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Note

Separation of phenols on a polyphenyl ether with six rings. II

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Dihydric phenols are valuable raw materials for the chemical industry. Industrially they are produced by synthetic methods, or they are present in liquid products of the carbonization or gasfication of coal, shales, wood and other solid fuels from which in some instances it is of economic and technical interest to extract them.

In view of the present industrial need to increase the production of dihydric phenols, we focused our attention on the application of previous results[1] to the separation and determination of C_6–C_{10} dihydric phenols and some accompanying methoxyphenols in mixtures with other monohydric tar phenols.

As well as classical analytical methods[2–8], there are chromatographic methods for the solution of this problem using, for example, paper chromatography[9–13], liquid–liquid chromatography[14,15] and gas–liquid chromatography[16–24].

Kusý[22] pointed out that the elution of dihydric phenols from non-inert supports is not quantitative. For the separation of dihydric and monohydric phenols he used porous polymers based on styrene–divinylbenzene (Porapak Q) wetted with Carbowax 20M. Sidorov *et al.*[23] have recommended the use of the system 10% Apiezon L on Polychrom I. Other stationary phases used for the separation of dihydric phenols alone, or as their ethers, include SE-30 silicone gum, PMFS-4 (ref. 21) and PPG 20,000 (ref. 24).

In this work we investigated the use of a polyphenyl ether with 6 rings (PPE) as a stationary phase.

EXPERIMENTAL

The GC separations were carried out using the conditions described previously[1]. A Chrom-4 gas chromatograph (Laboratorní přístroje, Prague, Czechoslovakia) with a flame-ionization detector was used. The glass chromatographic column (2.4 m × 2 mm I.D.) was filled with PPE, at a concentration of 5% (w/w) as stationary phase. Chromaton N (AW, HMDS) (0.16–0.20 mm) was used as the support. The carrier gas was hydrogen at a pressure of 133.9 kPa, the amount of feed was 0.4–0.6 μl and the temperature of the feed cell was 300–350°. The separation of phenols was studied under isothermal conditions at 140, 160 and 180°.

Dihydric phenol standards were purified by preparative chromatography. The same stationary phase at a concentration of 5% (w/w) on Chromaton N (AW, HMDS) (0.20–0.25 mm) was used. The preparative column (3.6 m × 0.6 cm I.D.) was made of stainless steel and the carrier gas was hydrogen.

Mixtures were then prepared from these pure standards, and were repeatedly chromatographed with added *n*-alkanes. From the elution data the retention indices were calculated according to the relationship valid for the isothermal process.

RESULTS AND DISCUSSION

The Kováts retention indices for the dihydric phenol standards and some selected methoxyphenols were determined at 160°. In order to evaluate their thermal relationship, for the phenols with Kováts retention indices in the range 1400–1750 at 160°, their Kováts retention indices were also determined at 140°; for those with Kováts retention indices between 1550–2000 at 160°, Kováts retention indices were also determined at 180°. The results are given in Table I.

The results obtained show that the Kováts retention indices lie in the range 1400–2000, and that for none of the standards studied did the Kováts retention

TABLE I

KOVÁTS RETENTION INDICES (*I*) OF DIHYDRIC PHENOLS AND METHOXYPHENOLS IN A GC COLUMN CONTAINING 5% PPE ON CHROMATON N (AW, HMDS)

No.	*Substance*	*I*			ΔI_1	ΔI_2
		140°	*160°*	*180°*		
1	2-Methoxyphenol	1414	1426	—	12	—
2	3-Methoxyphenol	1598	1607	—	9	—
3	4-Methoxyphenol	1598	1607	—	9	—
4	2-Methoxy-4-methylphenol	1507	1520	—	13	—
5	2-*tert*.-Butyl-4-methylphenol	—	1815	—	—	—
6	2,3-Dimethylphenol	1590	1600	—	10	—
7	Pyrocatechol	1565	1576	1587	11	11
8	Resorcinol	1717	1727	1737	10	10
9	Hydroquinone	1716	1724	1733	8	9
10	3-Methylpyrocatechol	1621	1635	1650	14	15
11	4-Methylpyrocatechol	1667	1678	1688	11	10
12	2-Methylresorcinol	—	1759	1768	—	9
13	4-Methylresorcinol	—	1793	1800	—	7
14	5-Methylresorcinol	—	1793	1804	—	11
15	Methyl-1,4-dihydroxybenzene	—	1797	1803	—	6
16	3-Ethylpyrocatechol	1695	1706	1718	11	12
17	4-Ethylresorcinol	—	1868	1876	—	8
18	Ethyl-1,4-dihydroxybenzene	—	1873	1881	—	8
19	3,5-Dimethylpyrocatechol	1732	1740	1748	8	8
20	3,6-Dimethylpyrocatechol	1674	1687	1700	13	13
21	2,6-Dimethyl-1,4-dihydroxybenzene	—	1858	1866	—	8
22	4-*n*-Propylpyrocatechol	—	1861	1870	—	9
23	4-*n*-Propylresorcinol	—	1938	1950	—	12
24	3-Isopropylpyrocatechol	—	1758	1765	—	7
25	4-Isopropylpyrocatechol	—	1832	1830	—	7
26	Isopropyl-1,4-dihydroxybenzene	—	1917	1921	—	5
27	4-*tert*.-Butylpyrocatechol	—	1894	1899	—	5
28	3,5-Di-*tert*.-butylpyrocatechol	—	1990	2001	—	11

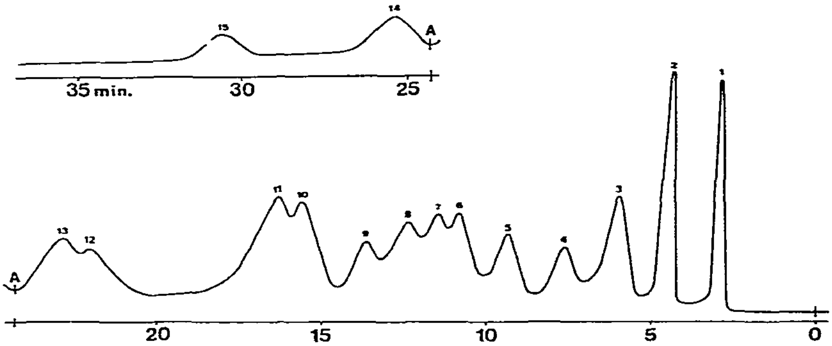

Fig. 1. GC separation of a mixture of dihydric phenols in a column packed with 5% (w/w). PPE at 160°. Peaks: 1 = pyrocatechol; 2 = 3-methylpyrocatechol; 3 = 4-methylpyrocatechol; 4 = 3-ethylpyrocatechol: 5 = resorcinol; 6 = 3,5-dimethylpyrocatechol; 7 = 2-methylresorcinol; 8 = 4-methylresorcinol; 9 = methyl-1,4-dihydroxybenzene; 10 = 4-ethylresorcinol; 11 = ethyl-1,4-dihydroxybenzene; 12 = 4-*tert*.-butylpyrocatechol; 13 = 4-*n*-propylresorcinol; 14 = 4-*tert*.-butylpyrocatechol; 15 = 4-*n*-propylresorcinol.

index (*I*) remain constant when the temperature was changed; the value increased with increasing temperature. Most frequently the value $\Delta I/20^\circ$ varied in the range 7–11. The greatest change in *I* was found with 2-methylpyrocatechol, being *ca.* 14.5 $\Delta I/20^\circ$ units. The next most significant changes in $\Delta I/20^\circ$ were found with 3,6-dimethylpyrocatechol (*ca.* 13) and 3-ethylpyrocatechol (*ca.* 12). Thus it can be seen that of the set of standards studied the greatest change in $\Delta I/20^\circ$ on the PPE stationary phase was found with *n*-alkylpyrocatechols with at least one substituent in the 3-position.

The possibility of separating pyrocatechols from the other two principal members of the homologous series of dihydric phenols (1,4-dihydroxybenzene and resorcinol) proved to be good. It is disadvantageous, however, that resorcinol and 1,4-dihydroxybenzene are not separated from each other with the PPE stationary phase.

Others pairs that are not separated are 2-methylresorcinol and 3-isopropylpyrocatechol; 4-methylresorcinol and 5-methylresorcinol; and 2,6-dimethyl-1,4-dihydroxybenzene and 4-*n*-propylpyrocatechol. The separation of 2-, 3- and 4-methoxyphenol is good, but 3- and 4-methoxyphenols are not separated. The Kováts retention indices for 2-methoxy-4-methylphenol and 2,3-dimethoxyphenols confirm the formation of intermolecular hydrogen bridges in phenols that have a methoxy group in the 2-position. Although the above phenols have a higher molecular weight than 3- and 4-methoxyphenol, they are eluted more quickly. The intermolecular hydrogen bridges weaken the strength of the intramolecular bridges between the phenol eluted and the weakly polar stationary phase used, thus accelerating the elution of the phenol.

REFERENCES

1 P. Buryan and J. Macák, *J. Chromatogr.*, 139 (1977) 69.
2 R. Scholder and M. Wolf, *Z. Anorg. Allg. Chem.*, 210 (1933) 184; *Chem. Zentralbl.*, (1933) 2661.
3 *GFR Pat.*, 854,523 (1952); *Chem. Zentralbl.*, (1953) 2521.

4 S. P. Burke and S. Caplan, *Ind. Eng. Chem.*, 19 (1927) 34.
5 *GFR Pat.*, 851,948 (1952); *Chem. Zentralbl.*, (1953) 7931.
6 *DR Pat.*, 743,572 (1943).
7 J. T. Edwards and R. J. Robinson, *J. Chem. Soc.*, (1952) 1080.
8 F. Boeck and G. Look, *Monatsh Chem.*, 53 (1931) 888.
9 V. Mráz, *Chem. Listy*, 44 (1950) 259.
10 L. L. Ingrahanc, *J. Amer. Chem. Soc.*, 74 (1952) 2297.
11 J. Franc, *J. Elektrochem.*, 61 (1957) 1059.
12 H. A. Schroeder, *J. Chromatogr.*, 30 (1967) 537.
13 J. Macák and F. Řehák, *Brennst.-Chem.*, 43 (1962) 80.
14 T. E. Young and J. R. Maggs, *Anal. Chim. Acta*, 38 (1967) 105.
15 J. Macák, P. Wimmer and J. Zacher, *Technology of Fuel, No. 5, Scientific Papers*, Institute of Chemical Technology, Prague, 1961, p. 251.
16 J. Janák and R. Komers, *Collect. Czech. Chem. Commun.*, 24 (1959) 1960.
17 W. Nauke and F. Tarkmann, *Brennst.-Chem.*, 9 (1964) 263.
18 Ju. E. Lille, L. A. Bitter, A. G. Murd, U. L. Pejnar and Ch. A. Kundel, *Tr. Tallin. Politekh. Inst., Ser. A*, No. 311 (1971) 127.
19 P. A. Hedin, J. P. Minyard, Jr., and A. C. Thompson, *J. Chromatogr.*, 30 (1957) 43.
20 Ch. A. Kundel, Ju. E. Lille, L. A. Bitter and E. Ju. Sorokinová, *Proceedings Conference on "Shale Alkylresorcinols, their Separation and Application"*, NIIS, Tallin, 1972.
21 T. A. Rudolfi, A. S. Leščiner and V. I. Luščik, *Sb. Anal. Khim.*, 24 (1970) 274.
22 V. Kusý, *J. Chromatogr.*, 57 (1971) 132.
23 R. V. Sidorov, V. I. Lebeděva, V. G. Lavrentěv and A. P. Lapan, *Khim. Tverd. Topl.*, 5 (1973) 95.
24 H. Pichler, P. Hennenberger and G. Schwarz, *Brennst.-Chem.*, 49 (1968) 175.