Pestic. Sci. 1987, **19**, 61–66

The Photodegradation of Parathion and Chlormephos

Simon J. Buckland and R. Stephen Davidson

Department of Chemistry, The City University, Northampton Square, London EC1V 0HB, UK

(Received 27 November 1985; accepted 25 February 1986)

ABSTRACT

Irradiation (~350 nm) of oxygenated acetonitrile solutions of parathion containing sensitisers such as benzoin and α-dicarbonyl compounds leads to oxidative desulphurisation at phosphorus, producing paraoxon in reasonable yield. Other degradation reactions also occur, probably as a result of the presence of the 4-nitrophenyl group in parathion. Under similar irradiation conditions, chlormephos is desulphurised at both the thionate and thiolate moiety. The reactions are rationalised as occurring via peroxy radicals which are generated from the sensitisers. Reaction was not observed when dyes, e.g. rose bengal, were used as sensitisers, which accords with the view that thionates and thiolates are not reactive towards singlet oxygen.

1 INTRODUCTION

A considerable number of organophosphorus esters, which contain either the thionate (P=S) and/or thiolate (P–S) moiety, find widespread use as agricultural insecticides.[1,2] Oxidative desulphurisation plays an important role in activating some materials, e.g. parathion and malathion,[3] to give more toxic acetylcholinesterase inhibitors and in the detoxication of other pesticides.[1] Two of the most important biochemical processes that are involved in the metabolism of organophosphorus pesticides containing P–S bonds are the oxidative desulphurisation of the thionate group to give the corresponding oxo analogue (P=O), and oxidative desulphurisation via de-esterification of the thiolate moiety. Other methods of degradation include photodegradation, and studies have been made of the kinetics and products from the direct irradiation of parathion.[4] As a continuation of earlier studies into methods of oxidative desulphurisation of pentavalent thiophosphorus compounds,[5,6] the reaction of

photochemically generated peroxy radicals with parathion and chlormephos has been investigated.

2 EXPERIMENTAL METHODS

2.1 Irradiation conditions

The solutions, contained in Pyrex tubes (26×1·9 cm), were flushed with oxygen for 10 min and then stoppered. The irradiation apparatus consisted of a circular array of sixteen 8-W black-light fluorescent lamps (Sylvania FT875/BLB) having a maximal emission at 350 nm. The tubes containing the solutions were rotated within the array of lamps, the closest distance between a single lamp and the tube being 3 cm.

2.2 Preparation of solutions for irradiation

Stock solutions of parathion and chlormephos were prepared by dissolving 0·40 g and 0·80 g, respectively, of the compounds in acetonitrile (100 ml). To 5 ml of the stock solutions, a known amount of sensitiser (see Tables 1 and 2) was added.

2.3 Analysis of solutions after irradiation

The g.l.c. analysis was carried out with a Perkin–Elmer Sigma 3 gas chromatograph fitted with a flame ionisation detector, using nitrogen as the carrier gas. The detector was checked for linearity over the range of concentrations used. All the columns used were fabricated from stainless steel. Parathion and paraoxon were separated on a 50 cm×3 mm column of 10% methyl silicone on 80–100 mesh Chromosorb W-AW-DMCS at 190°. Chlormephos was analysed using a 2 m×3 mm column of 1·5% OV 225 on 80–100 mesh Chromosorb W-AW-DMCS at 175°. Acids were detected and analysed as their methyl esters following their reaction with diazomethane. All the methyl esters were analysed using 2 m×3 mm columns of 10% SE 30 on 60–80 mesh Chromosorb at 140°. The mixture of methyl esters of **V** and **VI** could not be separated under these condi-

TABLE 1
The Photooxidative Desulphurisation of Parathion

Sensitiser		*Yield[a] of Recovered* **I** *(%)*	*Yield[a] of Recovered* **II** *(%)*
None		81	0
Benzoin	(2 Eq)	0	38
Benzil	(2 Eq)	35	29
Acenaphthaquinone	(1 Eq)	38	44
2,3-Dicyano-5,6-dichloroquinone	(2 Eq)	64	17
Biacetyl	(4 Eq)	27	23
Pyruvic acid	(4 Eq)	46	11
Methyl pyruvate	(4 Eq)	66	7

[a]Determined by g.l.c.

TABLE 2
The Photooxidative Desulphurisation of Chlormephos

Sensitiser		*Yield[a] of Unreacted* **III** *(%)*	*Yield[a] of Products*		
			IV *(%)*	**V+VI**[b] *(%)*	*Diethyl Phosphate (%)*
None		100	0	0	0
Benzoin	(2 Eq)	3[c]	27[c]	15	46
Benzil	(2 Eq)	68[d]		12	10
Biacetyl	(6 Eq)	2[c]	16[c]	<2	66
Pyruvic acid	(6 Eq)	58[d]		12	28
Methyl pyruvate	(6 Eq)	61[d]		8	26

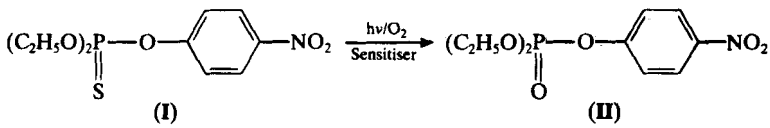
[a]Determined by g.l.c.
[b]Determined as methyl esters.
[c]Combined yield of **III** and **IV** determined by g.l.c. and relative yields by g.l.c.–m.s.
[d]G.l.c.–m.s. indicated that little of **IV** was present in these materials.

tions. Use of g.c.–m.s. (a Pye 104 gas chromatograph interfaced with a Kratos MS30 mass spectrometer), using helium as the carrier gas, led to separation of the g.c. peaks, and the components could be identified by m.s. Similarly, using g.c.–m.s., esters **III** and **IV** could be separated. The relative amounts of each ester were estimated from the ratio of the areas of the g.c. peaks.

3 RESULTS AND DISCUSSION

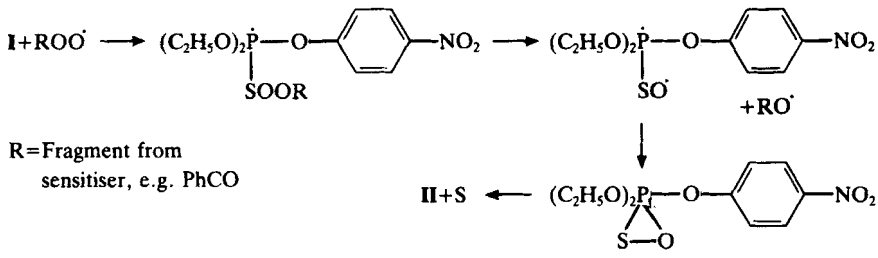
3.1 Parathion

From earlier studies[5] it was anticipated that irradiation of solutions containing parathion (**I**) and α-dicarbonyl compounds and benzoin would produce paraoxon (**II**):



(**I**) (**II**)

The results obtained, shown in Table I, show that as expected, oxidative desulphurisation of the thionate group does occur. The non-quantitative yields of phosphorus-containing compounds (as detected by g.l.c.) are probably due to reactions emanating from absorption of light by the 4-nitrophenyl groups. It has been shown that irradiation of both parathion and paraoxon in the absence of the sensitisers leads to decomposition and this probably involves *O*-dearylation.[7,8] Thus, in the presence of sensitisers, the desired desulphurisation occurs in competition with other non-sensitised decomposition reactions. The sensitised reactions, based on earlier work,[5] are proposed as involving peroxy radicals as shown in Scheme 1.



Scheme 1

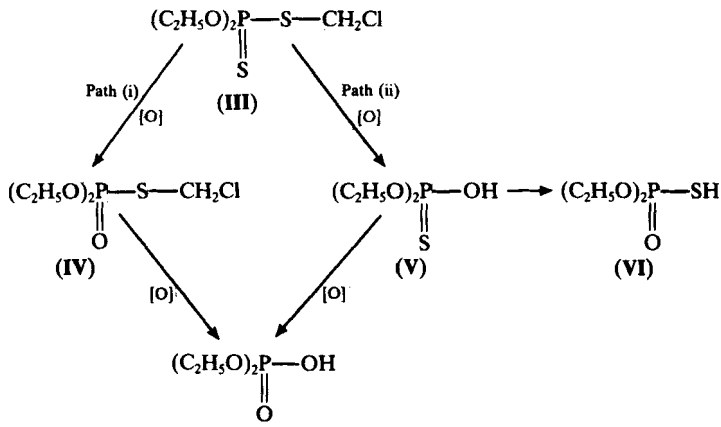
In none of the reactions was the fate of the extruded sulphur determined. From Table 1 it is seen that all the α-dicarbonyl compounds and benzoin enhance the yield of oxidative desulphurisation products, i.e. paraoxon. It could be argued that the reactions sensitised by benzil and acenaphthaquinone involve singlet oxygen since it is known that irradiation of these compounds in the presence of oxygen produces singlet oxygen.

Irradiation of solutions of parathion containing dyes such as rose bengal (a known efficient sensitiser of singlet oxygen)[9] led to no perceptible reaction (t.l.c. and g.c. analysis) suggesting that the P=S bond is not attacked by singlet oxygen. This result is in agreement with the findings by Grunwell and Erickson.[7]

3.2 Chlormephos (III)

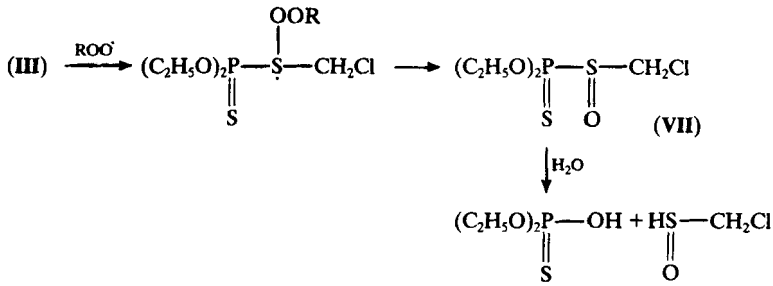
The photooxidation of chlormephos, sensitised by α-dicarbonyl compounds and benzoin gives a number of products (Table 2) by oxidation at the thionate group (Path (i)) and the thiolate group (Path (ii)) (Scheme 2).

From the g.l.c. analysis, the reaction mixtures were found to contain a peak corresponding to unchanged **III**. However, it turned out that **III** and **IV** showed



Scheme 2

similar retention times on the column used and therefore these mixtures were analysed by g.c.–m.s. With benzoin and biacetyl as sensitisers, respectable yields of **IV** are observed. Oxidative desulphurisation of the thiolate group leads to the formation of *O,O*-diethylphosphorothiolic acid (**V**), which may isomerise to its more stable thiono isomer (**VI**). Treatment of this mixture with diazomethane leads to alkylation at sulphur and oxygen. The desulphurisation reaction is thought to involve attack by the peroxy radicals to give a phosphorothiolate *S*-oxide (Scheme 3). Such compounds are reported to be powerful phosphorylating agents.[10]



Scheme 3

The formation of **V** and hence **VI** is thought to be due to **VII** reacting with adventitious traces of water present in the solvent. From the results, it is not possible to say whether oxidative desulphurisation occurs preferentially at the thionate or the thiolate group. However, in all cases the ultimate oxidation product is *O,O*-diethyl phosphate.

4 CONCLUSION

The ability of peroxy radicals to activate parathion (by oxidation to paraoxon) and to detoxify chlormephos has been demonstrated. Of particular significance is the finding that α-oxocarboxylic acids such as pyruvic acid and α-ketoglutaric acid can sensitise the reactions since such compounds are present in a number of biochemical systems.[11] Since such species show absorption at wavelengths >300 nm, their photooxidation by sunlight at surfaces, e.g. skin, may yield several peroxide intermediates. These may be partly responsible for the metabolism of organophosphorus compounds in the body and subsequent related toxicological side effects. Oxythionate derivatives such as **VII** are thought to be involved in the enzymic metabolism of organophosphorus pesticides.[12] The reported investigations have shown that photosensitised oxidation of organophosphorus compounds in which oxygen atom transfer occurs may be regarded as one of the models for biological oxidation. Other reagents for this purpose include *m*-chloroperbenzoic acid.[13,14]

ACKNOWLEDGEMENTS

The authors express their thanks to Dr R. Hall (C.D.E. Porton Down) for enthusiastic support of the work, the SERC in cooperation with the MoD for a CASE Award and Dr H. Hudson (North London Polytechnic) for a sample of chlormephos.

REFERENCES

1. Eto, M., *Organophosphorus Pesticides, Organic and Biological Chemistry,* CRC Press, Cleveland, OH, 1974.
2. *The Pesticide Manual* (Worthing, C. R., Ed.) The British Crop Protection Council, Croydon, 1983, 7th edn.
3. Gage, J. C. *Biochem. J.* 1953, **54,** 426–430.
4. Meallier, P.; Nury, J.; Pouyet, B.; Coste, C.; Bastide, J. *Chemosphere* 1977, **6,** 809–814, 815–820.
5. Buckland, S. J.; Davidson, R. S., *J. Photochem.* 1987, **36,** 39–49.
6. Buckland, S. J.; Davidson, R. S., *J. Chem. Res. (S),* 1986, 192–193.
7. Grunwell, J. R.; Erickson, *J. Agric. Food Chem.* 1973, **21,** 929–931.
8. Frawley, J. P.; Cook, J. W.; Blake, J. R.; Fitzhugh, J. *J. Agric. Food Chem.* 1958, **6,** 28–30.
9. Kearens, D. R., *Chem. Rev.* 1971, **71,** 395–427.
10. Segall, Y.; Casida, J. E., *Phosphorus and Sulfur* 1983, **18,** 209–212.
11. Jenson, D. *The Principles of Physiology,* Appleton-Century-Crofts, New York, 1980, Ch. 56 and 58.
12. Kamataki, T.; Belcher, D. H.; Neal, R. A. *Mol. Pharmacol.* 1976, **12,** 921–932.
13. Bellet, E. M.; Casida, J. E. *J. Agric. Food Chem.* 1974, **22,** 207–211.
14. Segall, Y.; Casida, J.E. *Tetrahedron Lett.* 1982, **23,** 139–142.