Rate of Hydrolysis of Seven Organophosphate Pesticides

by RUBEL P. COWART, FRANCES L. BONNER, and E. A. EPPS, JR.
Feed & Fertilizer Laboratory
Louisiana Agricultural Experiment Station
Baton Rouge, Louisiana 70803

One of the principle advantages claimed for organophosphate pesticides, as opposed to such "hard" chlorinated hydrocarbons as aldrin, dieldrin, and DDT, is the ability of the organophosphates to break down or be altered chemically only a few hours or days after their application. These pesticides are broken down usually by oxidation or hydrolysis.

The products of organophosphate oxidation may be more toxic than the original pesticide; whereas hydrolysis leads to detoxification, although the products of this process are not completely harmless (1). Rainfall, atmospheric water vapor, and soil moisture all provide ample opportunity for hydrolysis.

Since hydrolysis is the principle detoxification mechanism for the organophosphate pesticides, a study was made to determine just how rapidly seven of these compounds are degraded in a neutral aqueous medium.

Experimental

Standard solutions of malathion, phosdrin, methyl parathion, parathion, diazinon, ronnel, and ethion were prepared in redistilled acetone. Standards suitable for injection into the gas chromatograph were then prepared by making dilutions in redistilled hexane from these acetone solutions. The concentration of the acetone solutions and of the hexane dilutions made from them were as follows:

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TABLE 1

Concentrations Test Solutions

Organophosphate	Conc. in acetone (mg/ml)	Conc. in hexane (ng/ul)
Malathion	0.513	5.13
Phosdrin (alpha)	0.94	3.76
(beta)	0.43	1.72
Methyl parathion	0.26	1.30
Parathion	0.745	2.98
Diazinon	1.31	13.1
Ronnel	0.102	0.51
Ethion	0.665	6.65

Each of the following volumes of the acetone standards was pipetted into a flask containing 500 ml of distilled water: 1.0 ml malathion, 0.4 ml phosdrin, 0.5 ml methyl parathion, 0.4 ml parathion, 1.0 ml diazinon, 0.5 ml ronnel, and 1.0 ml ethion. The acetone solutions and the water were mixed thoroughly by vigorously swirling each flask. Immediately after swirling, and at regular intervals thereafter, a 25 ml aliquot was withdrawn from each flask and pipetted into a glass-stoppered graduated cylinder. Five mls of redistilled hexane were added, the graduated cylinder stoppered, and the mixture shaken vigorously for one minute. After the layers had separated, one ul of the hexane extract was injected into the gas chromatograph. The peak height obtained from this injection was compared with that obtained from the injection of one ul of each of the above mentioned hexane standards. The volumes of the acetone standards added to the water were chosen so that the hexane extracts and hexane standards would be directly comparable.

Results and Discussion

The degree of degradation by hydrolysis of each organophosphate, expressed in percent of pesticide undegraded, is given in the following table:

TABLE 2

Degradation by Hydrolysis of Seven Organophosphates

Percentage of Organophosphate Undegraded

Time Interval	Mal	Phos*	MeP	Par	Diaz	Ron	Eth
Immediately	91.9	5.6	94.8	99.1	101.4	101.2	102.2
2 hrs.	90.3	5.8	95.1	102.1	98.4	99.5	92.0
24 hrs.	93.5	10.0	91.2	96.0	95.2	88.4	84.2
2 days	80.9	4.6	85.5	93.3	90.5	60.4	71.3
1 week	59.3	5.4	68.0	81.8	62.6	4.9	38.9
2 weeks	30.7	4.6	43.5	67.3	46.3	-	37.9
3 weeks	20.5	1.7	26.2	56.2	21.6	-	31.2
4 weeks	9.0	2.8	-	31.2	8.3	-	13.4
5 weeks	-	-	-	25.1	4.6	-	6.0
6 weeks	-	-	-	17.8	-	-	5.2

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*The GC column used in this experiment apparently did not separate the alpha- and beta-isomers, since only one peak was observed.

The extremes in this study were represented by phosdrin and parathion. Phosdrin seems to have been almost completely hydrolyzed immediately. Its behavior in this experiment - immediate degradation to a very low level, and the maintenance of this level for a period of several weeks - is curious.

Our results seem to confirm the low chemical residual reported for phosdrin by Porter (2) and indicate that this lack of persistence is due primarily to hydrolysis of the compound. However, our observation of rapid phosdrin hydrolysis in water is not in accordance with values given by that author (3), who stated that the half-life of phosdrin in slightly acidic aqueous solutions (the pH of the distilled water used in this study was about 6.0) is of the order of 3 months.

Parathion, an unsatisfactory organophosphate pesticide because of its great toxicity to humans, was shown in this study to be one of the more persistent compounds of this class. Its relative resistance to hydrolysis would seem to make even more desirable the use of substitutes for parathion.

The general rule that the rate of hydrolysis in distilled water increases with decreasing sulfur content of the organophosphate ester (4) seems to have been confirmed in this study. Phosdrin, the only sulfur-free compound observed, was rapidly hydrolyzed, whereas such high-sulfur pesticides as malathion and ethion were shown to be quite persistent.

Conclusion

All of the organophosphates studied were degraded by hydrolysis at varying rates in a slightly acidic aqueous medium. Of course the conditions of this study were not intended to duplicate conditions in the field, but the results indicate that, while all of these pesticides are eventually hydrolyzed, most of them seem to have a much greater residual life than might have been anticipated. This is especially surprising when it is realized that the hydrolysis conditions in our study were probably more rigorous than those encountered in the field.

Organophosphate pesticides may therefore retain their toxicity for a longer period than expected after application, and as a consequence are more hazardous than commonly supposed.

It should also be remembered, as pointed out earlier, that the products of hydrolysis (such as p-nitrophenol in the case of parathion) are, in themselves, quite toxic.

REFERENCES

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2. Porter, P. E., Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, II, 351, (1964).
3. Ibid., 354.
4. Hindin, E., Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives, I, 89, (1967).