Effect of Water Vapor Pressure on the Thermal Decomposition of 2-Chloroethylphosphonic Acid

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ABSTRACT

Decomposition of 2-chloroethylphosphonic acid (Ethephon) was studied in dried films at various water vapor pressures (0.6 to 86.9 millimeters Hg, 3.2 to 93.9% relative humidity) and temperatures (20, 30, 40, and 50 C) at pH 6.3 and 7.0. The rate of decomposition could be determined equally well by [14C]Ethephon or ethylene measurements. The rate increases at increasing water vapor pressures at a constant temperature and pH, up to an optimum. The optimum vapor pressure for decomposition approximately doubles for each 10 C increase. The activation energy for the decomposition reaction in water vapor pressures of 3.2 to 12 millimeters Hg is 8.7 and 14.3 kilocalories per mole at pH 6.3 and 7.0, respectively.

Decomposition of Ethephon is inhibited above an optimum vapor pressure. The inhibition is stronger at lower temperatures and at pH 6.3 than at pH 7.0. The rate of decomposition and the inhibition observed at a low temperature (20 C) was found to be similar on various surfaces, including olive leaves.

Failure to induce olive (Olea europaea L.) fruit abscission under certain environmental conditions can be readily attributed to rapid breakdown of Ethephon at elevated temperatures and low relative humidities.

2-Chloroethylphosphonic acid, which readily decomposes to yield ethylene, is widely used to regulate plant growth and development (1). Decomposition of Ethephon increases rapidly above pH 5 (8) and at elevated temperatures (4). Inasmuch as decomposition proceeds only above pH 4.5, Maynard and Swan (8) concluded that breakdown occurs when both hydroxyls on the phosphonate group are ionized. A mechanism of nucleophilic attack of water or OH⁻ on the phosphonate dianion was proposed by Yang (10). A kinetic study of the thermal decomposition of Ethephon in aqueous solutions by Biddle et al. (4) showed that the rate of breakdown at different temperatures is proportional to the acid fraction in the dianion form. They (4) also claimed that decomposition rate of Ethephon was independent of the hydroxyl ion concentration. The mechanism of breakdown was described as a base-catalyzed elimination reaction (5) and as a second order reaction (9). Later measurements showed that the decomposition is a first order, not a second order reaction (4). From measurements of decomposition rates at different temperatures, the activation energy of the reaction in aqueous solutions was calculated to be 29.8 ± 1 kcal mol⁻¹ and claimed to be independent of pH (4).

Experiments to induce olive fruit abscission, conducted over a period of several years, indicated that application of Ethephon at pH 7.0 was more effective than at lower pH (2, 3, 6). The higher efficiency at pH 7.0 could be rationalized by the accelerated release of ethylene. It was found that application of Ethephon, which was very efficient under moderate temperatures and humidity (23–28 C, 50–70% RH), completely failed to induce fruit abscission at elevated temperatures and low humidity (34–39 C, 30–40% RH) (7). Failure to induce olive abscission under an environmental condition of high temperature and low humidity could have been attributed either to an extremely rapid breakdown at high temperature (4) or to insufficient breakdown, due to the low humidity and lack of water molecules necessary for the nucleophilic attack on the phosphonate dianion. It may also be attributed to a limited uptake under these climatic conditions. The effect of water vapor pressure on thermal decomposition of Ethephon was studied in order to distinguish between the first two possibilities.

MATERIALS AND METHODS

Different water vapor pressures were obtained by carrying out the decomposition reactions in closed systems above solutions of sulfuric acid at densities of 1.10, 1.25, 1.40 and 1.70 g/mL. Vapor pressures obtained at these densities at 20, 30, 40 and 50 C (Table I) were calculated from data in the "Handbook of Chemistry and Physics" (3rd ed., 1972–1973). Thermal decomposition was measured using [14C]Ethephon in 0.2 m phosphate buffer at pH 6.3 and by ethylene release of [14C]Ethephon in 0.4 m phosphate buffer at pH 7.0. On several occasions dried films were solubilized with deionized H₂O at the end of the decomposition reaction to verify that initial and final pH were identical. In order to verify if results obtained by the two methods of measurements are comparable, an additional measurement of decomposition, using three replicates, was taken with [14C]Ethephon at pH 7.0 and by ethylene release at pH 6.3.

Unless otherwise specified, decomposition measurements were carried out on 10-ml samples of [14C]Ethephon (1 × 10⁶ cpm, 0.7 μCi/14 μmol) containing 0.025% Triton X-100 buffered to pH 6.3 to 7.0. [14C]Ethephon samples were placed in scintillation vials and dried overnight at 20 C. Six scintillation vials containing dried [14C]Ethephon were sealed in 700-ml glass jars containing 30 ml of sulfuric acid solution at the different densities described above. Jars were incubated at 20, 30, 40, and 50 C for 5 h. Initial concentrations of [14C]Ethephon were measured immediately before the decomposition reaction was started. Following incubation, the remaining [14C]Ethephon was solubilized in 1 ml of water and 10 ml of scintillation liquid (4 g PPO, 0.2 g dimethyl POPOP in 1,000 ml toluene mixed with Triton X-100 at a ratio of 2:1) was added. Samples were counted in a Packard Tri-Carb liquid scintillation counter. Decomposition was measured in each experiment by three jar replicates per treatment, with six scintillation vials per jar. Experiments were repeated three to nine times.

Unless otherwise specified, measurements of decomposition by ethylene release were conducted by introducing 0.0117 μmol Ethephon in 17.5 μl buffered solution into 3-ml vials which were dried overnight at 20 C. Each vial with the dried Ethephon was placed inside a 35-ml test tube containing 5 ml of sulfuric acid solution at a different density. Tubes were stoppered and incubated in a...
Table I. Vapor pressure and RH of sulfuric acid solutions at four different temperatures

These data were calculated from the "Handbook of Chemistry and Physics" (53rd., 1972-73).

<table>
<thead>
<tr>
<th>Sulfuric acid density (g/ml)</th>
<th>Temperature (°C)</th>
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<tbody>
<tr>
<td>1.70</td>
<td>3.2</td>
</tr>
<tr>
<td>1.40</td>
<td>37.1</td>
</tr>
<tr>
<td>1.25</td>
<td>70.4</td>
</tr>
<tr>
<td>1.10</td>
<td>93.9</td>
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</table>

water bath at 20, 30, 40, and 50 °C. One-ml air samples were withdrawn from each sample at 1.5, 3, and 4.5 h for gas chromatography analysis of ethylene. Sampling for measurements at 50 °C were taken at 30-min intervals.

Ethephon loss overnight, while samples were dried at 20 °C, amounted to approximately 10 and 20% at pH 6.3 and 7.0, respectively.

A preliminary experiment was carried out to estimate possible gain or loss of ethylene under the experimental condition. It consisted of injecting 8.2 µl/ethylene into experimental test tubes under identical conditions as in decomposition tests of Ethephon. The concentration of ethylene injected declined gradually with time. The gradual decline was uniform (3.5%/h) and within experimental error, regardless of variation in density of sulfuric acid and temperature in the test tubes. Ethylene concentration in Ethephon decomposition measurements was therefore corrected according to the loss measured in the preliminary experiment. The initial concentration, before Ethephon decomposition measurement started, was estimated from samples incubated in test tubes without sulfuric acid at 50 °C for 2 h. Rate constants were calculated from the Ethephon which remained at the 3- and 4.5-h measurements, except at 50 °C, where decomposition was rapid and rates were calculated from measurements taken at 1 and 1.5 h.

The magnitude of standard errors indicated that the experimental errors at 3.2% RH were larger than at other vapor pressures. Experimental error was also larger in samples which had short half-life, since it took 15 to 20 min to reach the indicated temperature and vapor pressure. Measurements of RH showed that after equilibrium of vapor pressure was reached, it was maintained throughout the decomposition reaction.

Triton X-100, changes in total pressure or partial pressure of ethylene had no effect on the decomposition rate of Ethephon (data not shown). The effect of Triton X-100 (0.025%, and 0.25%) was measured at 20.5 and 51.9 mm Hg at 40 °C. Changes in total pressure were measured by releasing excess pressure generated inside test tubes in reactions carried out at 40 and 50 °C at 20.5 and 51.9 mm Hg. The effect of partial pressure of ethylene was measured in reactions where ethylene was absorbed in mercuric perchlorate.

Decomposition was linear to log₁₀ concentration up to the time that 90% of Ethephon had decomposed. The remaining 10% could not be degraded even after a long period of incubation at 50 °C.

RESULTS

Thermal decomposition of Ethephon was proportional to its concentration. A plot of log₁₀ concentration versus time was linear for the breakdown reaction at a constant pH, temperature, and vapor pressure (Fig. 1). The rate of the reaction could be measured equally well by counting [¹³C]Ethephon or by measuring ethylene release and calculating the molarity of Ethephon which remained at time t. The rate constants, as measured by the two methods at pH 6.3 and 40 °C (Fig. 1), were 0.295 × 10⁻⁴ and 0.499 × 10⁻⁴/s at 20.6 mm Hg and 0.129 × 10⁻⁴ and 0.193 × 10⁻⁴/s at 51.7 mm Hg. A similar comparison of the two methods of measurement at pH 7.0 and 40 °C yielded 1.303 × 10⁻⁴ and 1.143 × 10⁻⁴/s at 20.6 mm Hg and 1.075 × 10⁻⁴ and 1.092 × 10⁻⁴/s at 51.7 mm Hg.

Rate constants measured at pH 6.3 and 7.0 at increasing vapor pressures and various temperatures are shown in Figure 2. Rates were higher at pH 7.0 than at pH 6.3 and increased at higher temperatures in both pH values.

Increasing the vapor pressure, up to a certain level, at a constant temperature, increased breakdown of Ethephon. Above an optimum vapor pressure, breakdown decreased (Fig. 2). The decrease in rate constant at higher vapor pressures, at a constant temperature, was more pronounced at pH 6.3 than at 7.0 and greater at lower temperatures at both pH values. The decline of rate constant at higher vapor pressures at 50 °C and pH 6.3, and at 40 and 50 °C at pH 7.0, was very small (Fig. 2).

The optimum vapor pressure at 20, 30, and 40 °C in both pH 6.3 and 7.0 was approximately 6, 12, and 24 mm Hg, respectively. The approximate optimum vapor pressure at 50 °C was 50 mm Hg at pH 6.3 and 65 mm Hg at pH 7.0 (Fig. 2). It appears that the optimum vapor pressure doubles with every 10 °C increase, except at 50 °C at a pH of 7.0.

The half-life of decomposition of Ethephon, calculated from rate constants, was less than 24 h at a temperature above 30 °C in both pH values, and as low as 1.7 ± 0.1 h at 40 °C, at pH 7.0 and a vapor pressure of 20.6 mm Hg (Table II).

The activation energy for the decomposition reaction was measured from the slope of plotting the log₁₀ rate constant versus 1/T (Fig. 3). The activation energy, in vapor pressures of 3.2 to 12 mm Hg, was estimated as 8.7 and 14.3 kcal mol⁻¹ at pH 6.3 and 7.0, respectively. Activation energies were not calculated above 12 mm Hg, at which point the reaction is inhibited.

A comparative breakdown measurement of Ethephon at pH 7.0 was carried out on surfaces of glass, Parafilm, and detached olive leaves at two vapor pressures and temperatures (6.5 and 16.5 mm Hg at 20 °C, and 20.5 and 51.9 mm Hg at 40 °C). The rate of decomposition in this experiment was estimated by ethylene measurements. Ethylene release from Parafilm and olive leaves, with-

![Fig. 1. Time course of Ethephon decomposition as measured by ethylene released from 1.5 µmol Ethephon (A) and 3750 dpm [¹³C]Ethephon (B). Values plotted are Ethephon remaining during the decomposition reactions at 20.6 (C) and 51.9 mm Hg (D) vapor pressures, at 40 °C and pH 6.3.](image-url)
vapor pressures, Ethephon, was subtracted from measurements with Ethephon. Rate constants for decomposition of Ethephon on the three surfaces varied slightly (data not shown). The pattern of inhibition of decomposition, however, was similar, regardless of surface type and in agreement with data in Figure 2.

**DISCUSSION**

Decomposition of Ethephon was described by Warner and Leopold (9) as a second order reaction. Biddle et al. (4) presented data which showed clearly that the rate is a first order reaction. The present investigation confirms the fact that the rate is a first rather than a second order reaction.

Decomposition of Ethephon was measured in a buffer with sufficient ionic strength to maintain a constant pH. The pH of a dried film, however, may not be identical to the pH of its buffered solution. The increased breakdown rate of Ethephon in response to increased vapor pressure up to a certain optimum may result merely from an increase in the pH of the film itself. According to this interpretation, pH and decomposition rates should have increased up to a complete solution of the film, rather than be inhibited at high vapor pressures.

A mechanism of nucleophilic attack of water molecules on the phosphonate dianion of Ethephon molecules was postulated (4, 10). The breakdown reaction in homogeneous aqueous solutions is pH-dependent and requires the presence of water molecules. Ethephon breakdown in dried films is, similarly, pH-dependent and requires water molecules. The mechanism of Ethephon break-

**FIG. 2.** Log₁₀ rate constants for decomposition of Ethephon at various vapor pressures, temperatures, and pH levels. Decomposition was measured at 20 (○), 30 (△), 40 (●), and 50 C (▲). (±SE).

**FIG. 3.** Arrhenius plots (log₁₀ of rate constants versus 1/T) for decomposition of Ethephon at vapor pressures of 3.2 (●), 4.8 (○), 6.5 (△), 8.0 (▲), 10 (■), and 12 (□) mm Hg at two pH levels. Log₁₀ rate constants at the specified vapor pressures were taken from Figure 1.

<table>
<thead>
<tr>
<th>Table II. Half-life of decomposition of 2-chloroethylphosphonic acid at different temperatures, vapor pressures and pH levels</th>
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<tbody>
<tr>
<td>Temp. (C)</td>
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<tr>
<td>pH 6.3, t₁/₂ (hr)</td>
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<tr>
<td>20</td>
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<td>30</td>
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<td>40</td>
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<tr>
<td>pH 7.0, t₁/₂ (hr)</td>
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<td>20</td>
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<td>30</td>
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<td>40</td>
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<td>50</td>
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1 For vapor pressures and RH of the sulfuric acid solutions at the various densities and temperatures, see Table I.
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down may be similar in aqueous solution and dried films.

Decomposition rates of Ethephon in dried films at a maximum vapor pressure are similar to decomposition rates measured in aqueous solution (4), i.e. at pH 7.0 rates of 1.092 and 3.892 \times 10^{-4}/s were calculated in dried films at 40 and 50 C, respectively. The comparable values in aqueous solution, as measured by Biddle et al. (4), were 1.00 and 4.30 \times 10^{-4}/s. Decomposition rates at lower temperatures (20–30 C) and a pH below 7.0 were not measured in aqueous solution. Measurements in dried films showed that the rate of decomposition at a maximal vapor pressure can be as low as one-third of the rate at an optimal vapor pressure, i.e. at pH 6.3 and 30 C the rate is 0.322 \times 10^{-4}/s at 11.8 mm Hg as compared with 0.092 \times 10^{-4}/s at 29.9 mm Hg. Since vapor pressure has a considerable effect on the rate of decomposition at temperatures of 20 to 30 C, measurement in dried film is a better estimate of breakdown of Ethephon in outdoor spray application.

Rate measurements and the half-life of decomposition calculated from the rate constants indicated that raising the temperature from 20 to 50 C increases the rate constant and decreases the half-life of decomposition. The effect of a 10 C change is considerably greater at the lower temperature range and diminishes with every 10 C rise. Temperature change in the 20 to 30 C range appears to be as important as pH change with respect to breakdown.

Ethephon sprayed at pH 7.0 to induce olive fruit abscission, a treatment found to be effective when applied at moderate temperatures and humidity (23–28 C and 50–70% RH), failed completely at elevated temperatures and lower RH (34–39 C and 30–40% RH) (7). The vapor pressure at 35 C and a RH of 30 to 40% is 12.6 to 16.8 mm Hg—a range which is just slightly below the optimum vapor pressure for breakdown. Failure to induce olive fruit abscission at elevated temperature and low RH cannot be explained by lack of H2O molecules required for the nucleophilic attacks on Ethephon molecules, but is more likely the result of its extremely rapid breakdown. The half-life of Ethephon decomposition at pH 7.0 and at 30 and 40 C is 5.1 (±0.9) and 1.7 (±0.1) h, respectively.

At temperatures of 34 to 39 C, where Ethephon sprays are ineffective, the half-life is of the order of a few hours, thus reducing the effective concentration for uptake.

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LITERATURE CITED

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