

Notes

CHROM. 4900

The gas chromatographic behaviour of some isomeric derivatives of thiophene and furan

In this paper the gas chromatographic behaviour of the derivatives of thiophene and furan with different substituents on the 2 and 3 positions is examined on glass capillary columns with two different liquid phases. Previous work on these compounds is confined to the separation of the 2- and 3-isomers of acetylthiophene by PUCKNAT¹ at 125° with a 23 ft. × 1/4 in. column containing 20% Dow Corning F 1265 fluid on Diatoport, 60–80 mesh, and the separation of the 2- and 3-isomers of formylthiophene which were separated by OSTMAN² at 100° with an 10 ft. × 1/8 in. column containing 3% TCEPE on Aeropak, 80–100 mesh.

Experimental

Two glass capillary columns were used, containing, as liquid phases, trimer acid and Carbowax 20M. To obtain a uniform distribution of the liquid phase the two capillaries were precoated, the first one with a thin layer of carbon black³ and the other with polytrifluoroethylene⁴. They were then coated, respectively, with 10% trimer acid in methylene chloride and 15% Carbowax 20M in methanol. Table I gives the column characteristics.

TABLE I
COLUMN CHARACTERISTICS

	<i>Carbowax 20 M</i>	<i>Trimer acid</i>
Length (m)	30	88
Internal diameter (mm)	0.32	0.29
Capacity ratio <i>K'</i>	3.8 ^a	2.3 ^b
Number of theoretical plates	50,000 ^a	132,000 ^b

^a For *n*-tetradecane at 80°.

^b For *n*-hexadecane at 130°.

All the measurements were carried out with a Carlo Erba gas chromatograph Model G.I. equipped with a flame detector and using N₂ as carrier gas.

The following pairs of isomers have been examined. Thiophene derivatives: 2-acetylthiophene⁵, 3-acetylthiophene⁶, 2-formylthiophene*, 3-formylthiophene⁷, 2-trifluoroacetylthiophene⁸, 3-trifluoroacetylthiophene⁹, 2-benzoylthiophene¹⁰, 3-benzoylthiophene⁶, 2-acetylbenzothiophene¹¹, 3-acetylbenzothiophene¹¹. Furane derivatives: 2-acetylfuran⁵, 3-acetylfuran¹², 2-formylfuran*, 3-formylfuran¹², 2-benzoylfuran⁵, 3-benzoylfuran¹³. The references give the methods used for their preparation. The experimental data measured on the two columns are reported in Table II. The influence of the liquid phase polarity (trimer acid, slightly polar, and Carbowax, more

* Technical product.

TABLE II
GAS CHROMATOGRAPHIC RESULTS FOR THE SEPARATION OF THE 2- AND 3-ISOMERS OF THIOPHENES AND FURAN DERIVATIVES

No.	Compounds	Column temp. (°C)		$\alpha = V_R' (2)/V_R' (3)$		K'	Analysis time (min) (U opt.)		$R^2/t \times 10^2$ (sec ⁻¹)		
		Carbowax 20M	Trimer acid	Carbowax 20M	Trimer acid		Carbowax 20M	Trimer acid	Carbowax 20M	Trimer acid	
1	Acetylthiophenes	90	130	1.031	0.949	11.0	1.0	51	30	0.9	10.6
2	Formylthiophenes	80	80	1.138	0.987	8.8	2.4	41	73	8.6	0.1
3	Trifluoroacetylthiophenes	80	80	1.393	1.181	4.5	1.1	21	33	8.4	13.7
4	Benzoylthiophenes	175	175	1.168	1.071	4.3	4.8	19	144	80.0	13.1
5	Acetylbenzothiophenes	170	170	1.082	1.040	4.4	5.2	20	156	30.0	2.2
6	Acetylfurans	65	65	0.942	1.033	10.8	2.0	50	60	2.8	0.3
7	Formylfurans	80	65	1.102	1.000	4.0	1.6	18	47	16.5	—
8	Benzoylfurans	170	170	1.462	1.210	4.5	1.6	21	48	416	8.3

polar) is shown by the values of the separation factor as given by the ratio of the corrected retention volumes of the isomers substituted on position 2 and position 3.

$$\alpha = V_{R'}(2) / V_{R'}(3)$$

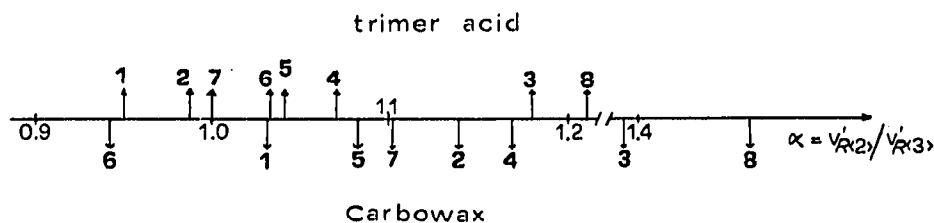


Fig. 1. Separation factors (α) on trimer acid and Carbowax columns for the compounds reported in Table II.

$\alpha < 1$ indicates a reversed elution order. By comparing the values for each couple of 2 and 3 isomers an inversion of the elution order ($\alpha < 1$) is observed for the acetyl and formyl thiophenes on trimer acid while with Carbowax the 2-isomer is eluted after the 3 isomer ($\alpha > 1$).

This behaviour can be explained by the fact that with these pairs of compounds the 2-isomer is more volatile and also more polar than the 3 isomer and consequently with the trimer acid column, which is less polar, the 2-isomer is eluted earlier, while with Carbowax, which is more polar, it is eluted after the 3 isomer.

The polarity and volatility act in opposite direction and on Carbowax the

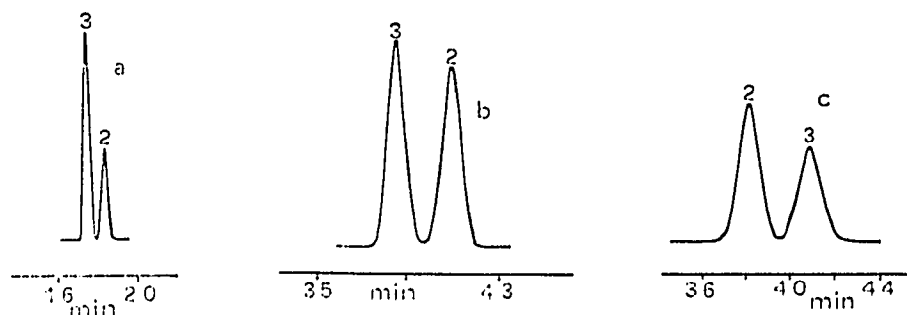


Fig. 2. Gas chromatographic separation on a Carbowax column of the 2- and 3-isomers of: (a) formylfuranes; (b) formylthiophenes; (c) acetylfuranes.

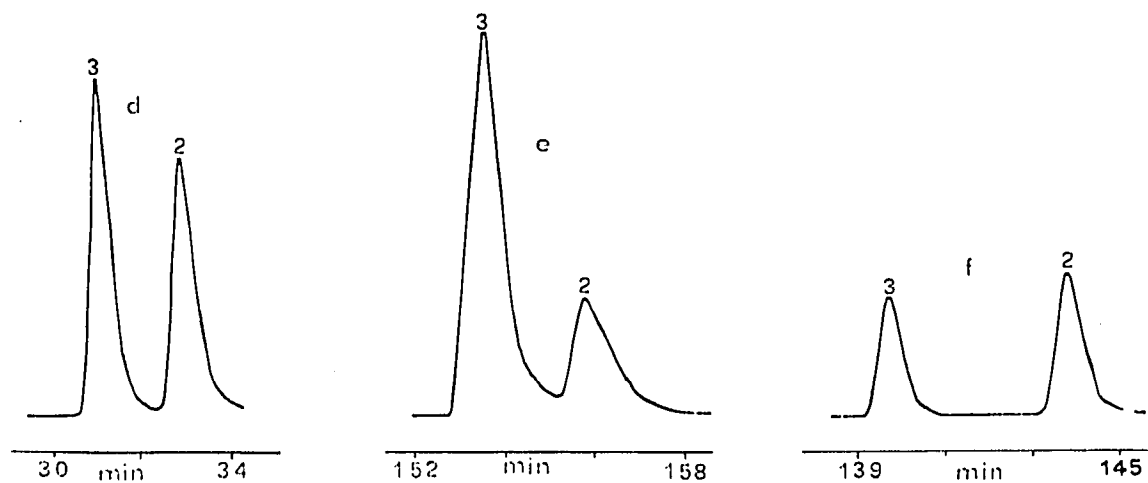


Fig. 3. Gas chromatographic separation on a trimer acid column of: (d) trifluoroacetylthiophenes; (e) acetylbenzothiophenes; (f) benzoylthiophenes.

first effect predominates and consequently the 2-isomer is retained more strongly than the 3-isomer.

For the other compounds, there is also an increase of α values on the Carbowax column with respect to the trimer acid, but since the 2-isomers are always eluted later from both the columns it is not possible to state if they are less volatile or more polar than the 3-isomer. With the formyl furans the values of α , very near to one, in the trimeric acid can be due to the fact that the 2-isomer is slightly more volatile than the 3-isomer but also more polar, as seen by their behaviour on the Carbowax column, and thus as the two effects almost compensate, the separation is very small. The stronger interaction observed from the gas chromatographic behaviour of thiophene and furan derivatives when a polar group is in position 2, as opposed to 3, can be explained from the stronger formation of hydrogen bonding with the free hydroxyl groups of the liquid Carbowax phase.

The α values on the liquid phases used for the compounds reported in Table II are plotted in Fig. 1. For all the compounds, except No. 6 (acetyl furan), separation factors on the trimer acid columns are less than those on Carbowax.

For the great majority of the compounds examined the gas chromatographic separation of the two isomers in 2 and 3 position is more easily achieved with a very polar liquid phase. With Carbowax the difference in polarity between the two molecules is enhanced. In a few cases, where the differences in vapour pressure are higher, as in the case of the acetylthiophenes, it is more convenient to use a less polar phase, such as the trimer acid; for the other pairs of compounds the vapour pressure differences are small and have an opposite effect to the polarity and consequently with Carbowax the α values differ more from unity. The Carbowax column in spite of a lower number of theoretical plates than the trimer acid column, generally gives a better separation with shorter retention times. This situation is shown from the last column of Table II where the ratio between the resolution and the analysis time measured under the best column conditions is reported. In Figs. 2 and 3 are shown some of the separations achieved.

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