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Note

Investigation of the isomeric composition of polyphenyl ethers by high-temperature gas chromatography

L. B. ITSIKSON and L. A. SHULGAITSER
All-Union Scientific Research Institute of Oil Refining, Aviamotornaya St. 6, Moscow E-116 (U.S.S.R.)
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The development of a method for the chromatographic analysis of polyphenyl ether isomers containing 4–6 phenyl groups in the molecule is described. These compounds have exceptionally low vapour pressures at temperatures up to 200–300° and also very high boiling points (up to 500–600°). They are therefore often used as the stationary phase in gas chromatography at temperatures up to 200° or higher (OS-124, OS-138)[1].

There is only one paper[2] in the literature concerning the analysis of polyphenyl ethers with 2–5 phenyl groups, performed in a column packed with SE-30 silicone elastomer, with temperature programming over the range 175–400°. The separation of the isomers was, however, inadequate.

Singlair *et al.*[3] showed the possibility of the chromatographic separation of tetra- and hexaphenyl ethers. One cannot, however, judge the efficiency of the recommended column packed with SE-52 silicone for separating isomers because each of the chromatograms presented contains only one peak. Perhaps it is necessary to use liquid phases characterized by a stronger molecular interaction with aromatic systems, compared with methyl silicones, in order to achieve effective separations of polyphenyl ether isomers. Therefore, in this work we used OV-17 methylphenylsilicone with a McReynolds constant, x', as high as 119, whereas the values for SE-30 and SE-52 silicones are 15 and 32, respectively[4].

EXPERIMENTAL AND RESULTS

The experiments were carried out using an LKhM-8MD instrument equipped with a differential dual flame ionization detector, with a 2 m × 2 mm I.D. column packed with 60–80 mesh Celite 545 coated with 5% OV-17. The column was conditioned at a nitrogen flow-rate of 30 ml/min, with temperature programming from 200 to 370° at the rate of 1.5°/min, followed by conditioning for 5 h at 370°. The column efficiency was 2100 theoretical plates, as calculated for the bis-(*p*-phenoxy)-*m*-phenoxyphenoxybenzene peak.

All the experiments on the separation of polyphenyl ethers were performed with high-purity nitrogen as the carrier gas. The carrier gas flow-rate was 26 ml/min, with hydrogen and air flow-rates of 30 and 240 ml/min, respectively, and a maximum sample size of 0.02 μl. The best separation was observed at 280° for tetraphenyl

TABLE I

RETENTION INDICES OF POLYPHENYL ETHER ISOMERS

*Peak No.**	*Compounds*	*Isomer*	*Column temperature (°C)*	*b***	*Retention index, I*
1	Tetraphenyl ethers	Bis-(*o*-phenoxy)phenyl ether	280	0.714	3272
2		*o,m'*-Diphenoxyphenyl ether			3347
3		*o,p'*-Diphenoxyphenyl ether			3434
4		Bis-(*m*-phenoxy)phenyl ether			3450
5		*m,p'*-Diphenoxyphenyl ether			3517
6		Bis-(*p*-phenoxy)phenyl ether			3646
1	Pentaphenyl ethers	Bis-(*o*-phenoxy)-*m*-phenoxy-phenoxybenzene	320	0.651	4179
2		*o,m'*-Diphenoxy-*m*-phenoxyphenoxy-benzene			4252
3		Bis-(*m*-phenoxy)-*m*-phenoxy-phenoxybenzene			4368
4		*m,p'*-Diphenoxy-*m*-phenoxy-phenoxybenzene			4445
5		Bis-(*p*-phenoxy)-*m*-phenoxy-phenoxybenzene			4527
1	*p*-Bis-(phenoxy-phenoxy)diphenyls	Not identified	360	0.553	5551
2		*p*-Bis-(phenoxyphenoxy)diphenyl			5648
3		Not identified			5766

* See Fig. 1.

** Tangent of the angle of inclination of the curve of log V'_R *vs.* the number of carbon atoms in the molecule for normal paraffins.

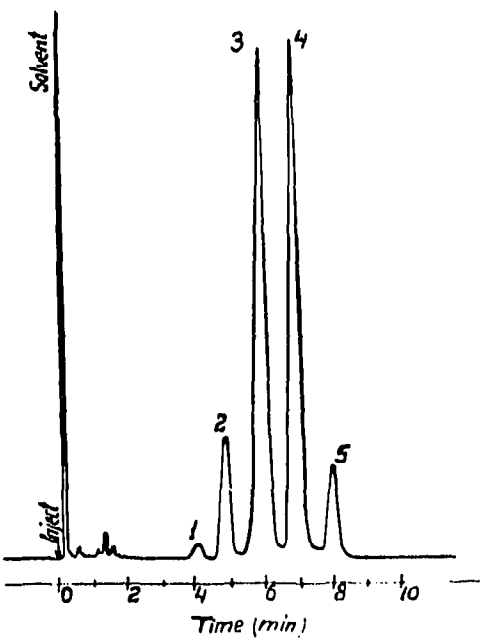

Fig. 1. Chromatogram of pentaphenyl ether isomers. Peaks: see Table I.

ethers, at 320° for pentaphenyl ethers and at 360° for *p*-bis-(phenoxyphenoxy)diphenyl. The retention indices of the isomers investigated are given in Table I, and the chromatogram of the pentaphenyl ether isomers is shown in Fig. 1. Peak identification was carried out by comparison with specially synthesized individual isomers, with the exception of the *p*-bis-(phenoxyphenoxy)diphenyl chromatogram, where only the largest peak was identified.

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