Reaction Gas Chromatographic Analysis of Pesticides. I.

On-Column Transesterification of *N*-Methylcarbamates by Methanol

H. A. Moye

A method is described for the on-column transesterification of *N*-methylcarbamate pesticides to methyl *N*-methylcarbamate, chromatography on Porapak P, and detection by Rb_2SO_4 pellet alkali flame ionization detector. Reproducible high yields were obtained for transesterification with methanol. Distinguishing gas chromatographic peaks were also obtained when an *N*-methylcarbamate pesticide was injected in ethanol, 1-propanol, and *n*-butanol.

Procedures for the gas chromatographic analysis of *N*-methylcarbamate pesticides have been developed which employ gas chromatography of the intact carbamate (Riva and Carisano, 1969; Strother, 1968; Zielinski and Fishbein, 1965a,b,c) or gas chromatography of a derivative of the carbamate (Bowman and Beroza, 1967; Crosby and Bowers, 1968; Tilden and Van Middelem, 1970). Generally the derivative is designed to make the carbamate sensitive to detection by either the electron capture detector (Crosby and Bowers, 1968; Tilden and Van Middelem, 1970) or the flame photometric detector (Bowman and Beroza, 1967).

Carbamates have been used by the polyurethane industry to provide a blocked, capped, or disguised isocyanate which, upon heating to temperatures in the 150° to 200° C range, would split to produce the isocyanate (Saunders and Frisch, 1967)

$$RNHCOOR' \xrightarrow{\Delta} RNCO + R'OH$$

This type of decomposition is predominant when R′ is an aryl group, which is the case for nearly all carbamate pesticides.

Another reaction exhibited for certain carbamates is the transesterification type (Gaylord and Sroog, 1953).

$$RNHCOOAr + R'OH \quad RNHCOOR' + ArOH$$

The term reaction gas chromatography was coined in 1960 (Drawert *et al.*, 1960) and has evolved to include any structural change of a compound occurring within the gas chromatograph. High temperature pyrolysis of a compound to obtain a fingerprint is the most common technique and is used frequently in the petroleum industry.

Esposito and Swann (1969) formed trimethylsilyl derivatives of some polyols by an on-column reaction. More recently, Jaglan and coworkers (1969) esterified the desalkyl metabolites of methyl parathion and methyl paraoxon on a gas chromatographic column.

The work described here investigates the possibilities of analyzing *N*-methylcarbamate pesticides by either thermally degrading them to methyl isocyanate or transesterifying them with a unique method for the analysis of carbamates at levels as low as 10^{-9} g by on-column transesterification, with methanol giving reproducibly high yields.

Department of Food Science, University of Florida, Gainesville, Fla. 32601

EXPERIMENTAL

A Varian model 1200 gas chromatograph was used with the rubidium sulfate alkali flame ionization detector, which is specific for organic nitrogen or phosphorus.

All solid supports and liquid phases were obtained from Applied Sciences, State College, Pa., as were the 80/120 mesh regular glass beads. The Porapak and Porasils were obtained from Waters Associates, Framingham, Mass.

The carbamate pesticides were obtained from their respective manufacturers in 99%+ form. The methyl *N*-methylcarbamate was made by addition of methyl isocyanate to methanol at room temperature.

RESULTS

A search was made for a gas chromatographic column that would efficiently separate the expected *N*-methylcarbamate decomposition product, methyl isocyanate, from the various common laboratory solvents which are used for extracting carbamate pesticides from agricultural products. These solvents were ethanol, acetone, ethyl ether, ethyl acetate, benzene, hexane, isopentane, methanol, and isopropyl alcohol. A great many activated charcoals were tested for gas–solid chromatography of methyl isocyanate, without measurable success. Also, the commercially available liquid phases that were obtained were tested. Of 15 liquid phases tested, none was able to separate satisfactorily methyl isocyanate from all the solvents used. Porasil C and D were also unsuccessful in separating the solvents from methyl isocyanate.

Porapaks P, Q, S, and QS were tested, and only Porapak P was able to perform the separations. Methyl isocyanate gave the same retention time in all the solvents listed except for the alcohols. Methanol, ethanol, and isopropyl alcohol gave methyl isocyanate peaks of different retention times and in the order methanol < ethanol < 1-propanol. When large amounts of methyl isocyanate were added to methanol, it was observed that an exothermic reaction was taking place. The reaction product had a melting point and infrared absorption spectrum identical to methyl *N*-methylcarbamate.

A preliminary test of Mobam (4-benzothienyl *N*-methylcarbamate) injected onto the Porapak P column in methanol gave a peak identical in retention time to that of methyl *N*-methylcarbamate. When injected in large amounts, in ethyl ether a small peak appeared where methyl isocyanate should be, but no peak occurred where methyl *N*-methylcarbamate was located. It appeared then that the methanol was reacting with the Mobam to give methyl *N*-methylcarbamate. This

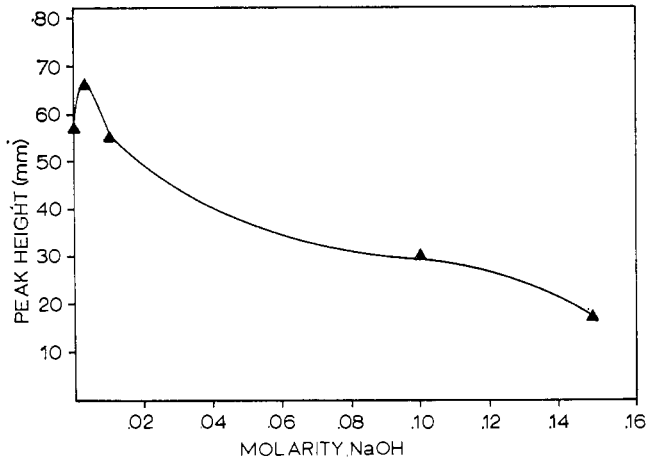


Figure 1. Effect of sodium hydroxide concentration in 98% methanol on response of 100 ng of Mobam

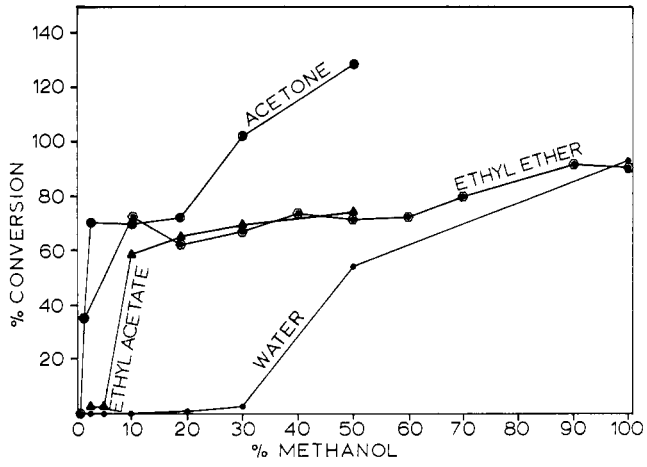


Figure 3. Effect of other solvents on Mobam conversion efficiency in methanol-sodium hydroxide

was confirmed by trapping the eluting peak in an air-cooled capillary tube and comparing the infrared and nmr spectra with those of methyl *N*-methylcarbamate. They were identical.

The various parameters which might be involved in the gas phase reaction of Mobam with methanol were studied. These were: injection port packing; sodium hydroxide concentration; injection port temperature; solvent effects; and presence of crop coextractives. The percentage conversion of Mobam was studied as a function of Mobam concentration in methanol as were the percent conversions of Mobam in ethanol, isopropyl alcohol, *tert*-butanol, and *n*-butanol.

Injection Port Packing. When Mobam was injected onto the Porapak column with crop (lettuce) coextractives present, very poor yields of methyl *N*-methylcarbamate resulted, on the order of a few percent of theoretical at the 100 ng level. The first 6 in. of the glass column were packed with the following materials and checked for their ability to aid in the conversion of Mobam in the presence of crop coextractives: glass wool; silanized glass wool; glass beads; sodium hydroxide treated glass beads; phosphoric acid treated glass beads; Fluoropak; High Performance Chromosorb W; and Porasil C (porous glass beads). No measurable conversion was obtained for glass wool, phosphoric acid treated glass beads, or porous glass beads. For those materials which have a detectable amount of methyl *N*-methylcarbamate upon the injection of 100 ng Mobam in lettuce extract, the conversion efficiency followed the order: sodium hydroxide treated glass beads > silanized glass wool > untreated glass beads > Fluoropak > High Performance Chromosorb W. The conversion efficiency for 100 ng of Mobam in lettuce extract was 60% on the first injection onto clean sodium hydroxide treated glass beads; however, this gradually diminished upon subsequent injections.

It was felt that the sodium hydroxide, which was providing a catalytic surface for the reaction of Mobam with methanol, was gradually becoming coated with crop coextractives upon repeated injections.

Sodium Hydroxide Concentration. Figure 1 shows the effect of NaOH concentration in a methanol-water standard of Mobam at 100 ng/μl. The water was held constant at 2% volume. For this study, untreated glass beads were used in the injection port. Equally good conversion efficiency was obtained and maintained for Mobam in the presence of lettuce extract (which did not deteriorate upon repeated lettuce extract injections) when the optimum amount of sodium hydroxide was present in the sample. Addition of small amounts of either HCl or H_2SO_4 to the methanolic Mobam created no enhancement of conversion over that obtained when methanolic Mobam was injected without any catalyst.

Injection Port Temperature. Figure 2 shows the effect of injection port temperature on the conversion efficiency of

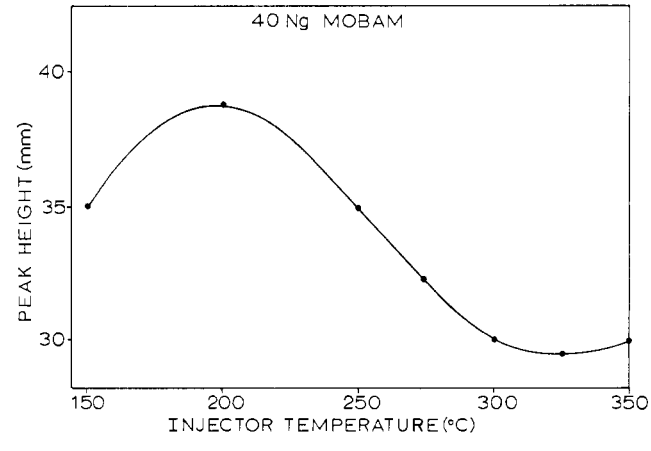


Figure 2. Effect of injection port temperature on the conversion efficiency of 40 ng of Mobam

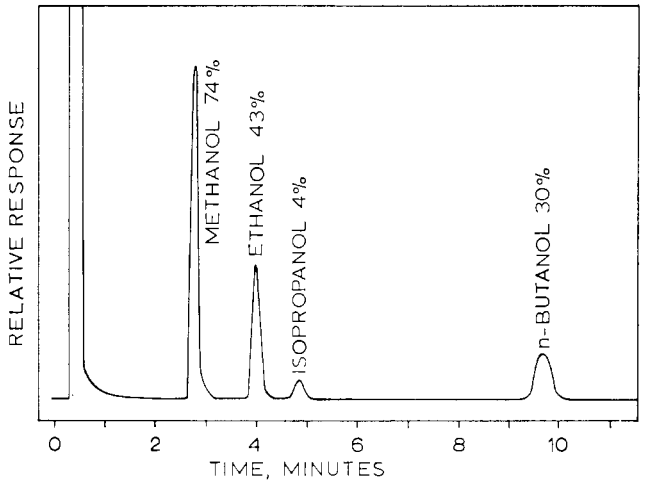


Figure 4. Peaks obtained upon individual injections of Mobam in various alcohols

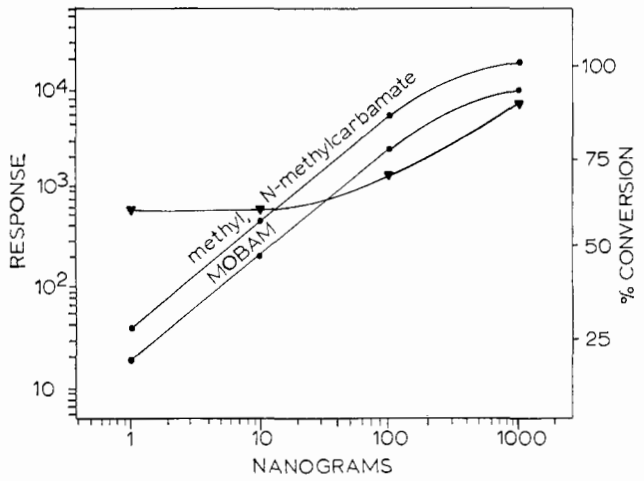


Figure 5. Extended range analytical curves of Mobam and methyl *N*-methylcarbamate ●, and Mobam percent conversion, ▼

Mobam. An optimum temperature of 215° C was determined although good conversion occurs at temperatures as low as 150° C. On several types of crop extracts that were analyzed, it was possible to markedly reduce crop contaminant peaks by lowering the injection port temperature to 150° C. This probably provided a sweep codistillation type of cleanup on the glass beads in the injection port, trapping some of the involatiles at the lower temperature.

Solvent Effects. In the analysis of crops for carbamate pesticides, solvents other than methanol are generally recommended for extraction. Since methanol is required for the conversion to methyl *N*-methylcarbamate, a study was done to see what effect various extraction solvents would have when mixed with methanol-NaOH containing 100 ng of Mobam As seen in Figure 3, for all the solvents studied other than water, yields of greater than 55% are obtained with as little as 10% methanol by volume. Acetone appears even to enhance the conversion or improve the chromatography of Mobam when present in the 50 to 75% range, as compared to methanol alone The appropriate amount of aqueous NaOH was included in these solvent pair samples

Alcohols other than methanol will react with Mobam in the injection port of the chromatograph. Figure 4 shows peaks obtained by making Mobam up in ethanol, isopropyl alcohol, and *n*-butanol. *Tert*-butanol produced no peak.

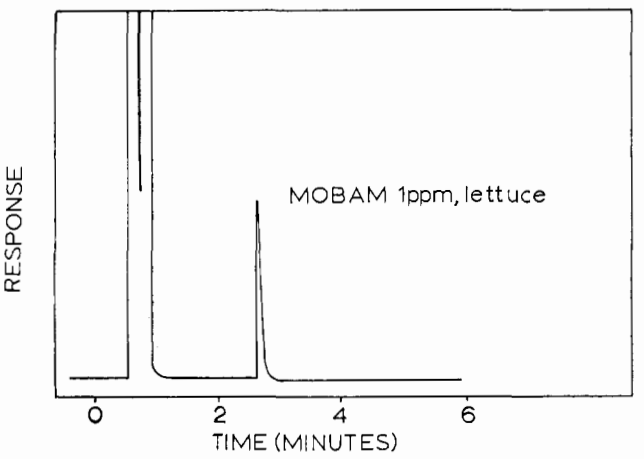


Figure 6. Chromatogram of Mobam extracted from lettuce

Table I. Transesterification Conversion Efficiencies of Carbamate Pesticides

Carbamate	Nanograms	% Conversion
U.C. 10854 (3-isopropylphenyl *N*-methylcarbamate)	33.9	78
Furadan (2,2-dimethyl-2,3-dihydrobenzofuranyl-7 *N*-methylcarbamate)	38.8	87
Mobam (4-benzothienyl *N*-methylcarbamate)	36.3	81
Sevin (1-naphthyl *N*-methylcarbamate)	35.1	79
Zectran (4-dimethylamino-3,5-xylyl *N*-methylcarbamate)	38.9	78
Bayer 37344 (4-methylthio-3,5-xylyl *N*-methylcarbamate)	39.5	76
Tranid [*exo*-3-chloro-*endo*-6-cyano-2-norbornanone-*O*-(methylcarbamoyl)-oxime]	42.4	76
Temik [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime]	33.4	58
Matacil (4-methylamino-*m*-tolyl *N*-methylcarbamate)	36.5	80

These peaks would presumably be ethyl *N*-methylcarbamate, isopropyl *N*-methylcarbamate, and *n*-butyl *N*-methylcarbamate, respectively, although they were not trapped and identified as such.

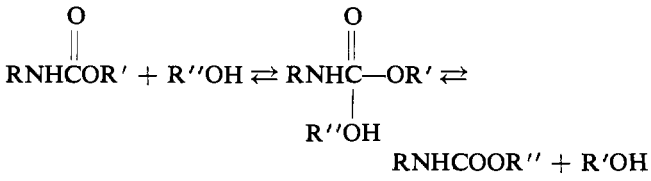
Conversion Efficiency and Linearity of Response. After the solvent, injector temperature, injector packing, and NaOH concentrations were optimized for Mobam conversion, a survey was made of the available *N*-methylcarbamate pesticides for conversion efficiency. Table I shows the results obtained. An amount of carbamate was injected so as to give a theoretical yield of 14 ng of methyl *N*-methylcarbamate. Also included in the table are Temik and Tranid. Temik [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)-oxime] gave a peak corresponding to methyl *N*-methylcarbamate and also a second peak with almost twice the retention time of methyl *N*-methylcarbamate. Tranid [3-chloro-6-cyano-2-norbornanone *O*-(methylcarbamoyl)oxime] gave only the characteristic methyl *N*-methylcarbamate peak. The percentage conversion is calculated on the first peak only.

A 36-ng Mobam standard was injected six consecutive times with a relative standard deviation in response of 1.7%. An extended range analytical curve is shown in Figure 5, along with the percentage conversions obtained.

Crop Extract. Lettuce was extracted after spiking with Mobam at 1 ppm. Methanol was used as the extraction solvent. Figure 6 shows the chromatogram obtained when the extract was injected. Methanol was the injection solvent made 5×10^{-3} *M* with NaOH. The 5 ft × 1/8 in. glass column of 80/100 Porapak P had the first 6 in. packed with untreated glass microbeads. The instrument temperatures were: injector, 220° C; detector, 225° C; column, 180° C. The gas flow rates were: He (carrier), 27 ml/min; H_2, 25 ml/min; air, 188 ml/min. The electrometer was operated at 16×10^{-12} AFS. Although the extract was highly colored and viscous, no extraneous peaks could be seen.

DISCUSSION

A mechanism for an ester interchange or transesterification of carbamates subject to basic catalysis has been proposed by Gaylord and Sroog (1953). They claim a carbonyl addition of the type



This reaction is favored when R′ is aromatic rather than aliphatic.

Attempts to perform the transesterification between Mobam and methanol by refluxing with various amounts of NaOH at atmospheric pressure were unsuccessful. The Mobam would simply hydrolyze to methylamine and an unidentified product or products.

The on-column transesterification reaction is not impeded by the presence of large amounts of coextractives; no differences can be seen in percent conversions of Mobam with and without crop present. The technique has been routinely used in this laboratory and in soil. The only difficulties encountered have been precipitation of waxes from the methanolic extract upon addition of aqueous NaOH. This was eliminated when a small amount of methanol was used in a large amount of ethyl acetate or ethyl ether.

The procedure described here is unique in that an easily chromatographed derivative of the carbamate pesticide is formed with facility in the chromatograph injection port which would otherwise be difficult or impossible to form in a reaction vessel. The conversion is near quantitative, even at the 1 ng level, and is as reproducible as injections not involving on-column reaction. No reagents are required for the transesterification of the carbamate on the injection port other than the methanolic NaOH, which is completely compatible with the rubidium sulfate nitrogen detector. The lack of column bleed from the Porapak P allows extended use of the rubidium sulfate salt tip without repacking. The chromatographic qualities of the Porapak P did not seem to be appreciably altered even when discolored by crop extractives, allowing continued use without column repacking.

This procedure should be useful when a survey of a suspect sample is desired to confirm or deny the presence of any *N*-methylcarbamate pesticide. It has been useful in this laboratory for those cases where disappearance curves of a single carbamate are desired after known applications to a field crop.

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