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The gas chromatography of isothiocyanates and 3-substituted rhodanines

Gas chromatography (GC) has already been applied to isothiocyanates such as of alkyl isothiocyanates[1,2] and some results have appeared in the literature[2–5]. The separation of isothiocyanates from 3-substituted rhodanines using thin-layer chromatography has also been reported[6]. However, no data have been given on the separation of 3-substituted rhodanines by GC.

The results obtained from a study of the reactions of isothiocyanates with thioglycolic acid showed an extraordinarily high reactivity of ionized mercapto derivatives. By their reactions it was found that 3-substituted rhodanines were formed[7,8].

The present research was undertaken to develop a possible method for the separation of various substituted isothiocyanates and 3-substituted rhodanines by GC. The influence of substituents attached to the benzene ring of compounds investigated on retention time was also studied.

Experimental

The appropriate isothiocyanates were prepared according to refs. 9 and 10 and 3-substituted rhodanines according to ref. 11.

The instrument used was a Hewlett-Packard 5756 B gas chromatograph with a flame-ionisation detector. A 183 × 0.2 cm column packed with Diatoport (80–100 mesh) and coated with 10 % silicone gum UCW 98 was used. The flow rate of the carrier gas (nitrogen) was 20 ml/min. The injector port and detector temperatures were

TABLE I

RETENTION TIMES FOR COMPOUNDS R–NCS

No.	*R*	*Mol. weight*	*B.p./m.p.* (°C(*torr*))	t_R (*min*)
1	4-Ethoxyphenyl	179.24	60	18.03
2	4-Methoxyphenyl	165.21	145/12	16.85
3	4-Acetylphenyl	177.22	112/0.2	18.50
4	4-Carbethoxyphenyl	207.25	58	19.76
5	4-Nitrophenyl	180.18	121–122	19.06
6	4-Bromophenyl	214.09	61	17.48
7	4-Tolyl	149.21	20	15.12
8	4-Dimethylaminophenyl	178.25	67	20.00
9	Phenyl	135.18	120/35	12.09
10	3-Nitrophenyl	180.18	58	17.80
11	Methyl	73.11	35.9 119(756)	3.78
12	*n*-Butyl	115.19	166	10.00
13	Benzyl	149.21	140–141/17	16.68
14	1-Naphthyl	185.24	58–58.5	21.72
15	2-Naphthyl	185.24	61–62	21.42
16	4-Bromobenzyl	218.12	144/5	20.16
17	4-Bromo-4'-biphenyl	290.19	132–133	27.87
18	4-Bromo-1-naphthyl	264.14	135–137	25.20
19	1-Naphthylmethyl	199.27	40	23.54
20	4-Nitro-1-naphthyl	230.24	73.5–75	26.28

250° and 260°, respectively. The column temperature was programmed between 50 and 350° at 10°/min.

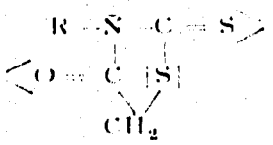
Results

We investigated various substituted isothiocyanates and 3-substituted rhodanines. Retention times for isothiocyanates determined in a non-polar liquid phase are given in Table I and those for 3-substituted rhodanines in Table II.

From the data, it can be seen that the isothiocyanates studied differ in retention

TABLE II

RETENTION TIMES FOR COMPOUNDS



No.	*R*	*Mol. weight*	*B.p.* (°C)	t_R (*min*)
1	4-Ethoxyphenyl	253.34	180–181	24.02
2	4-Methoxyphenyl	239.32	156–158	23.45
3	4-Acetylphenyl	251.33	147–148	20.54
4	4-Carbethoxyphenyl	281.36	114–115	25.01
5	4-Nitrophenyl	254.20	220–228	27.24
6	4-Bromophenyl	288.20	102–103	25.43
7	4-Tolyl	223.32	106.5–108	21.73
8	4-Dimethylaminophenyl	252.36	204–206	20.14
9	Phenyl	209.29	102–103	20.70
10	3-Nitrophenyl	254.20	105–106	25.51
11	Methyl	147.22	66–70	13.08
12	1-Naphthyl	259.35	168	25.23
13	2-Naphthyl	259.35	185–186	26.01
14	1-Naphthylmethyl	273.38	111	28.35
15	Benzyl	223.32	82.5–83	22.60
16	4-Bromobenzyl	302.21	95–96	25.04
17	4-Bromo-4′-biphenyl	364.30	188–190	31.02

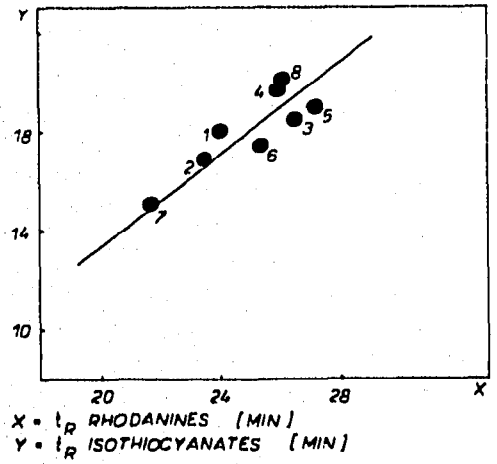


Fig. 1. Relationship between retention times (t_R) of 3-substituted rhodanines and 4-substituted isothiocyanates. Numbers refer to compounds listed in Tables I and II.

times, and the same is observed for the 3-substituted rhodanines. The retention times were 5.9 min higher for the 3-substituted rhodanines than for the isothiocyanates. The results indicate that the mixture of these compounds could be successfully separated by gas–liquid chromatography.

We found that the plot of the Hammett constants against retention times for 4-substituted isothiocyanates and 3-substituted rhodanines was not linear (correlation coefficients $r = 0.54$ and $r = 0.36$, respectively)[12]. However, a linear relationship between the retention times (t_R) of 3-substituted rhodanines and 4-substituted isothiocyanates was observed (correlation coefficient $r = 0.86$) (Fig. 1).

From the data in Tables I and II it might be assumed that electron-releasing substituents shift the retention times to the lower values whilst electron-withdrawing substituents have the opposite effect.

In comparing the adsorption coefficients (liquid–solid phase)[6] and partition coefficients (liquid–gas phase), it was found that both methods can be applied to the separation of the compounds studied. However, the differences in retention times are greater than those in R_F values of variously substituted isothiocyanates and 3-substituted rhodanines.

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1 H. BINDER, *J. Chromatogr.*, 41 (1969) 448.
2 AA. JART, *Acta Chem. Scand.*, 15 (1961) 1223.
3 H. BRANDENBERGER AND E. HELLBACH, *Helv. Chim. Acta*, 50 (1967) 658.
4 J. HRIVŇÁK, AND J. KALAMÁR, *Chem. Zvesti*, 20 (1966) 402.
5 J. KALAMÁR, K. ANTOŠ, J. HRIVŇÁK AND F. BOCÁN, *Chem. Zvesti*, 22 (1968) 674.
6 Ľ. DROBNICA, V. KNOPPOVÁ AND E. KOMANOVÁ, *Chem. Zvesti*, in press.
7 V. KNOPPOVÁ, *Dissertation*, Slovak Technical University, Bratislava, 1969.
8 Ľ. DROBNICA AND J. AUGUSTÍN, *Collect. Czech. Chem. Commun.*, 30 (1965) 1018.
9 G. M. DYSON AND H. J. GEORGE, *J. Chem. Soc.* (1924) 1702.
10 K. ANTOŠ, A. ŠTULLEROVÁ, V. KNOPPOVÁ AND P. KRISTIÁN, *Chem. Zvesti*, 19 (1965) 353.
11 J. L. GARRAWAY, *J. Chem. Soc.*, (1961) 3733.
12 O. EXNER, *Collect. Czech. Chem. Commun.*, 31 (1966) 65.

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