yield with improved GC characteristics. By this criteria, the reaction of TFAA with compounds containing a sulfoxide group appears to offer some real advantages for both GC quantitation and confirmatory tests, together with increased sensitivity to electron-capture detection.

As this study shows, most pesticides with a sulfoxide moiety react readily with TFAA under mild conditions (RT/15 min) to give a product, the nature of which is dependent on the type of substitution. Regardless of the ease of the Pummerer reaction, the presence of an NH group in the same molecule necessitated forcing conditions (100 °C) to form the di-TFA derivative in order to obtain a single product. Although phorate and Counter sulfoxide do not undergo the normal Pummerer reaction with TFAA, the reaction is both rapid and complete, thus providing a good confirmatory test. This also holds for the reaction of oxydemeton-methyl, which forms two dehydro products due to thermal decomposition.

The last figure (Figure 9) illustrates an application of the Pummerer reaction for the chemical confirmation of dasanit residues in soil. Analysis of a sandy loam soil extract after clean-up showed the presence of the insecticide (t_R 9 min) at a level of 1.1 ppm. Treatment of the extract with TFAA (RT/15 min) gave the TFA derivative with a t_R of 2.31 min (Dasanit TFA standard t_R, 2.34 min). The impurity present in the extract was not affected by TFAA and its retention time remained the same at 11.1 min.

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Gas Chromatographic Determination of Organophosphorus Pesticides by In-Block Methylation

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Microgram quantities of selected organophosphate, phosphorothioate, and phosphorodithioate pesticides were mixed with methanolic solutions of trimethylanilinium hydroxide (TMAH) and injected into a gas chromatograph equipped with a phosphorus-sensitive flame photometric detector. The efficiency of the reaction of TMAH with the various pesticides was determined by measurement of the quantity of trialkyl phosphates formed. The efficiency of the in-block reaction in 0.01 M TMAH varied from 61% for phoxim to 100% for azinphosmethyl. The rate of reaction of the pesticides with TMAH at ambient temperatures was also determined. Under these conditions the rate varied from 0% per day for malathion to 75% per day for chlorphoxim. The derivitization technique is useful for the identification and quantitation of many organophosphorus pesticides.

Brochmann-Hanssen and Oke (1969) developed a method for determination of barbituates, phenolic alkaloids, and xanthene bases based on the methylation of these materials with trimethylanilinium hydroxide (TMAH) in the block of a gas chromatograph. Prior to this, tetramethylammonium hydroxide (TAH) was used in a similar manner for determination of carboxylic acids by Robb and Westbrook (1963), for barbituates by Stevenson (1966), and for purine and pyrimidine bases by McGee (1966). It was concluded that TMAH was superior to TAH as a methylating agent when used in this manner. The first use of TMAH for analysis of a pesticide was reported by Dale et al. (1976), who used the technique for analysis of residues of chlorphoxim. They found that TMAH in methanol solution reacted slowly with chlorphoxim at room temperature to form diethyl methyl thiophosphate (DEMTP) but reacted instantaneously when injected into the block of a gas chromatograph at 280 °C. The efficiency of the in-block reaction varied from 40% in 0.0005 M TMAH to 74% in 0.1 M TMAH. The purpose of the present work was to explore the use of TMAH as a derivitizing reagent for other pesticides.

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EXPERIMENTAL SECTION

Apparatus. Gas chromatograph, Micro-Tek MT-220, equipped with a Melpar flame photometric detector with interference filter for spectral isolation of phosphorus emission at 526 nm. Chromatographic columns: 6 ft × 0.25 in. o.d. aluminum packed with 5% OV-225 on 100–120 mesh Chromosorb W (HP) and 6 ft × 0.25 in. o.d. aluminum packed with 3% OV-275 on 100–120 mesh Chromosorb W (HP). Inlet and outlet blocks were maintained at 280 °C, detector 280 °C; nitrogen carrier gas 145 mL/min at 70 psi; hydrogen 50 mL/min at 20 psi; and

oxygen 25 mL/min at 40 psi.

Reagents. (a) *Chlorphoxim.* Chemagro Corp., Kansas City, Mo. Recrystallized from benzene–hexane (1:1); mp 65.8 °C. (b) *Phoxim.* Analytical standard. Chemagro Corp. (c) *Malathion and Temephos (Abate).* Analytical standards, 99%. American Cyanamid Co., Princeton, N.J. (d) *Dichlorvos (DDVP), 99%, and Mevinphos (Phosdrin), Technical Grade.* Shell Chemical Co., Modesto Calif. (e) *Parathion, Methyl Parathion, Chlorpyrifos-methyl (Reldan), and Azinphosmethyl (Guthion).* Analytical reference standards. Quality Assurance Section, EPA, Research Triangle Park, N.C. (f) *Trimethyl Dithiophosphate (TMDTP).* American Cyanamid Co. (g) *Trimethyl Phosphate (TMP).* ICN Life Sciences Group, Plainview, N.Y. (h) *Diethyl Methyl Thiophosphate (DEMTP).* Prepared by refluxing 10 mL of diethyl chlorothiophosphate with 100 mL of anhydrous methanol for 2 h. After evaporation of HCl and excess methanol, product was distilled at 47.2 °C at 0.9 mmHg. (i) *Trimethyl Thiophosphate (TMTP).* Prepared by the same procedure used to prepare DEMTP with dimethyl chlorothiophosphate and methanol as starting reagents. Product distilled at 27.5 °C at 0.25 mmHg. (j) *Trimethylanilinium Hydroxide (TMAH).* 0.1 M in methanol. Eastman Organic Chemicals, Rochester, N.Y.

Procedures. Standard solutions containing known quantities of each of the selected pesticides were prepared in absolute methanol. Solutions of TMAH in absolute methanol were prepared by serial dilution of 0.1 M TMAH. Appropriate volumes of the pesticide solutions were added to the TMAH solutions to give a series of solutions containing 1 to 10 μg/mL of the given pesticide in TMAH ranging in concentration from 0.0001 to 0.1 M. Aliquots of each of these solutions were injected into the gas chromatograph operated under the conditions described above. Standard solutions of each of the expected methyl derivatives were prepared in methanol and injected into the gas chromatograph to establish standard curves. The OV-225 column was used for analysis of TMDTP, DEMTP, and TMTP and pesticides yielding these esters. The OV-275 column was used for analysis of TMP and pesticides yielding this ester.

The heights of the peaks of the methyl derivatives formed when the pesticide–TMAH mixtures were injected into the chromatograph were compared with those of the pure methyl derivatives to determine the efficiency of the in-block derivitization.

The pesticide–TMAH mixtures were then allowed to stand at room temperature for 24 h and aliquots were again injected and the efficiency determined as described above. This experiment was repeated after allowing the solutions to stand for 48 h. An increase in efficiency was an indication that some reaction was taking place between the TMAH and the pesticide at room temperature.

In another series of experiments the samples of the various pesticides were prepared in 0.01 M solutions of TMAH in methanol and allowed to stand for periods up to 96 h. Aliquots of the solutions were taken periodically and analyzed for the expected derivative. This was accomplished by adding water to the methanol solutions and extracting the methyl derivatives with hexane.

RESULTS AND DISCUSSION

Parathion and chlorphoxim react with TMAH to form DEMTP. The efficiency of the in-block reaction with parathion increases with increasing concentrations of TMAH up to 0.02 M. The efficiency also increases with the time TMAH and parathion are in contact, which shows that some reaction is taking place at room temperature.

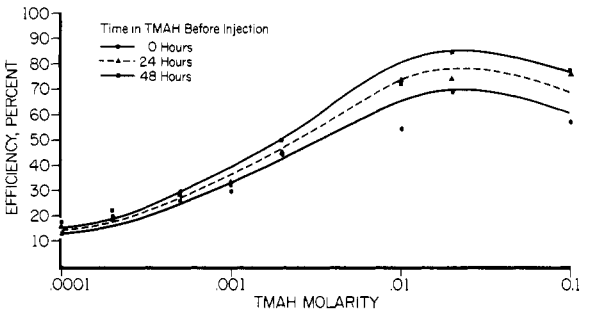

Figure 1. The efficiency of the in-block methylation of parathion in various concentrations of TMAH in methanol.

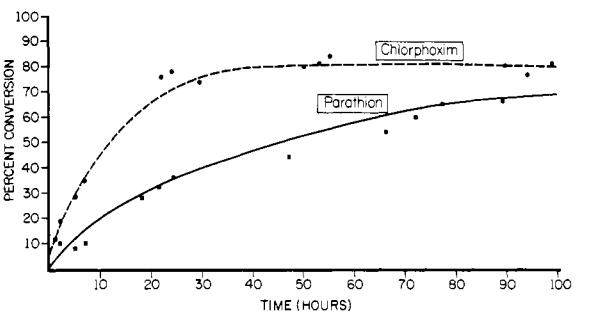

Figure 2. Rate of reaction of chlorphoxim and parathion with 0.01 M TMAH in methanol at room temperature.

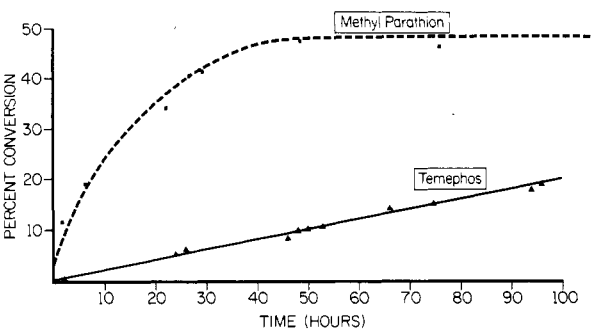

Figure 3. Rate of reaction of methyl parathion and temephos with 0.01 M TMAH in methanol at room temperature.

The efficiency of the reaction of parathion with varying concentrations of TMAH is shown in Figure 1. Chlorphoxim reacts in-block with TMAH in a similar manner; however, the maximum efficiency is reached in 0.1 M TMAH. Chlorphoxim also reacts slowly with TMAH at room temperature. The rate of reaction of parathion and chlorphoxim with TMAH at room temperature is shown in Figure 2. The formation of the derivative, DEMTP, was measured by extraction of the solutions with hexane and injection of the extract into the gas chromatograph.

Temephos and methyl parathion react with TMAH to form TMTP. The efficiency of the in-block methylation of methyl parathion is slightly higher than parathion. The efficiency of this reaction reaches a maximum in 0.02 M TMAH and as in the case of parathion, increases with time in contact at room temperature. The efficiency of the in-block methylation of temephos increases with increasing concentration of TMAH up to 0.01 M. No appreciable enhancement of efficiency was observed in solutions of temephos held 24 and 48 h prior to injection. The rate of reaction of temephos and methyl parathion at room temperature is shown in Figure 3. In 24 h only about 5% of temephos is converted to TMTP.

Malathion and azinphosmethyl react with TMAH to form TMDTP. Azinphosmethyl reacts with TMAH in the block with high efficiency, approaching 100% in 0.002 to

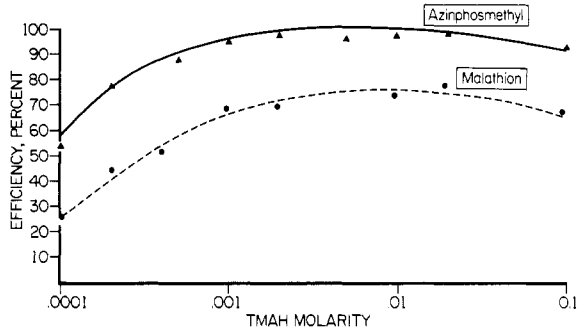

Figure 4. The efficiency of the in-block reaction of azinphosmethyl and malathion in various concentrations of TMAH in methanol.

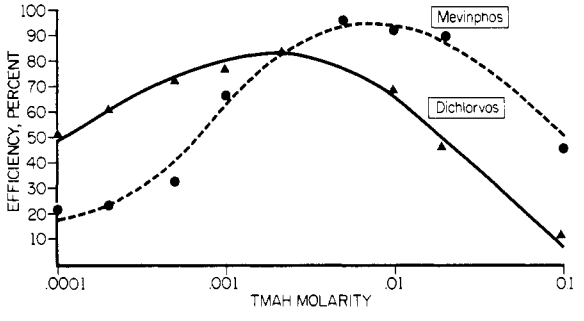

Figure 5. The efficiency of the in-block methylation of mevinphos and dichlorvos in various concentrations of TMAH in methanol.

0.02 M TMAH. The in-block reaction of malathion with TMAH is less efficient than that of azinphosmethyl as shown in Figure 4. Interestingly, neither malathion nor azinphosmethyl react with TMAH at room temperature. When these pesticides were left in contact with 0.01 M TMAH for 96 h, no TMDTP was found.

Dichlorvos and mevinphos react with TMAH to form TMP. The efficiency of the in-block reaction with mevinphos is very high in concentrations of 0.005 to 0.01 M. Dichlorvos reacts in a similar manner; however, maximum efficiency was reached at lower concentrations of TMAH. The efficiencies of the reactions of dichlorvos and mevinphos with TMAH are shown in Figure 5. Trimethyl phosphate is not extracted by hexane from an aqueous–alcohol solution and the rate of reaction of dichlorvos and mevinphos at room temperature was not measured.

In addition to the pesticides mentioned above, phoxim and chlorpyrifos-methyl were mixed with 0.01 M TMAH in methanol and injected into the gas chromatograph. The efficiencies of the reactions of these compounds along with the others described above are presented in Table I. The efficiencies ranged from 61% for phoxim to 100% for azinphosmethyl.

Solutions of dimethyl dithiophosphoric acid and its potassium salt were prepared in 0.01 M TMAH and injected into the gas chromatograph. In both cases the expected derivative, TMDTP, was formed in the block. The mechanism of the in-block pesticide derivatization, however, is different from that of salt methylation. Studies on these mechanisms and the application of in-block methylation to the determination of the dialkyl phosphate and thiophosphate degradation products of organophosphorus pesticides are in progress.

Table I. Efficiency of the In-Block Reaction of Various Pesticides in 0.01 M TMAH

Compound	Derivative	Efficiency, %
Phoxim	DEMTP	61
Temephos	TMTP	64
Parathion	DEMTP	65
Chlorphoxim	DEMTP	66
Dichlorvos	TMP	68
Malathion	TMDTP	76
Methyl Parathion	TMTP	76
Mevinphos	TMP	94
Chlorpyrifos-methyl	TMTP	95
Azinphosmethyl	TMDTP	100

SUMMARY AND CONCLUSIONS

TMAH reacts with most organophosphorus pesticides to form short-chain trialkyl phosphates which can easily be separated and quantitated by gas chromatography. In most cases, the reaction takes place in the block of the gas chromatograph with high efficiency. Many of the pesticides react slowly with TMAH at room temperature; however, malathion and azinphosmethyl gave no measurable yield of the expected derivative after 96 h in contact with TMAH at 25 °C. The derivatization technique is useful for confirmation of the identity of organophosphorus pesticides and for their quantitation. In practice, one may quantify samples of a pesticide of interest by simultaneously diluting the pesticide standards and samples in methanolic TMAH and then performing the GLC analysis.

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