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Note

Qualitative and quantitative analysis of propylnaphthalenes by gas chromatography on silicone stationary phases

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Several stationary phases have been suggested for the gas chromatographic analysis of alkylnaphthalenes[1–4] and in some instances the Kováts retention indices are known[5,6].

The need for rapid and accurate qualitative and quantitative evaluations in our kinetic investigations of the propylation of naphthalene[7] required the development of a suitable method for the rapid gas chromatographic analysis of the four isomeric propylnaphthalenes that are formed simultaneously under the reaction conditions used. Because of their relatively short retention times and the large number of samples involved, packed columns were chosen.

EXPERIMENTAL

Propylnaphthalenes

The individual pure propylnaphthalene isomers were prepared by the Wurtz method[8]. 2-Isopropylnaphthalene containing up to 2% of the 1-isomer, an almost equimolar mixture of 2-isopropylnaphthalene with 2-*n*-propylnaphthalene and a mixture containing all four propylnaphthalenes in about equal proportions were obtained by Friedel–Crafts reactions[7].

Preparation of columns

Glass columns of length 2.5 and 6 m and I.D. 1.8 mm were used. Chromosorb W HP was coated with 4% of liquid stationary phase by rotary evaporation. When mixed stationary phases were used, packings were prepared by coating the support with both stationary phases simultaneously.

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Measurements

The optimal conditions, the Kováts retention indices and the retention time (R_t) *versus* $1/T$ (T = absolute temperature) plots were constructed from the data obtained with a Carlo Erba Fractovap P and a Pye Series 104 gas chromatograph, both equipped with a flame-ionization detector, using a 2.5-m column. The peak resolution was estimated with the Pye chromatograph using both 2.5- and 6-m columns. Argon at a flow-rate of 15 ml/min (inlet pressure about 1.4 bar, Δp *ca.* 140,000 Pa) was used as the carrier gas. The vaporizer temperature was maintained at 300°C.

RESULTS AND DISCUSSION

First we investigated the liquid stationary phases that had been applied by other workers[1–4] or seemed suitable to give a high resolution of the four propylnaphthalene isomers. The results obtained on various stationary phases under identical conditions are summarized in Fig. 1.

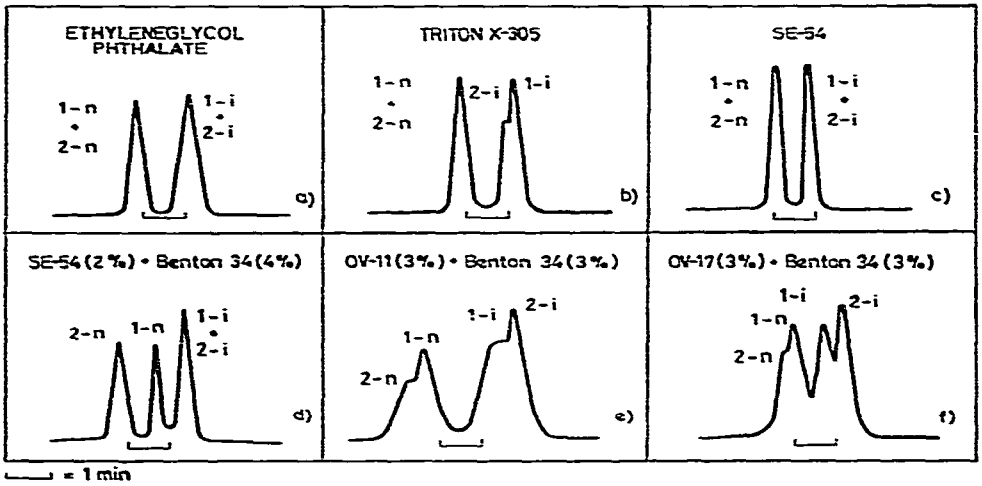

Fig. 1. Separation of the four propylnaphthalenes on various stationary phases. Temperature 150°C; carrier gas argon (15 ml/min).

Ethylene glycol phthalate, Triton X-305 and SE-54 (2.5-m columns) were not suitable for separating the four propylnaphthalene isomers but did show a good resolution of the side-chain isomers without any selectivity towards the positional isomers.

Benton 34 is widely used for the separation of positional isomers of alkylbenzenes[5], which suggested a test of the mixed stationary phases shown in Fig. 1d–f.

The use of a mixture of SE-54 and Benton 34 as the stationary phase showed some improvement: the *n*-propyl isomers were fully separated but the isopropyl isomers remained unresolved. Benton 34 seems to have selectivity towards the positional isomers of the *n*-propylnaphthalenes only.

In an earlier study some members of the UV series were found to be efficient for the separation of the isopropylnaphthalenes. Therefore, we decided to investigate OV-11 and OV-17 mixed with Benton 34. As can be seen in Fig. 1e and f, these packings do not give good resolution. This was caused by the different elution sequences of the *n*-propyl isomers on the Benton 34 and OV phases used in this instance, a tendency which became apparent after the determination of the Kováts retention indices (see Table I).

The investigations were extended to the higher members of the OV series. After optimal conditions had been found to be invariable over a wide range of

TABLE I

KOVÁTS RETENTION INDICES OF THE FOUR PROPYLNAPHTHALENES ON OV STATIONARY PHASES AT 150°C

Stationary phase	*Phenyl content (%)*	*Propylnaphthalene*			
		1-iso-	*2-iso-*	*1-n-*	*2-n-*
OV-1	0	1443	1442	1463	1470
OV-7	20	—	—	1552	1553
OV-11	35	1596	1582	1618	1616
OV-17	50	—	—	1669	1664
OV-22	65	—	1674	1717	1711
OV-25	75	1737	1713	1756	1748

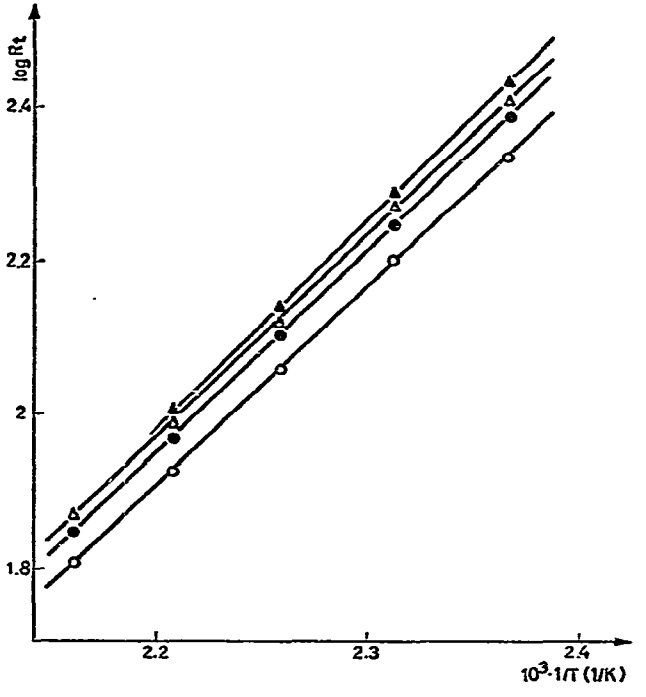

Fig. 2. Plots of log R_t *versus* $1/T$ on OV-25 stationary phase. Propylnaphthalene isomers: ▲, 1-*n*-; △, 2-*n*-; ●, 1-iso-; ○, 2-iso-.

flow-rates (argon, 10–20 ml/min), the effect of temperature on the retention times of the individual components was investigated. The plots of R_r *vs.* $1/T$ on OV-25 are shown in Fig. 2. The parallelism indicates that the interactions between the stationary phase and the components to be separated are similar and that the peak resolution will be not affected by temperature.

The Kováts retention indices of the four propylnaphthalenes were determined using the most important members of the OV series at 150°C. Table I shows that with increasing phenyl content of the stationary phase the difference between the retention indices of the isopropylnaphthalenes increases whereas the *n*-propyl isomers change their elution sequence. The values estimated on OV-1 are in good agreement with those determined by Engewald *et al.*[5] using a Golay-type column. Accordingly, OV-25 seemed the most suitable for the resolution of all four isomers.

Table II gives the peak resolution values on 2.5- and 6-m columns, and the chromatogram of an original sample is shown in Fig. 3. The latter shows that the 6-m OV-25 column gives nearly complete resolution of the four components, not only when all isomers are present in nearly equal amounts but also when the concentrations of the 1-isomers are low.

The analysis of a sample containing all four isomers required about 15 min.

TABLE II

PEAK RESOLUTION OF PROPYLNAPHTHALENES ON OV-25 STATIONARY PHASE AT 170°C

Column length (m)	*1-iso-/2-iso-*	*2-iso-/1-n-*	*1-n-/2-n-*
2.5	0.96	0.60	0.15
6	1.00	0.86	0.83

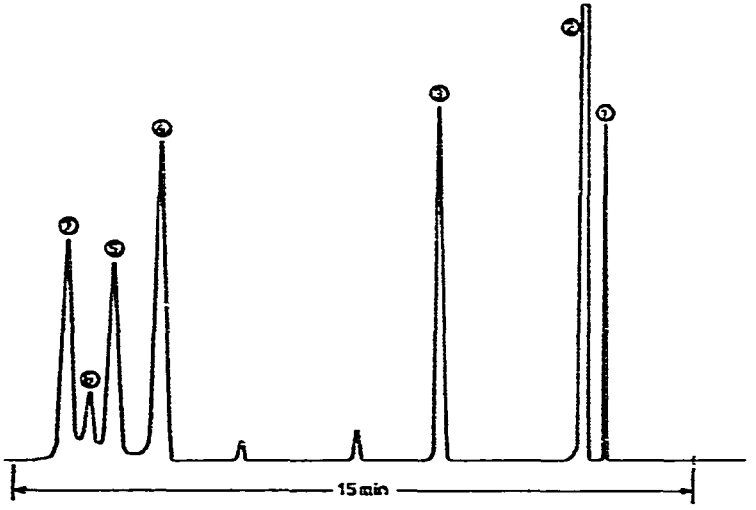

Fig. 3. Chromatogram of an original sample obtained on a 6-m OV-25 column. Temperature, 170°C; carrier gas, argon (15 ml/min). Peaks: 1 = isopropyl bromide; 2 = solvent; 3 = naphthalene; 4 = 2-isopropylnaphthalene; 5 = 1-isopropylnaphthalene; 6 = 1-*n*-propylnaphthalene; 7 = 2-*n*-propylnaphthalene.

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