# Hydrolysis and Solvent Partition of Phosdrin and Related Organophosphates

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In a recent study of the rate of hydrolysis of seven organophosphate pesticides it was reported that, of the compounds studied, Phosdrin was the most hydrolytically unstable, being 95% reacted within minutes of addition to distilled water at pH 6 (1). This finding was, as the authors mentioned, in disagreement with the hydrolysis half life, $T_{1/2}$ = 94 days at pH 6, reported by Porter (2); it is also in disagreement with the reported hydrolysis rates of the related organophosphates DDVP, $T_{1/2}$ = 35 hr at 37.5° and pH 6 (3), and Azodrin, $T_{1/2}$ = 23 days at 38° and pH 7 (4).

In the report of rapid Phosdrin hydrolysis (1) unhydrolyzed organophosphates were measured by extracting aliquots of aqueous solutions with hexane, then analyzing the hexane extract by gas chromatography. The possibility occurred to us that in this procedure the bulk of the Phosdrin would not be extracted into hexane, and thus not measured, since it is known that upon partition of Phosdrin between petroleum ether and 15% methanol in water most of the compound remains in the aqueous phase (5), and that 20% benzene in hexane will not remove the related organophosphate Azodrin from water (6).

To check this possibility we have reexamined the solvent partition behaviour and hydrolytic stability of Phosdrin. We include data for Azodrin, Bidrin, DDVP, and methyl parathion for comparison and to serve as a guide for choosing conditions in studies of compounds of this type which involve extraction of aqueous solutions.

## Experimental

Gas chromatographic analyses of Phosdrin and DDVP were carried out using a Varian model 1700 gas chromatograph equipped with a $Rb_2SO_4$ alkali-flame ionization detector and a 4 ft by 1/8 in 2% Reoplex 400 on A/W, DMCS, Chromasorb G, 80 mesh column. Column, injector and detector temperatures were 190°, 205°, and 205° respectively. Nitrogen, hydrogen and air flow rates were 24, 30, and 200 ml/min respectively. Analyses of Azodrin, Bidrin and methyl parathion were carried out using a Varian model 600-D gas chromatograph equipped with a KCl thermionic detector and a 4 ft by 1/8 in 2% DEGA on A/W, DMCS, Chromasorb G 100/120 mesh column. Column and injector temperatures were 200° and 210° respectively. Nitrogen, hydrogen, and air flow were 25, 30, and 300 ml/min respectively. Pesticide samples were

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analytical grade standards. The Phosdrin consisted of 60.4% _α_-isomer and 39.0% _β_-isomer; the isomers were completely resolved on the 2% Reoplex 400 column.

Partition p-valves (7) were determined by adding 50 μg of compound to 5.0 ml of water (previously equilibrated with organic solvent), analyzing a 2 μl aliquot by glc, adding 5.0 ml of organic phase and shaking for one minute, then again analyzing a 2 μl aliquot of the aqueous phase by glc. The p-valve (fractional amount found in organic phase) was calculated as:

$$1-\frac{\text{peak height after solvent equilibration}}{\text{peak height before solvent equilibration}}$$

The conditions of Cowart, _et al._ (1) were duplicated as closely as possible in studying hydrolytic stabilities. Thus 50 μl of 10 μg/μl of organophosphate standards in acetone was added to 500 ml of rapidly stirred deionized water, pH 6.2, at room temperature (26 ± 1°). A 5 μl aliquot was analyzed within 10 minutes by glc. The ratio of the peak height from the water to the peak height of 5 ng of organophosphate standard in acetone, about 0.90 for both Phosdrin isomers and Azodrin, was assigned a value of 100, for time 0. This analytical procedure was repeated at intervals, the ratio of peak heights then giving a measure of the amount of organophosphate undegraded. The aqueous solutions were kept in the dark when not being analyzed; acetone standards were kept at 10°.

## Results and Discussion

The partition p-valves (Table 1) clearly indicate that a single hexane extraction does not remove the bulk of the Phosdrin from water. This, we believe, explains the anomalous "rapid hydrolysis" of Phosdrin. Chloroform, on the other hand, extracts about 95% of both _α_- and _β_-isomers of Phosdrin after a single extraction and is thus a suitable solvent for performing this operation. The partition behaviour of Azodrin and Bidrin resembles that of Phosdrin quite closely. The less polar organophosphate DDVP can be extracted from water with hexane, providing more than one partition is carried out.

TABLE 1

Partition p-Valves of Organophosphates at 27°

| | Hexane / water | Chloroform / water |
|---|---|---|
| Phosdrin, _α_-isomer | 0.14 | 0.94 |
| Phosdrin, _β_-isomer | 0.02 | 0.95 |
| Azodrin | 0.25 | 0.87 |
| Bidrin | 0.13 | 0.98 |
| DDVP | 0.66 | 0.99 |
| Methyl parathion | 0.95 | 0.97 |

Thiophosphates, exemplified by methyl parathion, are nearly completely extracted from water with hexane.

After 1 week in water very little hydrolysis of Phosdrin occurred (Table 2). Analyses were performed directly upon the aqueous solution to rule out any losses in extraction and concentration steps. The slow hydrolysis of Phosdrin in pH 6 aqueous solution reported by Porter (2) is thus confirmed. The related organophosphate Azodrin likewise was quite stable in pH 6 aqueous solution, also in accord with earlier studies (4,6).

TABLE 2

Hydrolysis of Phosdrin and Azodrin

| | Percentage of Organophosphate Undegraded | | |
|---|---|---|---|
| Time interval | α-Phosdrin | β-Phosdrin | Azodrin |
| Immediately | 100% | 100% | 100% |
| 20 hrs | 108 | 106 | 92 |
| 2 days | 111 | 105 | 90 |
| 1 week | 99 | 94 | 91 |

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