Gas-Liquid Chromatographic Inlet Block Derivatization of Organophosphorus Pesticides and Related Dialkyl Phosphorothioates

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Trimethylphenylammonium hydroxide in methanol is demonstrated to be a useful reagent for the inlet block (in-block) GLC derivatization and subsequent quantification of not only many organophosphorus pesticides but also their dialkyl phosphorothioate hydrolysis products. Methyl parathion is shown to derivatize in high yield by an in-block transesterification mechanism, while malathion reacts by rapid β-elimination in solution, followed by in-block pyrolytic methylation. Efficiencies are determined for the methylation of potassium *O,O*-dimethyl phosphorodithioate and potassium *O,O*-dimethyl phosphorothioate and methods for the quantification of these salts are outlined.

Considerable interest exists in the development of analytical methods for the determination of organophosphorus pesticides and their dialkyl phosphate hydrolysis products. Such methods find use in studies involving environmental monitoring, human exposure, pesticide metabolism, and formulation stability, among many others.

Gas-liquid chromatography (GLC) is the most widely used technique for the analysis of pesticides, and most organophosphorus pesticides may be determined directly by GLC, requiring no derivatization. Although derivatization of pesticides results in some loss of specificity, such an approach can be useful in the confirmation of pesticide identity and for screening purposes (Shafik et al., 1971; Moye, 1973) and in increasing the sensitivity and/or convenience of analysis in studies involving the environmental stability or formulation stability of a specific pesticide. Further, derivatization is very useful for pesticides such as chlorphoxim which may present problems in direct GLC analysis (Dale et al., 1976).

In contrast, the dialkyl phosphates (including the phosphorothioates and phosphorodithioates) must be derivatized for GLC assay to be possible. Most commonly, the dialkyl phosphates are reacted with diazoalkanes such as diazomethane to produce the trialkyl esters which are readily chromatographed (Stanley, 1966; Shafik et al., 1973; Daughton et al., 1976). These diazoalkanes are toxic, carcinogenic, and potentially explosive. Less hazardous, alternative methods of derivatization would seem to be desirable.

Quarternary ammonium hydroxides have found application in the GLC in-block methylation of compounds such as long-chain fatty acids (Robb and Westbrook, 1963), barbituates, phenolic alkaloids, and xanthine bases (Brochmann-Hanssen and Oke, 1969), and *N*-methyl and *N*-aryl carbamates (Wien and Tanaka, 1977), among others.

Apparently methylation is effected by thermal decomposition of the quaternary ammonium salt of the analyte in the GLC inlet block to yield the corresponding methyl ester (Robb and Westbrook, 1963; Brochmann-Hanssen and Oke, 1969).

On-column (in-block) transesterification of a number of organophosphorus pesticides using methanolic sodium hydroxide has been described (Moye, 1973). Recently, solutions of trimethylphenylammonium hydroxide (TMPAH) in methanol have been employed for the in-block derivatization and subsequent quantification of the pesticide chlorphoxim (Dale et al., 1976) and nine other organophosphorus pesticides (Miles and Dale, 1978). In the present work, evidence is presented which illustrates the nature of alcoholic TMPAH derivatization reactions for methyl parathion and malathion and suggests further analytical applications for determination of these and other pesticides. In addition, this study demonstrates for the first time the efficiency and convenience of alcoholic TMPAH in the quantification of dialkyl phosphorothioates by GLC in-block methylation to the corresponding trialkyl esters.

Table I. List of Abbreviations for Dialkyl Phosphorothioate Salts and Their Esters

compound	abbreviation
potassium *O,O*-dimethyl phosphorothioate	DMPT,K
potassium *O,O*-dimethyl phosphorodithioate	DMPDT,K
potassium *O,S*-dimethyl phosphorodithioate	SMe-DMPDT,K
O,O,O-trimethyl phosphorothionate	TMPT
O,O-dimethyl *O*-ethyl phosphorothionate	DMEPT
O,O,S-trimethyl phosphorothiolate	TMPTh
O,O,S-trimethyl phosphorodithioate	TMPDT
O,O-dimethyl *S*-ethyl phosphorothiolate	DMEPTh

EXPERIMENTAL SECTION

Standards. Malathion, potassium *O,O*-dimethyl phosphorodithioate, potassium *O,O*-dimethyl phosphorothioate, potassium *O,S*-dimethyl phosphorodithioate, and *O,O,S*-trimethyl phosphorodithioate were available from earlier studies, having been provided originally by American Cyanamid Corporation. The methyl parathion standard source was the Pesticides Research Laboratory Repository, presently located at Research Triangle Park, N.C.

The *O,O*-dimethyl *O*-ethyl phosphorothionate was produced by the ethanolysis of $(CH_3O)_2P(S)Cl$. The vacuum-distilled product had a boiling point of 62.0 °C at 0.25 mmHg.

The *O,O,S*-trimethyl phosphorothiolate standard was synthesized from potassium *O,O*-dimethyl phosphorothioate by methylation with methyl iodide in acetonitrile. The product was purified by vacuum distillation [bp 68 °C (0.75 mm)].

O,O-Dimethyl *S*-ethyl phosphorothiolate was produced analogously using ethyl iodide. The crude product was seen to be sufficiently pure by NMR to serve as a qualitative standard.

O,O,O-Trimethyl phosphorothionate was prepared by refluxing dimethyl phosphorochloridothionate in an-

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hydrous methanol for 2 h. After evaporation of the HCl and methanol, the product was distilled at 27.5 °C at 0.25 mmHg.

The structure of the above esters synthesized specifically for this study were confirmed by proton NMR spectrometry.

Table I consists of a reference list of abbreviations for dialkyl phosphorothioate salts and their esters.

Reagents. Trimethylphenylammonium hydroxide (TMPAH) reagent was diluted as necessary from a 0.100 M stock solution in methanol, available from Eastman Organic Chemicals. Reagent grade methanol was used. TMPAH in ethanol was made by vacuum rotary evaporation of the methanol, followed by anhydrous ethanol addition and evaporation. Anhydrous ethanol was used to dilute the residue to give 0.1 M TMPAH in ethanol which was the stock from which dilutions were made. The concentration of TMPAH was verified by titration. Tetramethylammonium hydroxide (TMAH) was purchased as the pentahydrate from Eastman Organic Chemicals. Forty percent tetrabutylammonium hydroxide in water available from Aldrich Chemical Company was lyophilized and then immediately reconstituted with either ethanol or methanol as required. All other chemicals were reagent grade.

Equipment. A Micro-Tek MT-220 gas chromatograph was used for in-block derivatization of the analytes and subsequent separation and quantification of the resulting trialkyl esters. A Melpar flame photometric detector was used with an interference filter for spectral isolation of the phosphorus emission at 526 nm. The detector was modified to prevent flameout upon sample injection (Burgett and Green, 1974). The chromatographic columns used were (1) 6 ft × 0.25 in. o.d. (0.18 in. i.d.) aluminum packed with 5% OV-225 on 100/120 mesh Chromosorb W(HP) and (2) 6 ft × 0.25 in. o.d. (0.18 in. i.d.) aluminum packed with 3% OV-275 on 100/120 mesh Chromosorb W(HP). Each column was packed to within an inch of the inlet end. Each was pushed up to a full stop at the top of the inlet block before the fitting was tightened down so that injections could be made onto the top of the column itself. The inlet block was held at either 220 or 260 °C, depending on the experiment. Detector temperature was 250 °C. Column temperature for the efficiency and linearity studies was 166 °C. Nitrogen carrier gas flow was 140 mL/min while the hydrogen flow was 200 mL/min, the airflow 50 mL/min, and the oxygen flow 20 mL/min.

Peak areas and retention times (t_R) were determined using an Infotronics Model CRS-100 Digital Integrator system with controls set as necessary for accurate, discriminatory peak area counting. Digital data were recorded by an interfaced Victor Digit-matic printer while analogue data were displayed on a model SRG Sargeant recorder.

Nuclear magnetic resonance spectra were run on a Perkin-Elmer Model R-12B NMR Spectrometer.

Method. In the methyl parathion studies GLC derivatization efficiencies were determined by comparing freshly diluted solutions of 5 to 10 μg/mL of methyl parathion in dilute derivatizing reagent in methanol or ethanol with a standard containing the appropriate ester in alcohol. Quantification was by peak area. The various derivatizing bases studied were trimethylphenylammonium hydroxide (TMPAH), tetramethylammonium hydroxide (TMAH), tetra-*n*-butylammonium hydroxide (TBAH), and potassium hydroxide.

For the malathion investigations, stock standard solutions of accurately known concentration about 1 mg/mL were made up in methanol and ethanol. These were diluted as needed to give concentrations in the range of 5 to 10 μg/mL of malathion in 0.01 M TMPAH in either methanol or ethanol. These were compared with alcoholic solutions of the appropriate trialkyl esters to identify the derivatives formed in the GLC inlet block and quantify them where appropriate.

For the derivatization studies on potassium *O,O*-dimethyl phosphorothioate (DMPT,K) and potassium *O,O*-dimethyl phosphorodithioate (DMPDT,K), standards were weighed into 50-mL volumetric flasks and diluted to volume with methanol to give concentrations of approximately 1 mg/mL. Standard salt concentrates thus formed were then diluted to give an accurately known final concentration of about 5 ng/μL. The diluent in each case was methanolic TMPAH and methanol in such proportions as to give final concentration of analytes in 0.0001 M, 0.001 M, 0.01 M, and 0.09 M TMPAH. The trialkyl ester comparison standards were diluted to appropriate concentrations in reagent grade methanol.

Methylation efficiencies were determined by alternating duplicate injections of alkyl phosphorothioates in varying concentrations of methanolic TMPAH with injections of standard trialkyl esters in methanol. Quantification by both peak area and peak height was employed and served to identify conditions which cause peak broadening. Efficiencies were determined for each of the two compounds at inlet temperatures of both 220 and 260 °C in several concentrations of TMPAH.

The peak height and peak area response was determined as a function of injection volume for given concentrations of the two alkyl phosphorothioates of interest in 0.01 M TMPAH in methanol. The same response parameters were then measured as a function of alkyl phosphorothioate concentration in 0.01 M TMPAH using constant injection volume.

RESULTS AND DISCUSSION

Methyl Parathion. An earlier study (Miles and Dale, 1978) has shown that methyl parathion in 0.01 M TMPAH in methanol yields *O,O,O*-trimethyl phosphorothionate (TMPT) at a slow rate in solution and with 76% efficiency or greater as a result of in-block derivatization. Hydrolysis followed by methylation would produce the *S*-methyl ester (see below) and it is difficult to envision a mechanism by which the trimethylphenylammonium ion could participate in O-methylation. Indeed a solution of 6.98 ng/μL of methyl parathion in methanol alone gave an in-block conversion to TMPT of about 10% at an inlet block temperature of 260 °C. This transesterification, or methanolysis, can occur only by nucleophilic attack on the phosphorus by the solvent with subsequent loss of the *p*-nitrophenolate moiety, a good leaving group. Evidence from work on the hydrolysis of phosphate esters (Westheimer, 1977), suggests the occurrence of a five-coordinate trigonal bipyramidal intermediate. A reasonable representation in the present case might then be as shown in Figure 1.

The in-block derivatization procedure utilizing an inlet temperature of 260 °C and a solution containing 6.98 ng/μL of methyl parathion in 0.01 M TMPAH in methanol yielded TMPT with 81.2% efficiency. A side reaction occurs which produces less than 5% of the S-methylated derivative, *O,O,S*-trimethyl phosphorothiolate. These preliminary results then suggested that the observed TMPT resulted from an in-block, base-mediated nucleophilic attack on the phosphorus of methyl parathion by the solvent as shown in Figure 2.

The experiments utilizing the various bases at concentrations of 0.003 M and 0.01 M in ethanol gave credence

Table II. GLC In-Block Derivatization Efficiencies for Methyl Parathion Using Various Bases in Ethanol or Methanol at an Inlet Temperature of 250 °C

base	concn, M	alcohol	conversion (%) DMEPT	conversion (%) TMPT	other products obsd
None	0.000	EtOH	0.5	0.0	None
	0.000	MeOH	0.0	9.2	None
TMPAH	0.003	EtOH	24.6	0.0	TMPTh and DMEPTh
	0.01	EtOH	4.6	0.0	TMPTh and DMEPTh
	0.01	MeOH	0.0	81.2	TMPTh
TMAH	0.003	EtOH	38.8	0.0	None
	0.01	EtOH	38.7	0.0	None
	0.01	MeOH	0.0	82.2	None
TBAH	0.003	EtOH	30.6	0.0	None
KOH	0.003	EtOH	33.5	0.0	None
	0.01	MeOH	0.0	79.3	None

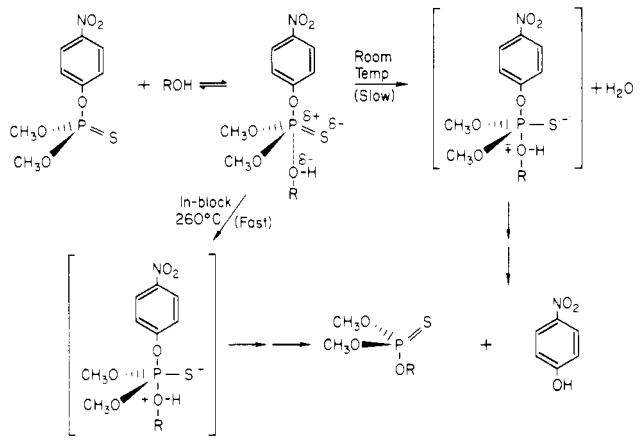

Figure 1. Transesterification of methyl parathion in alcohol alone.

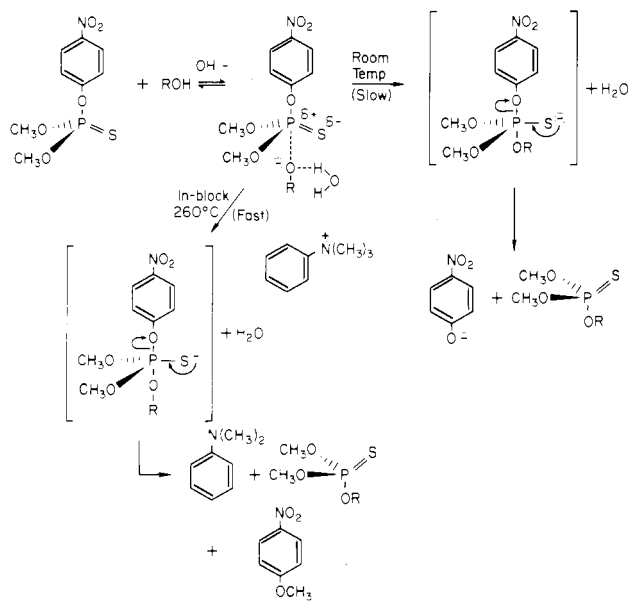

Figure 2. Basic transesterification of methyl parathion using alcoholic TMPAH.

to the above hypothesis, as may be seen from Table II. It is apparent that ethanolysis is less than half as efficient as methanolysis. This is easily rationalized by the relative pK_a's of water, methanol, and ethanol. Since water and methanol are of comparable acidities the dissolution of a hydroxide base in methanol will result in the extensive formation of methoxide ion, which then initiates transesterification. An analogous solution in ethanol will contain considerably less ethoxide because of the weaker acidity of ethanol and substantially more hydroxide will be present to allow hydrolysis and subsequent side reactions to occur. The four different bases each give similar yields in ethanol of the *O*-ethyl derivative with no *O*-methyl formation. TMPAH yields a substantial quantity of *S*-methyl and *S*-ethyl derivatives as side reaction products and is less efficient in producing DMEPT. It is seen that increasing the TMPAH in ethanol concentration from 0.003 M to 0.01 M decreases the yield of ethanolysis product. A corresponding increase is seen in the production of *S*-methyl and *S*-ethyl side reaction products. Figure 3 allows a comparison of methanolysis and ethanolysis under conditions in which only the identity of the alcohol solvent is varied. The identities of the side reaction products are inferred from t_R comparisons with authentic standard esters. It has not been conclusively established that the peak labeled $(CH_3O)_2P(O)SCH_2CH_3$ is not due to the isomeric possibility $(CH_3O)(C_2H_5O)P(O)SCH_3$.

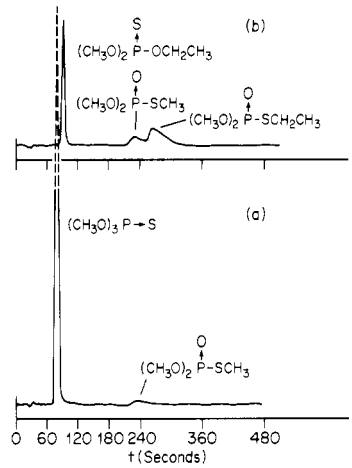

Figure 3. Comparison of GLC traces for the derivatization of 3.0 μL of 8.39 ng/μL of methyl parathion in 0.003 TMPAH in (a) methanol and (b) ethanol. Conditions: OV-225 column at 130 °C; inlet temperature, 260 °C.

The sequence in Figure 2 demonstrates the transesterification capability of TMPAH–methanol. Any hydroxide base in methanol would suffice, but trimethylphenylammonium hydroxide has an advantage in that any excess immediately pyrolyzes in the GLC block to form the volatile products methanol and dimethylanaline. In this way no unreacted hydroxide is left at the top of the column to artificially enhance analyte conversion upon successive GLC injections. TBAH, of course, cannot methylate and TMAH normally requires an inlet temperature of over 300 °C for efficient pyrolytic methylation (Robb and Westbrook, 1963). These reagents do not yield the S-alkyl side reaction products from methyl parathion under the derivatization conditions outlined in Table II. Both of the quaternary bases appear to decompose at the top of the column sufficiently rapidly, however, so that

Table III. GLC In-Block Methylation Efficiency for Potassium *O,O*-Dimethyl Phosphorodithioate in Methanolic TMPAH

TMPAH concn, M	block temp, °C	efficiency, % by peak area	broadening index
no TMPAH	220		
0.0001	220	96.4	1.34
0.001	220	97.3	1.32
0.01	220	92.1	1.89
0.09	220	97.2	3.11
no TMPAH	260	30.6	2.10
0.0001	260	94.4	0.824
0.001	260	95.8	0.829
0.01	260	87.3	0.832
0.09	260	90.5	1.063

there is not a buildup of hydroxide to provide spurious enhancement of subsequently injected samples. The TBAH excess undoubtedly decomposes in the block to yield 1-butene, water, and tri-*n*-butylamine (Lucas, 1953) while excess TMAH decomposes in the block over time to yield methanol and trimethylamine. Methanolic TMAH is convenient to prepare and is at least as efficient a transesterification reagent as methanolic TMPAH (see Table II). As alluded to previously, methanolic TMAH has the advantage of producing no *S*-alkyl side reaction peak in methyl parathion derivatization. Alcoholic KOH possesses this same characteristic, but excess KOH remains on the top of the column and produces memory effects upon subsequent injections.

GLC in-block transesterification using TMPAH–methanol may be applied to a wide range of organophosphorus pesticides containing good leaving groups. Other pesticides successfully analyzed by this method (Miles and Dale, 1978) which may be predicted to derivatize by this mechanism include parathion, chlorphoxim, and temephos. One may predict the prospects for successful application of the method to additional organophosphorus pesticides of interest by evaluating the strength of each pesticide as a phosphorylating agent. The better phosphorylating agent a pesticide is (Eto, 1974), the more facile will be the derivatization by methanolic TMPAH.

In practice a standard solution of a given pesticide is diluted in 0.01 M TMPAH in methanol and samples similarly prepared are quantified by direct peak height comparison of alternate duplicate injections of standards and samples. Samples and standards are diluted at the same time in TMPAH–methanol to allow compensation for any derivatization which takes place in solution prior to GLC analysis (Dale et al., 1976). Methyl parathion in 0.01 M TMPAH in methanol reacts to form TMPT with about 80% efficiency immediately after TMPAH dilution. After 48 h the apparent efficiency is nearly 90%, due to the occurrence of substantial in-solution reaction prior to the in-block transformation (Miles and Dale, 1978). The minimum detectable limit for methyl parathion using 0.01 M TMPAH–methanol is 400 pg.

Malathion. The in-block derivatization of malathion by TMPAH–methanol occurs by the salt pyrolysis methylation pathway. The malathion undergoes rapid β-elimination to form trimethylphenylammonium *O,O*-dimethyl phosphorodithioate, water, and diethyl fumarate upon dissolution in TMPAH–methanol reagent. Thus when the solution is injected into the inlet block, the reaction occurring is methylation of DMPDT anion by salt pyrolysis which occurs with about 90% efficiency in 0.01 M methanolic TMPAH (Table III). A small amount

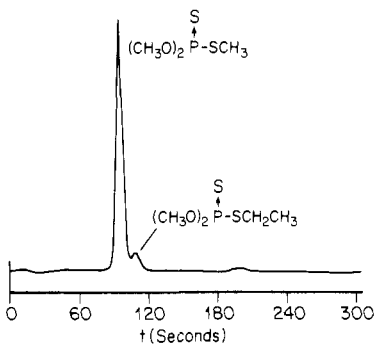

Figure 4. GLC trace for the derivatization of malathion in 0.01 M TMPAH in ethanol. Conditions: OV-225 column at 166 °C; inlet temperature, 260 °C.

(about 5%) of TMPT is also formed. This is probably due to side reaction by a transesterification mechanism. When the in-block derivatization is performed using 0.01 M ethanolic TMPAH, the predominant derivative again is TMPDT in about 90% yield. There is, however, also the formation of about 5% *O,O*-dimethyl-*S*-ethylphosphorodithioate (and/or possibly the *O*-ethyl-*S,O*-dimethyl isomer) and a trace of *O,S,S*-trimethyl phosphorodithioate. A typical GLC trace for methylation of malathion in ethanolic 0.01 M TMPAH is shown in Figure 4.

In practice the procedure for quantifying malathion is exactly analogous to that for methyl parathion. Methanol is used as the solvent. Minimum detectable limit for malathion is 400 pg.

Recent work on carbamate pesticides provides a further illustration of the capability of TMPAH–methanol to fulfill different derivitization functions. Wien and Tanaka observed that *N*-aryl carbamates methylate in the GLC block using TMPAH–methanol by replacement of the N hydrogen with methyl, while with an *N*-methyl, *O*-aryl carbamate such as carbaryl only the methyl ether of 1-naphthol was detected (Wien and Tanaka, 1977). These observations may be explained in terms of the ability of TMPAH–methanol to react by salt pyrolysis or by nucleophilic attack by solvent, depending on the substrate. The contribution of the aryl group and the carbonyl group to the acidity of the N hydrogen allows N-methylation to occur by salt pyrolysis in the case of *N*-aryl carbamates. Carbaryl, however, contains no *N*-aryl group to stabilize negative charge, but does contain an O-aryl moiety, a good leaving group for transesterification of carbamates by methanolic hydroxide (Moye, 1971). Thus the O=C–O bond is cleaved primarily by transesterification although some hydrolysis undoubtedly occurs also. In either event, the 1-naphthol anion is formed and then methylated by in-block pyrolysis to give the observed methyl naphthyl ether. The other carbamate derived product in this case is methyl *N*-methylcarbamate ($CH_3NHC(=O)OCH_3$) (Moye, 1971).

Quantification of Phosphorothioate Salts. Tables III and IV list the efficiencies of in-block methylation by methanolic TMPAH for potassium *O,O*-dimethyl phosphorodithioate (DMPDT,K) and potassium *O,O*-dimethyl phosphorothioate (DMPT,K) as a function of inlet temperature and TMPAH concentration. In addition a parameter designated the broadening index (B.I.) is listed where:

$$\text{B.I.} = \frac{\text{conversion efficiency by peak area}}{\text{conversion efficiency by peak height}}$$

Of course, any broadening of the peak formed by TMPAH–methanol methylation of a salt standard reduces

Table IV. GLC In-Block Methylation Efficiency for Potassium *O,O*-Dimethyl Phosphorothioate in Methanolic TMPAH

TMPAH concn, M	block temp, °C	efficiency, % by peak area	broadening index
no TMPAH	220		
0.0001	220	75.4	3.06
0.001	220	90.9	2.37
0.01	220	98.5	2.97
0.09	220	102.8	4.53
no TMPAH	260	2.4	
0.0001	260	60.1	1.42
0.001	260	94.4	1.12
0.01	260	97.1	0.899
0.09	260	99.5	1.26

the peak height from the "unbroadened" value and yields a value of B.I. greater than 1. The greater the broadening, the larger is the B.I. value. Should the sample give a narrower peak than the trialkyl ester standard, the B.I. will be less than 1.

Table III shows that methylation efficiency is high for all concentrations of TMPAH used to methylate DMPDT,K. The peaks are sharper when the higher block temperature (260 °C) is employed. Methylation results from pyrolysis of the trimethylphenylammonium salts of the analyte anions at the head of the column which is within the block region. At a 220 °C inlet temperature methylation occurs over a period of time sufficient to broaden the peaks and slightly increase the retention time compared to the methyl ester standard. At 260 °C, pyrolysis is rapid and the peaks of the methylated salts are sharp, although still late compared to the trialkyl ester standard. At the higher temperature and 0.01 M TMPAH, approximately 6% of *O,O,O*-trimethyl phosphorothionate and 2% of *O,S,S*-trimethyl phosphorodithioate are formed at the expense of the efficiency of formation of *O,O,S*-trimethyl phosphorodithioate. At the 0.09 M level of TMPAH at 260 °C, about 9% *O,S,S*-trimethyl phosphorodithioate is formed. The identities of both of these side reaction products are inferred from retention time comparisons with authentic standard esters.

Table IV reveals efficiency data for the formation of *O,O,S*-trimethyl phosphorothiolate from potassium *O,O*-dimethyl phosphorothioate. The methylation occurs exclusively on the sulfur of the bidentate anion and in high yield, except for the 0.0001 M TMPAH concentration. In this case the reaction is only 60% efficient at the higher temperature, but still no O-methylation occurs to form *O,O,O*-trimethyl phosphorothionate.

As for the DMPDT,K case, higher block temperature produces sharper peaks, and higher concentrations of TMPAH at 220 °C give broad, late peaks. However, there appear to be no side reaction products at the higher concentration of TMPAH and 260 °C in contrast to the DMPDT,K results. Both TMPDT and TMPTh elute at around 115 s under the reported conditions for the 5% OV-225 column. The use of 3% OV-275 selectively retards the TMPTh and allows easy resolution of a mixture of the compounds.

Plotting of peak area response vs. volume of 5.96 ng/μL of potassium *O,O*-dimethyl phosphorodithioate in 0.01 M methanolic TMPAH yielded a straight line. A similar peak height response plot showed response per nanogram injected falling off as the amount injected increased. This is consistent with earlier expressed observations that increased quantities of TMPAH in an injection can contribute to peak broadening (Table III). A linearity check utilizing the same injection volume of differing concentrations of potassium *O,O*-dimethyl phosphorodithioate in 0.01 M TMPAH showed linear plots of response vs. nanograms injected both by peak area and peak height.

The response curves for the methylation of DMPT,K were exactly analogous to those for DMPDT,K.

The above efficiency and linearity data provide guidelines in the use of TMPAH methylation for quantification of dialkyl phosphorothioates. In practice, samples containing the dialkyl phosphorothioates are ultimately diluted in methanolic TMPAH and compared by GLC to the corresponding dialkyl phosphorothioate standard similarly diluted. The best concentration of TMPAH to employ lies in the range of 0.001 to 0.01 M, sufficient to allow efficient methylation without causing the intrusion of side reactions and peak broadening seen at higher concentrations. Further, higher concentrations unnecessarily burden the GLC column, although no adverse effect on column life has been noted.

If one compares samples and standards on the basis of peak heights, then the TMPAH concentration and the injection volume should be the same for both, to cancel peak broadening effects. If one quantifies by peak area, neither TMPAH concentration nor injection volume need to be controlled particularly closely. The higher injection block temperature employed (260 °C) gave sharper peaks and is, therefore, more desirable.

With an inlet temperature of 260 °C and reagent concentration of 0.01 M TMPAH in methanol, the minimum detectable limit for both DMPDT,K and DMPT,K is 300 pg.

Methanolic TMPAH quantification of dialkyl phosphorothioates and phosphorodithioates should provide a safe, convenient alternative to the use of diazomethane in a final methylation step in the analysis of these pesticide metabolites.

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