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Article

An Immobilized Ortho-Palladated Dimethylbenzylamine Complex as an Efficient Catalyst for the Methanolysis of Phosphorothionate Pesticides

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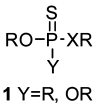
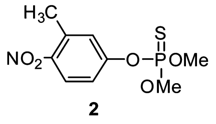
The methanolysis of a series of P═S phosphorothionate pesticides (fenitrothion, coumaphos, diazinon, and dichlofenthion) catalyzed by an ortho-palladated complex covalently attached to two different solid supports, macroporous polystyrene and amorphous silica gel, was studied. Both the polystyrene and the silica-based catalysts showed excellent activity in methanol near neutral pH (neutral $^{s}_{s}$pH = 8.38) at ambient temperature. These heterogeneous catalysts can be readily recovered and reused without significant loss of activity. Fifty milligrams of the silica-supported catalyst SiPd1 offered an acceleration of up to 8.6×10^9-fold for the methanolysis of fenitrothion (**2**) over the methoxide-promoted background reaction at $^{s}_{s}$pH = 8.8. For the same reaction, 50 mg of polystyrene-supported complex PSPd2 provided a 3.7×10^9-fold acceleration at $^{s}_{s}$pH = 8.8. When accounting for the amount of palladium in the solid, the slight superiority of silica over polystyrene as a solid support is believed to be a result of several possible factors including a higher concentration of active sites accessible to the reaction solvent and a more hydrophilic surface environment that allows better interaction of the methanol solvent with the attached palladacycle. Unlike the behavior in homogeneous solution, the rate of methanolysis of the substrates catalyzed by the solid catalysts was relatively insensitive to the nature of the substrate, probably indicating that a mass transport process is rate limiting. The solid-supported materials effectively decompose malathion at roughly stoichiometric ratios, but they are strongly inhibited by the thiol product resulting from the cleavage of the P═S(SR) linkage.

Introduction

The sulfur-containing phosphorothionate triesters of general structure **1** comprise a family of compounds that are commonly used as agricultural pesticides having potent insecticidal and acaricidal properties while maintaining lower levels of toxicity toward mammals.[1,2] Because of their widespread use and persistence, the environmental accumulation of these toxic materials presents an ecological and health threat that has spurred much research into finding efficient chemical and biological decomposition strategies.[3,4] Current chemical methodologies for the decomposition of organophosphorus (OP) compounds rely primarily on hydrolytic and oxidative processes, but only a few of these employ metal ions,[3] presumably because metal ion-catalyzed hydrolyses of OP substrates are relatively slow processes that also suffer from limited solubility of both the substrate and the active metal-hydroxo forms of the catalyst in water.



1 Y=R, OR
X=O, S



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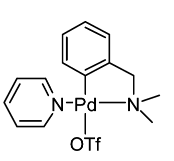

3 (OTf=$CF_3SO_3^-$)

Previous work in this laboratory demonstrated that neutral phosphate and phosphorothionate triesters,[5,6] phosphonates,[7]

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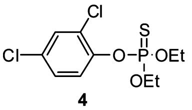
and phosphonothioates[8] are all cleaved rapidly in the presence of La^{3+} or a Zn(II) complex of 1,5,9-triazacyclododecane in methanol to yield relatively nontoxic products where the XR group of **1** is replaced by an OCH_3 group. We have also demonstrated that the Cu(II)($^{-}OCH_3$) complex of 1,5,9-triazacyclododecane catalyzes the methanolysis of phosphorothionate (P═S containing) triesters with billion-fold acceleration relative to the methoxide-promoted background reaction at the $^{s}_{s}$pH[9] where the catalytic reaction is conducted.[10] These results prompted us to initiate a program to investigate the catalytic potential of immobilized metal: ligand complexes affixed to solid supports, and we have recently reported the initial results wherein the methanolysis of a series of neutral organophosphorus esters was promoted by some polystyrene-supported Zn(II) and Cu(II) complexes.[11] The latter polymer-supported catalysts do not approach the activity of the corresponding complexes in solution, which is a general problem well-known for supported catalysts[12−15] and is usually attributed to surface and diffusion effects into the polymer matrix. However, the immobilized metal complexes still provide very good rate enhancements (up to 2.9×10^{6}-fold for the methanolysis of fenitrothion (**2**) by a Cu(II):1,5,9-triazacyclododecane-functionalized polystyrene) relative to the background reaction at $^{s}_{s}$pH = 9.05.[16] Thus, having demonstrated the successful immobilization of transition metal catalysts on solid supports, and their use as effective catalysts for promoting the methanolysis of some pesticides, we directed our attention toward developing more active and efficient anchored complexes.

Previously, we demonstrated that the palladacycle complex **3**, which had been shown to provide good catalysis of P═S OP materials in water,[17,18] is also an extremely efficient catalyst for the methanolysis of a series of phosphorothionate triesters including fenitrothion (**2**), where a 1 mM solution of catalyst at a near neutral $^{s}_{s}$pH = 8.75 in methanol accelerates the cleavage of **2** by 4.9×10^{9}-fold relative to the background methoxide-promoted reaction at that $^{s}_{s}$pH.[19] Complex **3** is also effective for the methanolysis of other phosphorothionate substrates including dichlofenthion (**4**), coumaphos (**5**), and diazinon (**6**). A kinetic analysis of the $^{s}_{s}$pH/rate profile revealed that all of these substrates react by a common mechanism involving formation of a transient complex (cis CH_3O^{-}−Pd−(S═P)), where subsequent intramolecular delivery of the methoxide with Lewis acid assistance leads to a methanolysis product. However, despite its high efficiency, **3** is sparingly soluble in water and methanol, and also is expensive when used for the purposes envisioned. Thus, it seemed likely that anchoring this palladacycle on a solid support might provide a proficient, reusable, and cost-effective heterogeneous catalyst for the decomposition of toxic P═S pesticide materials.



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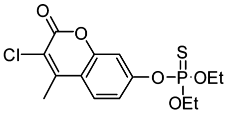

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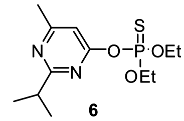

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While many examples of immobilized palladium catalysts for diverse processes exist, these have been generally investigated as potential catalysts for C−C bond forming and related cross-coupling reactions,[20] and the majority employ covalently anchored phosphines or imines for attachment of palladium to the surface. Some examples of immobilized (SCS)-type pincer palladacycles have been reported;[21] however, these complexes are known to be ineffective toward the methanolysis of phosphorothionate triesters.[22] The few examples of the immobilized ortho-palladated complexes that do exist have had variable success in their intended catalytic roles. In an example where the palladacycle was affixed to commercially available dicyclohexylphenyl phosphine-functionalized polystyrene, there was an apparent turnover of the catalyst, but no activity remained

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after the first run.[23] The ortho-palladated imine complexes developed by Nowotny et al.[24] and Bedford et al.[25] are thermally unstable in the organic media used, and all of the observed catalysis was found to be due to free palladium metal or nanoparticles in solution. More recently, Garcia et al. have reported that Suzuki-type cross-couplings could be promoted by an oxime carbapalladacycle immobilized on a variety of silica and polymeric surfaces.[26] While the SiO_2 anchored palladacycle showed no loss of activity after seven cycles,[26a] several of the polymeric materials exhibited decreased activity upon recycling.

Herein, we report on a simple method to generate an immobilized equivalent of complex **3** on commercially available polystyrene and silica supports and show that these have excellent catalytic activity and robustness for the methanolysis of phosphorothionate triesters **2** and **4**−**6** at ambient temperature and near neutral ^s_spH.

Experimental Section

Materials. Methanol (99.8% anhydrous), sodium methoxide (0.5 M solution in methanol), DMF (99.8%, anhydrous), K_2CO_3, Ag(OTf), $PdCl_2$, dimethylamine hydrochloride, dimethylamine (2.0 M solution in THF), and 4-benzyl chloride-functionalized silica gel (200−400 mesh, 1.2 mmol Cl/g) were purchased from Sigma-Aldrich and used as supplied. Acetonitrile was purchased from Fisher Scientific. PL-CMS MP-Resin (>12% of cross-linking with DVB, 2.8 mmol Cl/g, porosity size 100 Å, particle size 150−300 μm) was purchased from Polymer Laboratories. Fenitrothion (**2**, *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothionate), dichlofenthion (**4**, *O*,*O*-diethyl *O*-(2,4-dichlorophenyl) phosphorothionate), coumaphos (**5**, *O*-(3-chloro-4-methyl-2-oxo-2H-chromen-7-yl) *O*,*O*-diethyl phosphorothionate), diazinon (**6**, *O*,*O*-diethyl *O*-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothionate), and malathion (**8**, *O*,*O*-dimethyl-*S*-(l,2-dicarbethoxy)ethyl phosphorodithioate) were purchased from Chem Service Inc. and used as supplied.

The polystyrene- and silica-based catalysts (denoted PSPd and SiPd, respectively) were prepared by the same general methodology, starting from macroporous chloromethylated polystyrene and 4-benzyl chloride-functionalized silica gel, respectively.

Preparation of Dimethylbenzylamine-Functionalized Polystyrene. To a two-necked round-bottom flask were added 0.234 g (2.87 mmol) of dimethylamine hydrochloride and a small magnetic stir bar. The solid was dissolved in 20 mL of anhydrous DMF, and 0.602 g (4.36 mmol) of K_2CO_3 was added to the solution. The solid carbonate remained largely undissolved at the bottom of the flask, and the mixture was allowed to stir at room temperature for 2 h. At this point, 0.489 g of PL-CMS MP-Resin (1.37 mmol of Cl) was added to the reaction mixture along with an additional 0.19 g (1.37 mmol) of K_2CO_3, and the flask was equipped with a reflux condenser and thermometer. The mixture was heated to 100 °C in an oil bath and gently stirred to avoid crushing the polymer for 4 days. The polymer was then filtered and washed with excess water to dissolve all residual K_2CO_3, followed by washing with 100 mL of methanol. The pale yellow polymer was immersed in a solution of 0.1 M sodium methoxide in methanol overnight to remove traces of acid and cap any residual chloromethyl functionality. The polymer was filtered, washed with methanol (100 mL), and dried in an oven at 60 °C for 24 h.

Palladation of Dimethylbenzylamine-Functionalized Polystyrene. To a Teflon centrifuge tube were added 0.11 g (0.64 mmol) of $PdCl_2$ and 20 mL of anhydrous acetonitrile. The red solid was only sparingly soluble. To the mixture was added 0.33 g (1.3 mmol, 2 equiv) of Ag(OTf), whereupon an immediate formation of a thick beige precipitate (AgCl) ensued. A magnetic stir bar was added to the tube, and the mixture was stirred vigorously for 2 h until all of the red $PdCl_2$ was consumed. The solid precipitate was separated by centrifugation, and the yellow liquid phase was transferred to a 50 mL round-bottom flask containing 0.22 g of the dimethylamine-functionalized polystyrene prepared as above. Almost immediately after addition of the palladium solution, the pale yellow resin began to darken. The reaction flask was equipped with a small magnetic stir bar and a reflux condenser, and the two-phase mixture was heated to reflux for 24 h. After the mixture was cooled, the black polymer was filtered and washed with 100 mL of methanol, followed by drying at 60 °C for 24 h.

Preparation of Silica Gel-Supported Palladacycle. SiPd1. To a two-necked round-bottom flask were added 0.1195 g (1.47 mmol) of dimethylamine hydrochloride and a small magnetic stir bar. The solid was dissolved in 40 mL of anhydrous DMF, and 0.328 g (2.37 mmol) of K_2CO_3 was added to the solution. The solid carbonate remained largely undissolved at the bottom of the flask, and the mixture was allowed to stir at room temperature for 2 h. At this point, 0.614 g of 4-benzylchloride-functionalized silica gel (0.737 mmol Cl) was added to the reaction mixture along with an additional 0.11 g (0.8 mmol) of K_2CO_3, and the flask was equipped with a reflux condenser and thermometer. The mixture was heated to 100 °C in an oil bath and gently stirred to avoid crushing the silica for 4 days. The silica was then filtered and washed with excess water to dissolve all residual K_2CO_3, followed by washing with 100 mL of methanol. The pale yellow silica was immersed in a solution of 0.1 M sodium methoxide in methanol overnight to remove traces of acid and cap any residual benzylchloride functionality. The silica was filtered, washed with methanol (100 mL), and dried in an oven at 60 °C for 24 h. The palladium complex was formed analogously to what was described for the polystyrene-supported catalyst above.

SiPd2. To a heavy-walled glass pressure tube fitted with a Teflon screw cap was added 0.25 g of 4-benzylchloride-functionalized silica gel (0.3 mmol of Cl), and the gel was suspended in 10 mL of a 2.0 M solution of dimethylamine in THF (0.02 mol of dimethylamine, 67 equiv). The tube was sealed and heated in an oil bath at 80 °C for 72 h, after which the gel was filtered, washed with 100 mL of methanol, and then suspended in a 7 mM solution of $NaOCH_3$ in methanol overnight to remove all traces of acid. The resulting gel was washed by Soxhlet extraction with THF overnight and then dried at 60 °C for 24 h. The palladium complex was formed according to the procedure given above.

SiPd3. To a heavy-walled glass pressure tube fitted with a Teflon screw cap was added 1.0786 g of 4-benzyl chloride-functionalized silica gel (1.3 mmol of Cl), and the gel was suspended in 20 mL of a 2.0 M solution of dimethylamine in THF (0.04 mol of dimethylamine, 31 equiv). To the mixture was added 0.4768 g (1.3 mmol) of Bu_4NI. The tube was sealed and heated in an oil bath at 80 °C for 72 h, after which the gel was filtered, washed with 100 mL of methanol, and then suspended in a 7 mM solution of $NaOCH_3$ in methanol overnight to remove all traces of acid. The resulting gel was washed by Soxhlet extraction with $HOCH_3$

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overnight and then dried at 60 °C for 24 h. The palladium complex was formed analogously to what was described for the polystyrene-supported catalyst.

Analysis of Palladium and N Loading. Nitrogen microanalyses were performed by Canadian Microanalytical Services Ltd. in Delta, British Columbia. Samples of the palladium loaded material (0.01−0.1 g) were weighed into crucibles and burned in a muffle furnace at 500 °C for 4 h. The residual ash in the crucibles was dissolved in 4 mL of aqua regia (1 mL of HNO_3 + 3 mL of conc. HCl) and heated to 150 °C for 4 h on a hot plate to solubilize the palladium. The acid solutions were diluted with distilled water in a volumetric flask (10−100 mL) and analyzed for palladium at the Queen's Analytical Services Unit using a Varian AX-Vista Pro inductively coupled plasma-optical emission spectrometer. Samples were analyzed by monitoring the palladium emission line at 360.955 nm. The palladium content was determined on the basis of a four-point calibration curve using indium and scandium as internal standards.

Kinetics. All kinetics experiments with immobilized catalysts were conducted in 2.5 mL of a methanol solution buffered with *N*-iso-propylmorpholine (6.6 mM) at ${}^{s}_{s}\mathrm{pH} = 8.8 \pm 0.4$.[27] The rate of methanolysis of **2** (1×10^{-5} M) was monitored by observing the rate of loss of absorbance at 265 nm and the rate of appearance of the phenol product at 310 nm. The rate of disappearance of **4** (1×10^{-4} M) was followed at 220 nm, and the appearance of product was observed at 295 nm. For substrates **5** and **6** (1×10^{-4} and 1.5×10^{-4} M), the rates of starting material disappearance were observed at 293 and 245 nm and appearance of product from **5** at 195 nm. All reactions were monitored using a Cary 100 UV/vis spectrophotometer with the cell compartment thermostatted at 25.0 ± 0.1 °C. In a representative example monitored by UV/vis spectrophotometry, 0.05 g of PSPd2 was added to a quartz cuvette. In a separate vial, 25 μL of a 1×10^{-3} M stock solution **2** in methanol was added to 2.5 mL of *N*-iso-propylmorpholine buffered (6.6×10^{-3} M) methanol to give a final substrate concentration of 1×10^{-5} M. This solution was transferred to a UV/vis cuvette and immediately placed in the spectrometer to obtain a time-zero absorbance. Every minute, the cell was removed and shaken for 13 s (~30 times) and replaced in the spectrometer for a short time (1−5 s to allow settling) before collecting a new absorbance spectrum from 200−400 nm over 27 s. The reactions were run to completion, and the pseudo first-order rate constants (k_{obs}) were determined by fitting the absorbance versus time traces to a standard exponential model. As discussed later, the actual catalyzed reaction required agitation of the solutions, and control experiments establish that the reactions are at least 100 times slower when the catalysts are settled to the bottom of the cuvettes. Thus, only the collective times during which the reaction mixtures were actually shaken were used for the absorbance versus time profile.

Control experiments in which 0.05 g of nonfunctionalized chloromethylated polystyrene and 4-benzylchloride-functionalized silica gel were used as catalysts for the methanolysis of **2** showed no conversion of starting material to product, confirming that the reactions observed when PSPd and SiPd are catalysts are due solely to the palladacycle complex and not to the solid matrix.

Results and Discussion

Preparation of Immobilized Palladacycle. The chloromethylated polystyrene and 4-benzyl chloride-functionalized silica gels were chosen as solid supports on the basis of their commercial availability and our previous success in functionalizing various polystyrene-based materials.[11] Chloromethylated polystyrene is an attractive support matrix due to its chemical inertness and structural stability,[28] while silica gel has the advantage of a large surface area accessible to solvent. While past examples of immobilized palladacycle complexes have relied on grafting an already prepared complex onto the solid surface, the benzyl chloride moiety in both the commercially available functionalized polystyrene and the silica gel is a convenient point of attachment for the core structure of the immobilized palladacycle. Nucleophilic substitution of the chloride by dimethylamine gave the *N*,*N*-dimethylbenzylamine species, which is the starting point for the analogous preparation of complex **3** in solution.[29] As shown in Scheme 1, treatment of the anchored *N*,*N*-dimethylbenzylamine with $Pd(CH_3CN)_2(OTf)_2$, followed by immersion in methanol, gave the catalytically active species **7**. The respective palladium and nitrogen contents of the solid materials as determined by atomic absorption spectroscopy and microanalysis are given in Table 1. The analyzed loadings achieved by direct functionalization are comparable to those previously reported[26a] for grafting of oxime carbapalladacycle on polystyrene. In comparison to the chloride content in the commercial chloromethylated polystyrene, the Pd loadings represent 10−20% conversion of the chloride to the palladacycle complex, but the nitrogen loading is higher, and in the case of PSPd3 it is 55% of the stated Cl in the commercial polystyrene (2.8 mmol/g). The latter value represents the total chloride content, so it is possible that a considerable fraction of the Cl is located at sites inaccessible to, or of reduced reactivity for, the substitution or palladation

Scheme 1. Scheme for Preparation of Immobilized Palladacycle (**7**)

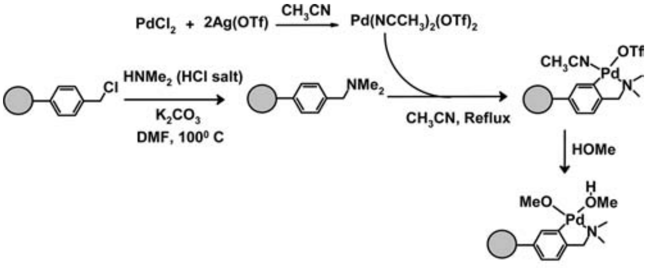

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Table 1. Palladium and Nitrogen Content of Immobilized Catalysts As Analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy and Microanalysis, Respectively

catalyst	Pd source	Pd content (mmol/g)[a,b]	N content (mmol/g)[c]
PSPd1	Li_2PdCl_4	0.85 (0.57)	
PSPd2	$PdCl_2$	0.40 (0.21)	
PSPd3	$PdCl_2$	0.58	1.55
SiPd1	$PdCl_2$	0.036	0.5
SiPd2	$PdCl_2$	0.20	1.03
SiPd3	$PdCl_2$	0.075	0.74

[a] The value quoted is the Pd content before the material was used in a reaction. The value in parentheses represents the Pd content after the first use of catalyst in solution. [b] Error limits are considered to be ±15% of the reported value based on replicate measurements and detection instrument error. [c] N loading determined by microanalysis.

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reactions. It is interesting that the Pd loading is only about 37% of the available N despite the fact that excess Pd reagent was used for all of the reactions. The reduced conversion to the palladium may be the result of the decreased reactivity of functional groups on rigid, highly cross-linked polymeric backbones,[30] or it may simply be a consequence of a slower reaction for the cyclopalladation reactions, but at this point we have not optimized the time/conversion profiles.

Three versions of silica-supported catalyst were prepared as described in the Experimental Section where the palladium loading represented between 3% and 17% conversion of the reported 1.2 mmol/g chloromethylated starting material. As was the case with the polystyrene material, the nitrogen loading is invariably higher, being 42−88% of the available Cl, so the Pd loading is 5−10 times less than the N loading for reasons that are not clear, but could be related to a slower palladation reaction. However, in the present study, we have not optimized the Pd loading because, as will be shown later, all of these materials, surprisingly, exhibited the same general catalytic activity, leading to the conclusion that there is no inherent advantage to create a more expensive, heavier loaded catalyst. Note that the Pd analysis is for total palladium in all forms so one cannot distinguish Pd in the form of active palladacycle, palladium black, or nanoparticles, but later we show that even if Pd^0 is present, this material does not catalyze the reaction in question.

Catalytic Studies. The catalytic activity of the materials was determined for the methanolysis of the phosphorothionate triesters **2**, **4**−**6**. The reaction rates were determined by measuring the change in UV/vis absorbance for both the loss of starting material and the formation of product in methanol solutions containing a known quantity of solid catalyst. The immobilized catalyst (0.009−0.090 g) was put into 2.5 mL of methanol solution, buffered at ${}^{s}_{s}$pH = 8.8 by *N*-isopropylmorpholine (6.6×10^{-3} M). In each case, the apparent concentration of the catalytic complex was determined as if the solid materials were completely dissolved in the reaction solution (denoted $[Pd]_T$) assuming that the Pd loading was completely in the form of palladacycle. Under these assumption, the $[Pd]_T$ ranged between 8.9×10^{-5} and 7.6×10^{-3} M when all experiments are considered.

As it is known that reproducible two-phase-catalyzed reactions require a reproducible method of solution agitation, the simple manual procedure for determining the reaction kinetics described in the Experimental Section proved effective. This involved manual shaking of the cuvette for 13 s followed by placing the cell in the spectrophotometer for a few seconds (1−5) to allow settling of the solids, followed by collection of the UV/vis spectrum from 200 to 400 nm over a 27 s period. The process was repeated every 60 s until the reactions were at least 95% completed. Magnetic stirring of the mixture was purposely avoided to prevent crushing of the solid catalyst that occurs quite readily with the silica catalyst even with a tiny stir bar, which in the latter stages of the reaction greatly increases the settling time of the solids. Control experiments established that the cleavage of the substrates occurs only while the solid catalyst is being actively agitated in the reaction mixture by shaking, and not when the catalyst is settled at the bottom of the cuvette. For example, when a 0.0426 g sample of the PSPd3 was placed in a cuvette with a 2.5 mL solution of 3×10^{-5} M **2** buffered at ${}^{s}_{s}$pH = 8.8, and the mixture was not shaken, contiguous UV/vis spectra do not show any change. After sitting unshaken for 6 min, there was an absorbance change of ΔAbs = 0.0084 at 272 nm (starting material wavelength). As compared to the total ΔAbs for complete conversion of starting material (ΔAbs = 0.1091 at 272 nm), the observed absorbance change represents $\Delta Abs/\Delta Abs_{total} = 0.0084/0.1091 = 7.7\%$ of the total absorbance change for the complete reaction or in terms of $\Delta Abs/dt = 0.0084/360\ s = 2.3 \times 10^{-5}\ Abs/s^{-1}$. However, when the same mixture is shaken for 13 s, the absorbance change was ΔAbs = 0.031, so the rate of change of absorbance was $\Delta Abs/dt = 0.031/13\ s = 0.0024\ Abs/s^{-1}$, or 100 times as great as without shaking.

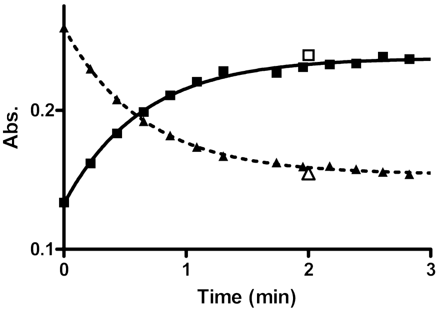

Figure 1. Absorbance vs time curves for the disappearance of **2** (3×10^{-5} M) (▲, absorbance at 272 nm) catalyzed by 0.0426 g of PSPd3 and for the appearance of 3-methyl-*p*-nitrophenol (■, absorbance at 310 nm) at *T* = 25 °C, ${}^{s}_{s}$pH = 8.8. The points Δ and □ represent the absorbances at 272 and 310 nm, respectively, after the same catalyst was shaken with a 3×10^{-5} M solution of **2** continuously for 2 min at *T* = 25 °C, ${}^{s}_{s}$pH = 8.8. The time scale on the *x*-axis is corrected to reflect only the time of shaking as described in the text. Lines through the data are computed on the basis of fits to a standard exponential model for appearance of product (1.56 ± 0.06 min^{-1}) and disappearance of **2** (1.53 ± 0.03 min^{-1}).

In view of the above, the Abs versus time plots that were used to determine the rate constant for the reactions reflect only the time period over which the reaction mixture was shaken (i.e., *n* × 13 s, where *n* is the number of repetitions). A typical Abs versus time plot for the methanolysis of **2** promoted by PSPd3 is shown in Figure 1, which also contains two data points for a second sample where the solution was continuously shaken for 120 s and then monitored by UV/vis spectrophotometry, which are in excellent agreement with the data acquired from the mixtures shaken for the equivalent number of 13 s intervals. In all cases for each substrate and catalyst, the observed rate of change in absorbance followed good pseudo first-order behavior and, when fit to a standard exponential model, gave the yielded first-order catalytic rate constants. These are normalized for 50 mg of catalyst, and the k_{obs} values are given in Tables 2 and 3. The tables also contain the apparent second-order rate constants for the PSPd- and SiPd-catalyzed methanolysis of **2**, **4**−**6**, defined as $k_{obs}/[Pd]_T$.

Plots of k_{obs} for the methanolysis of **2** catalyzed by PSPd2 and SiPd1 at ${}^{s}_{s}$pH = 8.8 as a function of the weight of catalyst

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[30] Guyot, A. *Pure Appl. Chem.* **1988**, *60*, 365.

Table 2. First-Order and Apparent Second-Order Rate Constants for the Methanolysis of Phosphorothionate Triesters Catalyzed by Polystyrene-Bound Palladacycle (PSPd2) in Methanol Buffered at $^{s}_{s}$pH = 8.8 by *N*-Iso-propylmorpholine (6.6 × 10^{-3} M), T = 25 °C

substrate[a]	k_{obs} (s^{-1}) for 50 mg of polymer[b]	k_2 (M^{-1} s^{-1})[c,d]	solution k_2 ($M^{-1}s^{-1}$)[e]	k_2^{OMe} (M^{-1} s^{-1})
2	2.68×10^{-2}	6.4	36.9	7.2×10^{-4}
4	2.15×10^{-2}	5.1	44.3	1.7×10^{-4}
5	2.07×10^{-2}	4.9	146.7	7.5×10^{-4}
6	1.63×10^{-2}	3.7	0.45	5.8×10^{-4}

[a] [**2**] = 1 × 10^{-5} M, [**4**] = 1 × 10^{-4} M, [**5**] = 1 × 10^{-4} M, [**6**] = 1.5 × 10^{-4} M. [b] For 50 mg of PSPd2 in 2.5 mL of solution, $[Pd]_T$ = 4.2 × 10^{-3} M. These kinetic data were gathered using the first use material where the Pd analysis was 0.40 mmol/g. [c] Error limits are considered to be ±20% based on errors in the determination of palladium loading and uncertainties in duplicate rate measurements. [d] k_2 is defined as k_{obs} (s^{-1})/$[Pd]_T$ (M). [e] Second-order rate constants for the methanolysis of substrates **2**, **4**−**6** catalyzed by **3** at $^{s}_{s}$pH 10.8 from ref 19.

Table 3. First-Order and Apparent Second-Order Rate Constants for the Methanolysis of Phosphorothionate Triesters Catalyzed by Silica-Gel Bound Palladacycle (SiPd1) in Methanol Buffered at $^{s}_{s}$pH = 8.8 by *N*-Iso-propylmorpholine (6.6 × 10^{-3} M), T = 25 °C

substrate[a]	k_{obs} (s^{-1}) for 50 mg of silica[b]	k_2 (M^{-1} s^{-1})[c,d]	solution k_2 (M^{-1} s^{-1})[e]	k_2^{OMe} (M^{-1} s^{-1})
2	6.22×10^{-2}	86.3	36.9	7.2×10^{-4}
2	4.8×10^{-2}[f]	12.4	36.9	7.2×10^{-4}
2	6.4×10^{-2}[g]	42.5	36.9	7.2×10^{-4}
4	4.13×10^{-2}	57.5	44.3	1.7×10^{-4}
5	4.07×10^{-2}	56.6	146.7	7.5×10^{-4}
6	2.38×10^{-2}	33.1	0.45	5.8×10^{-4}

[a] [**2**] = 1 × 10^{-5} M, [**4**] = 1 × 10^{-4} M, [**5**] = 1 × 10^{-4} M, [**6**] = 1.5 × 10^{-4} M. [b] For 50 mg of SiPd1 in 2.5 mL of solution, $[Pd]_T$ = 7.2 × 10^{-4} M. [c] Error limits are considered to be ±20% based on errors in the determination of palladium loading and uncertainties in duplicate rate measurements. [d] k_2 is defined as k_{obs} (s^{-1})/$[Pd]_T$ (M). [e] Second-order rate constants for the methanolysis of substrates **2**, **4**−**6** catalyzed by **3** at $^{s}_{s}$pH 10.8 from ref 19. [f] The methanolysis reaction was catalyzed by SiPd2 (0.2 mmol/g Pd) for which 50 mg in 2.5 mL of solution gives $[Pd]_T$ = 4.0 × 10^{-3} M. [g] Methanolysis reaction promoted by SiPd3 (0.075 mmol/g Pd) for which 50 mg in 2.5 mL of solution gives $[Pd]_T$ = 1.44 × 10^{-3} M.

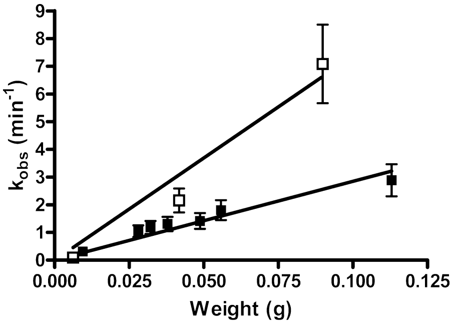

Figure 2. Pseudo first-order rate constant (k_{obs}) for the methanolysis of **2** (1 × 10^{-5} M) catalyzed by PSPd2 (■) and SiPd1 (□) vs weight of catalyst at $^{s}_{s}$pH = 8.8, *N*-iso-propylmorpholine buffer (6.6 × 10^{-3} M), T = 25 °C.

(Figure 2) are, within experimental uncertainty, linear and show no obvious saturation kinetics over the weight range investigated, which is consistent with the observations made for the methanolysis of **2** catalyzed by complex **3** in solution.[19]

The first three entries of Table 3 indicate that, while the experimental first-order rate constants (k_{obs}) for methanolysis of **2** promoted by the three variants of the SiPd catalyst are very similar, the computed second-order constants based on total Pd content vary up to 7-fold as a consequence of the different amounts of $[Pd]_T$. Cursorily, this signifies that there is no advantage to a higher loading, and perhaps that the rate of the reaction is not limited by a chemical step but probably by diffusion or surface effects. Despite the lower palladium content of the silica-based catalyst (SiPd1), the first-order rate constants for the methanolysis of all substrates were greater by roughly a factor of 2−3 than that provided by the polystyrene-supported catalyst. When corrected for the Pd loading to determine the apparent second-order rate constants for the catalyzed reaction, the silica catalyst is about 2−10-fold better than the polystyrene one due to the ~10-fold less amount of Pd on the silica-based catalyst, but the difference in reactivity is not strikingly large for the substrates investigated. Perhaps the greater activity of the Si-based catalysts is due to the larger concentration of accessible reactive sites on the surface of the silica particles in comparison to the polystyrene bead. Another important factor could be that the surface of the silica support is very hydrophilic, which may be of catalytic benefit in bringing the substrate to the surface, and also in allowing the methanol solvent to surround the catalytic groups on the surface, while the opposite could be true for the hydrophobic surface of the polystyrene-based catalysts.[31] Although the functionalization of the commercial chloromethylated polystyrene was performed in DMF and the cyclopalladation performed in acetronitrile (two solvents that are known to swell polystyrene), the solvolysis reactions are conducted in nonswelling methanol, and its hydrophobic surface may present a barrier to allowing the methanol solvent close to the surface attached catalytic groups and those in the interior, which are even less accessible.

The fact that the three silica-supported catalysts have very similar activity, as measured by the pseudo first-order rate constant for methanolysis of **2**, while the total analyzed loading of the Pd is quite different, can arise from two likely effects. One of these could be that there is a variable ratio of catalytically active/nonactive Pd in the three samples, with the larger loading arising from more of the nonactive forms that are occluded or attached to the solid support. This is probably also the case with the polystyrene catalysts, which are visibly black when made and where the Pd analyses show that considerable Pd is leached from the polymer after the first use, but the overall activity does not change much. We acknowledge the probability of Pd^0 and/or palladium nanoparticle formation on the surface of the solid materials as evidenced by the black color of the catalysts. The Pd^0 formation may be the result of the reduction of palladium(II) by trace amounts of methanol remaining after washing the *N*,*N*-dimethylbenzylamine-functionalized solids prior to palladation. However, even if formed, Pd^0 is not catalytically active. As a control experiment, unfunctionalized silica gel, which has no point of attachment for a palladacycle, was soaked in methanol overnight and then dried overnight at 60 °C and atmospheric pressure (the same drying procedure described for the other solid catalysts). This silica was then subjected to the same palladation conditions described in the Experimental Section. The resulting silica was found to be

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(31) Corma, A.; Garcia, H. *Top. Catal.* **2008**, *48*, 8.

dark gray, presumably as a result of Pd^0 formation, and when 0.043 g of this silica was introduced into a cuvette containing a solution of 3×10^{-5} M **2** with the usual shaking procedure, no change was observed in the UV spectrum over the course of 5 min.

A second likely possibility for the similar activity of the three Si-supported catalysts stems from the fact that the rate-limiting step for the overall conversion of starting material to product involves a nonchemical process such as surface penetration or diffusion. While the second-order rate constant for the methanolysis of substrates **2**, **4**−**6** in solution (given in Tables 2 and 3) ranges between 0.45 M^{-1} s^{-1} for diazinon **6** and 146.7 M^{-1} s^{-1} for coumaphos **5** (a 326-fold difference), the apparent second-order rate constants for methanolysis of the same substrates promoted by the supported catalysts reactions differ only by factors of ~1.3 and 1.7 for PSPd2 and SiPd1, respectively, and none of the reactivities of **2**, **4**−**6** follow the trend observed in solution. This too supports the contention that the rate-limiting process does not depend on the nature of the substrate. Interestingly, the second-order rate constants computed for the methanolysis of substrates **2**, **4**, and **6** catalyzed by SiPd1 are greater than the second-order rate constants for the methanolysis in homogeneous solution catalyzed by **3**, and in the case of PSPd2, the rate constant for its reaction with diazinon exceeds that of the solution reaction by about 8-fold. The reported apparent second-order rate constants in Tables 2 and 3 are lower limits because the computed values depend on the $[Pd]_T$, which is undoubtedly higher than the concentration of active species due to the presence of an inactive Pd^0 form. Nevertheless, the increased second-order rate constant for the heterogeneous reaction may be the result of an effect whereby substrate is concentrated on the catalyst surface. Hartshorn et al. also observed such phenomena when examining the hydrolysis of bis(*p*-nitrophenyl)phosphate and methyl parathion catalyzed by copper(II)-containing polymers.[32]

It is notable that the solid-supported palladacycles operate at near neutral ^s_spH values in methanol where the background methoxide reactions are very slow. This is an attractive feature of the system for removal of this sort of pesticide from sensitive surfaces, which may corrode easily under highly alkaline conditions. Comparing the methoxide ($k_2^{OMe} = (7.2 \pm 0.2) \times 10^{-4}$ M^{-1} s^{-1})[10] and solid promoted reactions of fenitrothion **2** at ^s_spH = 8.8, 50 mg of PSPd2 or SiPd1 provides a 3.7×10^9- and 8.6×10^9-fold acceleration when in excess of the substrate. When conducted in methanol buffered with 2,2,6,6-tetramethylpiperidine at ^s_spH = 11.5, the methanolyses of **2** catalyzed by both SiPd1 and PSPd3 were increased by only a factor of 2 relative to the same reaction at ^s_spH = 8.8. This suggests that the catalytically active complex, postulated as **7** having an associated lyoxide ($^-OCH_3$) by analogy with what we determined for the solution reaction mediated by **3**[19] and what was proposed by Gabbai and co-workers for a palladacycle operating in basic water with methyl parathion,[18] has a kinetic ^s_spK_a of 8.8 or somewhat lower and exists in its active form over a wide pH range. This is an important distinction from the free catalyst **3** in solution where the reported ^s_spK_a for formation of the active form is 10.8.[19] Indeed, these solid systems that bear a great number of ionizing sites must act as a large polybasic acid that undergoes numerous dissociations over a very wide pH range.[33] In fact, if the rate-limiting step for these catalyzed reactions is that of a nonchemical process such as surface diffusion or penetration, it is not required that all of the palladacycles exist in an active Pd−$^-OCH_3$ form, only a sufficient number to react with the substrate more rapidly than it is presented to the catalytic domain.

Catalytic Turnover. A turnover experiment was performed to demonstrate that the solid materials are indeed catalytic. A small amount of SiPd1 catalyst in 2.5 mL of methanol (6.2 mg, 8.9×10^{-5} M = $[Pd]_T$) was used to catalyze the methanolysis of 3.4×10^{-4} M **2** ([**2**] = $3.8[Pd]_T$) buffered at ^s_spH = 8.8 with *N*-iso-propylmorpholine (6.6×10^{-3} M). The UV/vis absorbance showed a complete loss of substrate and release of product with good first-order kinetics (k_{obs} = 0.092 min^{-1}) and no observed product inhibition. In this case, for the entire reaction under turnover conditions, the acceleration for the degradation of **2** relative to the background reaction at ^s_spH = 8.8 was 2.1×10^8-fold. The data do point out, however, that the reactions conducted under turnover conditions are somewhat slower than when the catalyst is in excess of substrate, a phenomenon also observed for the methanolysis of **2** promoted by **3** under turnover conditions.[19,34] Thus, the observed turnover second-order rate constant for methanolysis of fenitrothion of 17.2 M^{-1} s^{-1} (based on the total amount of Pd on 6.5 mg of silica) is about 5 times lower than that determined for the kinetic determination with an excess amount (50 mg) of functionalized silica given in Table 3, entry 1 (k_2 = 86 M^{-1} s^{-1}). The reduction in the observed rate of reaction with increasing substrate concentration might be indicative of a saturating transport phenomenon.

Catalyst Recycling. The oft-quoted advantages of polymer/solid-supported catalysts are the ability to store and to reuse the catalyst when recovered from the reaction mixture.[20,21,35] As a control experiment to test the effects of catalyst storage, the methanolysis of **2** was conducted using two batches of PSPd2, one of which was dried and stored in air, and a second that was stored for 5 days in *N*-iso-propylmorpholine buffer (6.6×10^{-3} M) at ^s_spH = 8.8. A reaction was conducted in which 0.0488 g of PSPd2, soaked in buffer,

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[32] Hartshorn, C. M.; Singh, A.; Chang, E. L. *J. Mater. Chem.* **2002**, *12*, 602.

[33] As is known for polybasic acids bearing numerous ionizing sites, the pK_a values are spread over several pH units due to statistical effects and, more importantly, electrostatic effects.

[34] When in excess of substrate, the k_2 value determined for reaction of **2** with **3** at ^s_spH 10.8 by UV/visible spectrophotometry is 1880 M^{-1} s^{-1}, while that determined under turnover conditions by ^1H NMR is 36.9 M^{-1} s^{-1}. The drop in reactivity was attributed[19] to the large concentration of inhibitory buffer in the NMR experiment, which was required to control the ^s_spH, as well as the larger concentrations of substrate (7×10^{-2} M) and catalyst, which can alter the solution properties. It is possible, however, that the diminution of rate is attributable to a saturation binding of substrate and catalyst.

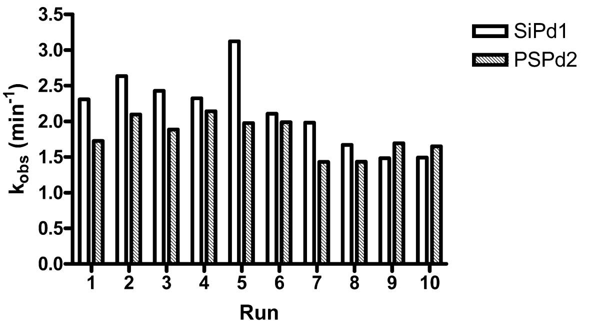


Figure 3. Pseudo first-order rate constants (k_{obs}) for the methanolysis of **2** (1×10^{-5} M) catalyzed by PSPd2 (0.0558 g) and SiPd1 (0.0418 g) at ${}_{s}^{s}$pH $= 8.8$ and $T = 25$ °C. Average k_{obs}(PSPd2) $= 1.79 \pm 0.26$ min^{-1}. Average k_{obs}(SiPd1) $= 2.16 \pm 0.52$ min^{-1}.

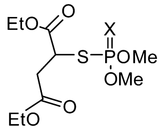
was used to catalyze the methanolysis of **2**. The catalyst was soaked in *N*-iso-propylmorpholine buffer (6.6×10^{-3} M) at ${}_{s}^{s}$pH $= 8.8$ in a quartz cuvette for 5 days. After this period, the buffer solution was decanted, and the catalyst was washed with three portions of clean methanol (3 mL each). To the cell was then added 2.5 mL of a 1×10^{-5} M solution of **2** in *N*-iso-propylmorpholine buffer (6.6×10^{-3} M) at ${}_{s}^{s}$pH $=$ 8.8. This experiment gave the same observed rate constant (within experimental error) for the methanolysis of **2** as obtained with catalyst, which was dried and stored in air (see Table 2).

The reusability of the immobilized catalysts was demonstrated by performing a series of sequential methanolysis reactions with the same sample of catalyst. Shown in Figure 3 are 10 consecutive reactions with 1×10^{-5} M fenitrothion promoted by both PSPd2 and SiPd1. Each experiment involved following the time course of the reaction to completion, removal of the reaction solution from the cuvette by careful pipetting, washing the solid material in the cuvette with five portions of clean methanol (3 mL each), each of which was removed by careful pipetting, and then charging the remaining solid with 2.5 mL of buffer along with inoculation with 1×10^{-5} M fenitrothion and remonitoring the reaction.

Given the relatively crude assessment of the activity as a function of time, both catalysts show a good stability toward subsequent use. It is possible that, during the washing cycles, some loss of active, but more flocculent, solid could have occurred, which might account for the gradual diminution and apparent plateauing of activity. As shown in Table 1, the polystyrene-based catalysts (PSPd) typically undergo some 30−50% loss of palladium upon the first use of the material, but the Figure 3 data indicate there is not much of a loss of the catalytic activity of the remaining material. This is consistent with desorption of a catalytically inactive palladium species, which was chemi- or physisorbed into the polymer matrix. In the case of the silica-based materials, the palladium contents before and after the first reaction do not differ, which is probably a consequence of having the loosely adsorbed Pd removed during the washing procedures prior to any kinetic experiments.

Control Experiment Showing Putative Solution Pd Is Not Active. To further demonstrate the truly heterogeneous nature of the catalysts and to confirm the robustness of the immobilized palladium species, leeching experiments were conducted to show that all of the observed catalysis is due to immobilized palladium, and not due to palladium free in solution. Samples of PSPd3 and SiPd1 (0.035 and 0.033 g, respectively) were added to separate UV cuvettes, and to each was added 2.5 mL of a 1×10^{-5} M solution of **2** in *N*-iso-propylmorpholine buffer (6.6×10^{-3} M) at ${}_{s}^{s}$pH $= 8.8$. The reactions were monitored and allowed to progress to ~50% completion, at which point the reaction solution was carefully removed from the UV/vis cell and transferred to a clean cuvette. The cuvettes containing the reaction solution were again placed in the spectrometer, and the reactions were monitored over the next 15 min. During this time, no change was observed in the UV spectrum of either reaction solution, indicating that in the absence of solid catalyst, the reactions proceed only at their slow background rate. Reintroduction of the reaction solutions into the cuvettes containing the solid catalyst and carrying out the shaking/monitoring the UV/vis spectra, as described above for the solid-catalyzed reactions, showed a continuation of the expected reaction until all of the substrate had disappeared.

Methanolysis of Malathion. The structures of substrates **2**, and **4**−**6**, with chromophoric leaving groups, make their reactions convenient to study using UV/vis spectrophotometry, but these are not as widely used as some other P═S pesticides such as malathion (**8**), which is the most commonly used organophosphorus insecticide in the United States[36] for applications ranging from protection of agricultural crops to the treatment of head lice. While it has relatively low toxicity in humans, the major oxidative metabolite and contaminant in the commercial product is malaoxon (**9**), which is roughly 60 times more toxic for mammals. The widespread use of malathion, the toxicity of its metabolite, and its slow rate of spontaneous hydrolysis make it an appealing target for catalytic degradation.



8 X=S
9 X=O

Because malathion does not contain a chromophore, its catalyzed methanolysis reactions were followed using ^{31}P NMR. A solution of malathion (5.15×10^{-3} M) was prepared in an NMR tube in 0.8 mL of a 1:1 mixture of normal methanol containing *N*-iso-propylmorpholine buffer (6.6×10^{-3} M) and CD_3OD. The substrate appears in the ^{31}P spectrum at δ 96.43 ppm. The catalyst (PSPd3, 0.0436 g) was added to the NMR tube, giving $[\mathrm{Pd}]_T = 31.6 \times 10^{-3}$

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(35) (a) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345. (b) Dijkstra, H. P.; Slagt, M. Q.; McDonald, A.; Kruithof, C. A.; Kreiter, R.; Mills, A. M.; Lutz, M.; Speck, A. L.; Klopper, W.; Van Klink, G. P. M.; Van Koten, G. *J. Catal.* **2005**, *229*, 322.

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M, and the tube was shaken for 30 s. After 5 min, the ^{31}P spectrum was recorded and showed a new signal corresponding to the methanolysis product (*O*,*O*,*O*-trimethyl phosphorothionate) emerging at δ 74.26 ppm (lit.[37] 73.91 ppm). Collection of the ^{31}P spectrum was repeated after 14 and 24 min (relative peak intensities (starting material/product): 5 min = 1.00/0.26, 14 min = 0.696/1.00, 24 min = 0.274/1.00). After 32 min, the substrate peak at δ 96.43 ppm was completely replaced by the product peak at δ 74.26 ppm. An analogous experiment in which 0.0426 g of SiPd1 was used as the catalyst ($[Pd]_T = 1.9 \times 10^{-3}$ M) showed an initial conversion of starting material to product, but failed to decompose all of the substrate after 30 min, suggesting catalyst inhibition (relative peak intensities (starting material/product): after 15 min = 1.00/0.31, after 30 min = 1.00/0.38). This is consistent with an earlier ^{31}P NMR experiment using PSPd2, which rapidly decomposed an amount of malathion equal to one-half of the palladium content. In this experiment, 0.0378 g of PSPd2 was added to an NMR tube containing a solution of 5.15×10^{-3} M malathion prepared as described above, which showed the starting material peak at δ 96.41 ppm in the ^{31}P NMR spectrum. The tube was shaken for 30 s every 10 min, and after a total of 60 min the ^{31}P signal was collected and showed that the starting material peak at δ 96.41 ppm was completely replaced by the product peak at δ 74.25 ppm. Addition of a second aliquot of malathion (5.15×10^{-3} M) generated its customary signal at δ 96.41 ppm; however, the ^{31}P spectrum recorded 60 min after the addition of the second portion of substrate and shaking the sample as was done for the first aliquot showed no decrease in the starting material, and no additional product signal was observed. After a period of 96 h (4 days), 64% of the substrate was converted to product, and after 264 h (11 days), the ^{31}P NMR showed no sign of starting material and the product peak at δ74.26 ppm.

The incomplete conversion by SiPd1 and the prolonged reaction time for the methanolysis of the second portion of malathion by PSPd2 are attributed to inhibition by the thiol/thiolate product. In the case of substrates **2**, **4**−**6**, we do not observe product inhibition, even in the presence of excess substrate, because the leaving groups are all substituted phenols where the hydroxyl group oxygen is a hard ligand and does not bind strongly to the soft[38] palladium center. In the case of malathion, however, the leaving group is diethyl thiomalate, which strongly binds to palladium via sulfur. As expected, analysis of the reaction solution from the catalyzed methanolysis of malathion by mass spectrometry showed the presence of the *O*,*O*,*O*-trimethyl phosphorothionate product at $m/z = 156$ with 34% intensity, but not the diethyl thiomalate. The fact that less than a stoichiometric amount of malathion strongly inhibits the polystyrene-bound palladacycle supports our earlier hypothesis that the metal-containing sites have variable accessibility to solvent and substrate, such that only the accessible ones are inhibited by the reaction products.

Conclusion

We have shown here that derivatization and palladation of commercially available chloromethylated polystyrene and 4-benzylchloride-functionalized silica gels leads to efficient heterogeneous catalysts for the methanolysis of phosphorothionate triesters where the departing group does not contain a free thiolate. The materials both show good activity toward the methanolysis of fenitrothion (**2**), dichlofenthion (**4**), coumaphos (**5**), and diazinon (**6**), all of which are commercially available P═S pesticides. The catalytic activity is shown to be somewhat greater for catalyst immobilized on silica gel, probably dues to the former's higher surface area and hydrophilic nature, making it more accessible to solvent than its polystyrene counterpart. In the best case, the palladacycle immobilized on silica gel accelerates the methanolysis of **2** by a factor of 8.6×10^9 as compared to the background reaction at the same pH. However, this result is obtained only when the heterogeneous catalyst is in excess of the substrate, and in cases where the substrate is in excess to the catalysis, there is a small but noticeable drop in activity for reasons that are not clear but might be related to transport phenomena. Both the polystyrene and the silica gel-based catalysts show good stability over the course of several sequential reactions and show no product inhibition with substrate **2**.

A surprising aspect of this work is that Si-based catalysts having different amounts of total analyzed Pd show roughly the same activity toward the methanolysis of **2**, and in fact very similar reactivities toward different substrates despite the fact that the solution-based reactions of these vary by about 300-fold. This suggests that the rate-limiting steps for these reactions are not chemical ones, but rather steps having to do with surface diffusion and penetration. One benefit of this phenomenon is that creating more expensive, higher loaded, catalysts does not appear to be of any benefit in accelerating the rates of the observed reactions.

A major shortcoming of the palladacycle catalysts as used here concerns their inhibition by the products of methanolysis of malathion. Presumably, the inhibitor is the thiolate anion, which suggests that it might be possible to employ oxidizing agents to divert the latter into disulfides or S═O products that will not be inhibitory. Further work along these lines is underway and will be reported in due course.

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