Short Communication

Ethylene Evolution From 2-Chloroethylphosphonic Acid

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Strong growth regulating properties have been observed for 2-chloroethylphosphonic acid (Amchem 66-329) when applied to plants, and the regulatory effects have been attributed to the liberation of ethylene within plants (5). Many regulatory effects of this chemical resemble the effects of ethylene, including the induction of ripening in bananas and tomatoes (4), flowering in pineapple, and abscission and various epinastic responses (1). The present report provides evidence that 2-chloroethylphosphonic acid (CEPA) breaks down in the presence of a base to form ethylene with an apparent release of chloride and phosphonate.

To illustrate the decomposition reaction, 5 ml of CEPA at $2 \times 10^{-4}$ M in a 1000 ml reaction flask, with either NaOH ($8 \times 10^{-4}$ M) or 500 mg of etiolated pea epicytols, evolve ethylene as shown in figure 1. The production of ethylene occurs not only in the presence of the plant tissue, but also in the absence of added base. In this experiment 1.0 $\mu$ mole of CEPA was present initially and 0.98 $\mu$ mole of ethylene had been produced 48 hr after addition of NaOH, indicating essentially complete conversion of the CEPA to ethylene. The logarithmic type of time curve in the presence of added base suggests a second-order reaction, possibly involving the alkali in reaction with CEPA. The rate of the reaction is increased by higher levels of added alkali.

That the gas evolved is ethylene was determined by gas chromatography (2) and its identity was confirmed by reaction with mercury perchlorate (6). The gas chromatographic peak considered to be ethylene was 99.2% removed by introduction into the reaction flask of a paper wick moistened with Hg(ClO$_4$)$_2$.

The decomposition of CEPA to ethylene should bring about the release of phosphonate and chloride. As an indication of phosphonate formation, in a test run concurrently with the experiment in figure 1 phosphate was measured by Allen’s molybdate color test, assuming a fairly ready oxidation of the phosphonate ion to phosphate. The results in figure 2 show a time course similar to that of ethylene evolution, though only 36% yield of phosphate was obtained. Presumably the lesser yield was due to incomplete oxidation of phosphonate to phosphate. The presence of chloride ion was detectable at the end of the 48 hr reaction time, using silver nitrate as an indicator.

The effects of pH were examined in buffered 2.5 ml solutions of 1000 ppm CEPA (17.5 $\mu$ moles) maintained by 0.1 M citrate-NaOH between pH 4 and 6 or by 0.1 M tris malate-NaOH buffer between pH 6 and 8. The data presented in figure 3 indicate no optimum pH for ethylene evolution, but rather an increasing evolution with increasing pH. The minimum pH at which ethylene evolution was detected was pH 5. In buffered solutions, ethylene

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evolution proceeds linearly with time for the first 7 hr. The time curve for the formation of ethylene from CEPA in pea stem tissue was (fig 1).

Plant tissues of different acidity might be expected to show different capacities for ethylene evolution. To test this hypothesis plants of Bryophyllum cruentum Baker were placed under short-day and long-day conditions to obtain different degrees of tissue acidity. After 10 days of controlled photo-periods, leaves from plants in each condition were allowed to take up by transpiration 1000 ppm CEPA in \( \text{H}_2\text{O} \) for 2 hr. The leaves were then washed and placed in 250 ml flasks for measurement of ethylene evolution. Table I indicates that the leaves from the long-day conditions produced substantially more ethylene after removal from CEPA solutions than leaves from the short-day condition, as would be expected from their relatively greater pH (pH 4.6 and 4.0 respectively).

Table 1. Rate of Ethylene Evolution from Leaves of Bryophyllum

<table>
<thead>
<tr>
<th>Time</th>
<th>CEPA</th>
<th>H(_2)O</th>
<th>CEPA</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>hr</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td>367</td>
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<td>138</td>
<td>0.2</td>
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<tr>
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<td>0.3</td>
<td>102</td>
<td>0.4</td>
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<td>...</td>
<td>35</td>
<td>...</td>
</tr>
<tr>
<td>48</td>
<td>63</td>
<td>...</td>
<td>21</td>
<td>...</td>
</tr>
</tbody>
</table>

The breakdown of CEPA into ethylene in the presence of a base appears to be a second-order reaction and apparently leads to the production of phosphonate and chloride. We suggest that the reaction involves the removal of the phosphonate as a salt followed by dehydrohalogenation. The hydroxyl groups of the phosphonate would be dissociated in the presence of base to form a strong negative charge, the carbon-phosphonate bond would break with the donation of an electron to the double bond of the alkene, and the chloride would be eliminated as shown below.

\[
\text{Cl}-\text{C}==\text{C}-\text{H} + 2\text{NaOH} \rightarrow \text{Cl}==\text{C}==\text{C}==\text{H} + 2\text{NaCl} + \text{H}_2\text{O}
\]

It is likely that CEPA is taken up in plants as is any weak aliphatic acid and subsequently breaks down at cytoplasmic pH with the formation of ethylene which then may cause the regulation of various aspects of plant growth.

After the completion of this manuscript, a similar suggestion for the breakdown of CEPA was made by Cooke and Randall (3), though without presenting data or evidence for the nature of the gas produced. They suggest that the ethylene release may be responsible for the biological activities of CEPA, a suggestion which had been documented previously (5). They point out that enzymes in the plant may participate in the reactions leading to ethylene formation, especially where esters are present in the applied material.
Literature Cited