

Short Communication

Ethylene Evolution From 2-Chloroethylphosphonic Acid

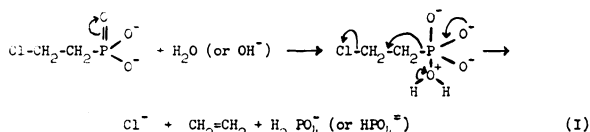
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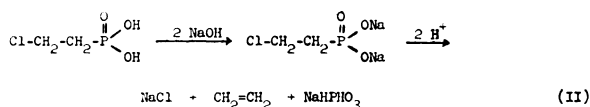
2-Chloroethylphosphonic acid (CEPA. "Amchem 66-329", "Ethrel"; ref. 1), a new plant growth regulator, degrades to yield ethylene in an alkaline solution. When applied to plants, it has been very effective in causing responses characteristic of ethylene treatment (3, 4, 6, 7). The formation of ethylene or its alkene homologs from CEPA or its homologs was studied and described in detail in 1963 by Maynard and Swan (5) including the probable reaction mechanism. Nevertheless, several reports have since appeared describing the same reaction without citing (4, 8) or properly acknowledging (3) their work. Some investigators (7) have since suggested that the growth regulatory action of CEPA is due to the stimulation of ethylene production within the plant tissues without discussing the fact that CEPA itself is the ethylene producer.

The chemical mechanism of ethylene production from CEPA suggested by Maynard and Swan (5) involves the nucleophilic attack on the phosphonate dianion by a water molecule and the concerted elimination of chlorine, leading to direct formation of phosphate and chloride as shown in equation (I). Probably the OH⁻ ion may also serve as a nucleophile in the reaction.



When tested, the yield of ethylene equals that of phosphate as shown in table I.

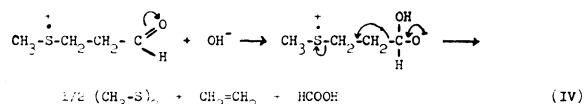
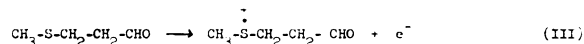
Recently Warner and Leopold (8) studied ethylene evolution from CEPA and suggested a reaction mechanism which involves the removal of the phosphonate as phosphonate salt, followed by dehydrohalogenation as shown in equation (II).



Their mechanism does not explain how the phosphonate group is removed or ethylene is formed.

They reported that the yield of phosphate was only a third of that of ethylene and interpreted this lesser yield of phosphate due to the incomplete oxidation of phosphite to phosphate. The results shown in table I do not confirm their finding that the yield of phosphate is less than that of ethylene. Furthermore, there is no evidence indicating that oxidation is involved in the reaction or that the initial product is phosphonate rather than phosphate. If dehydrohalogenation is involved in the ethylene-forming reaction, as suggested by Warner and Leopold (8), one of the α -hydrogens should be removed with the chlorine. The α carbon must then pick up a H⁺ ion from the solution to yield ethylene. In order to test this possibility, ethylene production from CEPA was conducted in the presence of tritiated water, and the ethylene produced was analyzed for radioactivity. As shown in table I, ethylene thus produced contained no radioactivity. The mechanism involving dehydrohalogenation as described by Warner and Leopold (8) appears, therefore, to be incorrect. The mechanism depicted in Equation (I) predicts that the tritium ions are not incorporated into ethylene, and is therefore consistent with the present data.

Methional, which is considered to be related to the precursor of ethylene *in vivo* (10), decomposes rapidly yielding ethylene by FMN and light (11) or by the sulfite-oxygen-peroxidase system (9). It has been postulated that the initial step involves the extraction of an electron from the sulfur atom of methional in either of these systems (equation III), followed by a concerted nucleophilic attack of OH⁻ ion or of H₂O on the aldehyde carbon and elimination of methylmercapto radical, leading to the formation of ethylene, formic acid, and methyldisulfide as depicted by equation (IV).



It is interesting to note that the mechanism depicted in equation (IV) to account for ethylene evolution is essentially identical to that depicted in equation (I) for ethylene production from CEPA, with the elec-

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Table I. *Ethylene and Phosphate Formation From CEPA*

The reaction mixture (flask 1) consisted of 0.5 ml of 0.05 N NaOH and 2 μ l of "Amchem 66-329" (a commercial formulation containing 2 lb. per gal. of a mixture of CEPA and its anhydride and the mono-2-chloroethyl ester of this acid; Ref. 1) in a 25-ml Erlenmeyer flask closed with a rubber serum cap. Flask 2 contained, in addition to the above components, 1 mc of tritiated water. The flasks were incubated at 50° for 2 hr. Reactions were stopped by injecting 0.5 ml of 4 N H₂SO₄. Total and radioactive ethylene were determined by gas chromatography and gas radiochromatography, respectively. Orthophosphate was determined by the molybdate reagent (2).

Flask	Ethylene		Orthophosphate
	μ mole	m μ c	μ mole
1	1.46	...	1.50
2	1.60	0	1.63

tron-withdrawing chlorine atom being replaced by

the CH₃-S- radical and the electrophilic phosphonate anion being replaced by a carboxaldehyde group. It appears that a molecule possessing a -CH₂·CH₂- grouping in the center of the molecule with 1 end attached to an electron-withdrawing leaving group and the other end attached to an electrophile (which is subject to a nucleophilic attack) is an excellent ethylene producer.

Acknowledgment

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