# NATURE OF THE YELLOW COPPER COMPLEX PRODUCED IN CERTAIN ANALYTICAL METHODS FOR THE DETERMINATION OF MALATHION

By A. C. HILL

Evidence is presented to show that the yellow copper complex, cupric O,O-dimethylphosphorodithioate (C), which is formed in certain colorimetric methods for the determination of malathion, can exist in reversible equilibrium with its two dissociation products, cuprous O,O-dimethylphosphorodithioate (A) and bis-(dimethoxyphosphorothiono) disulphide (B). At 20°, in solution in chloroform, equimolar proportions of A and B were found to be  $24 \cdot 86\%$  associated to form C, and the equilibrium constant for the association reaction,  $A + B \rightarrow 2C$ , was found to be 0.4378.

In view of these findings, a correlation is possible between colour intensities of yellow complex solutions obtained by two differing methods. This indicates that the yellow complex obtained by previous authors is initially undissociated. Hence, dissociation is considered to account, at least partly, for the instability of the yellow complex that has been reported by previous authors. The incorporation of B in the extractant, at a level of 450 moles of B per mole of yellow complex, is proposed as a means of limiting dissociation to a maximum of 1%.

## Introduction

In a recent paper a titrimetric method is reported<sup>1</sup> for the determination of S-[1,2-di(ethoxycarbonyl)ethyl] O,O-dimethylphosphorodithioate (I) in malathion insecticide and in its formulations. This method is based upon quantitative cleavage of I by alkali in methanol in the presence of phenol to give sodium O,O-dimethylphosphorodithioate (II), followed by complete reaction of II with cupric ions in the presence of sodium acetate-acetic acid buffer solution to give cupric O,O-dimethylphosphorodithioate (III).



When formed under these conditions and at the same time extracted into chloroform, III forms a yellow or yellowishbrown solution which shows only 2% decrease in colour intensity during one month of storage at room temperature. This method is based upon the same scheme of reactions as previously reported.<sup>2-6</sup>

All these authors have stated, without evidence, that the yellow copper complex produced in their analytical methods is cupric O,O-dimethylphosphorodithioate. However, their conclusions regarding the complex are warranted by the fact that it results from a double decomposition reaction between sodium O,O-dimethylphosphorodithioate and copper sulplate.

No report of the preparation and isolation of cupric O,O-dimethylphosphorodithioate could be found in previous reports and, in view of this, a preparation of the compound was attempted. This led to the observations which are reported in this paper.

## **Experimental and Results**

Preparation of sodium O,O-dimethylphosphorodithioate dihydrate

The sodium salt, which had been prepared by neutralising pure 0,0-dimethylphosphorodithioic acid with sodium methoxide in dry methanol, was recrystallised from ethyl acetate (Analar grade). At the solution stage, the ethyl acetate was heated below 45°, to avoid possible thermal decomposition of the sodium salt. On cooling to 0°, large colourless crystals of the sodium salt formed. Repeated recrystallisation from ethyl acetate yielded a product which melted at 65–66°. Elemental analysis was C = 11.3, H = 4.8 and P = 14.5;  $(CH_3O)_2P(S) \cdot SNa \cdot 2H_2O$  would require C = 11.1, H = 4.7 and P = 14.4.

To confirm this the sodium salt was subjected to iodometric titration by the method of Bode & Arnswald<sup>7</sup> for *O*,*O*-dialkylphosphorodithioic acids; the results indicated a purity of 99.8% for the dihydrate. Determination by the titrimetric method recently reported for malathion,<sup>1</sup> but omitting the hydrolysis stage, gave a purity of 99.77%. The salt was extremely soluble in water and did not appear to be hygroscopic when exposed to an atmosphere at 57% R.H. and  $20^{\circ}$  for 24 h.

# J. Sci. Fd Agric., 1969, Vol. 20, January

# Formation of the yellow copper complex

Stock solutions of sodium O,O-dimethylphosphorodithioate dihydrate in methanol, with the range of concentrations indicated in Fig. 1, were prepared. 10 ml aliquots of these solutions in separating funnels were each treated<sup>1</sup> with 25 ml buffer solution, 50 ml chloroform and 25 ml 0.02 M copper sulphate solution, in that order, and each mixture was shaken for 2 min. The chloroform layer, containing the yellow complex, was drained into a 100 ml measuring flask and the aqueous layer was washed with  $3 \times 10$  ml portions of chloroform. Each extract (80 ml) was made up to 100 ml and allowed to stand for 2 h at 20°, and then its optical density was measured at 420 nm in a 2 mm glass cell against a chloroform blank on a Unicam SP 500 spectrophotometer.

Stock solutions of 99.6% malathion in methanol, with the range of concentrations indicated in Fig. 1, were also prepared. 10 ml aliquots of these were transferred to separating funnels, and treated with methanolic sodium hydroxide in the presence of phenol<sup>1</sup> to convert the malathion to sodium *O*,*O*-dimethylphosphorodithioate. The hydrolysed malathion was neutralised by addition of 25 ml buffer solution and then converted to the yellow complex, extracted, and made up for colour measurement as described for the sodium salt.

The optical densities of the extracts were plotted against concentration of either the sodium salt or 99.6% malathion to give the curve shown in Fig. 1. The fact that one curve satisfies both sets of plotted points shows that the colour intensities obtained by converting molecularly equivalent quantities of the sodium salt and of malathion are the same; it also indicates that hydrolysis of malathion to the sodium salt under the conditions reported previously<sup>1</sup> is quantitative.

# Preparation of cupric O,O-dimethylphosphorodithioate

A solution of sodium O,O-dimethylphosphorodithioate dihydrate (4·32 g) in water (30 ml) was added to a solution of



FIG. 1. Curve showing optical densities of solutions of yellow copper complex in chloroform (100 ml)

Solutions prepared from 10 ml aliquots of various stock solutions of either malathion 99.6% ( $\bullet$ ), or sodium *O*,*O*-dimethylphosphoro-dithioate, 99.8% ( $\bigcirc$ )

J. Sci. Fd Agric., 1969, Vol. 20, January

cupric sulphate pentahydrate (2.60 g) in water (30 ml) in a separating funnel. The dark, yellowish-brown oil which formed was separated from the aqueous phase by several extractions with chloroform (100 ml total). The volume of the extract was reduced to 50 ml by evaporation at room temperature in a draught of air, and the buff-yellow material which separated was collected by filtration and dried (yield 3 g, m.p. 48–50°). Recrystallisation from 100 ml of 50 : 50 n-hexane/chloroform yielded 1.95 g of yellowish-white material, m.p.  $150-152^{\circ}$  (decomp.). This appeared to be crude cuprous O,O-dimethylphosphorodithioate.

The mother liquor from the initial crystallisation yielded 0.70 g of yellow material on evaporation. This material, though mostly microcrystalline, was observed to contain several large colourless crystals. Some of these were separated manually and were found to have a melting point of 47–49°, which corresponded to that of bis(dimethoxyphosphorothiono) disulphide (49–51°).

From these observations it appeared that recrystallisation was dissociating the yellow copper complex, thought to be cupric O,O-dimethylphosphorodithioate, into cuprous O,O-dimethylphosphorodithioate and bis(dimethoxyphosphoro-thiono) disulphide.

Subsequently, it was found that the yellow colour could be re-formed by mixing almost colourless solutions in chloroform of the materials separated by crystallisation. Thus, it appeared that recrystallisation was not of itself causing dissociation of the yellow copper complex. Rather it was leading to separation of dissociation products which already existed in equilibrium with the yellow copper complex, which when removed from the system allowed further dissociation to take place.

#### Preparation of bis(dimethoxyphosphorothiono) disulphide

230 ml 0.1 N iodine solution was added slowly with stirring to 5.0 g sodium *O*,*O*-dimethylphosphorodithioate dihydrate dissolved in 50 ml distilled water. The pale yellow syrup was extracted with chloroform and the chloroform extract evaporated. The residue (3.6 g) was crystallised from n-hexane, yielding colourless crystals (1.93 g), melting point 49-51° (lit. 51-52°).<sup>8</sup> The compound in chloroform solution showed no absorption of light in the visible range.

#### Preparation of cuprous O,O-dimethylphosphorodithioate

Cupric sulphate pentahydrate (3.75 g) was dissolved in 500 ml water and liquid sulphur dioxide (10 ml) dissolved in 50 ml water was added, followed by five drops of 1 N hydrochloric acid. The solution was then heated almost to boiling, and sodium *O*,*O*-dimethylphosphorodithioate (3.24 g)dissolved in 100 ml of water was added with stirring. The precipitate which formed, at first pale yellow, rapidly became white, and heating was stopped. After cooling, the cuprous complex was collected by filtration and washed with water. The filtrate was colourless and still retained the odour of sulphur dioxide.

The white material was dried for 1 h at 55°, powdered, and dried for a further hour at 55°. This gave the cuprous complex as a chalk-white material. The yield was  $3 \cdot 20 \text{ g} (96 \cdot 8 \%)$ . The material had no definite melting point; when heated it suddenly became brown at 149–151° and did not melt even when heated to 230°.

The cuprous complex was almost insoluble in carbon tetrachloride, chlorobenzene, benzene, n-hexane, methanol, acetone and water, and sparingly soluble in chloroform. After being washed with chloroform, the material showed no absorption in the visible range of wavelengths.

Elemental analysis on the washed material was C = 10.8, H = 2.6, P = 14.4 and Cu = 29.00;  $[(CH_3O)_2P(S)S]_2^{a-}$   $Cu_2^{a+}$  requires C = 10.9, H = 2.7, P = 14.1 and Cu = 28.8. Initial attempts to determine the copper content by various ashing techniques were unsuccessful owing to interference by phosphorus. The copper was finally determined by digestion with sulphuric and perchloric acids, neutralisation with ammonia until the first permanent blue colour was formed, buffering to pH 10 with an ammonia-ammonium chloride buffer solution and titration of the copper with EDTA using PAN [1-(2-pyridylazo) -2-naphthol] as indicator.

#### Reaction of the disulphide and the cuprous complex

Various quantities, 1, 2, 5, 10 and 15 ml, of a 0.02 M solution of the disulphide in chloroform were added to 10 ml quantities of a 0.01 M solution of the cuprous complex in a 100 ml measuring flask. The mixtures were made up to 100 ml with chloroform and allowed to stand at  $20^{\circ}$ . Table I shows the variation of optical density with mole ratio of the disulphide to the cuprous complex that was found after 18 h. The figures show that the disulphide and the cuprous complex are only partially associated in solution to form the yellow complex.

The optical density (1.023) of the solution containing the 1 : 1 mole ratio agrees well with the optical density (1.033) of a '0.002 M' solution of yellow copper complex read from Fig. 1. This shows that the position of equilibrium obtained on association of the disulphide and the cuprous complex (both initially 0.001 M in chloroform) is practically the same as that obtained on dissociation of the cupric complex (initially 0.002 M).

An average value for the degree of association of the cuprous complex and the disulphide when mixed together in equimolecular proportions was calculated from the data in Table I. In making calculations it was assumed that solutions of the yellow complex in chloroform obeyed Beer's Law and that the disulphide (IV) and the cuprous complex (V) associated to form the cupric complex (III) according to the following reaction:

$$\begin{array}{c} (CH_{3}O)_{2}P(S)S\text{-}S(S)P(OCH_{3})_{2} + [(CH_{3}O)_{2}P(S)S]_{a}^{2-}Cu_{a}^{2+}\\ \\ IV & V\\ \\ \leftrightarrows 2[(CH_{3}O)_{2}P(S)S]_{a}^{2-}Cu^{2+} \end{array}$$

#### III

#### TABLE I

Variation of optical density (O.D.) with mole ratio of bis(dimethoxyphosphorothiono) disulphide to cuprous O,O-dimethylphosphorodithioate in chloroform

Molar conc. of sulphide	O.D. after 18 h, 420 nm, 20°c, 2 mm cell				
	0.000				
0.0002	0.407				
0.0004	0.625				
0.001	1.023				
0.002	1.418				
0.003	1.688				

Then, representing the degree of association at the 1 : 1 mole ratio by 1.023 x, the equilibrium constant,  $K_e$ , was  $4(1.023x)^2/(0.001-1.023x)^2$ ; while at the 0.2 : 1 mole ratio  $K_e$  was  $4(0.407x)^2/(0.0002-0.407x)(0.001-0.407x)$ .

Equating these two expressions for  $K_e$  and solving for x, x was found to be  $2.535 \times 10^{-4}$ . Similarly, by equating the expression for  $K_e$  at the 1 : 1 mole ratio with those for  $K_e$  at the other mole ratios, three more values of x,  $2.401 \times 10^{-4}$ ,  $2.437 \times 10^{-4}$  and  $2.348 \times 10^{-4}$ , were calculated. Hence, the average value of x was  $2.430 \times 10^{-4}$  and the degree of association at the 1 : 1 mole ratio was  $1.023 \times 2.430 \times 10^{-4}$  mole per 0.001 mole of reactant  $\equiv 24.86\%$ . Finally, substituting  $y = 2.486 \times 10^{-4}$  in the expression  $4y^2/(0.001 - y)^2 = K_e$ ,  $K_e$  was found to be 0.4378.

Since the equilibrium constant contains no volume term, the dissociation products of the yellow copper complex formed from malathion should always be 24.86% associated at  $20^{\circ}$  regardless of the amount of malathion converted.

The results in Table II show the effect of temperature on the optical density of a solution of yellow copper complex that was 0.002 M expressed as undissociated cupric *O*,*O*-dimethylphosphorodithioate. This effect was completely reversible on cooling. The increase of optical density with temperature appears to be linear (0.0123/°C) and indicates that association of the dissociation products increases with temperature.

#### TABLE II

Optical densities (O.D.) at various temperatures of a solution in chloroform (100 ml) of cupric O,O-dimethylphosphorodithioate prepared from pure sodium O,O-dimethylphosphorodithioate dihydrate (0.4 m mole)

Temp, °c	17	20	25	30	35	
O.D., 420 nm, 2 mm cells	0.989	1.022	1 · 088	1 · 146	1 · 210	1

Unsuccessful attempts were made to calculate the degree of association of the dissociation products at the 1 : 1 mole ratio assuming either that other proportions of the disulphide and the cuprous complex associated to form the yellow copper complex, or that the cuprous complex existed as  $Cu^+S(S)$ -P(OCH<sub>3</sub>)<sub>2</sub>. Solutions of algebraic equations were obtained which either had no physical significance or did not fit the data.

#### Discussion

The calculations above prove that one molecule of cuprous O,O-dimethylphosphorodithioate and one molecule of bis-(dimethoxyphosphorothiono) disulphide associate to form two molecules of the yellow copper complex. From this it would appear that the yellow copper complex is cupric O,O-dimethylphosphorodithioate. No alternative formula seems possible, and, moreover, this formula affords the only reasonable explanation for the formation of the yellow colour.

The dissociation reaction proposed here is analogous in form to one that has been proposed by Busev & Ivanyutin<sup>9</sup> for cupric O,O-diethylphosphorodithioate.

There is a possible correlation between the data reported in Table I and in Fig. 1 and the data of Orloski<sup>6</sup> which are the only ones for optical density *versus* malathion concentration reported. From these data, which presumably relate to 1 cm spectrophotometer cells, it can be calculated that a 0.002 M solution of yellow copper complex in cyclohexane would have

#### J. Sci. Fd Agric., 1969, Vol. 20, January

an optical density of about 3.98 at  $26^{\circ}$  in a 2 mm cell, whereas a '0.002 M' solution of yellow complex as prepared by the method described above has an optical density of 1.023 (Table I). However, the '0.002 M' solutions reported here are only 24.86% associated at  $20^\circ$ . Assuming that Beer's Law is obeyed, it can be calculated that a 0.002 M solution of completely undissociated yellow complex would have an optical density of  $4 \cdot 12$  at  $20^{\circ}$  in a 2 mm cell. Allowing for possible differences between actual cell lengths and the nominal lengths used in making the calculations, these figures are in good agreement and indicate that the yellow copper complex as obtained by the method of Orloski is undissociated cupric O,O-dimethylphosphorodithioate. Other data reported by Orloski<sup>6</sup> show that the optical density of solutions of the yellow copper complex decreases slightly with increase in temperature. If it were possible to take this effect into account, this would improve agreement between the figures calculated above.

Since the complex as obtained by the method of Orloski appears to be the undissociated complex, it is probable that the instability of this complex is due to dissociation. Orloski reports<sup>6</sup> a 4% loss of colour after only a 15 second delay in measuring its intensity and a 40% loss after a 2 min delay.

From the data reported here, it can be calculated that the addition of  $\sim$  450 moles of the disulphide per mole of the yellow copper complex, produced in any of the colorimetric methods reported for the determination of malathion, would stabilise the vellow copper complex; first by greatly reducing the rate of dissociation and eventually by allowing not more than 1% dissociation. If this procedure were employed in the method of Orloski, it would entail extraction of the vellow copper complex, from a neutral or acetate-buffered aqueous phase, using a 1.6% (by wt.) solution of bis(dimethoxyphosphorothiono) disulphide in cyclohexane instead of cyclohexane alone; the same extractant would have to be used in preparing the standard curves.

Under the conditions reported here and elsewhere<sup>1</sup> for converting malathion to the yellow copper complex, dissociation probably proceeds so rapidly that it cannot be observed visually as fading of colour. The concentrations of yellow complex initially produced are approximately 100 times greater than those produced by the method of Orloski. Since the rate of dissociation is proportional to the square of the concentration of the yellow complex, this means that the rate of dissociation will be 10,000 times faster than that indicated by Orloski's figures for loss of colour with time.

Before the yellow complex in colorimetric methods for

malathion is formed, various authors<sup>4-6</sup> have employed a 'ferric-oxidation' step under neutral conditions to remove materials present in hydrolysed malathion, such as mercaptans and thiols, which would interfere by reducing cupric ions to cuprous. The purpose of this was to avoid subsequent reaction of 0,0-dimethylphosphorodithioate anions with cuprous ions to form cuprous O,O-dimethylphosphorodithioate-a colourless complex-instead of with cupric ions to form the required yellow complex. If a colorimetric version of the titrimetric method reported recently<sup>1</sup> is employed, this version may also require the inclusion of a 'ferric-oxidation' step under neutral conditions. However, in such a version, the rôle of the 'ferric-oxidation' step would be different. Its purpose would be to prevent formation of cuprous complex formed by direct reaction of O,O-dimethylphosphorodithioate anions with cuprous ions, because curpous complex formed in this way would interfere by altering the position of equilibrium between the yellow complex and its dissociation products.

## Acknowledgments

The author wishes to thank Mr. I. G. Blackwell, who carried out the elemental analyses reported and, also, Mr. J. Wood, who supplied a sample of sodium O,O-dimethylphosphorodithioate. The sample of 99.6% malathion used was supplied by American Cyanamid Company, Stamford, Conn., U.S.A.

Shell Research Limited, Woodstock Agricultural Research Centre, Sittingbourne, Kent

Received 24 May, 1968

#### References

- Hill, A. C., Akhtar, M., Mumtaz, M., & Osmani, J. A., Analyst, Lond., 1967, 92, 496
  Norris, M. V., Vail, W. A., & Averell, P. R., J. agric. Fd Chem.,
- 954, 2, 570
- Upham, S. D., J. Ass. off. agric. Chem., 1960, 43, 360
- Ware, J. H., J. Ass. off. agric. Chem., 1961, 44, 608 Ware, J. H., J. Ass. off. agric. Chem., 1962, 45, 529
- 6.
- Orloski, E. J., J. Ass. off. agric. Chem., 1964, 47, 248 Bode, H., & Arnswald, W., Z. analyt. Chem., 1962, 185, 99
- Kabachnik, M. I., & Mastryukova, T. A., Izv. Akad. Nauk SSSR, 8.
- 1953, p. 121; Chem. Abstr., 1954, **48**, 3244h Busev, A. I., & Ivanyutin, M. I., 'Soviet research on organo-phosphorus compounds 1949–1956', Part 1, p. 218 (New York: 9. Consultants Bureau, Inc.)