The Oxidation of Parathion to Paraoxon in Aqueous Media by Silver Oxide (AgO)

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Parathion (a thionophosphate) has been oxidized by many means to the biologically more active paraoxon (a phosphate). This conversion of P=S to P=O in this and some other organophosphorus insecticides increases minimum analytical detectability as much as a thousandfold in the widely used cholinesterase (ChE) assay of the organophosphorus and carbamate insecticides. Many modifications of this assay exist, the most recent being automated procedures (1, 2). Because it is clearly desirable to measure parathion and other thionophosphate residues routinely before and after oxidation so as to establish in situ conversions of parent compound to oxygen analog, in the automated procedure (1) it would have been desirable to split the sample stream so as to measure simultaneously both unoxidized and procedurally oxidized organophosphorus insecticides present. In the closed system of the automated procedure, however, otherwise standardized analytical oxidants[1] for the desired conversion cannot be adapted for this use or else fail

[1] Several such oxidants were discussed by R. C. BLINN (3).

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to work satisfactorily; for example, in the well-known manual procedure using bromine-water as oxidant the excess bromine escapes from the solution, but when automated (1) this necessary excess cannot escape and "poisons" the ChE added later. The literature has been exhaustively searched for promising oxidizing agents and excess oxidant "destroyers" for use in the automated system and all promising leads have been examined for suitability in this application with completely negative results. Oxidizing agents tested included bromine, N-bromosuccinimide, catalase, hydrogen peroxide, nitric acid, potassium permanganate, peroxidase, and intense ultraviolet energy; some excess oxident "destroyers" tested included catalase, cysteine, ferrous salts, and peroxidase. In the continuing search for the ideal universal oxidant for these stringent requirements it was suggested (4) that silver oxide (AgO) might achieve the desired thionophosphate-to-phosphate conversion; to our knowledge this reaction has not been reported previously. Unfortunately, it is not possible to incorporate fresh AgO continuously into a closed system; furthermore, subsequent fouling of the total system with the reaction by-products AgS, Ag_2S, and Ag would eventually occur.

The use of AgO in a manual method, however, is rapid and convenient and, under optimal conditions, may provide another means of converting thiono- and some thiolophosphates to their oxons in acceptable yields.

Methods

AgO was freshly prepared according to Bailar (5), air and oven dried, and stored four days *in vacuo* over concentrated sulfuric acid; the final product was kept at room temperature in a tightly closed amber bottle.

Finely divided AgO (5 to 150 mg.) was added to 1- or 5-ml. aliquots of parathion in 95% ethyl alcohol solution then incubated from 10 to 30 minutes in a water bath at 65° C. or at 80° C. After being cooled quickly to 0° C. and centrifuged, an aliquot of the supernatent was analyzed immediately by an anti-ChE method basically as reported earlier (1) after dilution with water to 25% ethyl alcohol or--after dilution with electrolyte solution[2/] to 50% ethyl alcohol--by oscillopolarography. Some polarographic assays were made following thin-layer chromatography (TLC) for isolative and supplementary qualitative purposes. Prior to TLC, excess water was added, the aqueous solution was extracted with chloroform, the chloroform extract was dried by passage through a short column of anhydrous sodium sulfate, concentrated to a few μl., then applied in entirety to a 250 μ thick, fluorescent silica gel Merck, (GF-254) TLC plate. After 10 cm. development of the plate

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[2/] Several were used, but 0.1 N potassium chloride in 0.2N acetic acid solution is preferred (see Discussion).

in hexane-chloroform-methyl alcohol (7+2+1), the observed (ultraviolet light) quenched spots were removed by scraping each spot area into a centrifuge tube then analyzed according to Hearth et al. (6) following mixing thoroughly with 1.0 ml. of 95% ethyl alcohol, mixing again with 1.0 ml. of electrolyte solution, centrifuging, and decanting of the clear supernatant into an oscillopolarographic cell.

Results and Discussion

Analysis by the automated anti-ChE method (1) of the parathion-AgO reaction mixture (11 μg. parathion in 1 ml. 95% ethyl alcohol solution 10 min. at 80° C. with 10 mg. AgO) indicated either the quantitative conversion of parathion to paraoxon or the conversion to some product(s) which inhibit(s) ChE to as great an extent as the theoretical yield of paraoxon. Reagent blanks and controls established the fact that the inhibition was directly attributable to the reaction of AgO with parathion.

Results from oscillopolarographic analyses also indicated conversion of parathion to paraoxon by AgO; with the present manual oxidative method, and under the conditions specified (see Table I), parathion was converted to paraoxon in 20-50% yields. In addition, p-nitrophenol was found in the oxidized mixture in approximately 30% yield as confirmed by both TLC and oscillopolarography.

TABLE I

Recoveries based on TLC-oscillopolarographic analysis of unreacted parathion and of resulting paraoxon and p-nitrophenol, following reaction of parathion with AgO in 5 ml. 95% ethyl alcohol

				Identified Products				
	Parathion			Paraoxon		p-Nitrophenol		
Treatment	µg. added	µg. found	% unreacted[a]	µg. found	% yield[a]	µg. found	% yield[a]	% Total accountable
10-Min. incubation, 65° C.; no AgO	50	31	110	None	--	None	--	110
	50	27	96	None	--	None	--	96
	50	27[b]	96	None	--	None	--	96
10-Min. incubation, 65° C.; 50 mg. AgO	50	13	46	6	21	Not analyzed		67
	50	15	54	9	32	4	29	115
	50	10	36	11	39	4	29	104
	50	11	39	13	46	5	36	121
	50	12	43	12	43	4	29	115

[a] Yields corrected on a mole per mole basis between compounds and for 56% recoveries in the total method.

[b] Some slight loss incurred during TLC application.

Figures 1 and 2 show relative amounts of unreacted parathion as a function of incubation time and mg. of AgO per unit of parathion, respectively. Figure 1 indicates that increased incubation time materially alters the amount of detectable unreacted parathion and, therefore, the amount of produced paraoxon and p-nitrophenol; the latter produced by alkaline hydrolysis of parathion and/or paraoxon. Another inverse relationship, between amount of unreacted parathion and

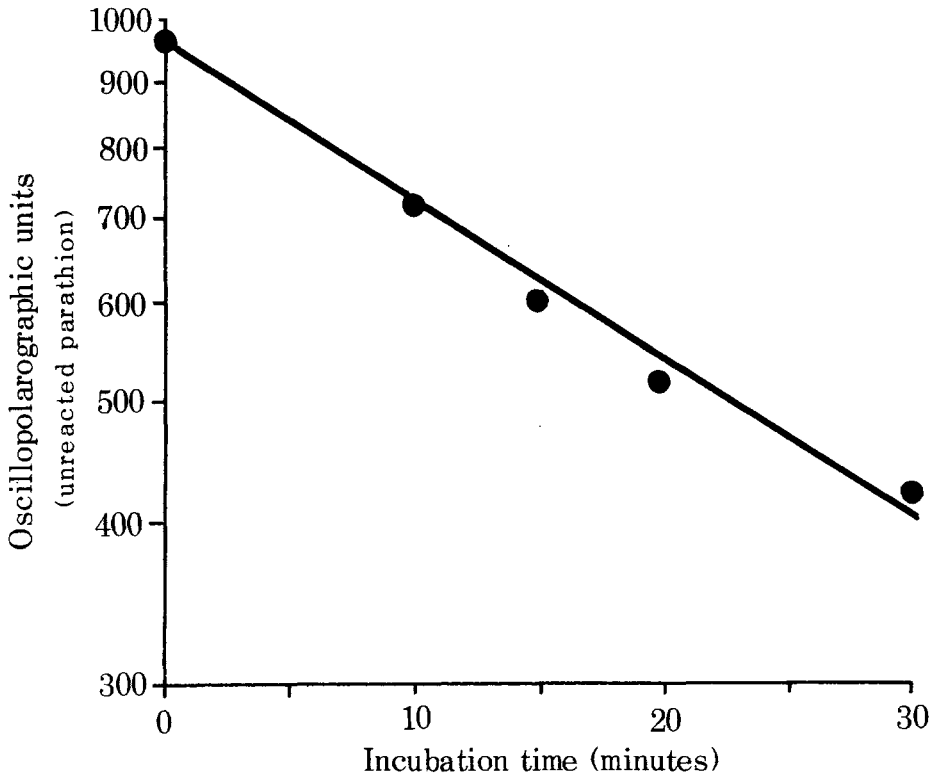

Fig. 1. Effect of increasing incubation time on parathion oxidation at 80° C., with 10 mg. of AgO/11 µg. of parathion; analyzed without TLC using 0.2 M tetramethyl ammonium bromide electrolyte solution

increased AgO added to the reaction mixture is seen in Figure 2. Although test solutions were evaluated polarographically with use of more than one supporting electrolyte solution, potassium chloride in acetic acid is preferred because it permits lower minimum detectability. It is clearly evident from these graphs that tests for final analysis by TLC-oscillopolarography as well as for ChE assay were conducted under less than optimal conditions. Nevertheless, sufficient evidence is available to indicate--even under these arbitrary

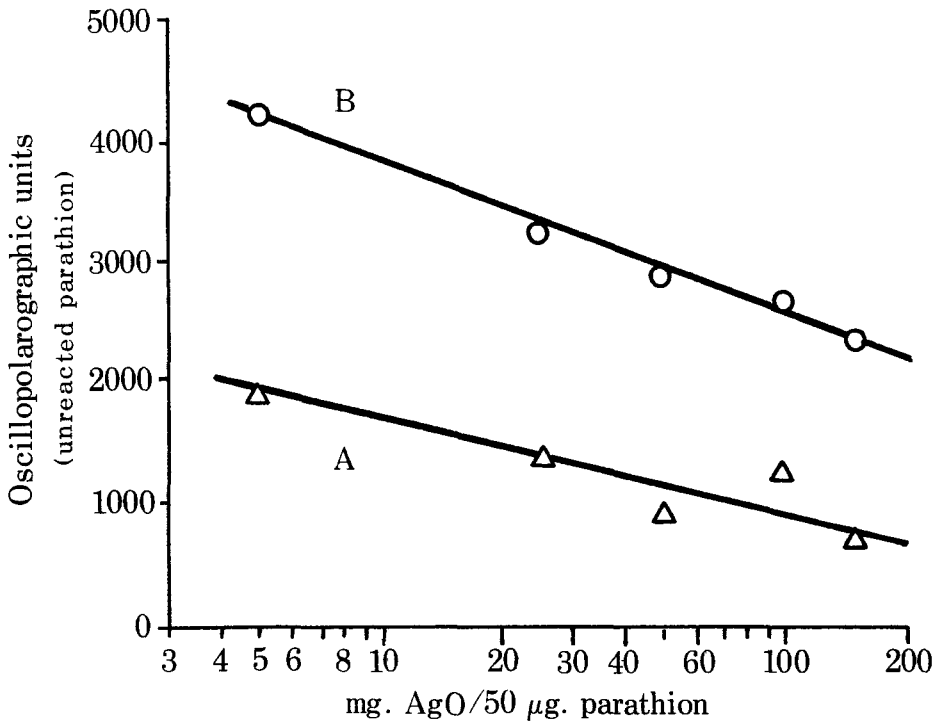

Fig. 2. Effect of increasing amounts of AgO on parathion oxidation with incubation at 65° C. for 10 minutes; analyzed without TLC using: A) 0.2 M tetrabutyl ammonium bromide electrolyte solution, B) 0.1 N potassium chloride in 0.2 N acetic acid electrolyte solution

conditions--a good recovery of paraoxon from the parent compound. It appears that the maximum quantity of paraoxon produced is limited only by the percent parent compound converted to p-nitrophenol by the competing hydrolytic side reaction.

Thimet (phorate) was not oxidized to a ChE inhibitor under the present conditions; TLC data indicates quantitative destruction of the parent compound, presumably also by hydrolysis.

Conclusions

The present preliminary report clearly justifies more detailed examinations of this previously unreported oxidative technique. AgO may prove to be a general reagent for oxidizing thiono-organophosphorus pesticides to their phosphates which are often more potent ChE inhibitors than the parent compounds; many other oxidants have been utilized for this purpose with reported conversion efficiencies ranging from a few percent to near quantitative, usually on a macro-scale; most micro methods in the literature are of very low efficiencies. Whether AgO will also oxidize any of the thiolo-organophosphorus compounds to their phosphates is not yet established, except for negative results with Thimet.

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