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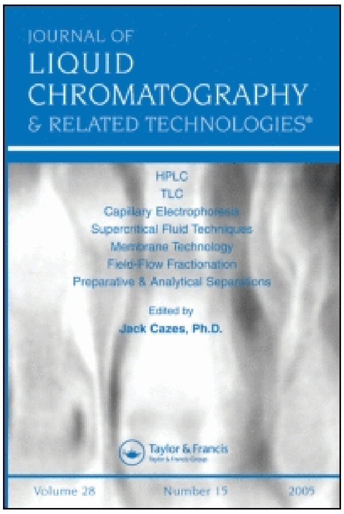

Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Aced, Gaby , Anklam, Elke and Mockel, Hermann J.(1987) 'Separation of Sulphonium Salts by Ion Chromatography: Five- and Six-Membered Cyclic Sulphonium Salts', Journal of Liquid Chromatography & Related Technologies, 10: 15, 3321 — 3327

To link to this Article: DOI: 10.1080/01483918708081875

URL: http://dx.doi.org/10.1080/01483918708081875

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JOURNAL OF LIQUID CHROMATOGRAPHY, 10(15), 3321-3327 (1987)

SEPARATION OF SULPHONIUM SALTS BY ION CHROMATOGRAPHY: FIVE- AND SIX-MEMBERED CYCLIC SULPHONIUM SALTS

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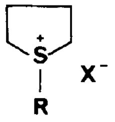
ABSTRACT

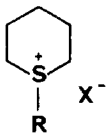
Several cyclic 5- and 6-membered sulphonium compounds were separated by ion pair chromatography on a opti-dbb ion pair column. The salts show specific retention behavior when using different mixtures of acetonitrile and aqueous sodium perchlorate solutions as eluents. The increase of retention times with extending chain length of the alkyl group R and with ring size is due to an increase of the solute molecular surface areas which were also calculated. The obtained retention parameters give additional information for structural determination.

INTRODUCTION

Only a few analytical methods for general characterization of sulphonium compounds have been described in the literature (1). Most of the procedures used paper and thin-layer chromatography (2,3,4) or ion exchange for purification and isolation (1). Liquid chromatography was only applied in a few cases e.g. to determine S-adenosylmethioninsulphonium salts (5,6), methylene blue and azure (7). We now report on the separation and determintion of several 5- and 6-membered cyclic (tetramethylene and pentamethylene) sulphonium compounds 1 - 12 which were synthesized by cyclization reactions of 1,n-halo(alkylthio)alkanes (8,9).



1 - 6



7 - 12

MATERIALS AND METHODS

Reagents

Sulphonium salts 1 - 12 were synthesized as described in the literature (8,9) and characterized by ^{1}H-NMR spectroscopy and elemental analysis. HPLC-grade acetonitrile was purchased from Baker Co., sodium perchlorate was obtained from Merck-Schuchardt. LC-qualitity water was obtained by passing distilled water through a Millipore water purification unit.

Apparatus

A Dionex 2010 ion chromatograph was used with a porous polymer 250 x 4.6 mm Opti-dbb-ion pair column (Melz-Analytik). The ion detection was achieved by a LCD 201 RI detector (Melz-Analytik) and the integration by a Shimadzu C-R3A integrator. Molecular surface areas were calculated on a Siemens 7880 computer.

Procedures

Analyses were carried out at room temperature. Aqueous sulphonium salt samples of 10 mg/ml were used, 50 µl were injected. The total column dead time was determined as the elution time of aqueous methanol ($t_{m,\,raw}$ = 3.415 min). For determination of the extra column dead time the column was replaced by a capillary of known volume (t_{extra}= 0.156 min), which yields a column dead time t_m = 3.258 min. Capacity factors were calculated as $k' = (t_{ms,raw} - t_{m,raw}) / t_m$. For calculating the molecular surface areas (TSA) the Fortran programs COORD and SAREA from Pearlman (10) were used. Structural data of 1 - 12 were taken from the literature (1, 11).

RESULTS AND DISCUSSION

The samples were eluted by different solvent mixtures of acetonitrile and aqueous sodium perchlorate solutions. Figure 1 shows the chromatogram of the 5-membered sul-

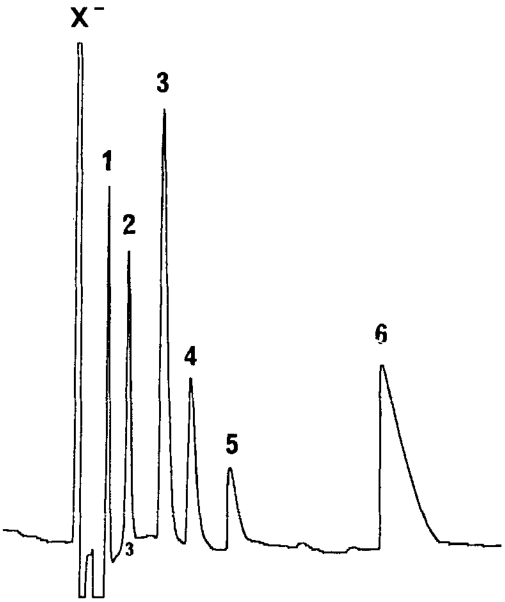


FIGURE 1: Ion pair chromatogram of 1 - 6 on a opti-dbb ion pair column with 0.1 M sodium perchlorate and 10 % acetonitrile as eluent (Retention times are given in Table 1)

phonium salts 1 - 6, Figure 2 that of the 6-membered samples 7 - 12. The appearance of the anions X^- (Cl^-, Br^-, I^-) which elute prior to the water peak is due to the ion pair chromatographic behavior of the column.

By varying the concentration of acetonitrile and sodium perchlorate the retention times of the sulphonium compounds are changed. Increasing the acetonitrile concentration leads to shorter retention times, while an increase of the molarity of sodium perchlorate increases the retention times of 1 - 12. These results are summarized in Table 1.

For both the 5- and 6-membered cyclic sulphonium compounds ln k′ increases regularly with extending chain length of the alkyl group R. For 1 - 6 with 10 % acetonitrile we found $\ln k' = -2.4507 + 0.9319 \times n_C$ ($r = 0.9985$) and for 7 - 12 with 15 % acetonitrile

$\ln k' = -2.0500 + 0.8000 \times n_C$ ($r = 0.9996$); (n_C = number of carbon atoms)

Both equations were calculated from data found for R = ethyl, n-propyl and n-butyl. With R = methyl, the experimental ln k′ is higher than expected from the above equations.

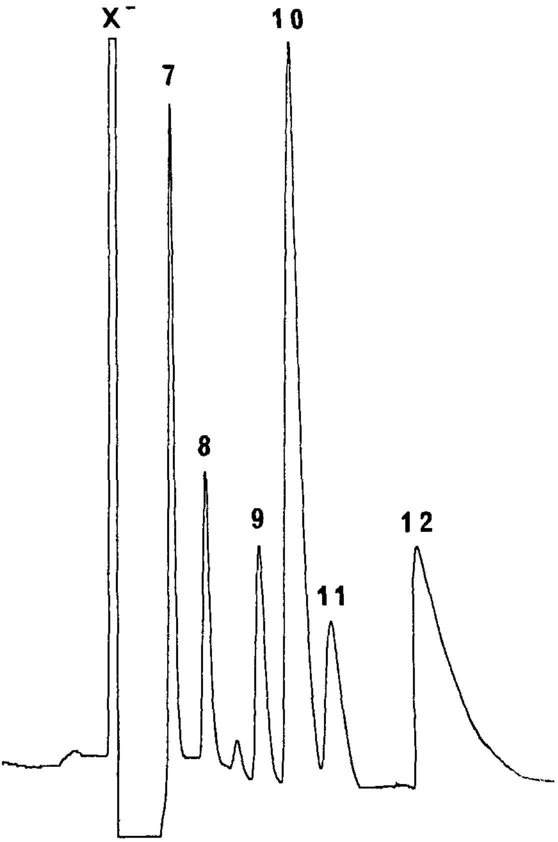


FIGURE 2 : Ion pair chromatogram of 7 - 12 on a opti-dbb ion pair column with 0.1 M sodium perchlorate and 15 % acetonitrile as eluent (*Retention times are given in Table 1*)

The high retention increment of the methyl-group is a well known effect in reversed phase liquid chromatography which, however, has not yet found a satisfactory interpretation. The increase of retention times with extended chain length of R is due to an increase of the solute molecular surface area (TSA) which, in turn, enhances solvophobicity (12).

The solutes 2 (R = ethyl) and 7 (R = methyl) cannot be separated with eluents in the 10 % to 30 % acetonitrile range, whereas all other sulphonium derivatives can be effficiently separated. Generally the 6-membered cyclic sulphonium compounds 7 - 12 have higher reten-

TABLE 1

Retention times of 1 - 12 using different eluents

Comp. No.	R	Retention times (min) 0.1M $NaClO_4$ 10 % CH_3CN	0.1 M $NaClO_4$ 15 % CH_3CN	0.1 M $NaClO_4$ 30 % CH_3CN	0.01 M $NaClO_4$ 15 % CH_3CN
1	CH_3	5.5	4.3	-	-
2	C_2H_5	6.6	5.6	4.7	-
3	i-C_3H_7	8.1	6.4	-	-
4	n-C_3H_7	9.7	7.2	-	-
5	t-C_4H_9	11.1	7.7	5.4	5.6
6	n-C_4H_9	19.3	9.3	-	-
7	CH_3	6.5	5.7	4.7	-
8	C_2H_5	7.2	6.9	5.1	-
9	i-C_3H_7	11.8	8.6	5.5	6.0
10	n-C_3H_7	13.4	9.9	5.7	-
11	t-C_4H_9	14.1	11.1	5.9	7.1
12	n-C_4H_9	-	17.3	-	-

TABLE 2

Molecular surface areas (TSA) and ln k′-values of 1 - 12

Comp. No.	ln k′	TSA	Comp. No.	ln k′	TSA
1	-1.1965	144.68	7	-1.0460	162.83
2	-0.5582	165.65	8	-0.4371	188.95
3	-0.0614	187.49	9	-0.0613	193.87
4	0.2876	188.33	10	0.3238	207.62
5	0.5169	204.04	11	0.5169	209.01
6	1.3056	211.00	12	1.1628	230.29

tion times than their 5-membered analogues 1 - 6. It is significant that the retention increment of the additional methylene group in the ring is slightly larger than in the chain.

Branching within R lowers the retention time. Changing propyl for iso propyl and butyl for tert. butyl reduces ln k′ by of 0.31 and 0.64, respectively (both in 15 % acetonitrile). With 10 % acetonitrile in the eluent the differences are slightly larger. This decrease of retention time is only partly due to a reduction of the solute molecular surface area. Steric effects in the interaction with the stationary phase play probably a significant role. The ln k′ -values and the molecular surface areas (TSA) of 1 - 12 are summarized in Table 2.

With higher acetonitrile concentrations in the eluent the solvophobicity of solutes is reduced and the retention time decreases(Table 2). Between 10 % and 30 % acetonitrile (0.1 M sodium perchlorate) the dependence of ln k′ on the acetonitrile volume percentage is nearly linear. The increase of ln k′ per % acetonitrile is around 0.08 , which indicates that an increase of modified concentration has no specific effect on the retention behavior on either of the investigated solutes.

The present work shows that the investigated different sulphonium salts can be efficiently separated retention behavior on the opti-dbb-column. Their separation by ion chromatography is an easy and rapid method and leads to additional information in characterization of cyclic sulphonium compounds. Application for other sulphonium derivatives is currently investigated and will be reported on separately.

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