

AGRICULTURE

Carbonyl Sulphide from the Decomposition of Captan

VOLATILE sulphur compounds such as carbon disulphide and thiocarbonyl chloride are considered to be formed when the agricultural fungicide captan (*N*-trichloromethyl-thio-4-cyclohexene-1,2-dicarboxyimide) reacts with fungal spores^{1,2}. During a general investigation³ of the fungitoxicity of captan we have examined by gas chromatography the vapours released when captan reacts with the conidia of *Neurospora crassa*, macroconidial wild-type Em 5297a, at 25° C.

A solution of 375 µg of captan in 0.5 ml. of ethanol was added to a 2 ml. aqueous suspension of 840 million *N. crassa* spores in a 35 ml. bottle. After 20 min a 1 ml. sample of the atmosphere above the suspension was removed with a Hamilton gas syringe and injected into a 'Microtek GC.2000' chromatograph provided with a dual thermal conductivity detector. Helium at 90 ml./min was the carrier gas and the column, inlet, and detector were at 165° C: the stainless steel column was filled with the uncoated solid absorbent 'Porapak Q' (80/100 mesh size). Commercially available compounds were used as standards with the exception of carbonyl sulphide (COS) which was prepared from the reaction between ethyl isothiocyanate and sulphuric acid and further purified by the preparation and decomposition of potassium ethyl thiocarbonate⁴. Fig. 1 shows that carbonyl sulphide was evolved when captan reacted with *N. crassa* spores: there was no trace of carbon disulphide. Captan is rapidly decomposed by cell thiols^{1,3} and when 750 µg of captan in 1 ml. of ethanol was added to an aqueous solution of excess glutathione, that is 3 mg, the resulting chromatogram (Fig. 2) of the vapours showed carbonyl sulphide but no carbon disulphide.

Infra-red gas analysis, in a 10 cm cell, with a Perkin-Elmer 237 spectrophotometer confirmed that carbonyl sulphide was produced from the reaction of glutathione and captan. The atmosphere above the solution was passed successively through acetone-solid carbon dioxide and liquid air traps⁵; the contents of the latter trap were then evaporated into the gas cell. The spectrum was identical to that of synthetic carbonyl sulphide with a doublet at 4.83 and 4.87 µ⁶. It was not possible to obtain sufficient carbonyl sulphide from the captan-spore reaction for infra-red analysis.

Lukens³ confirmed his earlier supposition¹ that thiocarbonyl chloride is a major product of the reaction of captan with fungal spores—presumably following reduc-

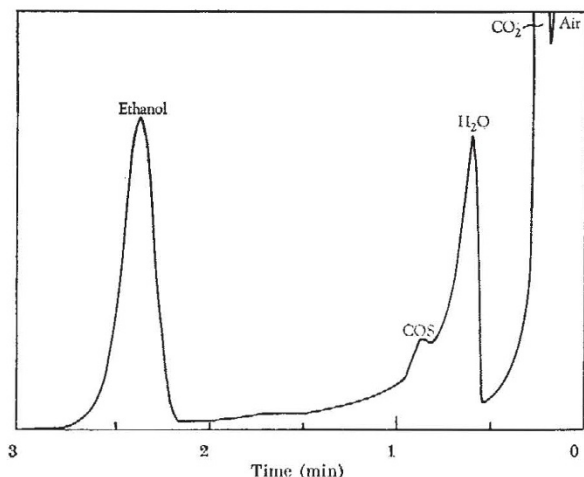


Fig. 1. Gas chromatogram of products of reaction between captan and *Neurospora crassa* conidia.

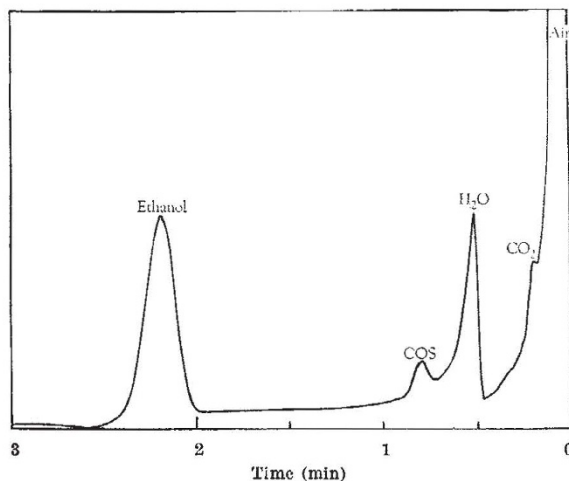


Fig. 2. Gas chromatogram of products of reaction between captan and glutathione.

tion by cell thiols. Although we were unable to resolve thiocarbonyl chloride by gas chromatography we have found that this compound is rapidly hydrolysed by excess water to form carbonyl sulphide the identity of which was confirmed, as before, by gas chromatographic and infra-red analysis. Haszeldine and Kidd⁶ reported a similar result, but as they used a lower water-thiocarbonyl chloride ratio the hydrolysis was much slower at room temperature. The most probable explanation for the evolution of carbonyl sulphide from mixtures of captan and fungal spores is that it is a product of the rapid hydrolysis of the thiocarbonyl chloride initially formed. A more complete discussion of this reaction is in preparation.

In view of the results of Lukens and Sisler¹ it seemed surprising that we could obtain no evidence of the formation of carbon disulphide from the reaction of captan with either spores of *N. crassa* or the model thiol, glutathione. These authors identified carbon disulphide by trapping the gas in Viles solution⁷ and measuring, at 440 mµ, the intensity of the yellow complex formed. We have found, however, that carbonyl sulphide also produces a yellow compound with Viles solution that gives an appreciable absorption at 440 mµ. It is apparent that this reagent is not specific for carbon disulphide and that, as Viles⁷ has suggested, other double bonded sulphur compounds can interfere.

The formation of carbonyl sulphide from captan has biological as well as chemical interest because it has been shown⁸ that vapours of this compound can be appreciably fungitoxic. Captan is used as a soil and seed fungicide⁸ and the release of carbonyl sulphide after its decomposition in the soil may well give a wider area of protection than has been previously supposed.

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