# The Loss of Five Thiolcarbamate Herbicides in Nonsterile Soils and Their Stability in Acidic and Basic Solutions

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A comparison of the degradation rates of five thiolcarbamate herbicides in two soils to their rates of hydrolysis in acidic and basic media was made to determine whether the ease of decomposition could be related to the chemical stability of the thiolcarbamate linkage. Fifty percent of the EPTC (*S*-ethyl *N,N*-dipropylthiolcarbamate), pebulate (*S*-propyl *N,N*-butylethylthiolcarbamate), vernolate (*S*-propyl *N,N*-dipropylthiolcarbamate), and diallate (*S*-2,3-dichloroallyl *N,N*-diisopropylthiolcarbamate) were lost within 2 to 4 weeks, while the loss of triallate (*S*-2,3,3-trichloroallyl *N,N*-diisopropylthiolcarbamate) was much slower. EPTC, pebulate, and vernolate were not affected by treatment with 10*N* sodium hydroxide solution at 95° C for 1 hr, whereas diallate and triallate were degraded in alkali under much milder conditions. In acidic solution a higher concentration of sulfuric acid was required for the hydrolysis of EPTC, vernolate, and pebulate than for diallate and triallate.

Thiolcarbamate herbicides are used extensively as preemergence treatments for the control of weeds in a variety of crops, and available evidence suggests that microorganisms can contribute to their breakdown in soils (Banting, 1967; Kaufman, 1967; Koren *et al.*, 1968; MacRae and Alexander, 1965; Sheets, 1959; Smith, 1970).

The mechanism involved in the microbial degradation of thiolcarbamate herbicides has not been established, although it has been postulated (Kaufman, 1967) that these molecules could undergo hydrolysis at the ester linkage with the formation of a mercaptan and a secondary amine. The mercaptan could then be converted into an alcohol by transthiolation and further oxidized to an acid prior to entering the metabolic pool. Such a mechanism has been proposed in plants and animals for both EPTC (*S*-ethyl *N,N*-dipropylthiolcarbamate) (Nalewaja *et al.*, 1964) and pebulate (*S*-propyl *N,N*-butylethylthiolcarbamate) (Fang and George, 1961; Fang *et al.*, 1964). Limited evidence for such a pathway during the microbial degradation of diallate in soil has been reported by Kaufman (1967), as in two separate experiments a bioassay analysis of treated soil indicated a partial loss of phytotoxicity followed by a temporarily increased phytotoxicity, with a subsequent complete loss of phytotoxicity. Hydrolysis of the diallate ester linkage followed by transthiolation of the allylic moiety could result in the formation of 2,3-dichloroallyl alcohol. The effect of such an alcohol on plants is unknown, although allyl alcohol has phytotoxic properties and is a known herbicide.

Thiolcarbamates are markedly resistant to chemical hydrolysis, and concentrated acids at elevated temperatures are required for the hydrolysis of EPTC and pebulate (Patchett *et al.*, 1964).

If the hydrolysis of the thiolcarbamate linkage does occur during microbial breakdown, then it is possible that a correlation may exist between the rates of biological degradation and ease of chemical hydrolysis. For this reason the breakdown of five thiolcarbamate herbicides in warm moist soils and their hydrolysis in acidic and basic media were investigated.

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## EXPERIMENTAL PROCEDURES

**Soils.** The composition and physical characteristics of Regina heavy clay and Weyburn loam are shown in Table I.

**Thiolcarbamates.** Analytically pure EPTC (*S*-ethyl *N,N*-dipropylthiolcarbamate), pebulate (*S*-propyl *N,N*-butylethylthiolcarbamate), vernolate (*S*-propyl *N,N*-dipropylthiolcarbamate), diallate (*cis*- and *trans*-*S*-2,3-dichloroallyl *N,N*-diisopropylthiocarbamate), and triallate (*S*-2,3,3-trichloroallyl *N,N*-diisopropylthiolcarbamate) were used in these studies.

**Reagents.** All solvents for gas chromatography were glass distilled, whereas other chemicals were reagent grade.

**Ultraviolet Absorption Measurements.** These were made on a Beckman DB spectrophotometer using 1-cm glass cells.

**Gas Chromatographic Analyses of Diallate and Triallate.** These were conducted on a Varian 204-2C gas chromatograph equipped with a tritium electron-capture detector using conditions previously reported (Smith, 1969a,b).

**Soil Degradation Studies.** To 40-g samples of the air-dried soils, sieved to pass a 2-mm sieve, in 70-ml screw capped bottles, were added 4 ml of an aqueous solution containing 50 ppm EPTC, vernolate, or pebulate so that a herbicide concentration of 5 ppm based on air-dried soil was achieved. Further water was added until field capacity moisture levels were obtained. This technique could not be used for diallate or triallate, as their water solubilities (14 and 4 ppm, respectively) were too low. Thus these two chemicals were applied in hexane to 2000-g batches of the dry soils as previously described (Smith, 1969b). Aliquots of 20 g (treated at the 5 ppm level) were then weighed into bottles and moistened to field capacity. After capping to prevent volatilization losses, all samples were stored in the dark at 25 ± 2° C.

At 2-week intervals, the EPTC, pebulate, or vernolate residues remaining in the soil were extracted by steam distillation (Koren *et al.*, 1969) and analyzed quantitatively following the colorimetric method of Patchett *et al.* (1964). In this procedure the secondary amine, formed by acidic hydrolysis of the thiolcarbamate, is treated with carbon disulfide and ammoniacal cupric sulfate to form the yellow cupric dithiocarbamate complex which absorbs at 440 mμ. Analysis showed that no interfering substances were present in untreated soils, and similarly, benzene extracts of the steam distillate from treated soils indicated the absence of any amine prior to acid hydrol-

Table I. Composition and Physical Characteristics of Regina Heavy Clay and Weyburn Loam

| Soil type | Composition % Clay | Silt | Sand | Organic content | pH | Field capacity moisture % |
|---|---|---|---|---|---|---|
| Regina Heavy Clay | 74.0 | 22.5 | 3.5 | 4.0 | 7.5 | 39.7 |
| Weyburn Loam | 18.0 | 37.0 | 45.0 | 6.5 | 7.0 | 28.0 |

ysis. This mode of analysis could not be utilized for either diallate or triallate as di-2-propylamine is so sterically hindered that formation of the cupric complex can occur only to an insignificant extent. Every 2 weeks soil residues of these two herbicides were solvent extracted and analyzed using electron-capture gas chromatography (Smith, 1969a,b).

Recoveries of all herbicides from fortified clay and loam soils, after a 24-hr equilibration period, were in excess of 90%.

**Acidic Hydrolyses.** Sulfuric acid solutions ranging from 4*N* to 36*N*, in intervals of two normality units, were used in these studies. To 10 ml of each of the acid solutions in 50-ml glass stoppered tubes was added 0.4 ml of a methanol solution containing 500 ppm EPTC, pebulate, or vernolate. After stoppering, the tubes were placed in an oil bath at either 95 ± 2° C or 75 ± 2° C for 1 hr. On cooling, the acid was diluted with 50 ml cold distilled water, basified with 50% sodium hydroxide while swirling in an ice bath, and finally extracted with 10 ml benzene. Any amine present in the organic layer was analyzed colorimetrically (Patchett *et al.*, 1964).

For diallate and triallate, aqueous solutions containing 8.5 and 0.9 ppm, respectively, were used. To 10.0-ml aliquots of the herbicide solutions in 50-ml glass stoppered tubes were added 10-ml portions of each of the sulfuric acid solutions, care being taken to keep the solution temperature below 30° C. The stoppered tubes were then heated in an oil bath at either 95 ± 2° C or 75 ± 2° C for 1 hr. After cooling, the contents were diluted with 50 ml cold distilled water and extracted with 20 ml benzene. The organic phase was dried over sodium carbonate and analyzed gas chromatographically for diallate or triallate.

**Basic Hydrolysis.** Aqueous solutions 2, 4, 6, 8, and 10*N* with respect to sodium hydroxide were used. The procedure was exactly the same as for the acid hydrolyses, 200 μg of EPTC, vernolate, or pebulate being added to 10 ml of the various basic solutions. After heating, the tube contents were cooled, diluted with 50 ml distilled water, acidified with 10*N* sulfuric acid, and finally extracted with two 20-ml portions of hexane. Any thiolcarbamate extracted into the hexane was analyzed in the usual manner (Patchett *et al.*, 1964).

The method used for the basic hydrolyses of diallate and triallate was analogous to that for the acidic hydrolyses, and the herbicide solutions 1, 2, 3, 4, and 5*N* with respect to sodium hydroxide were heated for 1 hr at either 95 ± 2° C or 50 ± 2° C. Following cooling, dilution, and benzene extraction, the diallate or triallate remaining was determined gas chromatographically.

## RESULTS AND DISCUSSION

The half-life values (the time for the initial concentration of the thiolcarbamates to be reduced by 50%) in the moist clay and loam are shown in Table II, and indicate that EPTC, vernolate, pebulate, and diallate are degraded considerably faster than triallate.

Table II. Time for 50% Degradation of Thiolcarbamate Herbicides in Regina Heavy Clay and Weyburn Loam

| Thiolcarbamate | Time in Weeks[a] Regina Heavy Clay | Weyburn loam |
|---|---|---|
| Pebulate | 2–3 | 2–3 |
| Vernolate | 2–3 | 2–3 |
| EPTC | 4–5 | 4 |
| Diallate | 5–6 | 4 |
| Triallate | 10–12 | 8–10 |

[a] Average of four replicates.

Table III. Normality of Sulfuric Acid Required to Hydrolyze Thiolcarbamates 50% in 1 Hr at 95° and 75° C

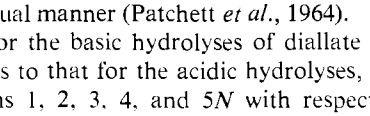
| Thiolcarbamate | Acid Normality[a] 95° C | 75° C |
|---|---|---|
| Diallate | 11 | 13 |
| Triallate | 10 | 13 |
| EPTC | 18 | 29 |
| Pebulate | 18 | 29 |
| Vernolate | 18 | 29 |

[a] Average of two replicates.

Percentage hydrolyses of EPTC and diallate in sulfuric acid solutions after 1 hr at 95° and 75° C are shown in Figure 1. The curves for pebulate and vernolate at both temperatures are virtually superimposable on those for EPTC. Similarly, the curves for triallate are almost identical to those for diallate. The normality of sulfuric acid solutions required for the 50% hydrolysis of the five thiolcarbamates within 1 hr at the two temperatures (Table III) suggests that EPTC, pebulate, and vernolate are all hydrolyzed at similar rates, while triallate undergoes hydrolysis at a rate comparable to that for diallate.

In basic solution, negligible hydrolysis (less than 10%) of EPTC, vernolate, or pebulate was noted, even on heating in 10*N* sodium hydroxide for 1 hr at 95° C. Both diallate and triallate underwent complete breakdown in 1*N* sodium hydroxide within 1 hr at 95° C. No triallate was detected in 1*N* base after 1 hr at 50° C, whereas 3*N* sodium hydroxide solution was required for the complete breakdown of diallate under the same conditions.

EPTC, vernolate, and pebulate have similar half-life values in both soils (Table II) and their hydrolytic half-lives in acidic solution (Table III) are identical. However, diallate and triallate, which are broken down in acidic and basic media under milder conditions than are the other three thiolcarbamates, have degradation rates in the clay and loam, indicating the opposite trend.

EPTC, pebulate, and vernolate are relatively simple compounds which can only undergo hydrolysis at the thiolcarbamate linkage  in acidic solution to give a secondary amine as hydrolysis product. Thus the quantitative analysis of the amine gives a direct measurement of the degree of hydrolysis of these three herbicides. As it is not possible to detect di-2-propylamine, the rate of disappearance of the diallate and triallate had to be studied, which may not be the same as the rate of hydrolysis at the thiolcarbamate linkage. For vernolate, pebulate, and EPTC, hydrolysis is much more rapid at 95° C than at 75° C (Figure I, Table III), while for diallate and triallate, the effects of temperature are relatively insignificant. This would tend to suggest that for these chlorinated thiolcarbamates, initial attack of the acid is not at the thiolcarbamate linkage but at the olefinic bond or

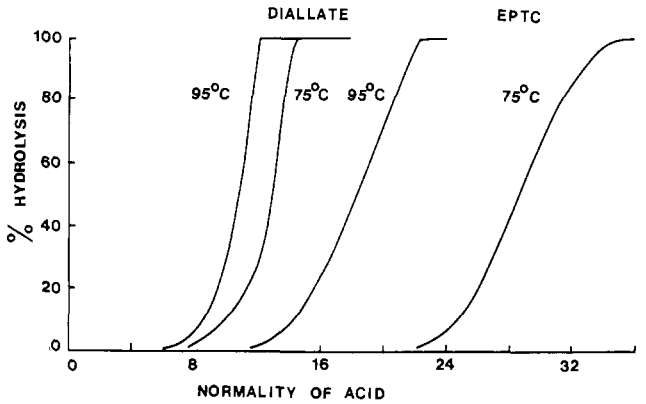



**Figure 1. Percentage hydrolysis of EPTC and diallate in sulfuric acid after 1 hr at 95° and 75° C**

some other point. During acidic hydrolysis of both diallate and triallate, an extra peak was noted on the gas chromatogram with a longer retention time than that of the parent compound. The nature of these products is unknown, though for detection by the electron-capture detector chlorine atoms must presumably be present.

The three saturated thiolcarbamates are stable to basic hydrolysis, while diallate and triallate are much more easily degraded. Again for these latter two compounds, initial attack by the base may rather be at the allylic moiety than the thiolcarbamate linkage. Triallate is less stable in base than diallate. Diallate is a mixture of *cis* and *trans* isomers (Harman and D'Amico, 1967) which may behave differently in basic solution. At present it is not possible to distinguish analytically between the two forms and thus determine whether one isomer is more stable in basic media than the other.

By conducting soil degradation experiments in sealed bottles, it was hoped to minimize volatilization losses so that only chemical and biological losses would be expected. Little is known about the chemical stability of thiolcarbamate herbicides in soils, though it has been observed (Smith, 1969b) that in warm moist sterile Regina heavy clay and Weyburn loam, negligible losses of diallate and triallate residues occurred over a 2- and 3-month period, respectively. Thus it is felt that in these soil experiments, losses of all five chemicals are due to biological processes rather than chemical.

Whether or not diallate and triallate undergo hydrolysis specifically at the thiolcarbamate linkage in acidic or basic solutions, under such conditions they are less stable than EPTC, pebulate, and vernolate. Consequently if biological breakdown is simply related to chemical stability, diallate and triallate should be more rapidly degraded in moist warm soils than they in fact are (Table I).

In the soil degradation experiments, other factors such as herbicide adsorption to soil colloids and water solubility could affect the rate of biological degradation (Alexander, 1965; Bailey and White, 1964). The water solubilities (Fang, 1969) of the thiolcarbamates used in these studies are EPTC (375 ppm), vernolate (107 ppm), pebulate (92 ppm), diallate (14 ppm) and triallate (4 ppm). Providing no adsorption to soil matter occurs, then all the applied residues of EPTC, pebulate, and vernolate could exist in soil solution, whereas the low water solubilities of diallate and triallate preclude this possibility. Studies with diallate and triallate (Smith, 1970) indicate that the adsorption of triallate by Regina heavy clay and Weyburn loam from aqueous solution is over 95%, whereas for diallate the amount is approximately 70%. These adsorptions are considerably greater than those reported for EPTC and pebulate (Koren *et al.*, 1969). Thus it is possible that diallate and triallate are adsorbed more strongly to soil colloids in the biological experiments than are EPTC, pebulate, and vernolate, and consequently are degraded at a relatively lesser rate. It is also possible that in culture media where no herbicide adsorption can occur, the rates of biological decomposition of EPTC, pebulate, vernolate, diallate, and triallate will be quite different from those observed in soils, and further work is planned to investigate this.

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