Chemical Stability of DDT and Related Compounds in Selected Alkaline Environments

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DDT was stable in soil treated with anhydrous ammonia (pH > 10.0) and in sterile, buffered, glass microbeads up to pH 12.0. The threshold pH for dehydrochlorination of DDT to DDE in microbeads was 12.5, with extensive conversion (>70%) at pH 13.0, where the amount of applied DDT unaccounted for increased from 20% at 140 hr to approximately 50% after 30 days, suggesting the formation of intermediates that were lost during extraction or not detectable by electron capture. Applied DDE was relatively stable in microbeads even at pH 13.0 where nearly complete recovery was obtained after 7 days. However, extended incubation to 28 days allowed a gradual disappearance of DDE with only 88 and 74% accounted for at pH 10.0 and 13.0, respectively, suggesting a time-dependent pH relationship for transformation under these conditions. Similar observations were observed in studying the effect of pH on the dehydrochlorination of DDD to DDMU. While DDD was stable for extended periods at pH 10.0, it converted rapidly to DDMU at pH 13.0 and then tended to disappear with time.

Because of its resistance to either microbial or chemical degradation, DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] tends to persist and accumulate in soils. Recently, however, it was shown that DDT degrades more rapidly in soils under biologically active, anaerobic conditions compared with well-aerated systems, with DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] as the major degradation product (Guenzi and Beard, 1967; Parr *et al.*, 1970; Burge, 1971). In solution cultures Johnson *et al.* (1967) observed that a rather large group of facultative and obligate anaerobic bacteria were capable of effecting this transformation under anaerobic, but not aerobic, conditions. Plimmer *et al.* (1968), in studies with *Aerobacter aerogenes*, concluded that the principal pathway of anaerobic biodegradation of DDT proceeds by direct reductive dechlorination to DDD, without the intermediate formation of DDE [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene]. These results suggest that the imposition of anaerobic conditions may have some practical application in decontaminating soils of DDT and related residues.

On the other hand, comparatively little is known about chemical mechanisms which might also contribute to the degradation of DDT in soils. López-González and Valenzuela-Calahorro (1970) reported that DDT adsorbed on homoionic clays was catalytically dehydrochlorinated to DDE, and that the reaction was influenced by the type of clay mineral and the exchangeable cations. The reaction was considerably enhanced with sodium compared with hydrogen clays. Whether this is a significant mechanism in natural soils has not been determined. Fleck and Haller (1945) observed that anhydrous chlorides of iron, aluminum, and chromium can actively catalyze the dehydrochlorination of DDT to DDE, though at elevated temperatures (115–120°C).

It is well known that DDT in alcoholic solution with strong alkali will undergo dehydrochlorination (Fleck and Haller, 1945). Moreover, the alkaline dehydrochlorination of DDD, under similar conditions, results in the formation of DDMU [1-chloro-2,2-bis(*p*-chlorophenyl)ethylene] which, according to Metcalf (1955), can also arise by enzymatic processes.

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Because pesticide residues in soil are often in close proximity to fertilizer components, there is some question whether certain fertilizers, alkaline in reaction, would accelerate the chemical decomposition of DDT. In this regard, a large number of fertilizers were tested *in vitro* by Fleck and Haller (1945), who found that dolomitic limestone was the only one which showed catalytic activity to dehydrochlorinate DDT. While the dissolution pH of dolomitic limestone is approximately 9.8, that of most commercially available fertilizers is in the acid to neutral range, and may account for the lack of activity. An exception is anhydrous ammonia, a widely used nitrogen source, which causes a temporary but marked pH increase in most soils (9.0–10.0) soon after application (Papendick and Parr, 1966).

The purpose of this paper is to report the effect of specific alkaline environments, including anhydrous ammonia, on the chemical stability of DDT and related compounds, and the critical pH values affecting their stability.

MATERIALS AND METHODS

The *p,p'* forms of DDT and DDE, 99.9% purity, were obtained by courtesy of Geigy Chemical Co., Inc., while *p,p'*-DDD was obtained from Rohm & Haas, Inc. DDMU was provided by courtesy of W. E. Beard, USDA–ARS–SWC, Ft. Collins, Colo., and prepared by alkaline dehydrochlorination of *p,p'*-DDD.

The soil experiment was conducted with Crowley silt loam (pH 6.0), obtained from the Louisiana rice area, which was air-dried, passed through a 2-mm sieve, and mixed in a large carboy on a special rotary table with enough DDT (in hexane) to achieve a concentration of 10 ppm, based on the oven-dry weight. The soil (3 kg) was then placed in polyethylene-lined gallon cans, adjusted to $^1/_3$ bar moisture percentage, and injected at the center with 450 mg of NH_3–N according to the method of Papendick and Parr (1966). After 15 min, 1, 24, and 48 hr, soil from appropriate cans was sampled concentrically (by zones) around the point of NH_3 release. Soil samples (25 g) from each zone were extracted with 150-ml aliquots of a 1:1 solution of hexane and acetone. The samples were sonified with a Branson Model J-17A Cell Disruptor for three 1.5-min periods, each followed by decanting, filtering, and addition of fresh aliquots of extracting solution. The extracts were partitioned in a separatory funnel, and the hexane layer was washed with distilled water,

Table I. Effect of pH of Glass Microbeads on Dehydrochlorination of DDT after 24 hr

pH of microbeads[a]	Recovery, % DDT	DDE
10.0[b]	95.0	...
12.2–11.7[c]	94.5	...
12.6–12.1[c]	89.9	2.6
13.0[d]	48.2	32.4

[a] Microbeads were wetted to approximately 0.1 bar, equivalent to a moisture content of 22.5% by weight. [b] pH of acid-washed, unbuffered microbeads. [c] pH of microbeads buffered with solutions of KCl + NaOH prepared according to Handbook of Chemistry and Physics, 52nd Edition. Values tended to decrease as indicated during the first 24 hr. [d] pH of microbeads adjusted with 2 *N* NaOH.

dried with anhydrous Na_2SO_4, and diluted for gas chromatographic analysis. Recovery of DDT from "spiked" soil samples after 48 hr exceeded 90%.

Glass microbeads (Class IV, No. 2027, supplied by the Cataphote Co., Inc., Jackson, Miss.), with a spherical diameter range of 53 to 74 μ, were used as a synthetic medium for studying the effect of alkalinity on chemical stability of DDT and related compounds. The physical properties of microbeads pertinent to this investigation were reported earlier by Parr and Norman (1964). The microbeads were washed with dilute HCl to remove surface alkali, rinsed thoroughly with distilled water, and dried. Samples (25 g) were placed in 225-cm^3 wide-mouth bottles and autoclaved (121°C) for 30 min at 15 psi. Concentration of DDT and related chemicals added to the microbeads (in 1 ml of *n*-hexane) was 10 ppm, based on the oven-dry weight of microbeads. After volatilization of hexane the microbeads were adjusted to 0.1 bar moisture percentage with sterile distilled water. The criterion of sterility was the lack of respiratory CO_2 from control systems amended with glucose, and absence of microbial growth on dilution plates. Incubation was conducted at 25°C using a multipurpose manifold assembly which provided for continuous aeration of each microbead system with CO_2-free air at a standard flow rate (Parr and Smith, 1969). The effluent air streams were scrubbed in ethylene glycol traps and analyzed for the presence of compounds removed by volatilization.

Periodically, the microbead systems were terminated, extracted in the manner described for soil, and assayed for DDT and other residues with a Micro-Tek Model GC-2000R gas chromatograph equipped with a ^{63}Ni electron capture detector operated at 295°C, with the inlet at 215°C, and the oven at 195°C. The carrier gas was prepurified nitrogen at a flow rate of 120 cm^3/min. The column, a coiled glass tube 180-cm × 6-mm, was packed with 80–100 mesh Chromosorb W (high purity, acid washed, DMCS) coated with 3% OV-1. Recovery of DDT, DDD, and DDE from sterile microbeads (pH 10.0) after 24 hr was approximately 95% in all cases.

The paste pH of washed, unbuffered microbeads, measured with a glass electrode, was 10.0, reflecting the natural alkalinity of their sodium–calcium silicate composition. Higher pH values were achieved with either buffer solutions of KCl + NaOH or by dropwise adjustment with 2 *N* NaOH.

RESULTS AND DISCUSSION

Injection of soil with anhydrous NH_3 creates a temporary but highly alkaline environment. The point source mode of application of this fertilizer is characterized by development of a concentration gradient, decreasing progressively outward from the point of release, which, in turn, is related to a pH gradient (Papendick and Parr, 1966). In the present studies, 15 min after injection, soil in the 0–5 cm (diam) zone reached a maximum pH of 10.7, dropping to 9.7 after 24 hr, and 9.2 after 48 hr. Based on previous information this should have been sufficient alkalinity to initiate some dehydrochlorination of DDT. However, this did not happen. There was no indication that this transformation had occurred, even to a limited extent. Soil concentration of applied DDT throughout the NH_3 retention zone, as well as unaffected (peripheral) regions, after 48 hr, was consistently 9.8 ppm, with no DDE detected.

These results prompted the use of glass microbeads for studying the alkaline stability of DDT and related compounds in the absence of complications associated with soil organic and inorganic fractions. Moreover, autoclaving of the microbead systems eliminated possible microbiological involvement, although this medium could probably be used advantageously in studying the biodegradation of pesticides (Parr and Norman, 1964). Microbeads provide a porous three-phase medium not unlike that of some soils, but with the distinct advantage that physical properties such as pore space, pore size, bulk density, internal surface, and moisture retention are more readily definable than for most soils. The use of microbeads in the present experiments demonstrates their potential utility for similar studies on the chemical stability of other pesticides.

The effect of pH on dehydrochlorination of DDT in microbeads after 24 hr is shown in Table I. The pesticide appeared to be quite stable up to a pH of about 12.0, with essentially complete recovery of the original compound. While transformation to DDE is apparent in the 12.0–12.5 range, these data suggest that the critical pH value for this reaction was closer to 12.5. The downward shift in pH of microbeads initially buffered at 12.2 and 12.6 is probably due to absorption of atmospheric CO_2, while systems buffered at pH 13.0 (2 *N* NaOH) remained unchanged because of their stronger alkalinity. At pH 13.0 a considerable amount of DDT was transformed to DDE. While about 50% of the DDT was recovered, the remainder was not entirely accounted for as DDE, nor did analysis reveal any other compounds detectable by electron capture techniques. Thus, at the highest pH, total recovery was about 80%, with 15 to 20% of the applied DDT unaccounted for. Incomplete recovery to a lesser extent was also observed in the 12.0–12.5 range.

The alkaline dehydrochlorination of DDT to DDE as affected by pH over a considerably longer time is shown in Figure 1. At pH 10.0 total recovery of applied DDT after 140 hr and even after 30 days (720 hr—not shown) was approximately 95%, indicating essentially no conversion. At pH 13.0, however, about 70% of the DDT was recovered as DDE after 140 hr, with only 10% remaining as DDT. Again, about 20% of the original DDT was unaccounted for. Total DDT and DDE recovered from volatilization traps during this time was less than 1%. Interestingly, the maximum amount of DDE (71.8%) was observed at this time, while after 280 and 720 hr the percent recovery of DDE had decreased to 55.4 and 42.1%, respectively. Corresponding recoveries of DDT at these longer incubation times were 8.9 and 5.0%. Thus, approximately half of the original DDT was unaccounted for after 30 days. These data suggest that DDT or DDE (or possibly both) is subject to further chemical degradation under extreme alkaline conditions, with the formation of polar products either lost in the aqueous phase during extraction, or not detectable by an electron capture

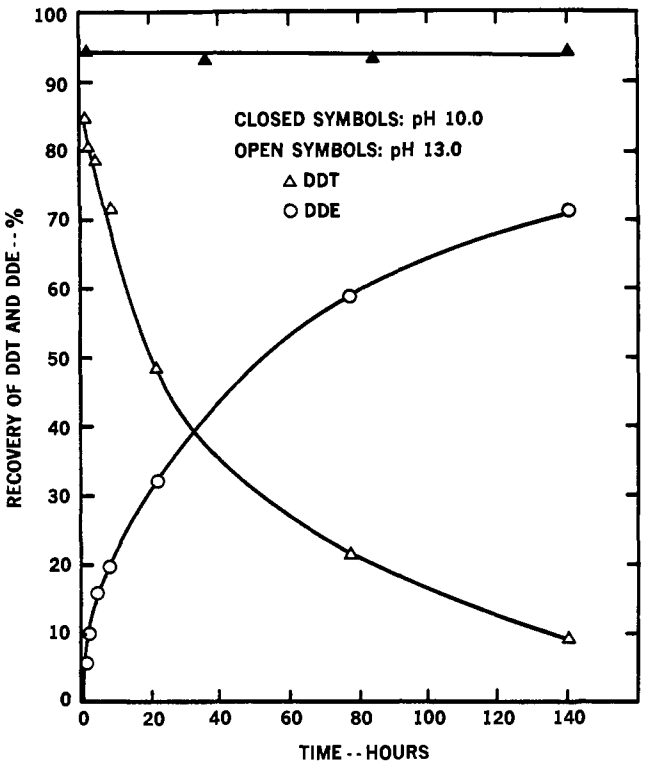

Figure 1. Percent recovery of DDT and DDE from sterile glass microbeads at two pH levels following the initial application of DDT

principle because of reduced electron sensitivity (Parr *et al.*, 1970).

An experiment was conducted to determine whether incomplete recoveries could be attributed to the alkaline instability of DDE. These results, shown in Table II, reveal that applied DDE was relatively stable in microbeads after 7 days (168 hr), even at pH 13.0. Moreover, when volatilization losses were considered, nearly complete recoveries were obtained. Recovery of applied DDE from microbeads after 28 days does, however, indicate a slow disappearance of this compound that is related to pH. Total DDE accounted for at pH 10.0 and 13.0 was 87.8 and 73.6%, respectively, and suggests that a time-dependent relationship with pH is involved. The extent of DDE volatilization after 28 days (>4.0%) was approximately four to five times greater than that occurring from systems containing DDT, reflecting the greater volatility of DDE compared with DDT recently reported by Spencer and Cliath (1972). Therefore, the aforementioned discrepancy apparently results from the further degradation of DDE to a compound, or compounds, not detected by the analytical methods employed.

Results of an experiment to determine the stability of DDD in highly alkaline environments and the effect of pH on dehydrochlorination to DDMU are shown in Table III. At pH 10.0 DDD is quite stable, with no detectable conversion to DDMU even after 28 days, where total recovery (<1.0% volatilization) was slightly less than that obtained for 7 days. In a previous paper, Barker and Morrison (1965) speculated on whether the conversion of DDD to DDMU by *Proteus vulgaris* resulted from enzymatic processes or the alkalinity (8.2) of their culture solutions. Based on these data (Table III) it is unlikely that chemical dehydrochlorination would have occurred because of the apparent stability of DDD at pH 10.0. Thus, enzymatic conversion would be a more plausible explanation of their results.

Table II. Effect of pH on the Disappearance of DDE from Glass Microbeads after 7 and 28 Days

pH of microbeads	Recovery[a] of DDE, % 7 days	28 days
10.0	90.2 (1.5)	83.5 (4.3)
13.0	92.2 (1.7)	69.4 (4.2)

[a] Values in parentheses denote the recovery of DDE from volatilization traps (ethylene glycol) during continuous aeration of the microbead systems.

Table III. Effect of pH on the Dehydrochlorination of DDD to DDMU in Glass Microbeads after 7 and 28 Days

pH of microbeads	Recovery, % 7 days DDD	7 days DDMU	28 days DDD	28 days DDMU
10.0	94.1	...	91.3	...
13.0	6.0	82.9	5.5	45.2

Almost 83% of the applied DDD was transformed to DDMU after 7 days in an alkaline environment of pH 13.0 (Table III). Based on total recovery, this conversion was essentially quantitative. However, after 28 days, while residual DDD remained the same, approximately half of the DDMU had disappeared. As with DDE (Table II) this may be indicative of a time-dependent pH interaction, allowing the conversion of DDMU to other products not detectable by the analytical methods used.

Because of the presence of atmospheric CO_2, it is unlikely that any natural environment would have a pH higher than 10.0 to 10.5, and that any strongly alkaline substance introduced into the environment would tend to undergo neutralization by CO_2. However, the essential considerations here would be the initial pH from artificial induction and the time required for neutralization, which in some cases may be sufficient to effect chemical changes in pesticide residues that might be present.

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