

STABILITY OF PARATHION AND DDT IN DILUTE IRON SOLUTIONS

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ABSTRACT

Dilute FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ solutions degraded parathion to paraoxon and p-nitrophenol. Initial hydrolysis products of iron appeared to have the greatest catalytic activity which decreased as these hydrolysis products aged. The Fe^{3+} ion was less catalytically active than its hydrolysis products for parathion degradation. pH was not a factor in parathion degradation in this study. AlCl_3 solutions did not degrade parathion over a 336 hour period. DDT was stable in dilute FeCl_3 and $\text{Fe}(\text{NO}_3)_3$ solutions for at least 56 days.

INTRODUCTION

The stability of the insecticide parathion is affected by various chemical factors in the environment such as pH, salinity, adsorption by various colloid surfaces, oxidants such as chlorine or permanganate, temperature and ultraviolet radiation^{10,14}.

Faust and Gomaa^{4,5} showed that parathion degradation in aqueous solution decreased with decreasing pH, the degradation half-life, $t_{1/2}$, at pH 10.4 being 33.2 and at pH 3.1, 4182 hr. Paraoxon, the oxygen analog of parathion showed an even greater decrease in degradation with decreasing pH over the same range. Faust and Gomaa¹ have also demonstrated that in neutral and acidic solutions, potassium permanganate oxidizes parathion to paraoxon without any significant hydrolysis to p-nitrophenol. There are several review articles which extensively discuss this subject^{10,12,14}. Weber¹³ found that the parathion degradation rate in neutral salt solution (30 g/l) was almost double that in distilled water in the pH 5.5-5.9 range. He attributed the higher degradation rate in salt solution to higher ionic strength, which influenced hydrolysis. Recently one of the authors (BTB)¹ observed that dilute FeCl_3 solutions (0.001-0.01 M) caused rapid conversion of parathion to paraoxon and p-nitrophenol in montmorillonite suspensions when no fulvic acid was present. With fulvic acid in the system, no parathion degradation was detected.

It has been suggested that there is a relationship between iron and DDT bioactivity in, and adsorption by soil^{2,3,11} but there appear to be no data published as to whether iron affects the stability of DDT in aqueous systems.

The purpose of this study was to investigate the role of ferric salts in the degradation of parathion and DDT in aqueous solutions and to briefly examine parathion stability in AlCl_3 solutions.

MATERIALS AND METHODS

Reagent Purity. The parathion used was 98.9% pure. The p,p'-DDT used was re-crystallized. Reagent-grade p-nitrophenol and paraoxon (95-99% purity) were used to identify decomposition products of parathion. FeCl₃, Fe(NO₃), and AlCl₃, all A.C.S. grade, were dissolved in distilled water. FeCl₃, after dissolution, formed a fine colloidal suspension which was passed through medium porosity filter paper to remove the larger colloidal particles. For some experiments this colloidal material was removed by centrifugation. Concentrations of salt solutions were confirmed by atomic absorption spectroscopy.

Analytical. Aqueous solutions of parathion, paraoxon, p-nitrophenol and p,p'-DDT were extracted three times with chloroform and eluted through anhydrous sodium sulfate. The chloroform was removed by flash evaporation and the solute taken up in benzene using proper precautions to avoid contact with the latter. The benzene extract was transferred to a suitable volumetric flask and made to volume for analysis by gas-liquid chromatography (GLC). Para-nitrophenol was derivatized with BSA [N,O-bis(trimethylsilyl)-acetamide] for detection by electron capture detector (ECD). To accomplish this 10 µl BSA was added to the benzene extracts in autosampler vials and allowed to react for five minutes prior to injection. Parathion, paraoxon, and p,p'-DDT were analyzed by GLC under the following conditions: column- 0.83 m x 2.0 mm I.D., 5% OV101 on Chromosorb W, 100/120 mesh; temperature -180°C; detector-tritium-ECD. Para-nitrophenol was analyzed under the following GLC conditions: column-1.83 m x 2.0 mm I.D., 5% Oronite 128 on Chromosorb W, AW DMCS, 80/100 mesh; temperature-135°C; detector-tritium-ECD.

Sample Preparation. Salt and parathion solutions were prepared at twice the required concentration and mixed 50/50 when initiating the experiment (duplicate samples). Sufficient volumes were pre-pared for successive samplings at appropriate time intervals. For DDT experiments, one volume of concentrated salt solution was added to 14 volumes of saturated DDT solution in order not to dilute the DDT below detection limit.

RESULTS AND DISCUSSION

Over a 1344 hr period (56 d.), p,p'-DDT (at 0.8-0.9 µg/L) loss from 0.046 M FeCl₃ solutions was within experimental error. In FeCl₃ solution containing colloidal forms of hydrolyzed iron, DDT levels decreased in the centrifuged supernatant solution, but were accounted for in the centrifuged material indicating no DDT breakdown. In 0.046 M Fe(NO₃)₃ solution p,p'-DDT decreased from 1.19 to 0.86 µg/L in 672 hr, but decreased by 0.02 µg/L in the next 672 hr. Parathion was quite stable in AlCl₃ solutions (<0.2 M) with less than 2.5% disappearance in 336 hr (14 d.).

Parathion stability was initially studied in 0.005, 0.01 and 0.05 M FeCl₃ solutions which had been filtered through medium porosity filter paper, but had not been centrifuged. These solutions exhibited some initial turbidity which increased considerably with time. Fig. 1 shows that the breakdown rates for parathion in all three solutions were considerably greater in the first seven hour period than throughout the remainder of the study.

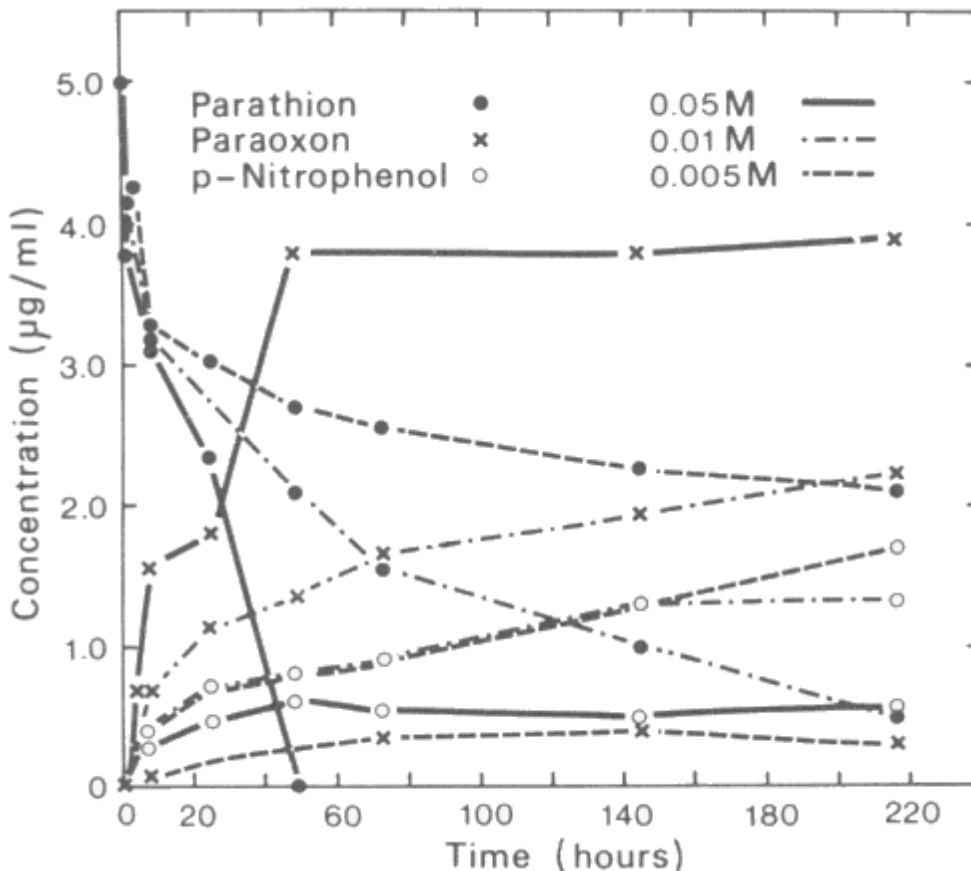


FIG. 1: Parathion degradation as a function of FeCl₃ concentration and time.

Parathion disappearance appeared to follow first-order kinetics in the initial stage of the study, but departed from this after the first 7-10 hours. The disappearance curves were replotted (Fig. 2) to correspond to first-order kinetics (natural logarithm of concentrations vs time) i.e.

$$\ln C = \ln C_0 - kt \quad (1)$$

Where C = concentration of parathion at time t
 C_0 = concentration of parathion at time $t=0$
 k = slope of regression equation = rate constant.

When $C = C_0/2$, $t = t_{1/2}$ and Eqn (1) reduces to

$$t_{1/2} = \ln 0.500 / k \quad (2)$$

The $t_{1/2}$ values (time required for 50% parathion disappearance), based on this initial

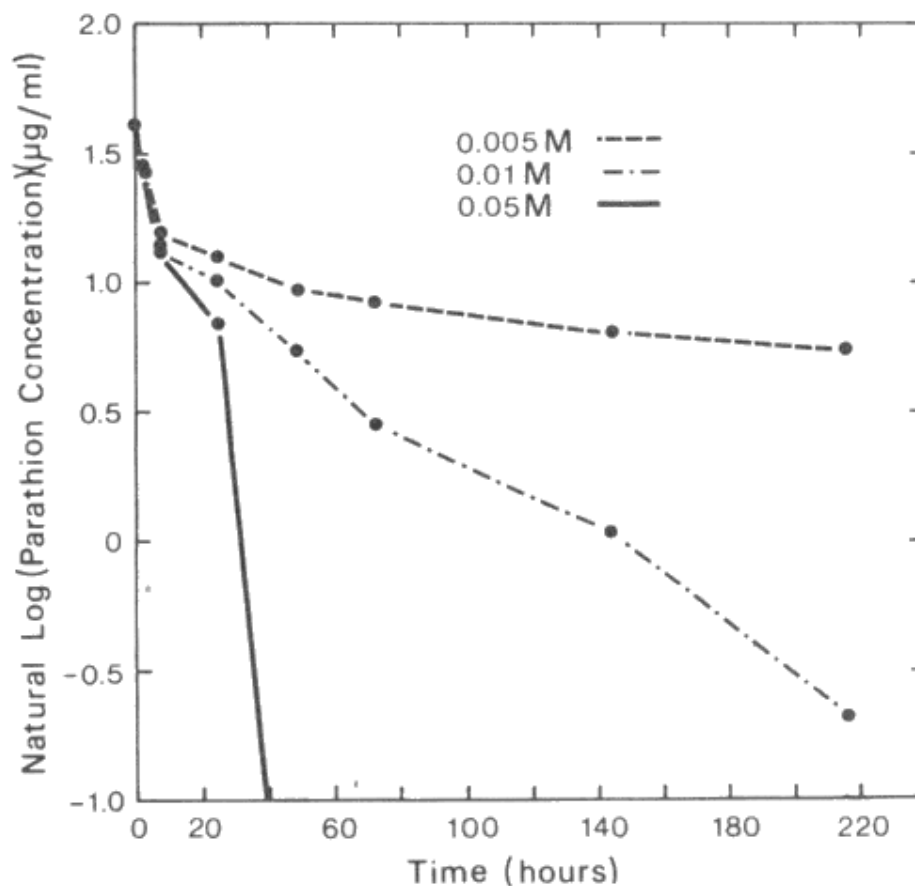


FIG. 2: Parathion degradation in FeCl_3 solutions plotted as a first-order reaction.

seven hour period, were projected to be 12.6, 12.0 and 11.7 hours, respectively, for the 0.005, 0.01 and 0.05 M FeCl_3 solutions (using Eqn 2). Because of the departure from first-order kinetics the actual measured $t_{1/2}$ values were 84, 36, and 22 hours for the 0.005, 0.01, and 0.05 M FeCl_3 solutions, respectively. The departure from first-order kinetics may be due to the onset of iron hydrolysis reactions which produced several interrelated hydrolyzed iron species⁶, each having its own rate constant for parathion degradation. The observed rate constant would be the summation of these individual rate constants, which would constantly change as the aging process of the iron

proceeded. There appeared to be a direct relationship between the FeCl_3 concentration and the parathion disappearance rate.

It was not apparent at this time whether parathion break-down in FeCl_3 solution was attributable entirely to the iron, or whether pH had an indirect effect i.e. pH values of FeCl_3 solutions decrease with increasing concentration. An experiment was conducted using 5 $\mu\text{g/ml}$ parathion in 0.01 M FeCl_3 which gave a pH of 2.28. The pH of a second 5 $\mu\text{g/ml}$ parathion solution in distilled water was adjusted to 2.28 with HCl. Parathion disappeared from the 0.01 M FeCl_3 solution in 96 hr whereas the parathion in distilled water adjusted to the same pH disappeared very slowly (Fig. 3). The final pH values of both solutions decreased slightly to 2.22 and 1.98 for the distilled water- and 0.01 M FeCl_3 -parathion solutions, respectively. These pH decreases may reflect the slightly acidic nature of the parathion degradation products, as well as the release of protons due to iron hydrolysis in the 0.01 M FeCl_3 solution. The $t_{1/2}$ for the 0.01 M FeCl_3 solution was about 8 hr. No accurate estimate for the $t_{1/2}$ of the acidified solution could be made, but it appeared to be comparable to the 4182 hr value quoted by Faust and Gomaa⁵ for parathion at pH 3.1. Thus pH, per se, can be ruled out as a significant factor in parathion breakdown in FeCl_3 solutions.

The slopes of the parathion disappearance curves (Fig. 1) for the 0.005 and 0.01 M FeCl_3 solutions radically changed with increasing time indicating a progressively decreasing disappearance rate. Solution turbidity also increased with time as the hydrolysis products of the FeCl_3 aged. To determine if aging of the FeCl_3 solutions had any bearing on parathion disappearance rates, a 0.02 M FeCl_3 solution was aged

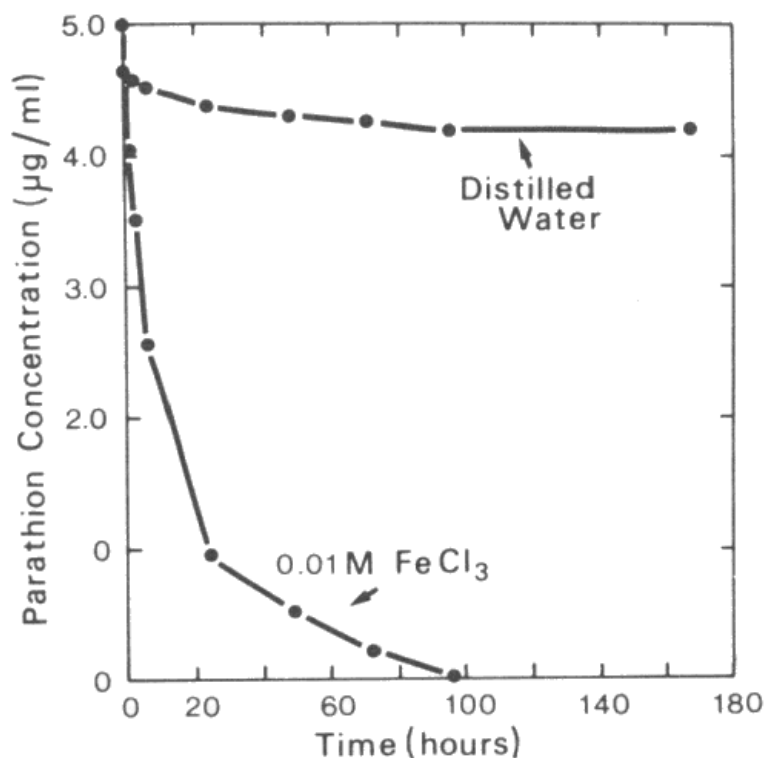


FIG. 3. Parathion degradation in 0.01 M FeCl₃ solution and in distilled water adjusted to the same pH as the 0.01 M FeCl₃ solution (pH 2.28).

for 17 days after dissolution, then diluted 50/50 with 10 µg/ml parathion to essentially reproduce the analytical conditions of the 0.01 M solution in Fig. 1. The $t_{1/2}$ for the aged 0.01 M solution was 180 hr compared to 36 hr for the freshly prepared solutions. For the first few hours following dilution of the aged 0.02 M FeCl₃ solution with parathion solution, the disappearance rate accelerated relative to rates later in the time sequence, similar to that observed for uncentrifuged FeCl₃ solutions in Fig. 1. Dilution of the FeCl₃ solution may have initiated a new set of hydrolysis reactions⁷ and some of the freshly produced hydrolyzed species such as monomeric Fe(OH)²⁺, Fe(OH)₂⁺ and Fe(OH)₃ may have catalyzed parathion breakdown⁶. After a short period, polymerization,

condensation and precipitation reactions of the hydrolysis products may have reduced their catalytic effect on parathion.

A second FeCl_3 aging study was set up using 0.092 M FeCl_3 and a 10 day aging period (from date of FeCl_3 dissolution) before diluting it 50/50 with parathion solution to give a 0.046 M solution. Fig. 4 shows disappearance curves for parathion in freshly prepared and in 10-day-aged FeCl_3 solutions. The measured $t_{1/2}$ values for parathion were 10 and 37.5 hr, respectively. The $t_{1/2}$ values for the 0.046 M FeCl_3 solutions were considerably less than for the 0.01 M solutions, as might be predicted. Because no attempt was made in the first experiment (Fig. 2) to immediately use the FeCl_3 solutions following preparation, the $t_{1/2}$ values were larger than those values obtained from

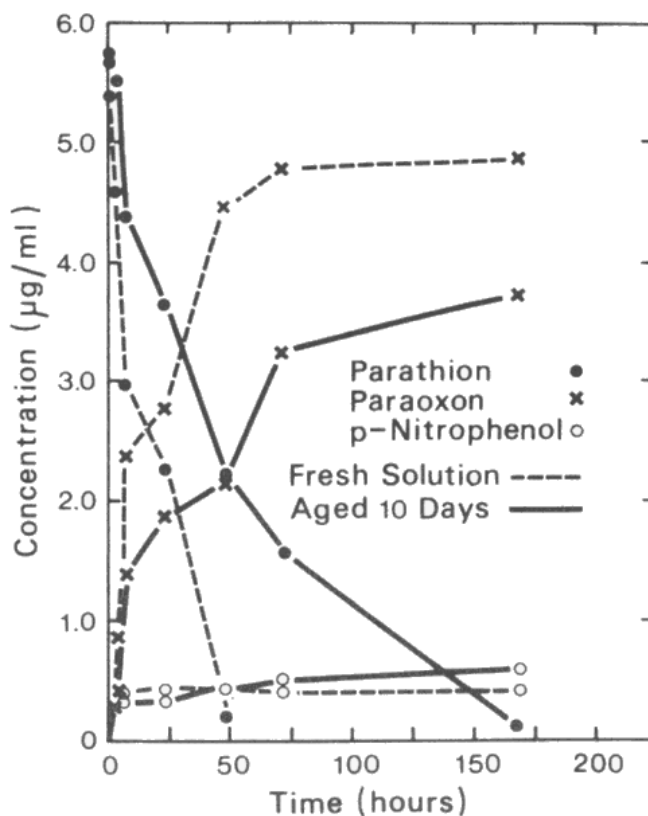


FIG. 4. Effect of aging FeCl_3 solutions (0.046 M) on parathion degradation.

Fig. 4 for similar FeCl_3 concentrations. Thus it is important in studies of this nature to control the preparation time of FeCl_3 solutions.

During preparation of another FeCl_3 solution, it was allowed to sit overnight, resulting in the partial settling out of the colloidal material. This solution was centrifuged to remove the colloidal material and the clear supernatant (0.092 M) was diluted 50/50 with parathion solution, as with the experiment shown in Fig. 4. The measured $t_{1/2}$ value (Fig. 5) was 195 hr, compared with 10 and 37.5 hr for the fresh and 10 day-aged solutions, respectively.

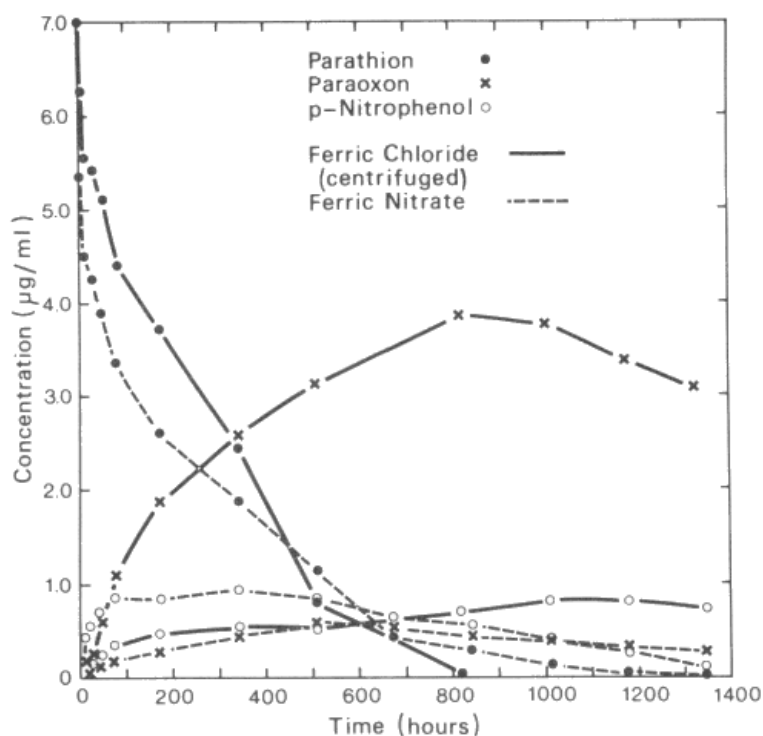


FIG. 5. Parathion degradation in centrifuged FeCl_3 solutions and in $\text{Fe}(\text{NO}_3)_3$ solutions (both 0.046 M).

The centrifuged FeCl_3 solution contained no visible material or cloudiness until the latter stages of the experiment, when most of the parathion had already disappeared. These results suggest that the Fe^{3+} ion degrades parathion, but at a slower rate than the mixture of iron colloidal species resulting from hydrolysis reactions.

Dilute $\text{Fe}(\text{NO}_3)_3$ solutions are subject to less hydrolysis than comparable FeCl_3 solutions^{8,9} $\text{Fe}(\text{NO}_3)_3$ at the same concentration as the FeCl_3 solution (0.046 M), degraded parathion faster in the early stages, giving a measured $t_{1/2}$ value of 160 hr, compared to 195 hr for the FeCl_3 solution (Fig. 5). There was no sign of colloidal material in the $\text{Fe}(\text{NO}_3)_3$ solution (making centrifugation unnecessary) throughout the study. The results of this experiment again suggest that the Fe^{3+} ion can catalyze parathion breakdown.

In all the FeCl_3 experiments in this study (Fig. 1, 4, 5), the predominant reaction was the oxidation of parathion to paraoxon. The hydrolysis of parathion and/or paraoxon to p-nitrophenol proceeded at a much slower rate. The data for the 0.05 M solution (Fig. 1) suggests that a significant amount of parathion was hydrolyzed to p-nitrophenol since there was a slight decrease in p-nitrophenol concentration after the parathion had disappeared when the paraoxon was approaching its maximum concentration. There was much less paraoxon development by $\text{Fe}(\text{NO}_3)_3$ than by FeCl_3 (Fig. 5) and the difference was not accounted for by increased p-nitrophenol development. After the mid-point of the $\text{Fe}(\text{NO}_3)_3$ experiment more than 70% of the original parathion was not accounted for as parathion, paraoxon or p-nitrophenol. There were no unidentified GLC responses that might be attributable to unknown breakdown products. As noted in Fig. 1

for the 0.05 M solution, the p-nitrophenol concentration increased rapidly up to about 72 hours, and decreased gradually after 336 hours coinciding with the decreasing parathion levels. This again suggests parathion hydrolysis to p-nitrophenol rather than the intermediate formation of paraoxon followed by hydrolysis. Further studies are planned to study parathion disappearance and lack of subsequent paraoxon formation in $\text{Fe}(\text{NO}_3)_3$ solutions.

In summary, the results of this study demonstrate that:

- (1) Fe^{3+} ion and some of its hydrolysis products can catalyze parathion breakdown in aqueous solutions.
- (2) The Fe^{3+} ion is less active than some of its hydrolysis products in catalyzing parathion breakdown. The catalytic effect of these hydrolysis products seems to decrease with time, because they tend to polymerize, condense and/or precipitate with time. The initial products of iron hydrolysis tend to be monomeric⁹, and these may be the most active catalysts.
- (3) pH does not seem to be a significant factor in parathion breakdown in acidic iron solutions, and in fact, increasing acidity (to at least pH 2.28) appeared to increase parathion stability.
- (4) Parathion breakdown in iron solutions is concentration dependent, but is complicated by the fact that iron hydrolysis proceeds faster in more dilute solutions, perhaps because dilution increases the pH which in turn speeds hydrolysis reactions. There was an indication that an iron solution aged for a

period of time and then diluted with parathion solution, initiated a new set of hydrolysis reactions. This caused greater parathion degradation rates for a short time until these hydrolysis products aged.

- (5) The predominate reaction of parathion in dilute FeCl_3 solutions is oxidation to paraoxon. The hydrolysis of parathion or paraoxon to p-nitrophenol proceeds at considerably slower rates.
- (6) AlCl_3 does not catalyze parathion degradation over the period of 336 hr.
- (7) Iron and its hydrolysis products do not catalyze DDT degradation in an aqueous solution.

The environmental significance of these findings is not clear. Iron and/or its hydrolysis products could play a role in parathion degradation in soil and aquatic systems. However this catalytic behavior may be diminished in natural systems because of the stable complexes that iron forms with organic matter¹.

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