Rapid Luminescent Detection of Phosphate Esters in Solution and the Gas Phase Using (dppe)Pt{S_2C_2(2-pyridyl)(CH_2CH_2OH)}

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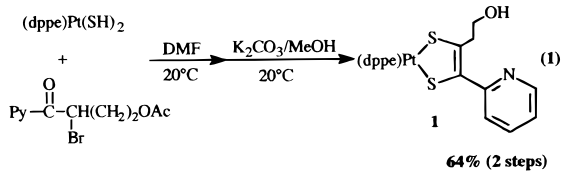
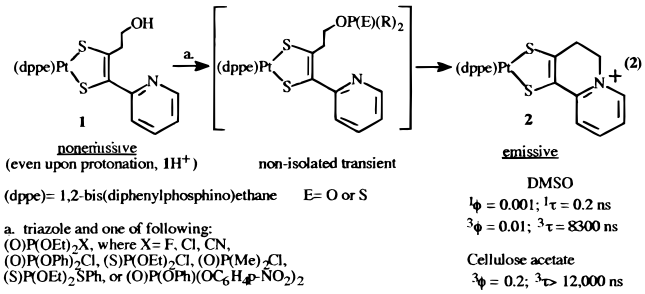
Organophosphate inhibitors of acetylcholine esterase (including phosphinates and phosphonates) are used as pesticides and as chemical warfare agents.[1−7] As such, their detection over a range of concentrations and conditions is required and has attracted considerable attention.[8−22] Several detection methods rely on an immobilized acetylcholine esterase detector coupled to a transducer (i.e., pH electrodes,[5,9,11−13,15,16,22] fiber optics,[10,21] and piezoelectric crystals[14]). Although the immobilized enzymes are sensitive and detect a broad spectrum of acetylcholine esterase inhibitors, they lack selectivity and are prone to false positives when exposed to choline mimics.[15,23,24]

The rapid detection of volatile fluoro and cyano phosphates is of particular interest since these are major constituents in the chemical warfare arsenal. Reported is a new selective method for the rapid detection of these esters. The method uses a new platinum 1,2-enedithiolate complex with an appended alcohol that upon exposure to selected phosphate esters is converted to a room-temperature lumiphore.[25]

Complex, **1**, was prepared by the literature procedure (eq 1).[26a,d]



The chemical conversion of **1** to [(dppe)Pt{$S_2C_2(CH_2CH_2$-*N*-2-pyridinium)}]$^+$, **2**, by activated phosphate esters (eq 2) can be



monitored by the emissions from **2** which have been assigned to a thiolate to heterocycle π^* intraligand charger-transfer singlet, ^{1}ILCT*, and triplet, ^{3}ILCT*. While **1**, and **1**H$^+$, are nonemissive ($\phi < 0.00001$), **2** is emissive in room-temperature solution ($^1\phi = 0.002$, $^3\phi = 0.01$, DMSO) and when immobilized in cellulose acetate/triethylcitrate films ($^1\phi \approx 0.01$, $^3\phi \approx 0.2$).[26]

Neutral pyridine-substituted complexes such as (dppe)Pt{S_2C_2-(2-pyridyl)(R)} R = H, and CH_2CH_2OH, are not emissive due to a lowest lying d to d transition which leads to rapid nonradiative decay of emissive excited states.[26] However, the emissive properties of **2** are similar to those of [(dppe)Pt{S_2C_2(2-pyridinium)(H)}]$^+$ suggesting that either the steric bulk or solution dynamics of the [(dppe)Pt{S_2C_2(2-pyridinium)(CH_2CH_2OH)}]$^+$ side-chain increases the nonradiative decay rate. The gross differences in the photophysical properties of **2** and [(dppe)Pt-{S_2C_2(2-pyridinium)(H)}]$^+$ from those of **1**H$^+$ could arise from the necessity for the 1,2-enedithiolate and heterocycle to be coplanar for emission from the ILCT excited states.[26d] Whereas in **2** the 1,2-enedithiolate and heterocycle are held coplanar in the ground state,[26d] the ability of the 1,2-enedithiolate and heterocycle to be coplanar in the [(dppe)Pt{S_2C_2(2-pyridinium)(R)}]$^+$ complexes depends on the bulk of the R group, and this could account for the emission from R = H and not R = CH_2CH_2OH.

Given the chemical reactivity of **1** and combined photophysical properties of **1** and **2**, activated phosphate esters serve to turn on the emission in this family of complexes. The reaction of **1** with phosphate, thiophosphate, and phosphinate esters (10^{-1}−10^{-6} M) leads to the generation of **2** (eq 2). These reactions can be followed by exciting a deaerated CH_2Cl_2 solution at 450 nm and monitoring the 605 and 710 nm emissions.

Sulfonyl chlorides and anhydrides convert **1** to **2** while carboxylic acid chlorides and anhydrides convert **1** to the corresponding nonemissive esters. As such, these reagents interfere with phosphate detection. However, amines and pyridines (common acetylcholine esterase inhibitors) have essentially no effect upon this phosphate detection.

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Table 1. Rates of Conversion of **1** to **2** Relative to the Rate of $(O)P(OEt)_2Cl$

phosphate ester	rates relative $(O)P(OEt)_2Cl$[a]
$(O)P(OEt)_2X$	
X = F	~1.1[b]
X = Cl	1.0
X = CN	0.71
$(S)P(OEt)_2Cl$	0.24
$(O)P(Me)_2Cl$	1.1
$(O)P(OPh)_2Cl$	1.0
$(O)P(OPh)(OC_6H_4p\text{-}NO_2)_2$	0.069
$(O)P(OPh)_2(OC_6H_4p\text{-}NO_2)$	<0.0003
$(S)P(OEt)_2SPh$	<0.0003

[a] Rates are relative to those required for the conversion of **1** (10^{-4} M) to **2** in the presence triazole (10^{-2} M) and 10^{-3} M $(O)P(OEt)_2Cl$ at 20 °C in CH_2Cl_2. All phosphate ester concentrations are 10^{-3} M. The maximum conversions of **1** to **2** are 70−90%. Under the pseudo-first-order conditions listed, **2** is generated with $(O)P(OEt)_2Cl$ at a rate of 1.2×10^{-5} M s^{-1}. [b] Generated from $(O)P(OEt)_2Cl$ and benzoyl fluoride and used without purification.

The relative conversion rates of **1** to **2** by various phosphate esters (10^{-3} M) with **1** (10^{-4} M) and triazole (10^{-2} M) in CH_2Cl_2 are shown in Table 1. Triazole, a common reagent used in phosphorylation strategies,[27] serves both to activate the phosphate and as a base in these reactions. The rates of reaction are dependent upon the leaving group attached to the phosphate ester. The relative rates are consistent with a rate-determining step that involves activation of the phosphate by triazole or addition of the phosphate to the alcohol. These results are inconsistent with a rate determining step that involves nucleophilic attack by the pyridine and loss of a phosphate monoanion. Support for this assertion is seen in the relative rates $(O)P(OPh)_2Cl > (O)P(OPh)(OC_6H_4p\text{-}NO_2)_2 \gg (O)P(OPh)_2(OC_6H_4p\text{-}NO_2)$. This is the expected sequence if initial addition of the phosphate is rate determining. If phosphate loss were rate determining, the relative rates should have been $(O)P(OPh)(OC_6H_4p\text{-}NO_2)_2 \gg (O)P(OPh)_2(OC_6H_4p\text{-}NO_2) \approx (O)P(OPh)_2Cl$. Additional support for this assertion is the rapid conversion of **1** to **2** with $(O)P(OEt)_2X$ X = F,[28] Cl and CN. These rates reflect the initial loss of X rather than the subsequent loss of $(O)P(OEt)_2O^-$ which is among the poorest phosphate leaving group in this study. Steric bulk is not a major factor since the rates for $(O)P(OR)_2Cl$ R = Et are essentially identical to those of R = Ph.

Complex **1** was immobilized in cellulose acetate/triethylcitrate (CA/TEC), RTV-108, and RTV-118 (~0.5-mm thick films) and its ability to serve as a gas-phase detector screened (Figure 1). The polymer/plasticizer ratios of the cellulose acetate/triethylcitrate films were varied and the $P(OEt)_2(O)X$, X = Cl, F,[28] and CN detection times monitored (Table 2).[25] For the CA/TEC films, the time required for both minimum detection of the phosphate as well as for complete conversion of **1** to **2** drops with increasing plasticizer (TEC) content. The addition of plasticizers to polymers such as CA are well-known to increase permeability and mobility of polar analytes.[29−34] Detection of the esters was not possible when the TEC content was below 20% of the CA weight. Using CA/50% TEC films and monitoring the emission spectra (following 470 nm excitation), the generation of **2** was found to be linear with phosphate exposure time.

These results demonstrate a new method for detecting volatile phosphate esters using an immobilized heterocyclic-substituted platinum 1,2-enedithiolate with an appended alcohol as the sensor molecule. The volatile fluoro and cyano esters were chosen for this study since they are suitable mimics for SARIN, SOMAN, and TABUN,[17] three chemical agents in the current arsenal. Our plans include preparing new molecules with reactive functional groups similar to those found in **1** and varying the immobilizing polymer in an attempt to optimize the conditions for fluoro and cyano phosphonate and phosphate ester detection.

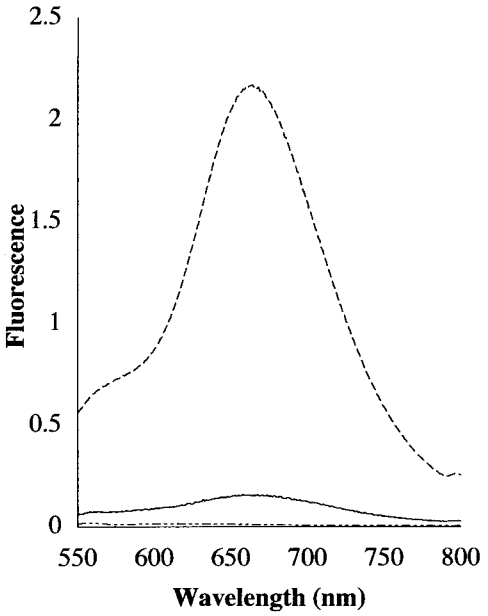

Figure 1. The luminescence spectra of **1** (0.3%/wt) immobilized in a cellulose acetate/150% triethylcitrate film (0.5 mm thick): (− · · −) Control film. (− − −) Film exposed to 0.9 g/m^3 $OP(OEt)_2Cl$ in N_2 for 2 min at 50 mL/s. (−) Film exposed to HCl.

Table 2. Exposure Times for the Conversion of **1** to **2** in Various Polymer/Pasticizer Combinations

polymer/plasticizer[a]	phosphate ester	minimum exposure time (s)[e]	complete exposure time (s)[f]
CA	$(O)P(OEt)_2Cl$[b]	not observed	not observed
CA/25% TEC	$(O)P(OEt)_2Cl$[b]	>600	not observed
CA/50% TEC	$(O)P(OEt)_2Cl$[b]	15	600
CA/100% TEC	$(O)P(OEt)_2Cl$[b]	<15	40
CA/150% TEC	$(O)P(OEt)_2Cl$[b]	<15	30
GE-RTV108	$(O)P(OEt)_2Cl$[b]	<15	15
GE-RTV118	$(O)P(OEt)_2Cl$[b]	<30	180
CA/150% TEC	$(O)P(OEt)_2F$[c]	<15	
CA/150% TEC	$(O)P(OEt)_2CN$[d]	<15	

[a] Cellulose acetate (CA), triethylcitrate (TEC). Percentages listed are for TEC wt % of CA. Loading of **1** is 0.3%/wt. Silicone films were impregnated in CH_2Cl_2 solution containing 0.1% NEt_3. [b] $(O)P(OEt)_2Cl$ at 0.093 Torr (0.90 g/m^3) in an N_2 flow of 50 mL/s. [c] $(O)P(OEt)_2F$ at 0.130 Torr (1.2 g/m^3) in an N_2 flow 50 mL/s. [d] $(O)P(OEt)_2CN$ at 0.054 Torr (0.88 g/m^3) in an N_2 flow of 50 mL/s. [e] Minimum exposure required for luminescence detection of a deareated sample, 470 nm excitation, 570 and 675 nm emission. [f] Minimum exposure required for maximum absorbance from the film at 470 nm.

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Supporting Information Available: The preparation and characterization of **1** and **2** and the details of phosphate ester detection are available (3 pages, print/PDF. See any current masthead page for ordering information and Web access instructions.

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