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Accelerated Degradation of Organophosphorus Pesticides with Sodium Perborate

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Most organophosphorus pesticides (OPs) exhibit high toxicity. Waste disposal is one of several operations with OPs that must take toxicity into consideration. Sodium perborate has been recommended as a detoxifying agent for hazardous OP wastes (Lee et al. 1984; Edwards 1976), but little data on the reactivity of sodium perborate with several widely used OPs are available in the literature.

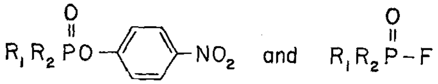
Sodium perborate reacts with water to form hydrogen peroxide ion (HO_2^-) and boric acid:

$$BO_3^- + 2\,H_2O \rightleftharpoons HO_2^- + B(OH)_3$$

In alkaline solution significant concentrations of HO_2^- are present because of the equilibrium (Lee et al. 1984):

$$H_2O_2 \rightleftharpoons HO_2^- + H^+$$

HO_2^- is extremely reactive towards organophosphorus esters, attributable to its nucleophilicity (Edwards et al. 1962). Fina and Edwards (1973) reported a study of the nucleophilic substitution of compounds with the general formulae:



in which it was found that HO_2^- was the most reactive reagent. In spite of its considerably lower basicity, HO_2^- was about 100 times more reactive than OH^-. They suggested that the reactivity of HO_2^- might be enhanced by the presence of unshared electrons on an atom adjacent to the nucleophilic center (alpha effect). Epstein et al. (1956) had shown

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the reaction rate of HO_2^- with paraoxon was about 100 times as rapid as that of OH^-, and ascribed this to hydrogen bonding by HO_2^- in the transition state.

The purpose of this work was to study the rate of reaction of sodium perborate towards several common organophosphorus pesticides in aqueous solutions and in soil-water mixtures. The latter was included in order to explore the possibility of using sodium perborate to rapidly degrade OPs in waste water ponds where soil may be present. The 5 OPs selected were mevinphos, diazinon, methyl parathion, malathion and parathion. While many OPs have short residual lifetimes in aqueous environments, the hydrolysis data for diazinon and parathion indicate that these compounds under natural water conditions are characterized by residual lives that vary between 3-6 months (Gomaa et al. 1972). The disposal of wastewater containing these compounds could be facilitated if accelerated degradation took place before the wastewater was released to a disposal site, or as a treatment in the site itself.

MATERIALS AND METHODS

Sodium perborate tetrahydrate ($NaBO_3 \cdot 4H_2O$), Mallinckrodt; sodium carbonate anhydrous powder, Mallinckrodt; mevinphos (E:Z isomer = 2:1) analytical grade, Shell Chemical; diazinon 87.2%, Ciba-Geigy; methyl parathion, 99.9%, Monsanto; malathion, 93.9%, American Cyanamid; parathion, 98.0%, Stauffer; ethyl acetate, Resi-analyzed, Baker; methanol, Resi-analyzed, Baker.

Clay loam soil was from agricultural plow layer in Brentwood, CA (fine, mont-morillonitic, thermic typic xerocrepts). The soil was air dried and crushed to pass through a 2 mm sieve before storage. The soil was not sterilized.

Tap water, deionized water and lake water were from Davis, CA.

The gas chromatograph was a Hewlett Packard 5700A equipped with an NP-TSD detector and a 30 m x 0.31 mm i.d. fused silica capillary column coated with a 0.25 µm film of DB-1 (J and W Scientific, Rancho Cordova, CA). The carrier gas was helium with a flow rate of 2.2 ml/min through the column; the split ratio was 1/73. The flow rates of hydrogen and air were 3 and 50 ml/min, respectively. The column temperature was 190° C and the detector and injector temperatures were 200°C. Under these conditions the 5 OPs resolved one from another but the E and Z isomers of mevinphos eluted as a single peak. A methanol solution containing the 5 OPs (2 mg/ml of each) was prepared. Tap water (200 ml) contained in an Erlenmeyer flask was brought to 26°C in a water bath. The methanol solution (1.0 ml) was added and mixed with magnetic stirring for 1 minute. An aliquot of the water solution (~10 ppm, 2 or 4 ml) was sampled and extracted with 2 or 4 ml of ethyl acetate by vortexing in a

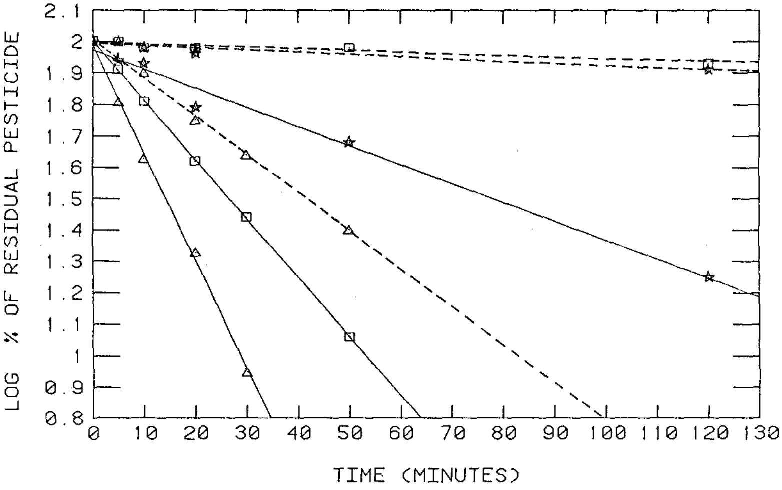

Figure 1. Comparison of degradation rate of three OP pesticides in sodium perborate (pH = 10) and sodium carbonate (pH = 10) solution
——— sodium perborate, ------ sodium carbonate,
△ malathion, ☆ diazinon, □ parathion

15 ml centrifuge tube. After centrifugation the ethyl acetate was adjusted to an appropriate volume for GC analysis to measure the initial concentration of each pesticide.

To start the reaction, sodium perborate (0.9 g) was added to the solution, mixed and dissolved with magnetic stirring; this gave a concentration of 0.03 M and a pH of 10. The aqueous solution was sampled at intervals by the aliquot method mentioned above for analysis of the percentage of pesticide remaining versus time.

Deionized water and lake water were also used instead of tap water in measuring the degradation rate. For soil-water experiments, 0.1, 1, or 5% of Brentwood clay loam soil were added to water, then the pesticide solution and sodium perborate were added as mentioned above. Sodium carbonate (0.15 g in 200 ml water) was used as a control solution (pH 10, but no perborate) in all experiments.

RESULTS AND DISCUSSION

Sodium perborate accelerated the degradation rate of all 5 OPs when compared with the sodium carbonate control (Figure 1). Half-lives in sodium perborate tap water solution were less than 1 hr (Table 1) while the control half-lives were too long to measure within the experimental time except for malathion.

Table 1. Half-lives (minutes) for degradation of pesticides with sodium perborate[a]

Pesticide	Tap water pH = 9.94[b]	Lake Water pH = 9.88[b]	Deionized Water pH = 9.68[b]	Tap water With 0.1% Soil pH = 9.98[b]	Tap water With 1% Soil pH = 9.98[b]	Tap water with 5% soil		
						pH = 9.83[b]	After centrifugation and addition of more sodium perborate[b]	0.12 M sodium perborate pH = 9.98
Mevinphos	13.9±0.7	18.8±0.5	33.6±0.8	16.2±1.0	14.6±1.0	>240	16.1±0.4	6.1±0.7
Diazinon	16.0±1.0	21.3±0.3	27.2	16.6±0.2	20.3±3.0	>240	16.1±2.0	9.4±2.0
Me parathion	12.3±0.8	15.4±0.2	27.2	13.1±0.1	14.4±3.0	>240	12.1±0.8	6.4±0.6
Malathion	8.6±0.4	13.0±0.1	18.7±0.6	8.7	8.4±1.0	23.4±5.3	----	5.0±0.4
Parathion	48 ±6	64 ±3	103 ±7	51 ±2	>240	>240	44 ±3	34 ±4

[a] When sodium carbonate was substituted for sodium perborate as a control, control half-lives were too long to measure within experimental time except for malathion which gave $t_{1/2}$ of 22, 34, and 30 minutes in tap water, tap water plus 1% soil, and tap water plus 5% soil, respectively. Triplicate runs at 26°C and pH 10 except for some deionized water and tap water with 0.1% soil runs which were duplicates.

[b] Contained 0.03 M sodium perborate at initiation.

These experiments confirmed that HO_2^- is a much more reactive nucleophile toward electrophilic phosphorus than hydroxide ion for a selection of common OPs. Plots of the log percent of residual pesticides vs time were linear, indicating a pseudo first order reaction rate when perborate was in excess.

When lake water and deionized water were substituted for tap water, no significant changes in degradation rates were observed. The slightly lower rates in deionized water may have been due to the lower pH (9.68) used in this run when compared with the others (Table 1).

There was no influence on degradation rate when the amount of soil in the water reaction medium was 0.1% but, above that amount, soil did influence the degradation rates noticeably. At 1% soil in water most of the reactions slowed somewhat when compared with 0.1% soil or soil-free solutions. There was no change for malathion whose degradation rate was very fast ($t_{1/2} \sim$ 8 min), and a large change for parathion whose degradation rate was very slow ($t_{1/2}$ for parathion changed from 50 min to >>240 min). When the amount of soil was increased to 5% the degradation reaction nearly stopped after 50 minutes except for malathion. In general, the presence of soil had less of an effect on degradation rates for pesticides such as malathion for which OH^- - mediated hydrolysis was rapid.

In one 5% soil-sodium perborate degradation experiment, the concentration of pesticides dissolved in water was measured after centrifugation to separate suspended soil. The percentage of pesticides remaining in water was nearly the same as in the unseparated soil-water mixture (Table 2), indicating that adsorption by soil was minimal. Thus the slowing of reaction in the presence of soil was not due to adsorption of the pesticides, but rather to the reaction of soil towards sodium perborate resulting in depletion of the reagent. To confirm this, 100 ml of clear supernatant was recovered from the 5% soil-water experiment after 120 min of reaction. At that time no malathion was left. When another portion of sodium perborate was added to this supernatant the degradation rates of the four remaining pesticides were nearly the same as in tap water (Table 1). This indicates that removal of soil from a soil-water mixture, or addition of a larger excess of sodium perborate to such mixtures may be required to effect complete degradation.

To test the latter, a 5% soil-water mixture was made 0.12 M in sodium perborate (4 times the prior concentration). The degradation reaction proceeded rapidly to completion. Half-lives of all pesticides were shorter than half-lives in water solution containing 0.03 M sodium perborate (Table 1). Thus, adding more sodium perborate can counteract the inhibition of the reaction by the soil.

Table 2. Percentage of residual pesticide remaining in 5% soil-water mixture containing 0.03 M sodium perborate.

Pesticide	Soil and Water (no centrifugation)		Water (after centrifugation)	
	120 min	240 min	130 min	250 min
Mevinphos	59 ±7	61 ±6	58 ±3	56
Diazinon	68 ±4	70 ±4	65 ±5	66
Me parathion	63 ±4	64 ±4	59 ±2	60
Malathion	14 ±6	<1	13 ±0	<1
Parathion	80 ±6	80 ±8	80 ±2	84

To check the possibility of using perborate to decompose other classes of pesticides, the tap water experiment was run with the carbamate pesticides molinate, propoxur and carbofuran. The degradation rate of molinate was very slow with sodium perborate or with sodium carbonate; at 240 min, the amounts degraded were 13 and 6%, respectively. The degradation rates of propoxur and carbofuran were faster in sodium carbonate solution than in sodium perborate solution. The half lives of propoxur in sodium perborate and sodium carbonate were 106 ± 6 min and ~ 50 min, respectively; for carbofuran corresponding values were 76 ± 2 min, and ~ 32 min, respectively. Further study of the reaction involving sodium perborate with other pesticides is needed, although these results indicate that the degradation of thiocarbamate and N-methyl carbamate pesticides is not accelerated by this reagent.

The dramatic effect of sodium perborate on OP degradation indicates that it could be used to rapidly degrade these pesticides in waste evaporation ponds. Given a pond volume of 40,000 liters (SCS Engineers 1979), 185 kg of sodium perborate would be required to achieve a 0.03 M solution. At the current cost of bulk technical sodium perborate tetrahydrate (35 cents a pound, Chemical Marketing Reporter, 1984) this treatment would cost $142. Further investigations are required to study the effect of other evaporation pond components, such as emulsifiers and oils, on the utility of this reagent. It is also possible that sodium perborate could be used for other purposes, such as detoxifying organophosphates spilled on paved surfaces or left in spent pesticide containers.

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