, the formation of *p*-nitrophenoxide was followed using UV/Vis spectroscopy (Scheme 1 b, Figure S2 in the Supporting Information); however, the $^{31}P\{^1H\}$ NMR spectrum of the product from the hydrolysis of methyl paraoxon (Scheme 1 b) did not show evidence of hydrolysis beyond dimethyl phosphate, thus demonstrating the highly selective nature of UiO-66. Figure 3 shows the percent conversion of methyl paraoxon as a function of time at room temperature and

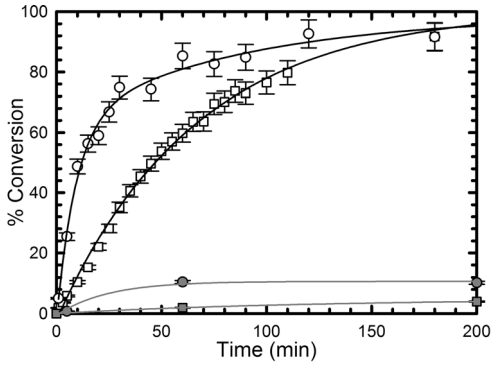

Figure 3. Conversion profiles for the hydrolysis of methyl paraoxon in the presence of UiO-66 at room temperature (□) and 333 K (○) as a function of time. Gray ■ and ● represent the conversion profiles for the uncatalyzed reaction at room temperature and 333 K, respectively.

333 K, with half-lives of 45 and 10 min and initial rates of 4.2×10^{-6} and 1.6×10^{-6} M s^{-1}, respectively. Attempts to determine the half-life of the uncatalyzed reaction were unsuccessful; in our hands at room temperature and 333 K, the reaction proceeded until approximately 15% conversion upon which no further hydrolysis was observed. Under similar conditions/concentrations, UiO-66 afforded a 40-fold shorter reaction half-life when compared to the previously reported MOF Cr-MIL-101 in the presence of dimethylaminopyridine (DMAP),[31a] thus making it the most effective MOF-based catalyst for the hydrolysis of phosphate esters reported to date.

To confirm that the catalysis is indeed heterogeneous, we filtered the reaction mixture through a 200 μm filter after 20 min, and continued to monitor the hydrolysis of methyl paraoxon in the filtrate. As expected for a heterogeneously catalyzed reaction, no catalysis was observed in the solution after filtration (Figure S4 in the Supporting Information). Given the known high mechanical stability of UiO-66,[39] it is not surprising that powder X-ray diffraction (PXRD, Figure 4), scanning electron microscopy (SEM, Figure S5 in the Supporting Information), and transmission electron microscopy (TEM, Figure S5 in the Supporting Information) confirm that UiO-66 is stable under our reaction conditions. Interestingly however, the surface area of UiO-66 decreased from 1450 to 880 and 750 m^2 g^{-1} after methanolysis and hydrolysis, respectively. We attribute this to clogging of the pores or apertures of UiO-66 by the various reagents and products in solution and not to degradation of the MOF. This hypothesis is supported by the observation that UiO-66 becomes yellow after catalysis and the fact that the $^{31}P\{^1H\}$ NMR spectrum of a postcatalysis sample of UiO-66 dissolved in D_2SO_4 showed the presence of an unidentified phosphorous-containing complex. In addition, the ^1H NMR spectrum of the same sample exhibited peaks from more than just benzendicarboxylate (BDC). Considering that catalysis can occur only on the MOF exterior surface (see below), we do not expect pore clogging to affect the rates of catalysis.

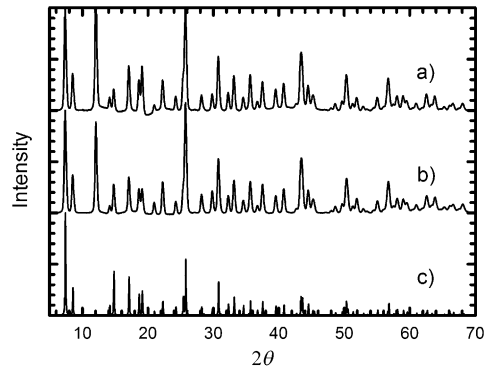

Figure 4. PXRD data for UiO-66 postcatalysis (a) and precatalysis (b) compared to a simulated pattern (c). No significant change in peak position or intensity is observed; the peaks from 10° on have been magnified by 10x for clarity.

The catalytic efficiency of UiO-66 is even more impressive when one considers that the actual number of active catalytic sites is only a fraction of the nominal 6 mol% loading. Even methyl paraoxon (ca. 11×4.5 Å), the smaller of the two substrates, is too large to access the interior of UiO-66 (the apertures of which are ca. 6 Å across), thus all of the catalysis occurs on the exterior surface of the MOF crystals and the local turnover frequency (TOF) is much higher than the apparent rates and half-lives described above. To get an estimate of the true TOF for UiO-66-catalyzed hydrolysis, we measured the particle size of our UiO-66 sample using SEM, TEM, and dynamic light scattering (DLS). Interestingly, in contrast to the octahedron-shaped crystals that have been reported,[37] the SEM image (Figure S6 in the Supporting Information) of our UiO-66 shows aggregates of 400 nm spheroid particles. DLS measurements of UiO-66 in a dilute aqueous medium (Figure S7 in the Supporting Information) also confirm the presence of 400 nm particles. The TEM image of UiO-66 (Figure S6) further suggests that the 400 nm particles observed by SEM/DLS are not agglomerates of even smaller particles. Based on this data and assuming an average particle size of 400 nm, only approximately 0.75% of the MOF nodes are accessible to the nerve agent simulant molecules. A nominal catalyst loading of 6 mol% thus corresponds to an accessible catalyst loading of a mere 0.045 mol% (assuming that each available hexazirconium node comprises one active catalytic site). The local TOF for the hydrolysis of methyl paraoxon by UiO-66 is then 0.4 s^{-1} at room temperature and 1.5 s^{-1} at 333 K; quite impressive numbers for a heterogeneous catalyst.

In conclusion, we have demonstrated that UiO-66 is an active biomimetic catalyst for the methanolysis of methyl paraoxon and PNPDPP. Most notably, UiO-66 is an exceptionally active and selective catalyst for the hydrolysis of methyl paraoxon. We attribute the performance of UiO-66 to the ability of the Zr–OH–Zr-containing node to functionally mimic the binuclear Zn^{II} active site of the phosphotriesterase enzyme. We are currently investigating the effects of introducing either electron-donating or electron-withdrawing groups onto the BDC linker of UiO-66.[40,41]

Experimental Section

All reagents were purchased from commercial sources and used without further purification. UiO-66,[40] methyl paraoxon,[15] and *p*-nitrophenyl diphenyl phosphate (PNPDPP)[21] were synthesized according to reported procedures. Nitrogen isotherm measurements were carried out on a Micromeritics Tristar II 3020 at 77 K. Samples were activated by heating overnight at 80 °C under vacuum prior to measuring the isotherms. NMR spectra were collected on a Varian Inova 500 MHz NMR spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker AXS APEX2 diffractometer equipped with a CCD detector and a $Cu_{K\alpha}$ IμS microfocus source with MX optics. Data were collected with an area detector as rotation frames over 180° in ϕ at 2θ values of 12°, 24°, and 36°, and exposed for 10 min for each frame. At a distance of 150 mm, the detector area covers 24° in 2θ. The resulting pattern was integrated using the Bruker APEX2 Phase ID program.

Methanolysis experiments were carried out at 333 K (60 °C). A solid sample of UiO-66 (2.5 mg, 6 mol %, 0.0015 mmol; 0.045 mol % of active surface sites) was added to an aliquot of methanol (1 mL) in a 1.5 mL vial. The resulting mixture was stirred for 30 min to finely disperse the UiO-66. To this suspension was then added either methyl paraoxon (6.2 mg, 0.025 mmol) or PNPDPP (9.3 mg, 0.025 mmol). The vial was then placed in a preheated oil bath at 333 K under stirring. Periodic monitoring was carried out by removing a 20 μL aliquot from the reaction mixture (the 333 K reaction vial was removed from the oil bath and quickly cooled for 10 s in a dry-ice/isopropanol slurry before the sample was taken) and diluting it with methanol (10 mL) prior to UV/Vis measurements. Progress of the reaction was monitored by following the appearance of the *p*-nitrophenol absorption at 315 nm. Owing to the convolution of the starting material absorption at 270 nm, the absorption spectrum was fit to two Gaussian peaks using fityk.[42] The background reaction was carried out under identical reaction conditions without the catalyst.

Hydrolysis experiments were carried out at room temperature and 333 K. A solid sample of UiO-66 (2.5 mg, 6 mol %, 0.0015 mmole; 0.045 mole % of active surface sites) was added to an aqueous solution of *N*-ethylmorpholine (1 mL, 0.45 M) in either a 1.5 mL Eppendorf vial (room temperature) or a 1.5 mL vial (333 K). The resulting mixture was stirred for 30 min to finely disperse the UiO-66. To this suspension was then added methyl paraoxon (6.2 mg, 0.025 mmol). Periodic monitoring was carried out by removing a 20 μL aliquot from the reaction mixture (the 333 K reaction vial was removed from the oil bath and quickly cooled for 10 s in a dry-ice/isopropanol bath before the sample was taken) and diluting it with an aqueous solution of *N*-ethylmorpholine (10 mL, 0.45 M) prior to UV/Vis measurements. Progress of the reaction was monitored by following the *p*-nitrophenoxide absorbance at 407 nm to avoid overlapping absorptions with other species. No spectral evidence for the *p*-nitrophenol was observed at this pH. The background reaction was carried out under identical reaction conditions without the catalyst.

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