DEGRADATION DYNAMICS OF FENITROTHION

IN AQUEOUS SYSTEMS

By

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INTRODUCTION

Fenitrothion (0,0-dimethyl 0-4-nitro-m-tolyl
phosphorothioate), an organophosphorus insecticide with a wide
range of pesticidal action and a low mammalian toxicity is now
widely used in liquid formulations for the control of insect
pests in Canadian forest spray programs (Fettes 1968). For a
formulation to be acceptable, however, it must meet certain
minimum chemical and physical stability requirements. An intensive
study of the hydrolytic decomposition of fenitrothion, under
controlled conditions simulating the natural environment, is use-
ful in assessing the stability of the insecticide formulations and
eventually in correlating their persistence in the aquatic environment.
Despite the increased use of this insecticide in forest spray
programs, there is little knowledge of the hydrolytic behaviour of
the toxicant and of the role of pH in affecting the kinetics of its
persistence. The present study was undertaken with the objective
of providing information on this.

MATERIALS AND METHODS

Buffer Solutions

Four buffer solutions covering the pH range of 5.40 to
8.20 corresponding to the pH of water samples present in the
natural environment (Faust and Suffet 1966), were prepared by
titrating 500 ml of either 0.10 M potassium hydrogen phthalate or
potassium dihydrogen phosphate with 0.10 M carbonate free sodium
hydroxide. The pH of the resultant solutions was measured at 25.0

+ 0.2°C using a Sargent-Welch pH meter (model NX). The values obtained were 5.42, 6.52, 7.32 and 8.22. Two hundred milliliters of the buffer solutions were placed separately in 500 ml stoppered conical flasks and kept in a shaker water bath (Blue M Model MSB-1122A-1) maintained at $25.0 \pm 0.2^{\circ}$C. A stock solution containing 2μg/ml of analytical grade fenitrothion (Sumitomo) in pesticide grade acetone was prepared. Fifty milliliter portions of this solution were added with a pipette to each of the conical flasks. The resulting solutions had an initial concentration $[A_o]$ of 1.44×10^{-6} M of the insecticide. At various time intervals, up to 15 days, aliquots of solutions (5 ml) were removed from each flask and analysed immediately by gas chromatography for fenitrothion to determine the extent of decomposition. Kinetic evaluations were conducted on each of the solutions.

Extraction Procedure

Aliquots of reactants (5 ml) were extracted thrice by vigorously shaking for a few minutes with 50 ml of pesticide grade benzene in a separatory funnel. The benzene fractions, after complete separation were collected quantitatively and combined. The combined extracts were then dried by passing through a 30 g (8 cm) column of anhydrous sodium sulphate, flashed to a small volume (0.5 ml) and estimated by GLC without further cleanup due to the tolerance of the phosphorus detector to any coextracted impurities.

GAS CHROMATOGRAPHIC ANALYSIS

Gas chromatographic analysis of fenitrothion in the water samples was carried out using a Hewlett-Packard F&M model 810 gas

chromatograph equipped with a Tracor flame photometric detector.

Operation conditions:

Columns:	glass, 4 ft x 1/4 in	
	loadings: (1) 5% OV1; (2) 3.8% SE30; on	
	Chromosorb W, 60/80 mesh. AW-DMCS	
Temperatures:	injection ports 200	
(^{o}C)	column oven	185
	transfer line	190
	detector	160
Gas flow:	N_2	60
(ml/min)	H_2	150
	air	50
	O_2	20
FPD filters:	P	526
($m\mu$)	S	394

The gas chromatograph was standardized on the same day as the samples were analysed by injecting aliquots (1-5 µl) of freshly prepared standard solutions of fenitrothion (analytical grade supplied by Sumitomo Chemical Company of Japan), measuring the peak heights, and preparing a calibration curve by plotting peak heights vs concentration. Quantitative results of the extracted samples were obtained by measuring each of the peak heights after injection (2 µl), under the same operating conditions, and reading the concentration from the calibration curve.

Reagents

Benzene used in the experiment was either pesticide grade or freshly distilled using all glass distilling apparatus. The middle fraction was collected and used. Potassium hydrogen phthalate, sodium hydroxide and potassium dihydrogen phosphate used were of analytical grades. Anhydrous sodium sulphate (Fisher) was of reagent grade, heated at $150^{\circ}C$ overnight and stored in a glass-stoppered bottle. Distilled water was obtained by passing tap water through a demineralizer followed by distillation in an all glass apparatus.

Laboratory sources of contamination were found to be minimal.

To determine the efficiency of the extraction method and the overall recovery of fenitrothion, water samples were fortified with known amounts, extracted immediately through the described procedure and analysed for the concentration of fenitrothion by GLC. The final recoveries averaged about 98 percent.

Hydrolysis of fenitrothion - kinetic procedure

Many hydrolytic reactions including the hydrolysis of phosphorothioate triesters are of S_N2 type and obey second order-rate law (O'Brien 1960). In conditions where one reactant is in large excess which is not the case in this study, the reactions obey first order rate law (Ebeling 1963, Ruzicka et al 1967) and are of S_N1 type. In the present study a simple kinetic approach was used where

$$- \frac{d\,[A]}{dt} = k\,[A]^n \quad \text{where} \quad n = \text{the order}$$

For n = 2, integration yields $\frac{1}{[A]} - \frac{1}{[A_o]} = kt$ where $[A_o]$ is the initial concentration of fenitrothion (1.44×10^{-6}M), $[A]$ is the concentration at time t and k is the rate constant. A plot of $\frac{1}{[A]}$ vs t should be linear, with a positive slope equal to k. For n = 1, integration of the above equation gives $\ln[A]/[A_o] = -kt$. A plot of $\ln[A]/[A_o]$ (logarithm of residual insecticide or preferably, its percentage) vs t should be linear. The progress of the hydrolytic reaction of fenitrothion in the laboratory, at the varying pH values (5.42, 6.52, 7.32 and 8.22) was followed by measuring the residual insecticide concentration at definite intervals of time by solvent extraction followed by quantitation using the GLC method as described above. The results obtained were fitted in the integrated rate expressions for first and second order rate laws to see which of the kinetic equation is obeyed during the hydrolytic decomposition of fenitrothion.

RESULTS

Fenitrothion content measured in the four buffer solutions with pH 5.42, 6.52, 7.32 and 8.22 at various time intervals up to 168 hours* and the calculated quantities therefrom are summarized in Table I. The residual concentration of fenitrothion is expressed in terms of percentage recovery ($[A]/[A_o] \times 100$) and molarity. The latter

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* Residue determinations of fenitrothion were carried out far beyond the 168 hours but the rate of hydrolysis of the insecticide was found to be very low; consequently the results are not included here.

is calculated from the former on the assumption that 100% recovery of the insecticide from the buffer solution is equal to 1.44×10^{-6}M. The initial concentrations $[A_o]$ when $t = 0$ were not measured owing to uncertainties involved in such measurements but assumed to be equal to the concentration of the standard fenitrothion (1.44×10^{-6}M) solution used in this hydrolytic study. The hydrolytic pattern of the insecticide obtained by plotting the percent recovery (i.e. residual insecticide concentration) against time (hours) is shown in Fig. 1. A plot of ln ($[A]/[A_o] \times 100$) i.e. ln of percent residual insecticide against time, t is given in Fig. 2. Curvilinear lines were obtained for the hydrolysis of the insecticide at various pH values studied showing that the process did not follow the first-order rate equation. On plotting $1/[A]$, reciprocal of percentage recovery vs t (Fig. 3), straight lines were obtained showing the second-order behaviour of the insecticide within the period of 120 hours and beyond which deviations occurred probably due to the low concentrations of the ester causing a lag phase in hydrolysis. Second-order rate constants k, were determined from the slopes of straight lines in Fig. 3. Half-lives ($t_{\frac{1}{2}}$), (time taken for the disappearance of fenitrothion to half its original value), were obtained from the Figs. 1 and 3. The rate constants (moles 1^{-1} hr^{-1}) and the half-lives are shown in Table 2. A plot of pH against $t_{\frac{1}{2}}$ [obtained from plots of percent recovery vs t (Fig. 1) and $1/[A]$ vs t (Fig. 3)] showing the sensitivity of the latter to the hydronium or hydroxyl ions of the medium is shown in Fig. 4. The variation of k with pH is curvilinear and is shown graphically in Fig. 5.

TABLE 1

Degradation of Fenitrothion in Solutions of Varying pH at 25 $\pm$ 0.2° C.

pH	5.42				6.52				7.32				8.22			
Time (Hours)	M x 10^6	Percent Recovery	$\ln[A]/[A_0]$	$1/[A]$	M x 10^6	Percent Recovery	$\ln[A]/[A_0]$	$1/[A]$	M x 10^6	Percent Recovery	$\ln[A]/[A_0]$	$1/[A]$	M x 10^6	Percent Recovery	$\ln[A]/[A_0]$	$1/[A]$
1	1.438	99.88	-0 002	0.010	1.408	97.81	-0.022	0.010	1.382	95.99	-0.041	0.010	1.354	94.00	-0.062	0.011
2	1.413	98.11	-0.018	0.010	1.352	93.88	-0.063	0.011	1.267	88.00	-0.128	0.011	1.223	84.92	-0.163	0.012
4	1.357	94.25	-0.059	0.011	1.298	90.11	-0.104	0.011	1.230	85.44	-0.157	0.012	1.152	80.03	-0.223	0.013
8	1.265	87.85	-0.130	0.011	1.182	82.06	-0.198	0.012	1.110	77.06	-0.261	0.013	1.008	70.02	-0.356	0.014
12	1.182	82.05	-0.198	0.012	1.109	77.00	-0.261	0.013	1.023	71.06	-0.342	0.014	0.928	64.43	-0.440	0.016
18	1.109	76.99	-0.261	0.013	0.994	69.02	-0.371	0.015	0.896	62.22	-0.474	0.016	0.793	55.10	-0.596	0.018
22	1.052	73.09	-0.313	0.014	0.938	65.12	-0.429	0.015	0.850	59.01	-0.527	0.017	0.722	50.11	-0.691	0.020
30	0.968	67.20	-0.398	0.015	0.863	59.90	-0.512	0.017	0.733	50.88	-0.676	0.020	0.622	43.22	-0.839	0.023
36	0.894	62.11	-0.476	0.016	0.785	54.49	-0.608	0.018	0.663	46.04	-0.776	0.022	0.521	36.21	-1.016	0.028
46	0.814	56.50	-0.571	0.018	0.691	48.01	-0.734	0.021	0.579	40.22	-0.911	0.025	0.484	33.61	-1.090	0.030
54	0.752	52.21	-0.652	0.019	0.634	44.02	-0.821	0.023	0.543	37.71	-0.975	0.027	0.451	31.30	-1.162	0.032
62	0.692	48.09	-0.732	0.021	0.592	41.11	-0.889	0.024	0.507	35.22	-1.044	0.028	0.406	28.20	-1.266	0.036
78	0.620	43.06	-0.843	0.023	0.524	36.41	-1.010	0.028	0.446	31.00	-1.171	0.032	0.346	24.01	-1.427	0.042
86	0.586	40.66	-0.900	0.025	0.492	34.19	-1.073	0.029	0.429	29.76	-1.212	0.034	0.332	23.09	-1.466	0.043
96	0.551	38.28	-0.960	0.026	0.469	32.54	-1.123	0.031	0.397	27.55	-1.289	0.036	0.320	22.20	-1.505	0.045
108	0.518	36.00	-1.022	0.028	0.439	30.50	-1.187	0.033	0.382	26.50	-1.328	0.038	0.304	21.11	-1.555	0.047
116	0.502	34.88	-1.053	0.029	0.429	29.82	-1.210	0.034	0.368	25.55	-1.365	0.039	0.297	20.65	-1.577	0.048
124	0.477	33.11	-1.105	0.030	0.422	29.33	-1.227	0.034	0.356	24.70	-1.398	0.041	0.281	19.52	-1.634	0.051
146	0.462	32.05	-1.138	0.031	0.393	27.26	-1.300	0.037	0.345	23.95	-1.429	0.042	0.274	19.05	-1.658	0.053
168	0.446	31.00	-1.171	0.032	0.367	25.50	-1.366	0.039	0.332	23.05	-1.468	0.043	0.262	18.20	-1.704	0.055

TABLE 2

Kinetic Results for the Rate of Hydrolysis of Fenitrothion

at $25 \pm 0.2\,^\circ C$

pH	$[OH]^-$ moles/liter	k (moles l^{-1} hour^{-1})	$t\frac{1}{2}$ (hours) from Fig 1	$t\frac{1}{2}$ (hours) from Fig 3
5.42	2.63×10^{-9}	2.39×10^{-8}	58	60
6.52	3.31×10^{-8}	3.01×10^{-8}	45	45
7.32	2.09×10^{-7}	3.67×10^{-8}	31	34
8.22	1.66×10^{-6}	4.95×10^{-8}	22	22
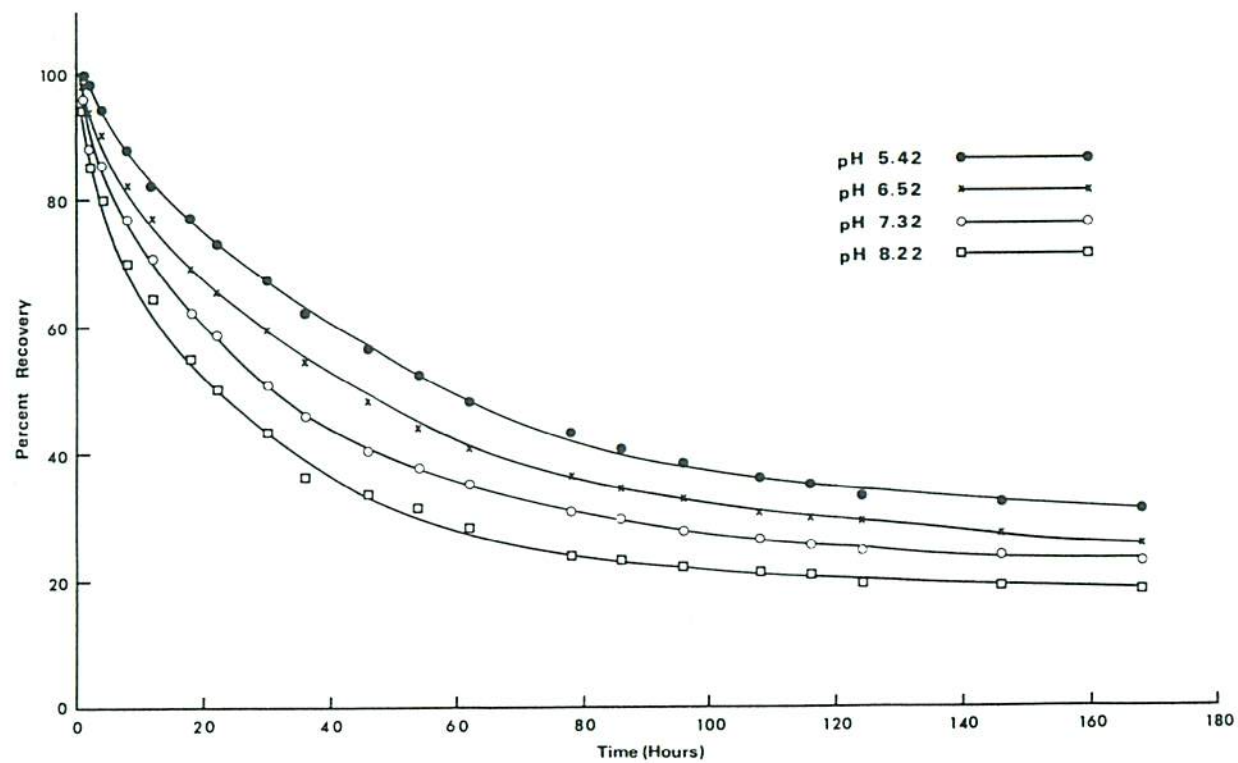
Fig. 1. Percentage of fenitrothion remaining in water samples at various pH levels.
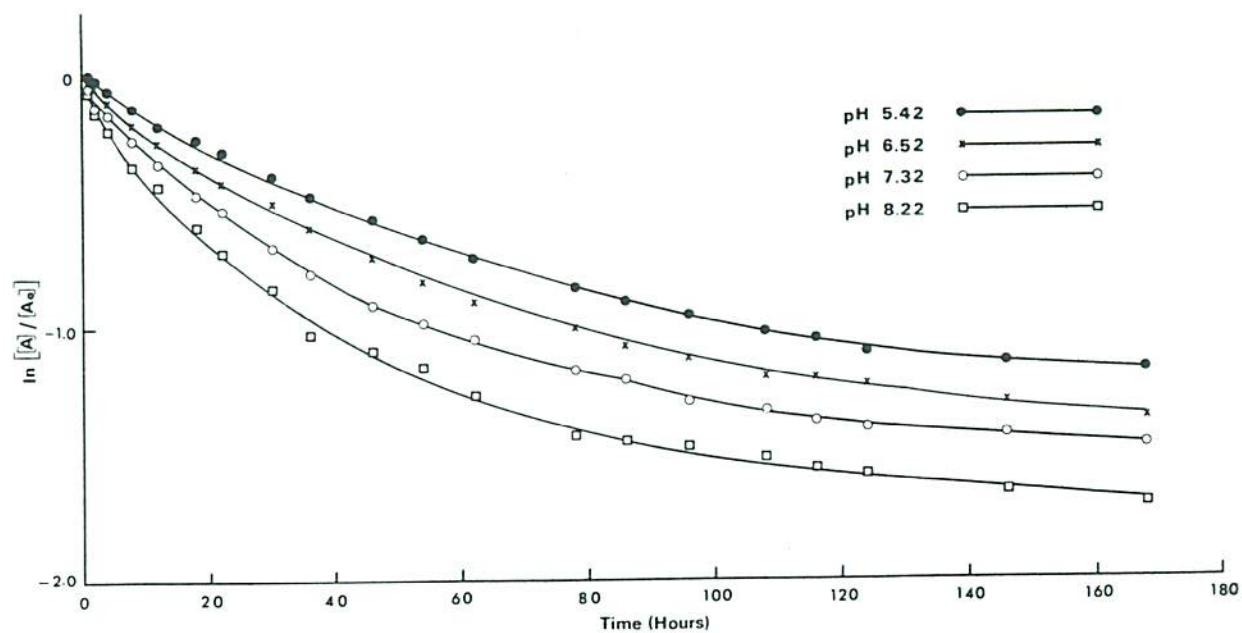
Fig. 2. First-order kinetic behaviour of fenitrothion hydrolysis
in aqueous systems.
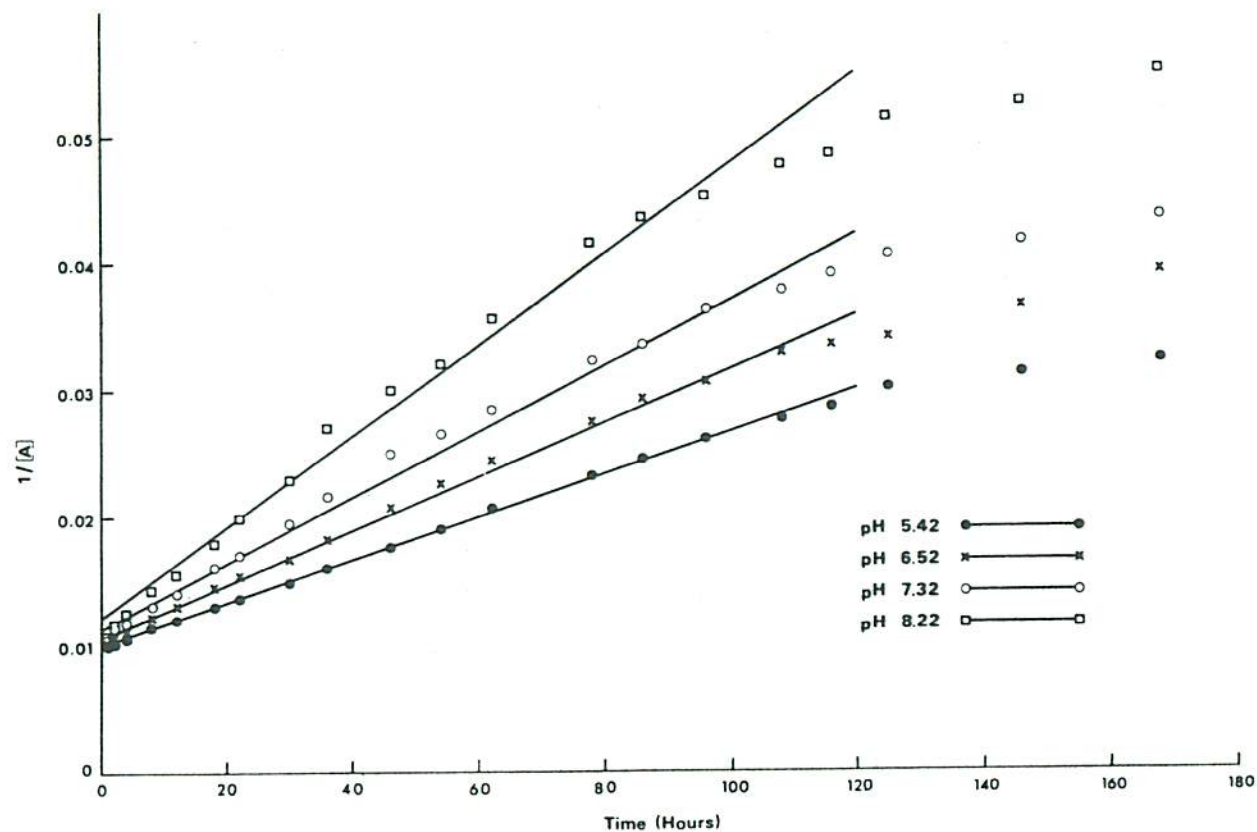
Fig. 3. Second-order kinetics of the hydrolytic rate of fenitrothion.

Regression equation for the straight lines:

pH 5.42 y = 0.00017 + 0.01005X
    6.52 y = 0.00021 + 0.01062X
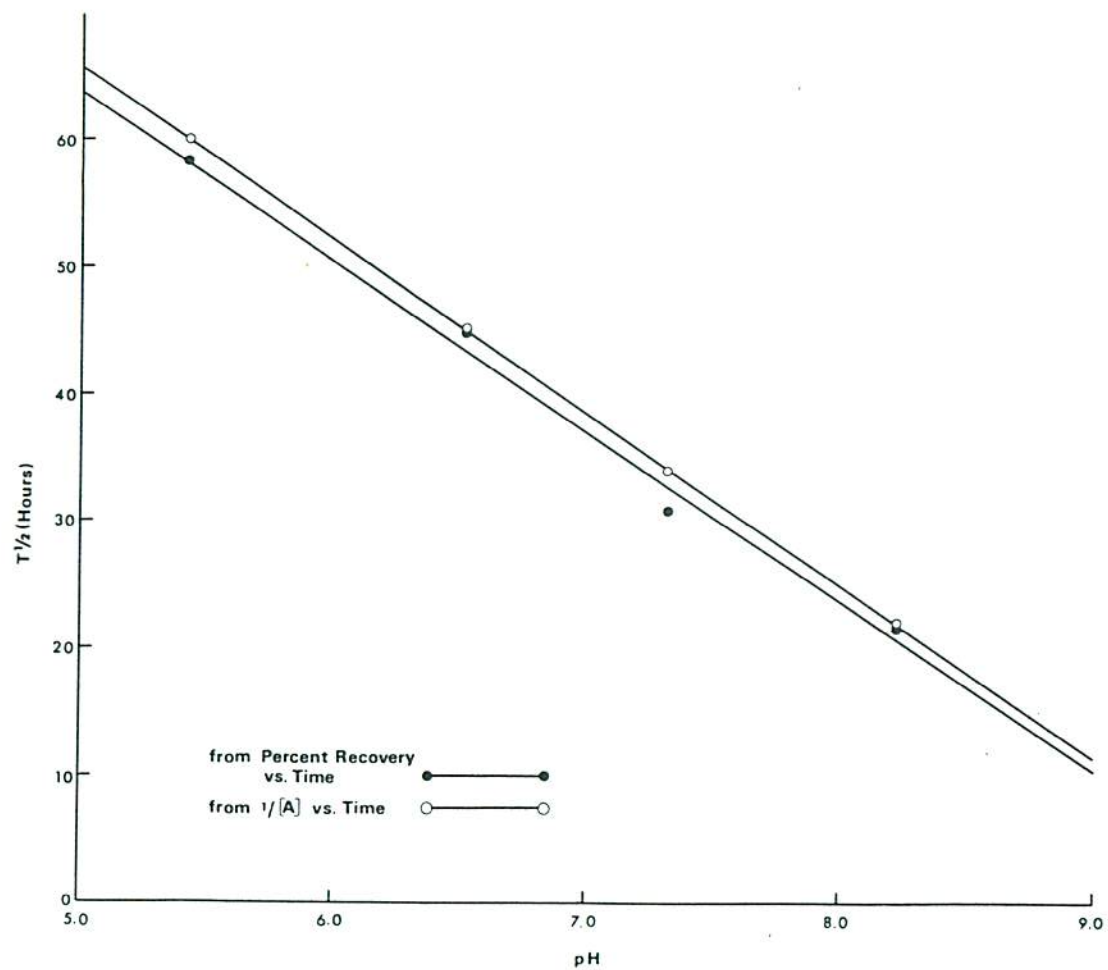   7.32 y = 0.00026 + 0.01146X
    8.22 y = 0.00034 + 0.01229X

Fig. 4. Half-life dependency of fenitrothion on the pH of aqueous systems
Regression equation for the straight lines:
Percent recovery vs Time y = -13.3756 + 130.8399 X
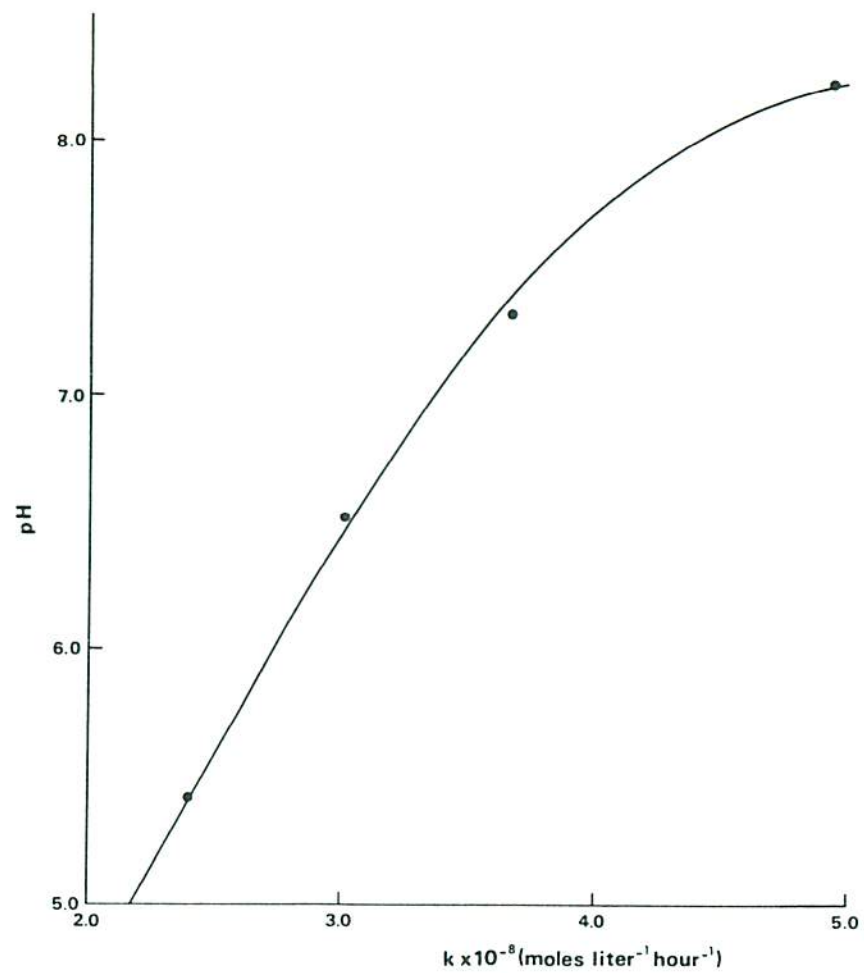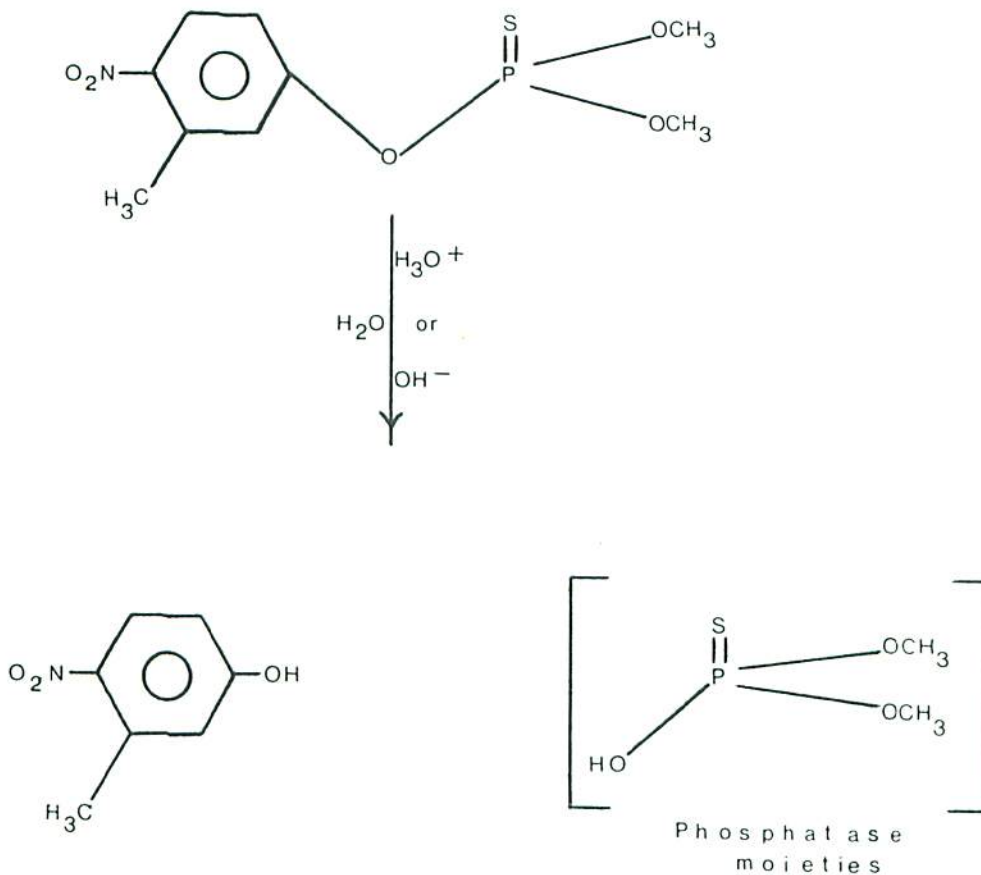1/[A] vs Time   y = -13.5872 + 133.5941 X

Fig. 5. Effect of pH on the hydrolytic rate constant of fenitrothion.

DISCUSSION

Hydrolysis of fenitrothion

Fenitrothion is a tertiary thiophosphate ester and undergoes hydrolysis in aqueous medium - acidic, neutral and alkaline - according to the following scheme:

Phosphatase
moieties

Whether the P—O or O—Ar bond is ruptured depends on the hydrolytic conditions. Various mechanistic studies of organo-phosphate esters in O^{18} rich water have shown that, in alkaline solutions the P—O bond is broken whereas in acidic medium a slow rupture of the O—Ar bond apparently occurs as an initial step (Faust and Gomaa 1972, Singleton 1973). The acid and neutral reactions are considered to operate under a mechanism of nucleophilic substitution, the nucleophile OH^- or H_2O attacking a relatively positive site, the central phosphorus atom, in the substrate molecule causing the rupture of labile P—O bond and the leaving nucleophile (4-nitrocresolete ion) undergoes protenation yielding the corresponding cresol with the simultaneous combination of OH group with the P forming the diester referred here as phosphatase moieties (O'Brien 1960). Under acidic conditions, the hydrolysis is slow; the hydronium ion protonates slowly the low electronegative sulphur atom of the thiono (P=S) group causing an inductive shift of electrons, thereby slowly breaking the Ar—O bond (Bunton 1968). The free energy changes (ΔG_o) for such hydrolytic reactions are highly negative for various organophosphorus insecticides (Faust and Hunter 1971) confirming their instability in aquatic media. The hydrolysis proceeds by a bimolecular mechanism, the rate being proportional both to the concentration of the ester and of the nucleophile (O'Brien 1960).

$$rate = k \, [Fenitrothion] \, [Nucleophile].$$

Effect of pH on hydrolysis

The decay data of fenitrothion (Table 1) show that the percent recovery of the toxicant decreases with time as well as with the increase of hydroxyl ion concentration or pH. At a concentration of 1.44×10^{-6}M and at pH 5.42 only 32.80 percent of the fenitrothion was hydrolysed at the end of 30 hours compared to 56.78 percent at pH 8.22. The hydrolytic rate was found to be dependent upon the pH of the medium, i.e., the reaction is catalyzed by hydronium or hydroxide ions, the latter being a strong nucleophile; hydrolyzability or detoxification increased with increase of $[OH^-]$ or pH. The rate of hydrolysis was found to be low in acidic medium (pH 5.42) (Table 1, column 3) probably due to the strengthening of P——O bond in P-O-Ar system by protonation of the oxygen (Rowlands and Dyte 1972). Therefore the toxicant will be stable in acidic waters and will persist for longer periods of time.

The residue data (Table 1) are plotted according to the second order rate equation, i.e. 1/[A] <u>vs</u> t. Straight lines were obtained (Fig. 3) for all the four pH media studied up to 120 hours, in agreement with the second-order reaction rates. Deviations from linearity occurred after this period probably due to the depletion of fenitrothion molecules in the reaction media. At constant catalytic concentration, i.e., in an appropriate buffer medium, normally first-order hydrolytic kinetics should be observed (Faust and Gomaa 1972); but here on the contrary, at very low nucleophilic concentration ranging from 2.63×10^{-9} to 1.66×10^{-6} moles/liter (Table 2) compared to the ester (1.44×10^{-6} moles/liter), the simplified second-order kinetic equation is obeyed. Second-order rate constants (Table 2) increased with pH; the value more than doubled when the pH rose from 5.42 to 8.22 showing that the compound is sensitive

to hydroxyl ions and is unstable in alkaline medium. The half-lives ($t_{\frac{1}{2}}$) decreased linearly (Table 2 and Fig. 4) with increase of pH; a fall of 38 hours for an increase of 2.80 units of pH from 5.42 to 8.22. Such a linear variation was not observed between pH and k (Fig. 5) especially at the lower hydroxyl ion concentrations.

Various other factors, in addition to pH, influence the hydrolytic rate of fenitrothion. Presence of trace cations such as Cu^{2+}, Fe^{3+} etc., ionic strength (salt effect) of solutions, solvent types and temperatures have considerable influence on the stability of the toxicant (O'Brien 1960). An extensive investigation would be necessary to study the influence of all the factors and their parameters which affect the overall stability and storage life of the insecticide formulations used in spray operations. Knowledge gained from such a study would be useful in the production of superior and stable spray formulations, custom made to the specific needs of various spray programs.

SUMMARY

The chemical stability of fenitrothion in four buffer solutions of pH 5.42, 6.52, 7.32 and 8.22 were studied in the laboratory at 25 ± 0.2°C by solvent extraction and quantitation by gas chromatography. The decay process obeyed a modified second-order kinetic equation. The compound was reasonably stable to hydrolysis under acidic conditions but the rate increased rapidly with alkalinity showing that the process was pH dependent. The rate constant was

sensitive to hydroxyl ions and increased with pH whereas the
half-life decreased. The half-lives ranged from 60 hours at pH
5.42 to 22 hours at pH 8.22 signifying that the compound as a
pesticide has little persistence in aqueous media. Knowledge
of such kinetic data is valuable in preparing environmentally
safe spray formulations of fenitrothion with desirable half-life.

ACKNOWLEDGEMENTS

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