GAS CHROMATOGRAPHY OF TRIMETHYLSILYL DERIVATIVES

I. PESTICIDAL CARBAMATES AND UREAS

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Silylation of diverse functions such as hydroxyl, amine and amide has been known for some time as an acknowledged organic procedure[1–3]. The development of gas chromatography, however, has resulted in recent years in the increased utility of trimethylsilyl derivatives in the analytical separation and measurement of steroids[4–7], amino acids[8,9], carbohydrates[10–14], phenols[15–20], alcohols[21,22], biological amines[23–25] and monoglycerides and fatty acids[26]. Organic compounds possessing sufficiently active proton substitution sites undergo facile silylation with the observed effects of enhanced volatility, stability and decreased polarity in the molecular structure.

In view of the attention being given to the area of the analysis of pesticides and because of the possibility of the enhancement of chromatographic results via silylation, the present study was undertaken to evaluate the behavior of the trimethylsilyl derivatives of pesticidal carbamates and ureas on gas chromatographic columns. The preparation of silyl derivatives of simple non-pesticidal carbamates and ureas has been reported[27,28] by other workers.

EXPERIMENTAL

Samples of the carbamates and ureas were obtained from commercial sources and purified by recrystallization. The carbamates included were Sevin (α-naphthyl N-methyl carbamate), IPC (isopropyl N-phenyl carbamate), CIPC (isopropyl N-3-chlorophenyl carbamate) and Zectran (4-dimethylamino-3,5-xylyl N-methyl carbamate). The pesticidal ureas were Monuron (N,N-dimethyl-N′-4-chlorophenyl-urea), Diuron (N,N-dimethyl-N′-3,4-dichlorophenyl-urea) and Hercules 7531 (N,N-dimethyl-N′-hexahydro-4,7-methanoindan-5-yl-urea). The trimethylsilyl derivatives of the purified standards were reacted in pyridine with hexamethyldisilazane in the presence of trimethylchlorsilane[11]. The reaction mixture was chromatographed directly.

The separations were performed alternately on 4% QF-1 (on 80–100 mesh HMDS-pretreated Chromosorb W), 4% SE-30 (on 80–100 mesh HMDS-pretreated Chromosorb W) and 3% Carbowax 20M (on 60–80 mesh acid-washed, DCMS-pretreated Chromosorb G). The columns were 6 ft. by 0.25 in. coiled pyrex glass tubes (Applied Science Laboratories, State College, Pa., U.S.A.). The QF-1 and SE-30 columns were purchased commercially prepacked, while the 3% Carbowax 20M column packing was prepared and the column packed in our laboratory. The columns were employed with an F & M model 1609 flame ionization gas chromatograph. Specific column operating conditions for chromatography are given in the footnotes to Table I.

RESULTS AND DISCUSSION

The preparation of trimethylsilyl (TMS) derivatives of carbamates and ureas may be illustrated by the general exchange reaction between the acceptor and silyl donor, as follows:

$$(CH_3)_3SiNHSi(CH_3)_3 + R_1\overset{H}{\underset{|}{N}}R_2 \rightleftarrows 2\ R_1\overset{Si(CH_3)_3}{\underset{|}{N}}R_2 + NH_3$$

Owing to the known effect of silylation producing derivatives of diminished polarity characteristics, one would expect concomitant decreases in chromatographic elution times when contrasting the elution values of TMS derivatives with those of the respective parent compounds. Gas chromatographic analyses were carried out on both the specific pesticidal carbamate or urea and its respective TMS derivative. The results for the carbamates are given in Table I; those for the ureas are given in Table II. Table I also includes values for α-naphthol and its TMS derivative since this compound is known to form from the thermal degradation of Sevin during its analysis by gas chromatography at high column temperatures[29,30].

On examining the data given in Tables I and II, one may observe that the

TABLE I

CHROMATOGRAPHY OF PESTICIDAL CARBAMATES AND THEIR TMS DERIVATIVES

Compound	*Mol. wt.*	*QF-1*[a]		*SE-30*[b]		*Carbowax 20M*[c]	
		Elution (min)	*Relative elution*[d]	*Elution (min)*	*Relative elution*[d]	*Elution (min)*	*Relative elution*[d]
Zectran[e]	222	2.02, 22.4	0.58, 6.4	2.70, 9.30	1.0, 3.4	4.86, 19.80	1.2, 4.9
TMS-Zectran[e]	294	1.46, 2.75	0.42, 0.79	2.56, 0.94	1.0, 0.35	4.86, 19.70	1.2, 4.9
α-Naphthol	144	3.55	1.0	3.24	1.2	20.30	5.0
TMS-α-naphthol	216	3.30	1.0	3.81	1.4	1.62	0.40
Sevin	201	3.80	1.1	3.35	1.2	20.35	5.0
TMS-Sevin	273	3.41	1.0	3.86	1.4	1.67	0.41
IPC	179	3.34	1.0	2.62	1.0	4.01	1.0
TMS-IPC	251	3.50	1.0	2.70	1.0	4.05	1.0
CIPC	213	8.28	2.4	6.83	2.5	11.75	2.9
TMS-CIPC	285	8.14	2.4	6.72	2.5	11.71	2.9

[a] 4% w/w on 80–100 mesh Chromosorb W (HMDS pretreated), 6 ft. by 0.25 in. O.D. glass column. Operating conditions: column 130°; injection port 50 V (cartridge-heated block); detector 220°; range 1000; nitrogen carrier 85 ml/min; hydrogen 54 ml/min; air 500 ml/min.
[b] 4% w/w on 80–100 mesh Chromosorb W (HMDS pretreated), 6 ft. by 0.25 in. O.D. glass column. Operating conditions: column 130°; injection port 50 V (cartridge-heated block); detector 220°; range 1000; nitrogen carrier 90 ml/min; hydrogen 57 ml/min; air 500 ml/min.
[c] 3% w/w on 60–80 mesh Chromosorb G (acid-washed, DMCS pretreated), 6 ft. by 0.25 in. O.D. glass column. Operating conditions: column 170°; injection port 50 V (cartridge-heated block); detector 220°; range 1000; nitrogen carrier 110 ml/min; hydrogen 72 ml/min; air 500 ml/min.
[d] Relative to TMS-IPC as 1.0. TMS-IPC eluted at 3.5 min on QF-1, 2.7 min on SE-30 and 4.05 min on Carbowax 20M.
[e] Major peak underlined.

TABLE II

CHROMATOGRAPHY OF PESTICIDAL UREAS AND THEIR TMS DERIVATIVES

Compound	*Mol. wt.*	*QF-1*[a]		*SE-30*[b]		*Carbowax 20M*[c]	
		Elution (min)	*Relative elution*[d]	*Elution (min)*	*Relative elution*[d]	*Elution (min)*	*Relative elution*[d]
Monuron	198	0.73	0.21	0.78	0.29	1.13	0.28
TMS-Monuron	270	0.77	0.22	0.94	0.35	1.13	0.28
Diuron	232	1.61	0.46	2.16	0.80	[e]	—
TMS-Diuron	304	1.96	0.56	2.43	0.90	[e]	—
Hercules 7531	210	2.76	0.79	2.75	1.02	1.38	0.34
TMS-Hercules 7531	282	2.80	0.80	2.62	0.97	1.34	0.33

[a] See Table I, footnote a.
[b] See Table I, footnote b.
[c] See Table I, footnote c.
[d] Relative to TMS-IPC as 1.0. TMS-IPC elution values on the three columns are given in Table I, footnote d.
[e] No peak; possible decomposition.

chromatographic behavior of the compounds is dependent to a degree upon the column substrate polarity; Carbowax 20M $\gg$ QF-1 (trifluoropropylmethyl silicone) $>$ SE-30 (methyl silicone). That is to say, elution of polar solutes is prolonged upon substitution of a more polar column for a less polar one, as may be seen in comparing the values for α-naphthol.

Several interesting points are suggested by the data. Despite a general improvement of peak appearance due to polarity decreases upon silylation, the elution values for the TMS derivatives lie very close to those of the parent compounds. Comparing α-naphthol to its TMS derivative, one may extend this to say that silylation produces much smaller elution differences on non-polar columns than on polar columns. It is also evident that the degree of elution differences produced by silylation is dependent upon the polarity of the molecular moiety to which the active hydrogen is attached. It is obvious then, that there is a considerable polarity expanse between hydroxyl and imino functional groups.

It had been reported earlier[33] that Sevin thermally degrades to α-naphthol. The analysis of Sevin itself, without degradation, at sufficiently low temperatures on low-loaded non-polar columns appears possible. At the analytical temperature required for chromatography on Carbowax 20M, it is evident that cleavage to α-naphthol occurred. It is of interest, however, that chromatography of Sevin as a TMS derivative may apparently be effected without thermal rupture of the naphthyl ester linkage. Neither Sevin nor its TMS derivative were found to give a positive α-naphthol test with *p*-nitrobenzene-diazonium fluoborate. The TMS α-naphthol gave a positive test.

Zectran produced two peaks on chromatography. If one assumes the major peak (see Table I) to be Zectran or its TMS derivative as the case may be, a possibility existing for the alternate peak is 4-dimethylamino-3,5-xylenol. If this is true, its TMS derivative could be expected to elute prior to TMS Zectran on SE-30 and after

it on QF-1. Owing to resonance considerations also, the TMS derivative of Zectran would be expected to possess lower stability to degradation than that of the TMS derivative of Sevin, and it was noted that the elution value on Carbowax 20M at 170°, for the secondary peak in the TMS Zectran preparation, corresponded very closely to that of the secondary peak of the unreacted Zectran sample. In addition, the delayed elution on Carbowax 20M of the secondary peak in either the Zectran sample or the TMS Zectran reaction mixture is suggestive of a compound possessing a fair degree of polarity. The above remarks are presented as suggestions to explain the chromatographic behavior of Zectran.

The retention of the pesticidal ureas was less than that of the carbamates and was in the order of Hercules 7531 > Diuron > Monuron. With the exception of Hercules 7531, the urea peaks were less definite than those of the carbamates. No elution value was observed for Diuron on Carbowax 20M, undoubtedly owing to its thermal decomposition[31]. Chromatography of Diuron was successful at the lower temperatures used for QF-1 and SE-30, however. A composite chromatogram of several of the TMS derivatives is given in Fig. 1.

TABLE III

EFFECT OF SILYLATION ON PESTICIDAL CARBAMATES AND UREAS

Compound	*% elution decrease by silylation*[a]		
	QF-1	*SE-30*	*Carbowax 20M*
Monuron	— 5	—17	0
Diuron	—22	—11	[b]
Hercules 7531	— 1	0	3
Zectran[c]	28, 88	0, 88	0, 0
α-Naphthol	0	—17	92
Sevin	9	—17	92
IPC	0	0	0
CIPC	0	0	0

[a] Values obtained from: $\frac{\text{R.E. (C)} - \text{R.E. (TMS-C)}}{\text{R.E. (C)}} \times 100$, where R.E. is relative elution, (C) is the unsilylated compound and (TMS-C) is the TMS derivative of the compound.
[b] No peaks; possible decomposition.
[c] Major peak underlined.

In an effort to estimate the effect of silylation, the percent of elution change by silylation is shown in Table III. It must be kept in mind that the elution differences in some cases were very small. The table is merely offered as an illustration of the apparent differences upon silylation between the different columns employed and between the carbamate and urea classes. In general, silylation decreased elution values on the polar column (Carbowax 20M); increased elution values on the nonpolar (SE-30) column (apparently due to molecular weight increase); and produced variable results on QF-1.

Extension of the investigation of silylation to other classes of compounds of pesticidal interest is at present underway.

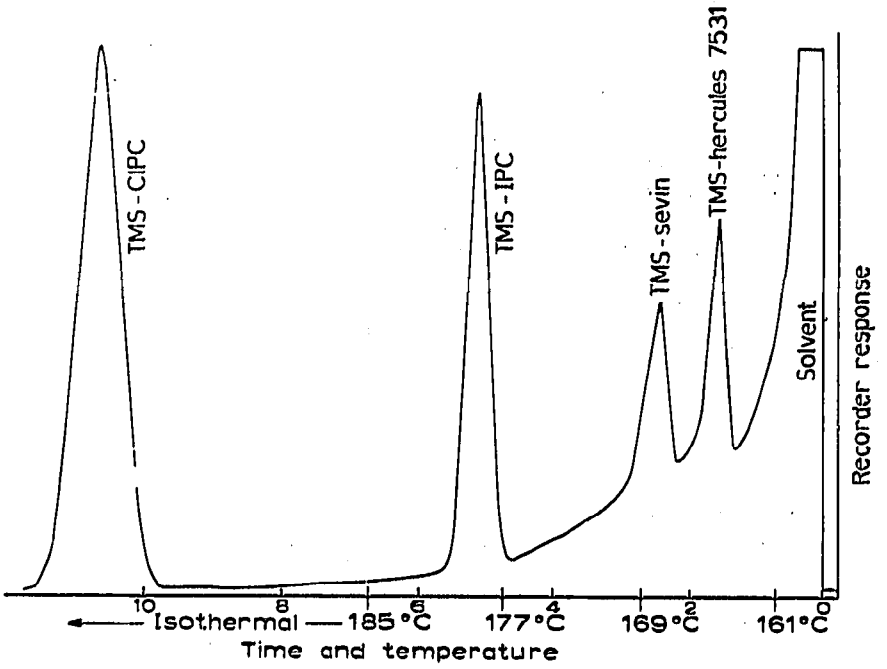

Fig. 1. Composite chromatogram of several carbamate and urea TMS derivatives. Column: 3% Carbowax 20M on 60–80 mesh acid-washed, DCMS-pretreated Chromosorb G, 6 ft. by 0.25 in. O.D. pyrex glass. Conditions: nitrogen carrier 96 ml/min (at 160°); hydrogen 75 ml/min; air 440 ml/min; programmed 160–185° at 4.0°/min; injection port block heater 50 V; detector temperature 230°; range 1000; flame ionization detector.

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SUMMARY

A study of the gas chromatographic behavior of trimethylsilyl derivatives of pesticidal carbamates and ureas has been carried out. The results suggest that silylation retards the thermal breakdown of Sevin and generally results in better peak symmetry and less tailing of the eluting solute bands. Contrasts between the parent compound and its TMS derivative are given for the carbamates and ureas. The investigation of the effect of silylation on other classes of pesticide derivatives is being continued.

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