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Mercury-Promoted Hydrolysis of Parathion-methyl: Effect of Chloride and Hydrated Species

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Mercury salts are commonly used in laboratory and field experiments as biocides. It has been previously reported that Hg(II) can enhance chemical hydrolysis of a number of pesticides. Earlier studies on metal-promoted hydrolysis have reported overall rate constants as a function of total metal concentration. There are three advantages in reporting the relative importance of the different species: (1) results can be extrapolated form one situation to another, (2) rates can be predicted for specific conditions, and (3) greater understanding of the catalysis mechanism can be gained. In this study, mercury-promoted hydrolysis of parathion-methyl (*O*,*O*-dimethyl-*O*-*p*-nitrophenyl phosphorothionate), a probe organophosphate compound (OP), was studied as a function of Hg(II) speciation. The observed rate of hydrolysis was a function of specific mercury species rather than of the total mercury in solution. Second-order rate constants were determined experimentally at various pH values. A pH-dependent kinetic expression, $k_{obs} = (\alpha_{Hg^{2+}}k_1 + \alpha_{HgOH^+}k_2 + \alpha_{Hg(OH)_2}k_3)$ where $k_i = K_i k'_i$, with K_i representing the Hg:OP equilibrium constant, k'_i the rate constant for Hg:OP hydrolysis for the different Hg(II) species, and α is the fraction of the total Hg(II) present as specific species, provides a plausible interpretation for the system. Mercury-chloride species proved to have little catalytic power, whereas the contributions for Hg^{2+} and $Hg(OH)^+$ were significant. Our results also suggest that a mixed mechanism (electrophilic and nucleophilic) may have to be considered for general metal-promoted hydrolysis of OPs.

Introduction

Many pesticides contain functional groups that make them susceptible to both biotic and abiotic transformations. Kinetic studies of pollutant transformations are often confounded by the complex array of reactions that can take place simultaneously in natural environments. To isolate, quantify, and mechanistically study the different processes controlling the fate of pollutants in natural systems, laboratory experiments must be performed under various controlled conditions.

One of the first tasks is to determine the relative importance of biotic versus abiotic processes. To distinguish between sorption and/or chemical and microbial degradation of pesticides in soils, researchers normally use a comparison between sterile and nonsterile systems (*1*). Soil-sterilization methods can alter the chemical environment to which the pesticide is exposed; consequently, not only biological reactions are terminated. These sterilization methods can also alter homogeneous and heterogeneous chemical processes (*2*). Such alterations need to be addressed before comparisons and extrapolations can be made.

Previous studies have used various methods to distinguish between biotic and abiotic transformations (*3*−*7*). In a study to illustrate the pH dependency of chemical processes, Blumhorst and Weber (*8*) used autoclaving to distinguish chemical versus microbial degradation of atrazine and cyanazine in several soil samples. A 0.02% NaN_3 solution was used by Lion et al. (*9*) to study the sorption of hydrophobic compounds on aquifer material, and Xing et al. (*10*) minimized biological activity by using a 10^{-5} M $HgCl_2$ solution in their study to predict partition coefficients of nonionic organic contaminants. Although studies have been conducted to assess the effect of sterilization methods on various soil properties, little has been reported on any of the possible secondary effects induced by the use of the biocides (*11*−*14*).

In this study, we investigated the use of $HgCl_2$ to control biological activity when the organic pollutants contain hydrolyzable functional groups. OPs represent one class of such pollutants. OPs are used extensively as insecticides, and they have replaced organochlorine compounds in many of their uses. A major transformation pathway controlling the fate of OPs in the environment is hydrolysis, both chemical and biotic. Typically, the products of chemical and biological hydrolysis are the same; thus, scientists rely on the use of biocides in controlled kinetic studies to distinguish between the two processes. Some of the most commonly used biocides can alter the kinetics of chemical degradations.

The use of a divalent metal ion, such as mercury, is of specific concern with OPs due to possible metal-ion activity in hydrolysis reactions. The role of various metal ions, such as Cu(II), Mn(II), and Zn(II), in the hydrolysis of phosphorus esters has long been established (*15*−*18*), yet the degree to which different aquo-metal species are responsible has not been evaluated. Normally, the effect of metal catalysis has been reported through a lumped parameter, $k_{Me}[Me_T]$, that is highly pH dependent (*19, 20*), making it impossible to extrapolate from one pH to another. For example, in the study conducted by Smolen and Stone (*20*), k_{obs} values for Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, and Pb^{II} catalyzed hydrolysis of five OPs were reported at different pH values and varied by as much as 2 orders of magnitude. When only k_{obs} values are reported, it is difficult to identify the specific metal-ion species involved in the reaction (e.g., Me^{2+}, $Me(OH)^+$, $Me(OH)_2$, ...). The separation of the lumped kinetic parameter for contribution of the Me-aquo species could provide a generalized pH-dependent rate law.

Different mechanisms for metal-catalyzed hydrolysis have been postulated where the metal can act as either an electrophile or a nucleophile (*21, 22*). In the case where the metal acts as an electrophile, coordination between the metal and the hydrolyzable moiety or the leaving group occurs, which facilitates the attack by a nucleophile (H_2O). In a nucleophilic mechanism, the metal ion coordinates with the nucleophile, forming metal-hydroxo ($MeOH^{+n}$) species that catalyze the reaction via improved nucleophilicity. Smolen and Stone (*20*) concluded that phosphorus-centered nucleophilic attack by Cu and Cd species was the mechanism for all the esters examined. However, we should expect such behavior to be metal specific. Sulfur is a good ligand for Hg that would facilitate the complexation of mercury to the sulfur

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moiety in the OPs; thus, mercury would act as an electrophile.

In a recent study, the following mechanism was proposed for the Hg(II)-promoted hydrolysis of OPs (*19*):

$$\mathrm{Hg(II)} + \mathrm{S{=}P(OR)_3} \overset{K}{\leftrightarrow} \mathrm{Hg(II)S{-}P(OR)_3} \xrightarrow{k_2} \underset{\underset{\mathrm{OH}}{|}}{\mathrm{Hg(II)S{=}P(OR)_2}} + \mathrm{ROH} \tag{1}$$

where Hg(II) coordinates with sulfur in the thionate moiety of the pesticide withdrawing electronic density from the "P" center and thus facilitating a nucleophilic attach by H_2O. In this mechanism, Hg acts as an electrophile and the observed hydrolysis is not a complete catalytic process (a 1:1 relationship exists between total mercury added and amount of OP compound hydrolyzed). However, as in other studies, the proposed mechanism lumps all mercury species into one term that fails to consider the contributions of the various Hg species, and the reported k_{obs} value is pH dependent.

The objectives of our study were (1) to quantify the effects of pH on Hg-promoted parathion-methyl hydrolysis, (2) to identify and quantify the rates of the active Hg species, and (3) to examine how chloride complexation with Hg affects hydrolysis rates. Parathion-methyl is used as a probe OP because of its high solubility and fast hydrolysis as compared to other OPs.

Materials and Methods

Chemical Reagents. $HgCl_2$ (99.5+% purity) and $Hg(NO)_3 \cdot H_2O$ (98+% purity) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Sodium acetate, acetic acid, sodium nitrate, sodium chloride, sodium hydroxide, ethylenediaminetetraacetate (EDTA) disodium salt dihydrate, and hydrochloric acid were purchased from J. T. Baker (Phillipsburg, NJ). Sodium perchlorate was purchased from EM Science (Gibbstown, NJ). All these chemicals were high-purity reagent grade and were used without further purification. Parathion-methyl (*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphorothionate) and paraoxon-methyl (*O,O*-dimethyl-*O*-*p*-nitrophenyl phosphate) were obtained from Chem Service (West Chester, PA) at purities greater than 97% and were used without further purification.

Experimental Setup. All solutions were prepared from double-deionized water (DW), Hydro, Durham NC]. All glassware was soaked with 6 N HNO_3, rinsed several times with DW, and baked at 550 °C before use. Experiments were performed in a rotary shaker at room temperature (25 ± 2 °C). Unless otherwise stated, solutions were prepared in 40 mL amber EPA vials containing 10 mM $NaNO_3$ as the electrolyte medium. Experiments were conducted at pH values from 3.5 to 5.5 with acetate buffer. Some experiments were conducted with Na_2HPO_4 to compare our results from those previously reported by Wan et al. (*19*). A Fisher Accumet pH meter with a combination electrode pH was used to measure pH. Throughout the reaction, the pH was always maintained within ±0.1 pH units of the initial pH. Hg(II) stock solutions were prepared by dissolving $HgCl_2$ or $HgNO_3$ with DW. For all these experiments, acetate buffer was used (with no phosphate), because, in the absence of chloride, mercury forms a di-metal low-soluble complex with phosphate. Concentration of Hg in stock solutions was measured via atomic-absorption spectroscopy. The stock parathion-methyl solution was prepared by dissolving in 100% methanol (MeOH), final reactor MeOH concentration of 6.6%. Pilot experiments conducted at lower parathion-methyl concentrations without MeOH indicated that this level of MeOH did not alter the reaction rates.

Hydrolysis Experiments. After the addition of parathion-methyl, samples were taken at specific predetermined time intervals and were analyzed by high-pressure liquid chromatography (HPLC). The loss of parathion-methyl and the formation of *p*-nitrophenol (hydrolysis product) were monitored using a Waters system equipped with a multiwavelength programmable UV detector and Millenium software. The HPLC stationary phase was a 150 mm Altech Altima C_{18} column, the wavelengths of study were $\lambda_{\text{parathion-methyl}} = 277$ nm and $\lambda_{p\text{-nitrophenol}} = 303$ nm. The mobile phase was a gradient method consisting of acetonitrile/0.01 M chloroacetic acid. Due to the extremely fast hydrolysis observed in the presence of Hg(II), EDTA (2:1 EDTA to Hg_{total}) was added to all samples to quench Hg(II) and halt the hydrolysis reaction at sampling time. To gain insight into the mechanism and the selectivity of Hg as a catalyst, experiments were conducted with the paraoxon-methyl, following the same procedure.

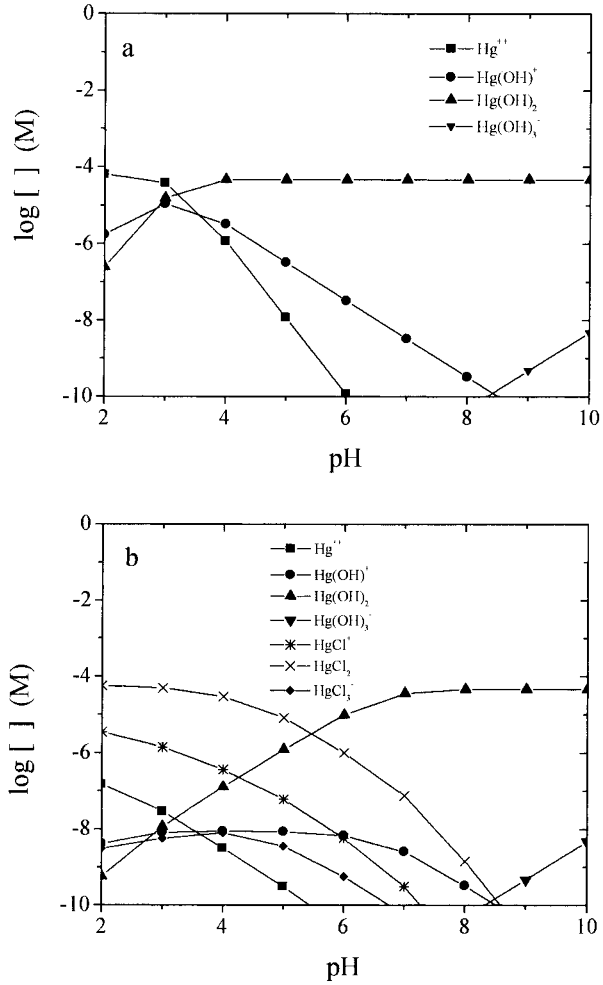


FIGURE 1. Mercury speciation in 10 mM $NaNO_3$ of (a) 65 μM $Hg(NO_3)_2$ and (b) 65 μM $HgCl_2$.

Results and Discussion

Mercury Speciation. The computer program HYDRAQL (*23*) was used to calculate mercury speciation in the absence and presence of chloride for the studied pH values. The equilibrium database was modified with equilibrium constants obtained from Smith and Martell (*24*). The results are presented in Figure 1. At pH 5.5, in the absence of chloride, more than 72% of the mercury exists as hydroxyl species [mostly $Hg(OH)_2$]. In the presence of chloride, approximately 49% of the mercury exists as chloride complexes (mostly $HgCl_2$). At pH 3.5, in the absence of chloride, approximately 84% of mercury is in $Hg(OH)_2$ form. In the presence of

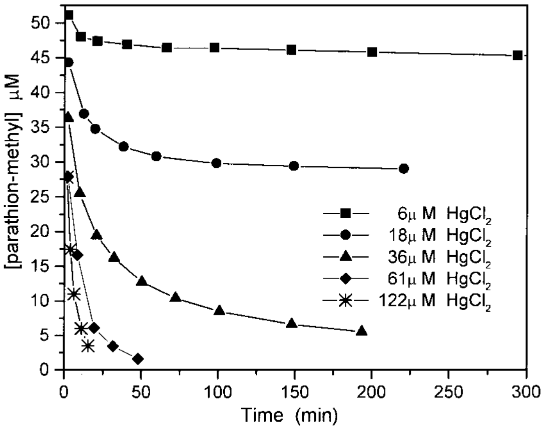


FIGURE 2. $HgCl_2$-promoted hydrolysis of parathion-methyl (60 μM) at pH 3.5 and varying $HgCl_2$ concentrations.

chloride, 65% of the mercury species is in the di-chloride species ($HgCl_2$). Therefore, chloride-complexed mercury species can play a significant role in the activity of mercury in catalyzed hydrolysis, especially at low pH values, where chloride species have an increased dominance.

Development of Analytic Method. In the absence of Hg(II), neither parathion-methyl nor paraoxon-methyl significantly hydrolyzed over our experimental time (up to 48 h). Mercury had a high ability to catalyze parathion-methyl hydrolysis significantly. For example, after 12 min, the typical time for an HPLC run, the reaction is more than 30% complete. Due to the fast hydrolysis (reaction is >90% complete within 30 min), we required a method to quench the reaction at sampling time before injection to the HPLC. EDTA had the ability to quench Hg and, hence, stop mercury-promoted hydrolysis of parathion-methyl. Residual hydrolysis was observed with the addition of equimolar concentrations of EDTA (1:1 EDTA:Hg_{total}; data not shown). Therefore, enough EDTA was added to yield a 2:1 EDTA:Hg ratio to all samples, at sampling times, to ensure no reaction during HPLC analysis.

Effects of Chloride on Kinetics. Figure 2 shows the hydrolysis of parathion-methyl at various mercury-chloride concentrations at pH 3.5. The disappearance of parent compound and the appearance of hydrolysis product, *p*-nitrophenol, increased with increasing mercury chloride. A molar-mass balance was maintained through the reaction, indicating that only one of the two possible hydrolysis mechanisms operates under our experimental conditions (i.e., nucleophilic attack to the P center, and no attack to the C center). However, this process was not truly catalytic; as Figure 2 illustrates, at sufficiently low Hg(II) concentrations, the reaction rate slows throughout its course without achieving complete hydrolysis of parathion-methyl. This slow indicates that mercury is consumed (i.e., complexed in an unavailable form) during the reaction. Similar findings were reported by Wan et al. (*19*) at pH 5.5 for fenitrothion (another OP pesticide). Assuming the mechanism proposed in ref *1*, the following rate law results:

$$\frac{-\mathrm{d}[\mathrm{PTM}]}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{PTM}][\mathrm{Hg(II)}] \qquad (2)$$

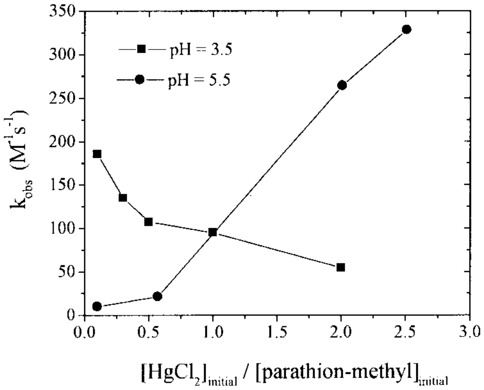


FIGURE 3. Concentration dependence of experimentally determined second-order observed rate constants (k_{obs}) for $HgCl_2$-promoted hydrolysis of parathion-methyl at pH 3.5 and 5.5.

TABLE 1. Second-Order Observed Rate Constants (k_{obs}) for Mercury-Promoted Hydrolysis of Parathion-Methyl at Various pH Values

pH	k_{obs} ($M^{-1}s^{-1}$)	R^2
4.62	320	0.99
4.62	330	0.99
4.62	320	0.99
5.04	130	0.99
5.08	170	0.99
5.11	140	0.99
5.52	51	0.98
5.61	56	0.90
5.61	73	0.89

where $k_{obs} = Kk_2$. We determined the second-order rate constants (k_{obs}) by fitting the experimental data using nonlinear kinetic software by Micromath: Scientist. As illustrated in Figure 3, at pH 3.5, the second-order rate constant (k_{obs}) decreased with increasing $HgCl_2$ added while at pH 5.5, k_{obs} increased with increasing $HgCl_2$ added. For example, at pH 5.5, the second-order k_{obs} more than doubled from 9.8 to 21.4 M^{-1} s^{-1} for initial mercury-chloride to parathion-methyl ratios of 0.5 and 1.0, respectively. However, at pH 3.5, k_{obs} decreased from 135.0 to 95.5 M^{-1} s^{-1} (a 30% reduction) for initial mercury-chloride to parathion-methyl ratios of 0.3 and 1.0, respectively. As shown in Figure 1, Hg-Cl species are more dominant at pH 3.5 than at pH 5.5, suggesting that chloride has an inhibitory effect on the Hg-promoted hydrolysis of parathion-methyl. These results emphasize the importance of metal speciation rather than total metal concentration on metal-catalyzed hydrolysis. Furthermore, we believe that the significant difference for observed rates at pH 3.5 and 5.5 (21.4 and 95.5 M^{-1} s^{-1}, respectively) for similar $HgCl_2$ to parathion-methyl ratios can also be attributed to different catalytic power by the different hydroxy−mercury species present at different pHs (e.g., Hg^{2+}, $Hg(OH)^+$, and $Hg(OH)_2$). Thus, the rate expression in eq 2 is inadequate to account for different Hg species.

To assess further the effects of chloride, studies with $HgCl_2$ at various NaCl concentrations at pH 5.5 were conducted. The hydrolysis of parathion-methyl decreased with increasing NaCl concentration, whereby the mercury-promoted hydrolysis of parathion-methyl was virtually nonexistent at NaCl = 0.1 M. To illustrate that this effect is one of Hg speciation and not solely an ionic-strength effect, experiments with other electrolytes ($NaNO_3$ and $NaClO_4$) were conducted. Neither NO_3^- nor ClO_4^- has a high complexation constant with Hg. For concentrations ranging from 0.001 to 0.1 M, neither $NaNO_3$ nor $NaClO_4$ showed any effect on the mercury-chloride promoted hydrolysis of parathion-methyl, where complete hydrolysis into *p*-nitrophenol was observed after 75 min at pH 5.5. However, for NaCl, the formation of the hydrolysis product (*p*-nitrophenol) ranged from 50% to less than 1% for electrolyte concentrations ranging from 0.001 to 0.1 M, respectively. Hence, the presence of chloride can affect significantly the mercury-promoted hydrolysis of OP pesticides. These results indicate that not all the added Hg is in a form capable of promoting hydrolysis.

Rate Law as a Function of Hydrated Mercury Species. $HgNO_3$ was used to determine the contributions of the various mercury species to the k_{obs} in the absence of chloride. Nitrate is not a good ligand for mercury, and mercury-nitrate species in solution are insignificant.

Metal-catalyzed hydrolysis, such as mercury with OP pesticides, should be viewed as a series of reactions of the parent compound with different metal species. A reasonable mechanism may be postulated as the addition of these reactions in series:

$$\mathrm{Hg^{+2} + S{=}P(OR)_3 \xleftrightarrow{K_1} Hg^{+2}{-}S{=}P(OR)_3 \xrightarrow{k'_1} Hg^{+2}{-}S{=}P(OH)(OR)_2 + ROH}$$

$$\mathrm{Hg(OH)^{+} + S{=}P(OR)_3 \xrightarrow{K_2} Hg(OH)^{+}{-}S{=}P(OR)_3 \xrightarrow{k'_2} Hg(OH)^{+}{-}S{=}P(OH)(OR)_2 + ROH}$$

$$\mathrm{Hg(OH)_2 + S{=}P(OR)_3 \xleftrightarrow{K_3} Hg(OH)_2{-}S{=}P(OR)_3 \xrightarrow{k'_3} Hg(OH)^{2}{-}S{=}P(OH)(OR)_2 + ROH}$$

and, assuming a fast complex formation, a reasonable mechanisms can be expressed as

$$\frac{-d[\text{parathion-methyl}]}{dt} = (\alpha_{\mathrm{Hg^{2+}}}k_1 + \alpha_{\mathrm{HgOH^+}}k_2 + \alpha_{\mathrm{Hg(OH)_3}}k_3 + ...)[\mathrm{Hg(II)}][\text{parathion-methyl}] \quad (3)$$

where $k_i = K_i k'_i$, and α is the fraction of the total Hg(II) present as specific species (ionization fraction) and can be determined from knowledge of the pH and the equilibrium constants for the different hydroxy−mercury complexes. The overall second-order rate constant can then be expressed as $k_{obs} = (\alpha_{Hg^{2+}}k_1 + \alpha_{HgOH^+}k_2 + \alpha_{Hg(OH)_2}k_3)$, assuming that no other active species are present, or that if they are present, they do not contribute significantly to the overall observed catalysis. A similar approach has been used to describe the reduction of chromium(VI) by iron(II) (*25*).

The rate constants k_1, k_2, and k_3 were extracted from the k_{obs} at various pH values by solving the three simultaneous equations:

$$\begin{bmatrix} \alpha_{\mathrm{Hg^{2+}(pH1)}} & \alpha_{\mathrm{HgOH^{+}(pH1)}} & \alpha_{\mathrm{HgOH(OH)_2(pH1)}} \\ \alpha_{\mathrm{Hg^{2+}(pH2)}} & \alpha_{\mathrm{HgOH^{+}(pH2)}} & \alpha_{\mathrm{Hg(OH)_2(pH2)}} \\ \alpha_{\mathrm{Hg^{2+}(pH3)}} & \alpha_{\mathrm{HgOH^{+}(pH3)}} & \alpha_{\mathrm{Hg(OH)_2(pH3)}} \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix} = \begin{bmatrix} k_{\mathrm{obs(pH1)}} \\ k_{\mathrm{obs(pH2)}} \\ k_{\mathrm{obs(pH3)}} \end{bmatrix} \quad (4)$$

At pHs lower than 4.5, the reaction was too fast to allow an accurate determination of k_{obs}. At pH above 6, Hg^{2+} and $Hg(OH)^{+1}$ become negligible and the catalytic effect too small to measure. k_{obs} values were used with MATLAB to solve for the k_i values by minimizing the mean square error with the condition that the minimum value for any $k_i \geq 0$. Values obtained from the various sets (Table 1) were used to determine the standard deviation. The calculated second-order rate constants are

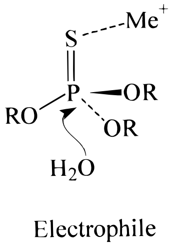
$$k_1 = 5023 \pm 210\ \mathrm{M^{-1}\ s^{-1}}$$

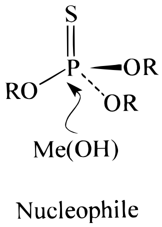
$$k_2 = 50 \pm 22\ \mathrm{M^{-1}\ s^{-1}}$$

$$k_3 = 0 \pm 0\ \mathrm{M^{-1}\ s^{-1}}$$

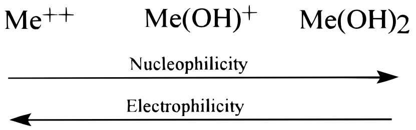
Clearly, different hydroxy−mercury species have different powers to promote the hydrolysis of organophosphate esters. The k_i values were then used to calculate the k_{obs} at different pHs. Figure 4a illustrates the calculated rate law versus the experimentally measured values and the measured rate for $HgCl_2$-promoted hydrolysis at the same mercury to compound initial ratio. At pH 3.5, the $Hg(NO_3)_2$ model predicts a k_{obs} value more than 1 order of magnitude greater than that measured for $HgCl_2$. This prediction is further evidence that chloride has an inhibitory effect and that the mercury-chloride species do not contribute to the overall Hg-promoted hydrolysis of OP pesticides.

The k_1, k_2, and k_3 values imply that Hg^{2+} is more active than $Hg(OH)^+$ and that $Hg(OH)_2$ is essentially inactive. This information provides insight into the metal-promoted hydrolysis mechanism. As stated in the Introduction, different mechanisms have been proposed, where the Me species act as either electrophiles or as nucleophiles:





The general trends of hydroxy-metal species for nucleophlicity and electrophilicity are as follows:



Therefore, a metal-promoted hydrolysis mechanism dominated by nucleophilic attack by the metal species would show increased rates with increasing pH; a mechanism dominated by the metal acting as an electrophile would show increased rates with decreasing pH. Figure 4b illustrates this hyphothesis for the mercury-promoted hydrolysis experiments of parathion-methyl and the results published by Smolen and Stone (*20*) for copper- and lead-promoted hydrolysis of parathion-methyl. Although, from the published data for the Cu(II)- and Pb(II)-promoted hydrolysis of parathion-methyl, we could not determine the contribution of the specific hydroxy-metal species to the overall observed rate because NaCl was used and the pH values studied resulted in very small ionization fractions for some metal species (e.g., $\alpha_{Cu(OH)_2}$ at pH 5.5 = 1.25×10^{-13}); the general trend shown in Figure 4b for Pb and Cu are clear. As the concentration of more nucleophilic species increases (pH increase), so does the observed rate for both lead and copper. Such trends support Smolen and Stone's (*20*) conclusion suggesting that Cu(II) and Pb(II) act mostly as nucleophiles. However, for the mercury-promoted hydrolysis, the maximum rates are observed at lower pH values, where the metal species are more electrophilic.

Experiments with paraoxon-methyl show no catalysis (data not shown) over the experimental time (24 h). This result suggests that the sulfur ("S") was involved in the interaction with Hg. The high affinity of Hg to coordinate with "S" over "O" centers has been documented and is evident from the relative stability constants for mercury sulfide and mercury oxide ($K_{s,HgS} = 10^{-52.3}$ vs $K_{s,HgO} = 10^{-13.3}$) (*24, 26*). Such a selectivity would play a major role when the dominant role of the metal is as an electrophile. When a nucleophilic attack by the metal at the P═S or P═O center is the dominant mechanism, we would expect the P═O center to yield higher observed rates, because the oxygen is more electron with-

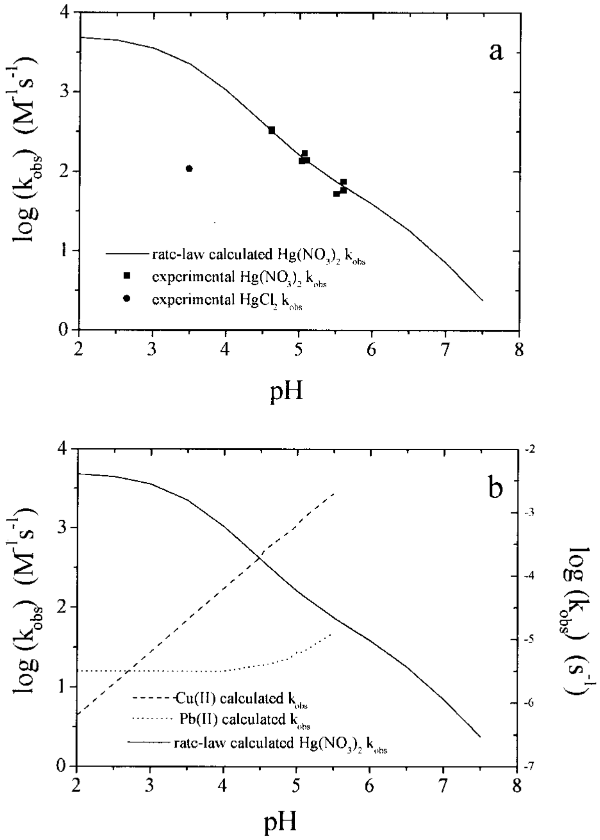


FIGURE 4. (a) pH dependence of k_{obs} from calculated rate law and experimentally determined values. (b) Predicted k_{obs} values for Hg(NO$_3$)$_2$ (this study), and for Cu(II), and Pb(II) [right *y*-axis, pseudo-first-order rate constants from Smolen and Stone, (*20*)].

drawing than sulfur and would leave the phosphorus center more receptive to a nucleophilic attack. Significant differences in observed hydrolysis rates for OPs between the oxo and thio forms have also been reported by Smolen and Stone (*20*) for Pb(II) and Cu(II). As discussed above, their data suggest that nucleophilic attack is dominant. However, both lead and copper showed higher observed hydrolysis rates for the “thio” than for the “oxo” OPs. This preference for “S” centers by the metals suggests that the sulfur center also plays a role in the catalyzed hydrolysis. Thus, although the metal species can act mostly as electrophiles or nucleophiles, a mixed mechanism may be involved.

Environmental Implications

Our results indicate that Hg(II) is capable of promoting the hydrolysis of organophosphate pesticides, thus, use of Hg(II) salts as biocides in the presence of hydrolyzable pollutants may lead to unexpected complications. Furthermore, the overall hydrolysis rate is a function of the concentration of specific Hg species rather than of the total Hg(II) concentration, with the dominant mechanism being electrophilic attach at the S atom.

The contributions of the various mercury species can be calculated from the observed rates and presented in a pH-independent rate law for use in the prediction of catalyzed-hydrolysis rates. Previous studies of metal-catalyzed or metal-promoted hydrolysis have reported k_{obs} values without further examination. There are three advantages to report the relative importance of the different species in catalyzed or promoted hydrolysis: (1) results can be extrapolated form one situation to another, (2) rates can be predicted for specific environmental conditions, and (3) greater understanding of the catalysis mechanism can be gained.

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