Kinetic Investigation of Malathion Degradation in Water

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Malathion [0,0-dimethyl-S-(1,2-dicarbethoxy)ethyl phosphorodithioate] is a widely used pesticide as indicated by a steady rise in production that reached 35 million pounds in 1971 (1). With increaseing emphasis on non-persistent pesticides this organophosphorus compound is anticipated to receive even greater useage in the future.

Malathion exhibits considerable biological selectivity and has been the subject of many comparative biological studies. The kinetics of microbial degradation of malathion by aquatic organisms has been reported by PARIS *et al.* (2), and a kinetic study in soils has been carried out by KONRAD *et al.* However, there are no available data in the literature describing the kinetics of malathion degradation in water.

Malathion has several chemical bonds that are potentially labile under anticipated environmental reaction conditions (Scheme 1). Sulfur-carbon cleavage proceeding through an elimination reaction would give 0,0-dimethyl phosphorodithioic acid and diethyl fumarate. Phosphorus-sulfur bond cleavage by water or hydroxide would give diethyl thiomalate and 0,0-dimethyl phosphorothionic acid which would be in equilibrium with its tautomer, 0,0-dimethyl phosphorothiolic acid. Carboxyl ester hydrolysis would give two possible products, malathion α- and β-monoacids. Another potential reaction under environmental conditions would be oxidation of the sulfur-phosphorus double bond to give malaoxon.

Degradation kinetics were studied under pseudo-first-order reaction conditions. Acid studies were carried out employing a large excess of acid while alkaline degradative studies were done using buffered pH solutions. All reactions obeyed first-order kinetics through at least one half-life.

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1. U.S. ENVIRONMENTAL PROTECTION AGENCY, EPA Report #TS-00-72-04 (1972).

2. PARIS, D. F., LEWIS, D. L., and WOLFE, N. L., Submitted for publication in Environ. Sci. and Tech. (1974).

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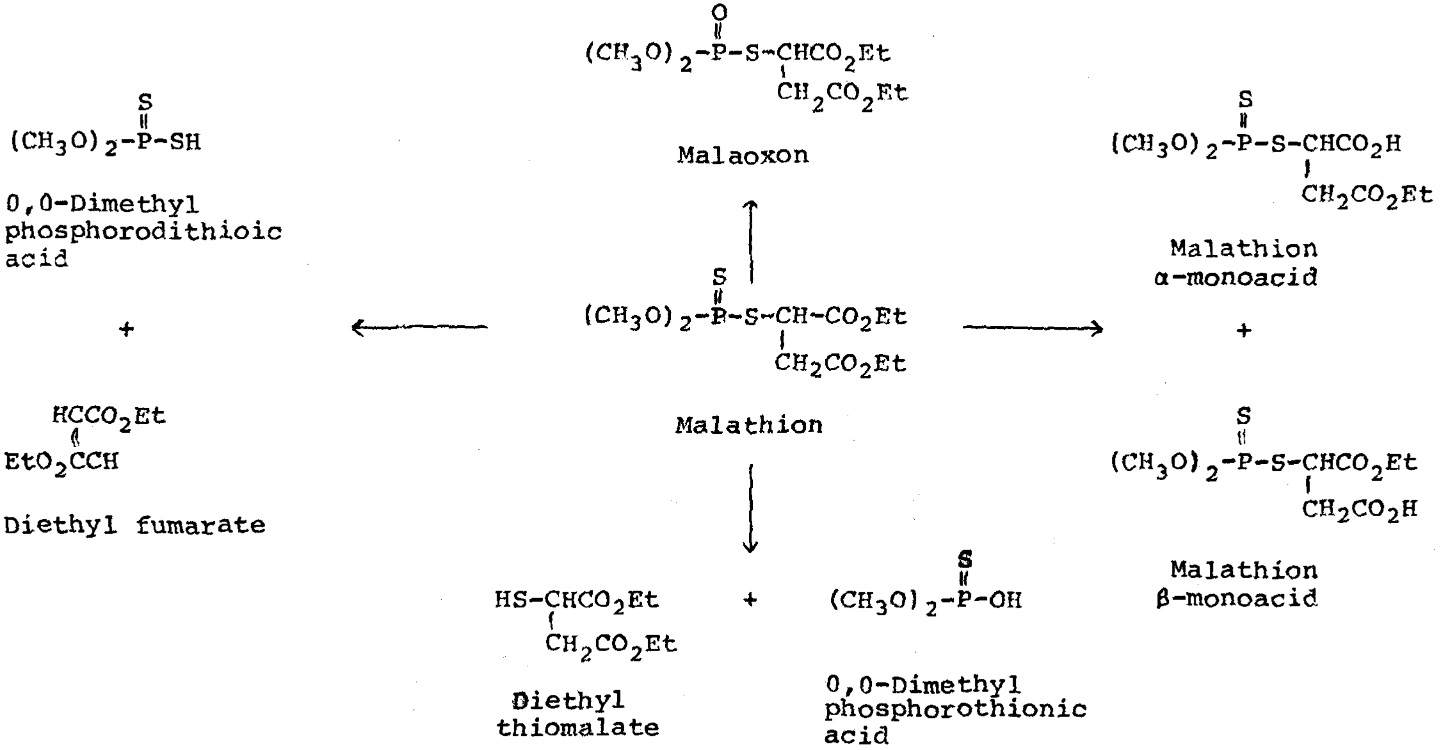
SCHEME 1

Potential Chemical Pathways for Malathion Degradation



Aquatic systems are generally buffered and as a result acid or base concentration is not affected by reaction. Under these conditions the convenient half-life expression is given by

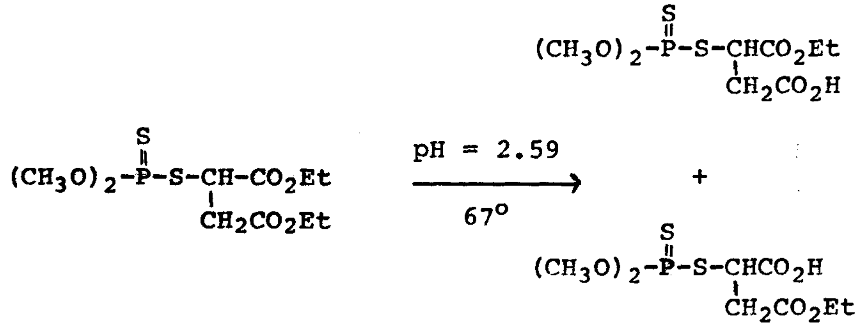
$$t_{\frac{1}{2}} = \frac{0.693}{k\ ([H^+]\ \text{or}\ [OH^-])}$$

where k is the second-order rate constant.

Malathion was stable in water at pH 2.59 for 10 days at 27°. Therefore, the kinetic studies were carried out at elevated temperatures (67° and 87°) (Scheme 2). The extrapolated rate constant (k_{ex}) is $(4.8 \pm 0.2) \times 10^{-5}\ M^{-1}\ sec^{-1}$ at 27°. Based on this rate constant, reaction with hydrogen ion is too slow to be significant at temperatures and pH's common to the aquatic environment.

SCHEME 2

Acid Degradation of Malathion in Water



$$(CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\underset{CH_2CO_2Et}{CH}\text{-}CO_2Et \xrightarrow[67^{\circ}]{pH = 2.59} (CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\underset{CH_2CO_2H}{CH}CO_2Et + (CH_3O)_2\overset{S}{\overset{\|}{P}}\text{-}S\text{-}\underset{CH_2CO_2Et}{CH}CO_2H$$

$$k_{ex}^{27} = (4.8 \pm 0.2) \times 10^{-5} M^{-1} sec^{-1}$$

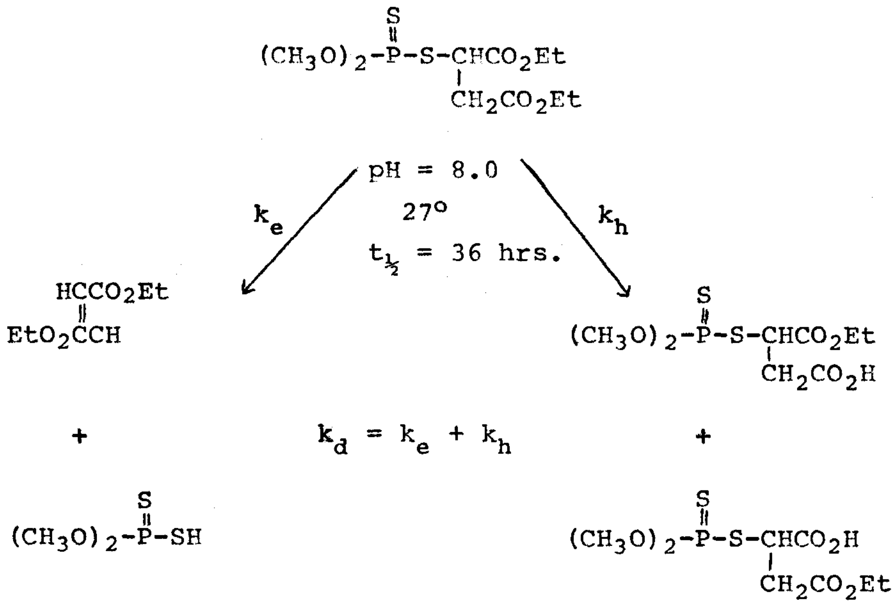
pH 4 $t_{\frac{1}{2}} > 1$ yr.

Product analysis after one disappearance half-life showed the presence of 49% malathion monoacid. Although no malathion diacid was found, it would be an anticipated product at extended reaction times.

The disappearance second-order-rate constant (k_d) for malathion basic degradation at 27° is $5.5 \pm 0.3\ M^{-1}sec^{-1}$. At pH 8 the malathion half-life is 36 hours (Scheme 3).

SCHEME 3

Competing Elimination and Carboxyl Ester Hydrolysis Reactions



$k_d^{27} = 5.5 \pm 0.3\ M^{-1}sec^{-1}$

$k_e^{27} = 3.9 \pm 0.2\ M^{-1}sec^{-1}$

$k_h^{27} = 1.4 \pm 0.1\ M^{-1}sec^{-1}$

Half-life product studies showed the presence of malathion, malathion monoacids, 0,0-dimethylphosphorodithioic acid, and diethyl fumarate. This demonstrates that two competing reactions are occurring, carboxyl ester hydrolysis and 0,0-dimethyl phosphorodithioic acid elimination. Carboxyl ester hydrolysis is favored at lower temperatures as shown by the amount of malathion monoacid present at one half-life. At 0° there was 25%; at 27°, 12%; and 47°, 5%.

Liquid chromatographic analysis showed the monoacid mixture (27°) to consist of 85% α-monoacid and

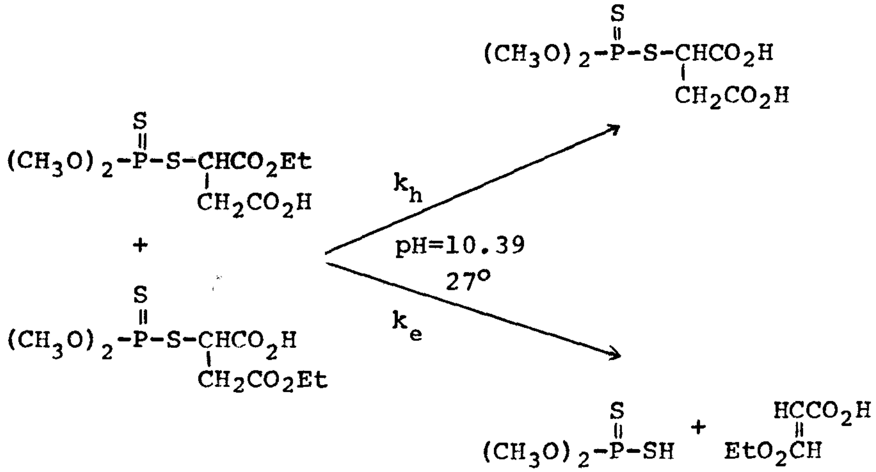
15% β-monoacid. This is in contrast to the results reported by PARIS *et al.* (2), who found that microbial degradation by aquatic organisms gave 99% malathion β-monoacid as product.

Malathion monoacids are anticipated environmental degradation products and therefore we examined their persistence under alkaline reaction conditions.

The disappearance second-order rate constant (k_d) obtained on starting with a mixture of 53% α-monoacid and 47% β-monoacid was $(3.1 \pm 0.2) \times 10^{-1} M^{-1} sec^{-1}$ (Scheme 4). Assuming no large difference in reactivity for the two isomers, at pH 8 the monoacids would have a half-life of about 24 days. Thus malathion monoacids are about 18 times more stable than malathion under the same alkaline conditions.

SCHEME 4

Competing Degradative Pathways for
a Mixture of Malathion α- and β-Monoacids



$$k_d = k_h + k_e$$

pH 8.0

$t_{1/2}$ = 24 days

$k_d = (3.1 \pm 0.2) \times 10^{-1} M^{-1} sec^{-1}$

$k_h = (1.3 \pm 0.1) \times 10^{-1} M^{-1} sec^{-1}$

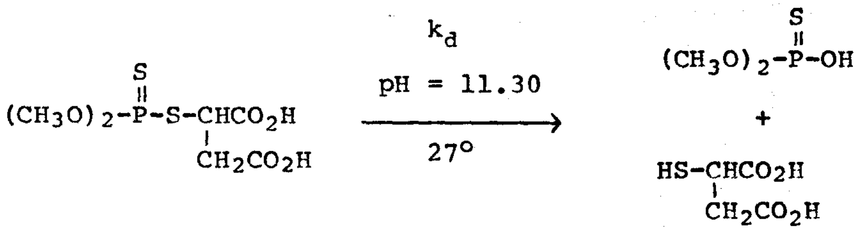
$k_e = (2.0 \pm 0.1) \times 10^{-1} M^{-1} sec^{-1}$

Half-life product studies by gas liquid chromatography (glc) demonstrated the presence of malathion monoacids, malathion diacid, ethyl hydrogen maleate, and 0,0-dimethyl phosphorodithioic acid. There are two possible mechanisms to account for these products. Either the monoacids are undergoing competing carboxyl ester hydrolysis and 0,0-dimethyl phosphorodithioic acid elimination or one isomer is reacting by a carboxyl ester hydrolysis pathway and the other isomer by an elimination pathway.

Because malathion diacid might be a significant breakdown product, we determined its stability under alkaline reaction conditions. The malathion diacid disappearance second-order rate constant (k_d) is (1.8 ± 0.2) x $10^{-2}M^{-1}sec^{-1}$ at 27° (Scheme 5). Thus at pH 8.0 the diacid would have a degradation half-life of about a year. Under the same alkaline conditions malathion diacid is approximately 200 times less reactive than malathion. Product studies (glc) at one half-life showed the presence of malathion diacid, thiomalic acid, and 0,0-dimethyl phosphorothionic acid.

SCHEME 5

Malathion Diacid Degradation in Water



k_d = (1.8 ± 0.2) x $10^{-2}M^{-1}sec^{-1}$

pH 8.0 $t_{1/2} > 1$ yr.

Malathion was stable in oxygen saturated water at acidic pH's for up to two weeks. Whereas malathion is readily oxidized to malaoxon by a variety of mild oxidizing reagents, oxidation by molecular oxygen does not appear environmentally significant.

Malathion photolysis half-life is 990 hours in distilled water (pH 6) with wave lengths greater than 290 nm. However in a Suwannee River water sample which contained a large amount of colored material, malathion was 50% degraded by sunlight in 16 hours.

Malathion basic degradation occurs at a rate fast enough to be a competitive degradative pathway under certain environmental conditions. At acidic pH's degradation is slow and microbial degradation, or in some cases photochemical degradation, might be competitive degradative pathways.

Reference

KONRAD, J. G., CHESTERS, G., and ARMSTRONG, D. E., Soil Sci. Amer. Proc. 33,259 (1969).