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GAS–LIQUID CHROMATOGRAPHY AND MASS FRAGMENTOGRAPHY OF S-*n*-PROPYL N-MONOALKYL DITHIOCARBAMATES

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SUMMARY

An investigation was undertaken to evaluate Apiezon L, silicone oil DC-200 and Reoplex 400 liquid phases for the separation of S-*n*-propyl N-alkyl dithiocarbamates where the alkyl group contained one to four carbon atoms. The Kováts retention indices for these liquid phases were determined in the range of 160° to 210°. Individual mass spectra of the N-monoalkyl dithiocarbamates by electron impact were recorded and the fragmentation pathways were evaluated. A method using mass fragmentography for the quantitative determination of N-alkyl dithiocarbamates was developed using their molecular ions at *m/e* values of 149, 163, 177 and 191 for single-ion monitoring.

INTRODUCTION

This study was undertaken to develop a method for the analysis of sodium salts of N-monoalkyl dithiocarbamates (MADTCs) through esterification with 1-iodopropane to form S-*n*-propyl MADTCs followed by chromatographic separation. The publications of Halls[1] and Zahradnik and Zuman[2] describe polarographic studies of N,N-dialkyl dithiocarbamates and MADTCs and briefly mention that MADTCs may be detected by this technique. Gas chromatography and gas chromatography–mass spectrometry (GC–MS) have recently been applied to the separation of S-alkyl N,N-dialkyl dithiocarbamates[3,4].

The separation of S-alkyl MADTCs may be accomplished by using the same alkylating agent and slightly modified conditions. The importance of mass spectrometry for pesticide chemistry, particularly for the identification of small quantities in residues, is rapidly being realized. Dithiocarbamates (DTCs) are well suited for mass spectral residue analysis because these compounds usually yield intense molecular ions or fragment peaks and can be easily identified by the characteristic peak pattern

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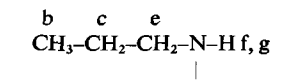
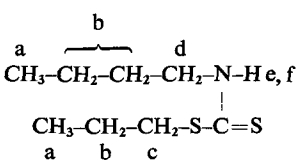
TABLE I

ANALYTICAL DATA FOR S-*n*-PROPYL MADTCs

Tri = triplet; mu = multiplet.

Name	*Formula*	*Composition (%)*		*MW*	*IR* (cm^{-1})	*NMR* (δ)
		Calculated	*Found*			
S-*n*-Propyl N-methyl-dithio-carbamate	d CH_3–N–H e, f | CH_3–CH_2–CH_2–S–C=S a b c	C: 40.26; H: 7.38; N: 9.39; S: 42.97	C: 40.11; H: 7.53; N: 8.93; S: 43.43	149	3225 1505 955 825	a = 1.02 (tri) b = 1.70 (mu) c = 3.08 (doublet) d = 3.28 (tri) e = 7.75 f = 8.40
S-*n*-Propyl N-ethyl-dithio-carbamate	b e CH_3–CH_2–N–H f, g | CH_3–CH_2–CH_2–S–C=S a c d	C: 44.17; H: 7.98; N: 8.59; S: 39.26	C: 43.32; H: 7.99; N: 9.22; S: 39.47	163	3220 1502 965 820	a = 0.99 (tri) b = 1.25 (mu) c = 1.77 (mu) d = 3.22 (tri) e = 3.73 (mu) f = 7.55 g = 8.25

S-*n*-Propyl N-propyl-dithio-carbamate 	C: 47.46; H: 8.47; N: 7.91; S: 36.16	C: 47.27; H: 8.67; N: 7.34; S: 36.72	177	3210 1500 985 885	a = 0.93 b = 1.00 c = 1.52 (mu) d = 3.30 (mu) e = 3.68 (mu) f = 7.32 g = 8.2
S-*n*-Propyl N-*n*-butyl-dithio-carbamate 	C: 50.26; H: 8.90; N: 7.33; S: 33.51	C: 50.09; H: 8.67; N: 7.30; S: 33.94	191	3210 1500 920 735	a = 0.92 (mu) b = 1.62 (mu) c = 3.28 (mu) d = 3.70 (mu) e = 7.35 f = 8.20

due to the ^{32}S and ^{34}S isotopes. These features have aided in the development of a mass fragmentography method for identifying the MADTCs in N,N-dialkyl dithiocarbamates. After a proper clean-up the method may be used for crude plant extracts, industrial wastewater or crude chemicals. The present paper deals with gas chromatographic conditions that are required for separating mixtures of MADTCs and with the evaluation of column performance using intermediate polar and non-polar liquid phases.

EXPERIMENTAL

Reagents

Abs. ethanol was used as a solvent for a preparation of the derivatives.

1-Iodopropane was obtained from BDH, Toronto, Canada.

Individual MADTC sodium salts were prepared by the following procedure: A mixture of carbon disulphide (0.1 mol), water (50 ml) and monoalkylamine hydrochloride (0.1 mol) in water (40 ml) was heated to 30° and a solution (40 ml) of sodium hydroxide (0.2 mol) was added dropwise with stirring. Stirring was continued for 2 h and the yellow reaction mixture was evaporated *in vacuo* to a small volume. The bulk of the sodium chloride crystallized and was filtered off. The filtrate was evaporated to dryness. The residue was dissolved in abs. ethanol, filtered through Whatman No. 1 filter-paper and then precipitated with abs. diethyl ether. The yellowish crystalline product was purified by dissolving it in acetone, precipitating with abs. diethyl ether and filtering. Drying of the compound *in vacuo* over diphosphorus pentoxide yielded a white powder.

S-n-Propylation of sodium MADTCs

Sodium MADTCs (1.1 g) (where alkyl is C_1 to C_4) were dissolved in abs. ethanol (25 ml). 1-Iodopropane (1 ml) was added and the mixture was kept at 40° for 1 h. The ethanol was evaporated and the yellow liquid extracted with abs. diethyl ether (5 ml). The ether was evaporated and vacuum distillation of the residual yellow liquid yielded S-*n*-propyl MADTCs as colourless liquids.

The NMR spectra showed broad bands at δ 8.1 for the proton on nitrogen. All other peaks integrated correctly (see Table I). The 70-eV mass spectra were obtained with a Varian CH-07 mass spectrometer by the direct introduction technique, using the standard sample probe. The ionization-chamber temperature was 200°. Elemental analysis (Table I) confirmed the expected empirical formulae.

Gas chromatography

A Varian gas chromatograph Model 1800 equipped with a flame ionization detector (FID) and a Varian Model 20 recorder was employed in this study. Stainless-steel columns of different lengths with 2-mm internal diameter were used. To prepare a coiled column, vacuum was applied, and the coated material was packed by adding small amounts while tapping the column at the packing level after each addition. Liquid phases (10%, w/w) were coated onto 80–100 mesh Chromosorb G-HP as given in Table II.

TABLE II

GAS CHROMATOGRAPHIC CONDITIONS

Column	*Length (cm)*	*Flow-rate (ml/min)*	*Column temperature (°C)*
Apiezon L	360	30.0	190, 200, 210
Silicone DC-200	245	29.3	190, 195, 200
Reoplex 400	215	20.0	160, 165, 170

Gas chromatography–mass spectrometry

A Finnigan Model 1015 quadrupole gas chromatograph–mass spectrometer was used to obtain conventional mass spectra from 1.5 μg/samples of the reference compounds. The gas chromatograph was interfaced to the mass spectrometer with a glass jet separator. The chromatograph was fitted with a 155 cm × 2 mm I.D. glass coil packed with 3% OV-1 coated on a 70–80 mesh Chromosorb W-HP. The flow-rate of helium carrier gas was 20 ml/min. The initial temperature was 110° with a 2-min isothermal operation prior to temperature programming to 170° at 8°/min. The temperature of the injection port was held at 200°.

For mass fragmentography, the instrument has been described earlier[5].

The computer used was a System 150, a small-scale, general-purpose computer with a 12-bit word length. The Model ASR 33 Teletype and 280 Automatic Peak Monitor with the four-pen Rikadenki KA-40 potentiometric recorder were employed.

The system was calibrated with perfluorotributylamine to assign mass numbers on spectra obtained in the subsequent GC–MS. A mass marker was used to centre a channel on its assigned ion peak.

Typical chromatograms are presented in Figs. 1–3.

Kováts retention indices were obtained at three different temperatures.

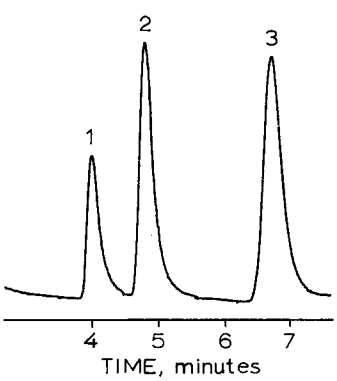
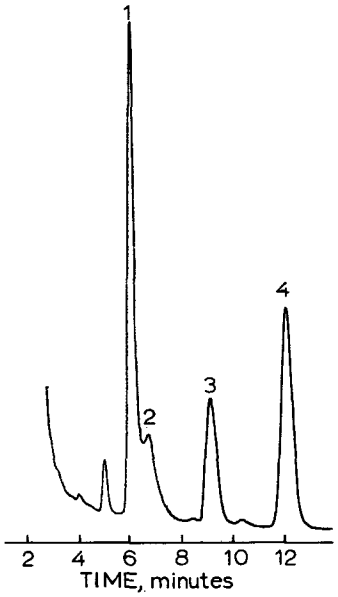


Fig. 1. Chromatogram of S-*n*-propyl MADTCs on Apiezon L at 190°. 1 = S-*n*-propyl N-methyl-DTC; 2 = S-*n*-propyl N-ethyl-DTC; 3 = S-*n*-propyl N-*n*-butyl-DTC.

Mass spectrometry

The S-*n*-propyl MADTCs were first examined with a Varian CH-07 mass spectrometer, which separates ions sufficiently for the determination of mass numbers.



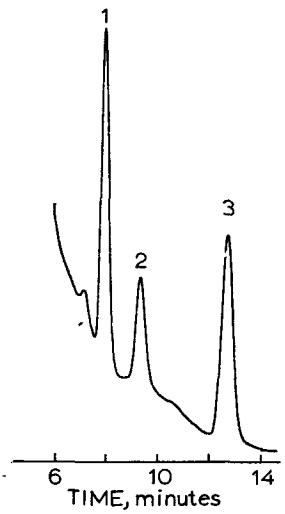


Fig. 2. Chromatogram of S-*n*-propyl MADTCs on silicone DC-200 column at 200°. 1 = S-*n*-propyl N-methyl-DTC; 2 = S-*n*-propyl N-ethyl-DTC; 3 = S-*n*-propyl N-*n*-propyl-DTC; 4 = S-*n*-propyl N-*n*-butyl-DTC.

Fig. 3. Chromatogram of S-*n*-propyl MADTCs on Reoplex 400 column at 160°. 1 = S-*n*-propyl N-methyl-DTC; 2 = S-*n*-propyl N-ethyl-DTC; 3 = S-*n*-propyl N-*n*-butyl-DTC.

Thereby the mechanism of fragmentation can be studied and valuable information may be obtained about the molecular structure. The mass spectral data obtained for S-*n*-propyl derivatives of MADTCs are given as bargraphs in Fig. 4.

RESULTS AND DISCUSSION

Gas chromatographic data for the S-*n*-propyl MADTCs and their retention ratios and Kováts retention indices on three stationary phases at three different temperatures are given in Tables III–V.

The data on S-*n*-propyl MADTCs were arranged according to increasing elution from a non-polar liquid phase. Typical chromatograms of MADTCs on the column packed with Apiezon L (Fig. 1), silicone oil DC-200 (Fig. 2), and Reoplex 400 (Fig. 3) showed that the elution of S-*n*-propyl derivatives of MADTCs correspond to that expected for any homologous series. The retention values increased with increasing chain length of a hydrocarbon (linked to nitrogen). Polypropylene glycol adipate (Reoplex 400), a liquid phase of intermediate polarity, substantially increased retention and the Kováts retention indices of S-*n*-propyl MADTCs. From this column, MADTCs were eluted in the same order as on Apiezon L and silicone DC-200. Since the polarity of the Reoplex 400 is the highest of the liquid phases employed for the study (Rohrschneider constant $Y_{Re} = 5.46$), hydrogen bonding of the free hydrogen

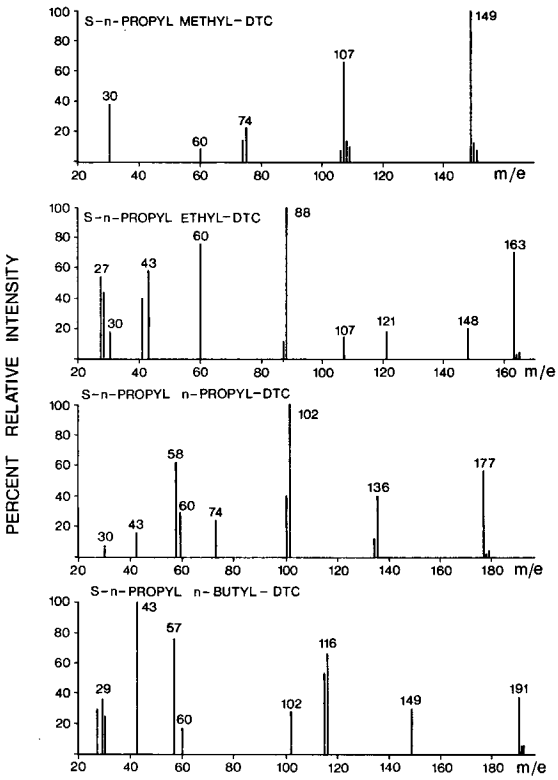


Fig. 4. Mass spectra of S-*n*-propyl MADTCs.

TABLE III

RELATIVE RETENTION VOLUMES (V_R) AND KOVÁTS INDICES OF S-*n*-PROPYL MADTCs ON APIEZON L

MADTC	V_R	$I^{190°}$	V_R	$I^{200°}$	V_R	$I^{210°}$
Methyl-	0.63	1411.3	0.66	1416.3	0.68	1421.4
Ethyl-	0.79	1465.2	0.83	1472.2	0.85	1479.3
n-Propyl-	1.00	1515.5	1.00	1518.3	1.00	1521.2
n-Butyl-	1.44	1594.9	1.42	1599.7	1.39	1604.8
n-C_{15}- (standard)	0.92	1500.0	0.95	1500.0	0.91	1500.0

TABLE IV

RELATIVE RETENTION VOLUMES AND KOVÁTS INDICES OF MADTCs ON REOPLEX 400

MADTC	V_R	$I^{160°}$	V_R	$I^{165°}$	V_R	$I^{170°}$
Methyl-	0.85	1822.2	0.86	1828.7	0.87	1835.0
Ethyl-	0.92	1842.8	0.92	1849.3	0.93	1855.8
n-Propyl-	1.00	1866.0	1.00	1871.0	1.00	1876.0
n-Butyl-	1.36	1952.3	1.34	1954.4	1.34	1956.5
n-C_{19}- (standard)	1.12	1900.0	1.13	1900.0	1.08	1900.0

TABLE V

RELATIVE RETENTION VOLUMES AND KOVÁTS INDICES OF S-*n*-PROPYL MADTCs ON SILICONE DC-200

MADTC	V_R	$I^{190°}$	V_R	$I^{195°}$	V_R	$I^{200°}$
Methyl-	0.64	1393.8	0.64	1395.9	0.65	1398.0
Ethyl-	0.80	1449.5	0.80	1452.0	0.81	1454.5
n-Propyl-	1.00	1506.6	1.00	1509.2	1.00	1511.8
n-Butyl-	1.53	1599.7	1.40	1608.7	1.37	1617.7
n-C_{15}- (standard)	—	1500.0	—	1500.0	—	1500.0

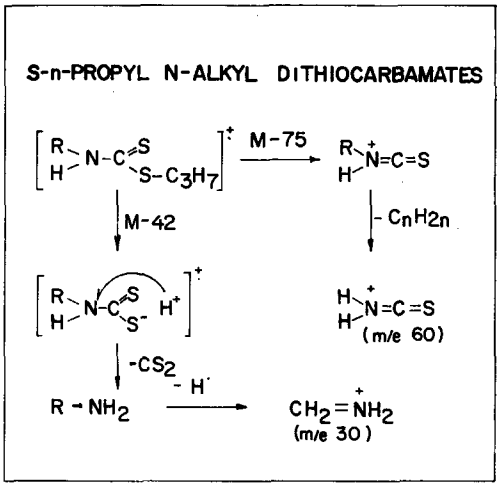
in the secondary amine causes a higher affinity for this liquid phase. The lowest Kováts indices were found for silicone DC-200. This type of liquid phase is less polar than Apiezon for MADTCs (Rohrschneider $Y_{DC} = 0.22$ and $Y_{AP} = 0.39$).

Mass spectral data for the individual S-*n*-propyl MADTCs are presented as bar charts in Fig. 4. All MADTC derivatives yielded significant peaks for molecular ions. A simplified fragmentation pathway under an electron impact at 70 eV can be generalized as it is shown in Fig. 5. Metastable peaks observed were generally broad owing to the presence of ^{32}S and ^{34}S isotopes. Identification of fragment ions was partially obtained by a calculation from the general equation $m_1/m_2 = m^*$. In all spectra peaks corresponding to the ion $RNHCS_2^+$ were found. When R^+ was a saturated aliphatic hydrocarbon group larger than methyl, partial fragmentation by elimination of this R^+ occurred. In MADTCs two simple fragmentations were observed. The molecular ion was most abundant in N-methyl-DTC. Initially, each S-*n*-propyl derivative lost its $(M - 75)^+$ ion followed by the expulsion of propylene $(M - 45)^+$. Also observed was an expulsion of methyl ion from the molecular ion $(M - 15)^+$. It is evident that the hydrocarbon moiety of an amine residue plays a less important role in the fragmentation processes. The spectra showed that a $CH_2{=}NH_2^+$ ion was formed (*m/e* 30). This fragment was an important feature of MADTCs and N,N-dialkyldithiocarbamates.

In N-ethyl-DTC derivatives generally the same fragmentation process occurred. A new feature in this fragmentation was observed where an ionized form of ethyl isothiocyanate expelled ethylene from the monoethylamine moiety giving an (*m/e* 60) ion. Propylene was expelled from N-*n*-propyl- and butylene from N-*n*-butyl-DTC.

Separating and collecting the MADTCs from a mixture was impractical or usually impossible. Therefore, GC–MS was used as a routine analytical approach. Although intensities of the magnetic type mass spectrum and quadrupole type mass spectrum varied significantly, especially at lower *m/e* ratios, the same fragmentation patterns were observed on both types of mass spectra.

Fig. 6 shows the selective monitoring of the molceular ions in individual MADTCs. The peak heights obtained by single-ion monitoring are proportional to the relative abundances of the molecular ions in the mass spectra. This technique seems to be feasible for the quantitative analysis of pesticides in biological or wastewater samples. Components of the mixture contained all S-*n*-propyl MADTCs and each of them represents 5 ng of S-*n*-propyl derivative. It showed that this amount of the particular derivative may be detected, identified and quantitated selectively by this technique.



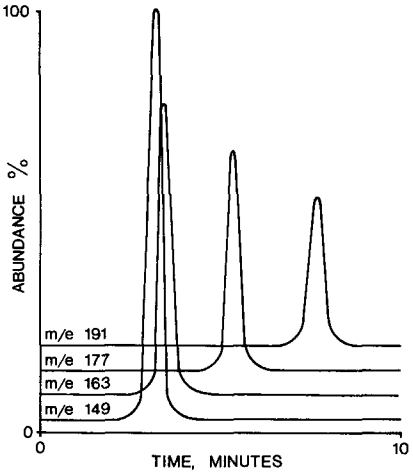


Fig. 5. Fragmentation pathway of S-*n*-propyl MADTCs under electron impact at 70 eV.

Fig. 6. Mass fragmentogram of S-*n*-propyl MADTCs.

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