UDC 547.222 + 543.544

CHROMATOGRAPHIC BEHAVIOR OF SOME FURAN DERIVATIVES

V. I. Yakerson, Ya. L. Danyushevskii, Ya. L. Gol'dfarb

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 25-30, 1965

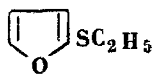
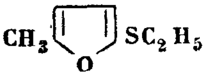
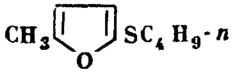
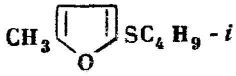
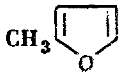
Sulfides of the furan series and derivatives of furylthienylmethane are separated by gas-liquid chromatography. Heats of solution in polyethylene glycol adipate supported on alkali-treated diatomaceous brick are calculated. Interaction with the stationary phase is considered.

Gas chromatography has now emerged as a significant technique beyond the limits of its analytical potentialities. Comparative chromatographic characteristics include the degree of polarity of a substance and its structural peculiarities. In this connection considerable interest attaches to a comparison of the chromatographic behavior of heterocyclic compounds, especially furan and thiophene derivatives of the same type. The similarity in electronic structure, geometry, and, within certain limits, boiling point, makes comparison quite interesting.

The present paper gives results of a study of certain furan derivatives, mainly sulfides, by gas-liquid chromatography. It should be mentioned that some years ago a chromatographic method for separating furan and tetrahydrofuran homologs was developed [1].

TABLE 1

Retention time (t_R), relative retention volumes (V_R^{rel}), heats of evaporation (ΔH_V) and heats of solution (ΔH_p) of furan sulfides in polyethylene glycol adipate (20% by wt.) supported on alkali-treated diatomaceous brick.

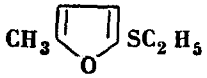
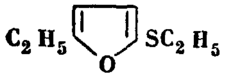
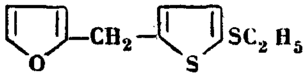
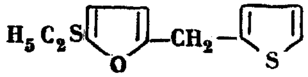
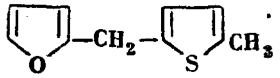
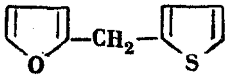
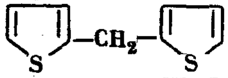
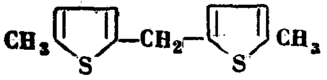
Compound no.	Compound	B.p. at 760 mm, °C	137°		180°		210°		ΔH_p, kcal./mole	ΔH_V, kcal./mole
			t_R min.	V_R^{rel}	t_R min.	V_R^{rel}	t_R min.	V_R^{rel}		
1		158—160	2.0	0.78	0.92	0.88	—	—	11.0	9.0
2		179—180	2.55	1.0	1.05	1.0	0.6	1.0	12.2	9.5
3		218—219	5.0	1.96	1.53	1.46	0.78	1.41	13.6	10.4
4		209—210	3.9	1.53	1.34	1.28	—	—	—	—
5		65	0.55	0.22	—	—	0.39	0.71	—	—

Tables 1 and 2 give values of the retention times (t_R) and relative retention volumes of some furan and thiophene derivatives at 137°, 180°, and 210°. In the case of derivatives with a single furan ring log V_R^{rel} is found to be a linear function of the boiling point (Fig. 1), the slope being $3.5 \times 10^{-3} \Delta \log V_R$ per 1° (at 210°), and this in particular can be used to identify unknown compounds in mixtures. The appearance of a subsidiary thiophene ring, joined to the furan ring by a methylene bridge, doubles the selectivity of separation ($7 \times 10^{-3} \Delta \log V_R$ per 1° at 210°) Dithienylmethane and furylthienylmethane both fit a single linear relation. Hence we may obviously conclude that the chief role in interaction with the phase is played by the mobile π electrons of the ring, and not the alkylmercapto group. The interaction of the stationary phase with the thiophene and furan rings is practically identical. It is interesting that the interaction of diphenylmethane with the phase is considerably less than for the corresponding furan and thiophene derivatives (even on a log scale the retention volume for diphenylmethane lies below the linear relation for furan and thiophene derivatives). As expected, when the experimental temperature was raised from 137° to 210°, the selectiveness of separation of the sulfides of the furan series decreased.

The temperature dependence of the corrected retention volume made it possible to find the heat of solution (ΔH_p) in polyethylene glycol adipate. The experimentally determined heat of solution (ΔH_p) includes the heat of vaporization (ΔH_V) and the excess heat of solution ($\Delta \overline{H}_S^E$) [5]. When ideal solutions are formed, the excess heat of solution is zero, and the heat of solution is equal to the heat of evaporation. $\Delta \overline{H}_S^E$ is always negative; thus solution is exothermic and the deviation from Raoult's law is negative, which testifies to the advantage of the interaction of the substance with the stationary phase.

TABLE 2

Retention time (t_R) and relative retention volumes (V_R^{rel}) for furan sulfides and dithienyl- and furylthienylmethane derivatives

Compound	B.p. at 760 mm, °C	210°	
		t_R, min	V_R^{rel}
	179—180	0.6	1,0
	195	0.63	1,05
	240—245	1.45	2,42
	305	5,2	8.7
	305	5,0	8,3
	230	1.6	2.67
	215	1.5	2.50
	260	2,65	4.42
	285	4.2	7,0

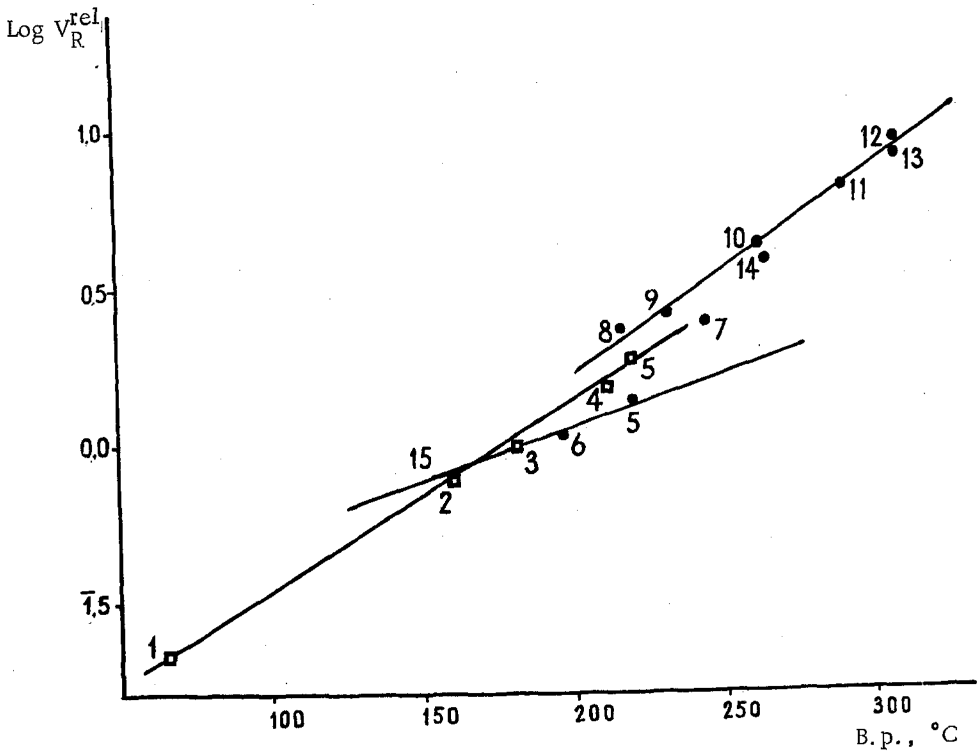


Fig. 1. Relation between relative retention volumes and boiling point. □ —137°, ● —210°. Key: 1 — sylvane, 2 — 2-ethylmercaptofuran, 3 — 5-ethylmercapto-2-methylfuran; 4 — 5-isobutylmercapto-2-methylfuran; 5 — 5-n-butylmercapto-2-methylfuran; 6 — 5-ethylmercapto-2-ethylfuran; 7 — 2,5-bis-(ethylmercapto)furan; 8 — 2-furyl-2-thienylmethane; 9 — 2-methyl-5-(2-furfuryl)thiophene; 10 — di(2-thienyl)methane; 11 — bis-(5-methyl-2-thienyl) methane; 12 — ethyl(5-furfurylthienyl-2)sulfide; 13 — ethyl[5-(thenyl-2)furyl-2]sulfide; 14-diphenylmethane; 15 — diethyl disulfide.

Figure 2 gives the separation at 137° of furan sulfides with one furan ring; the last component to emerge has b. p. 219°. The complete separation of a 5-component mixture takes 8 min. Retention time increases with increasing number of carbon atoms in the molecule. Boiling point falls with branching of the alkyl part of a substituent, and the retention time drops correspondingly. Figure 3 is the chromatogram, at 210°, of a 7-component mixture, mainly derivatives of 2-furyl-2-thienyl- and di-2-(thienyl)methane. The last component to emerge boils at 305°, and the entire separation takes 7 min. Unlike the preceding case, introduction of a methyl group is not enough to secure separation, and 2-methyl-5-(2-furfuryl)thiophene emerges as a kink in the peak of 2-furyl-2-thienylmethane. Di(2-thienyl)methane has a much higher boiling point than 2-thienyl-2-furylmethane, and correspondingly it is also eluted later. 5-n-butylmercapto-2-methylfuran and 2-furyl-2-thienylfuran have, for example, one and the same boiling point (215-218°), nonetheless, the latter emerges later, thus agreeing with the conclusion reached above that the interaction of the stationary phase with the thiophene or furan ring is greater than with the alkylmercapto group. A similar conclusion can be drawn on comparing the retention time of 2, 5-bis-(ethylmercapto)furan with that, for example, of 2-furyl-2-thienylmethane.

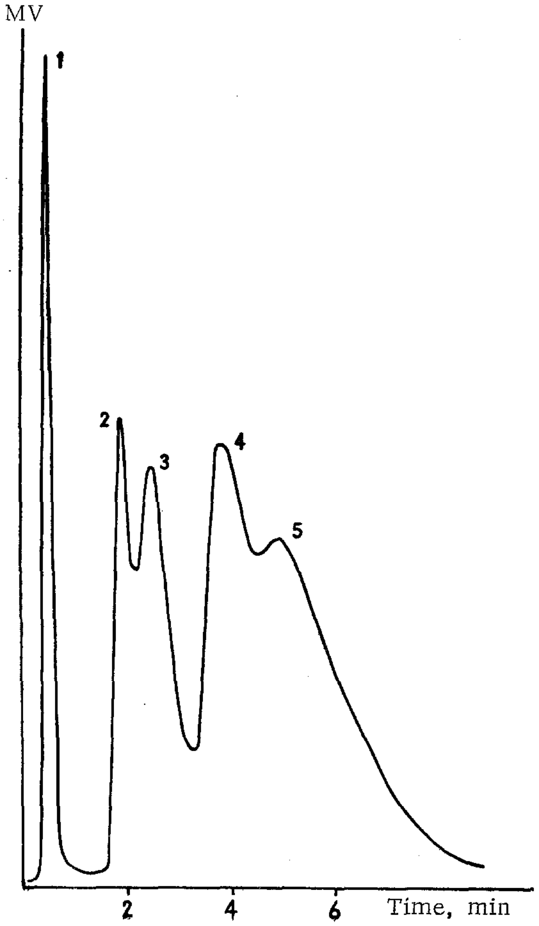


Fig. 2. Chromatogram of a mixture of sulfides of the furan series. Column: polyethylene glycol adipate on diatomaceous brick treated with alkali, 137°. Key: 1 – sylvane, 2 – 2-ethylmercaptofuran; 3 – 5-ethylmercapto-2-methylfuran; 4 – 5-isobutylmercapto-2-methylfuran; 5 – 5-n-butylmercapto-2-methylfuran.

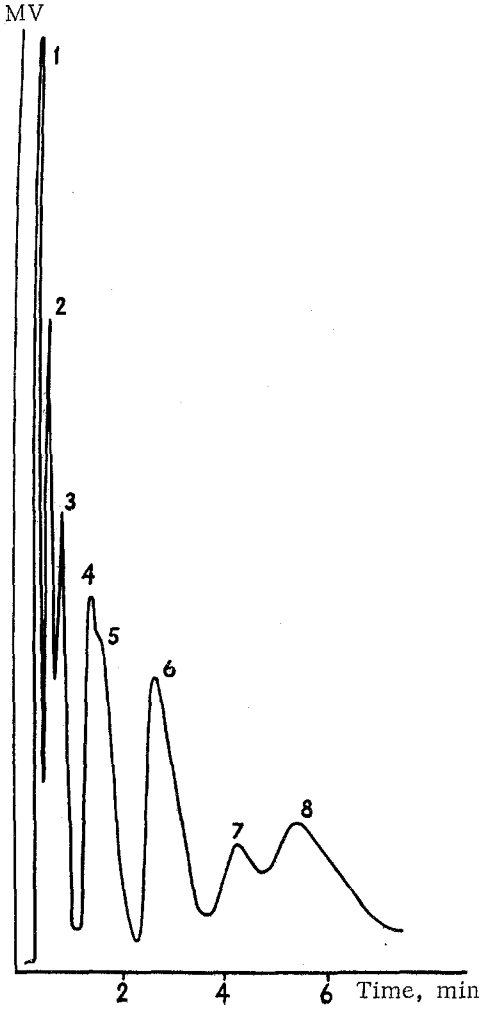


Fig. 3. Chromatogram of a mixture of furan and thiophene derivatives. Column: As in Fig. 2; 210°. Key: 1 – solvent, 2 – 5-ethylmercapto-2-methylfuran; 3 – 5-n-butylmercapto-2-methylfuran; 4 – 2-furyl-2-thienylmethane; 5 – 2-methyl-5-(2-furfuryl)thiophene; 6 – di(2-thienyl)methane; 7 – bis-(5-methyl-2-thienyl)-methane; 8 – ethyl[5-(thenyl-2)furyl-2]sulfide.

The method of chromatographic separation developed makes it possible to determine the individuality of substances and the way in which they change. Ethyl(5-furfurylthienyl-2)sulfide, prepared by the action of butyllithium, sulfur, and ethyl iodide on 2-furyl-2-thienylmethane, is actually not an individual compound, but a mixture of ethyl(5-furfurylthienyl-2)sulfide and ethyl [5-(thenyl-2)furyl-2]sulfide, i. e., metalation takes place not only in the thiophene ring, but also in the furan ring. Unlike the above, ethyl(5-furfurylthienyl-2)sulfide, prepared from 2-ethylmercaptothiophene [6] and furfuryl chloride, is an individual substance. Equally peculiar with respect to conditions of synthesis was ethyl(5-thienylfuryl-2)sulfide, made from ethylmercaptofuran [2], butyllithium, and thienyl chloride.

EXPERIMENTAL

The work was carried out with a LKhM-2 gas-liquid chromatograph built by the Institute of Organic Chemistry AS USSR and equipped with a thermal conductivity detector; the carrier gas was investigated on a stationary phase (polyethylene glycol adipate, 20% by wt.) supported on diatomaceous brick pretreated with an alcohol solution of alkali. The 0.25-0.5 mm fraction of the solid was used as carrier; the length of the copper spiral of the column was 2.6 meters, its diameter 6 mm. Gas flow was held constant at 66-72 ml/min. The alkali pretreatment made it possible to chromatograph into low- and high-boiling derivatives. The preparation of the compounds has already been described [2-4].

REFERENCES

1. N. I. Shuikin, V. V. An, V. L. Lebedev, Zav. lab., vol. 27, p. 976, 1961.
2. Ya. L. Gol'dfarb, Ya. L. Danushevskii, M. A. Vinogradova, DAN, vol. 151, p. 332, 1963.
3. Ya. L. Gol'dfarb, Ya. L. Danushevskii, ZhOKh, vol. 31, p. 3654, 1961.
4. Ya. L. Gol'dfarb, Ya. L. Danushevskii, Izv. AN SSSR, OKhN, p. 1361, 1956.
5. D. H. Desty, W. T. Swanton, J. Phys. Chem., vol. 67, p. 766, 1961.
6. Ya. L. Gol'dfarb, M. A. Kalik, M. L. Kirmalova, ZhOKh, vol. 29, p. 2034, 1959.

19 September 1964

Institute of Organic Chemistry AS USSR, Moscow