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Note

High-performance liquid chromatographic separation and identification of pyrolysis products of benzene

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The identification of the pyrolysis products of benzene is far from complete, even though many studies have been carried out. In the range 837–1020°K, hydrogen and biphenyl are the principal reaction products, but traces of isomeric terphenyl and triphenylene have also been observed¹. At temperatures above 1020°K, ring fission occurs and polycyclic aromatic hydrocarbons (PAHs) are sometimes strongly adsorbed by the carbonaceous materials that are formed¹.

The purpose of the present work is to optimize a high-performance liquid chromatographic (HPLC) method² for the separation and identification of the products formed in the flash pyrolysis of benzene, carried out at very low conversions. As many of the high-boiling pyrolysis products show a marked fluorescence, the eluted compounds are readily revealed by a fluorescence detector, which allows on-line scanning of the chromatographic peaks, in series with a UV detector.

EXPERIMENTAL

Apparatus

The HPLC chromatograph constituted of Millipore-Waters Model M6000 solvent pumps and M660 gradient programmer, Perkin-Elmer LC75 UV-visible detector, and 650-10S fluorescence detector, and a Rheodyne 7105 sample injector (5- μ l loop).

Materials

Benzene and cyclohexane were special products for fluorescence analysis (E. Merck, F.R.G.). All other solvents were HPLC-grade products (Carlo Erba, Italy). The following PAH and polyphenyl standards for chromatography were used: naphthalene, anthracene, biphenyl and *p*-terphenyl (E. Merck), fluorene (BDH, U.K.),

m-terphenyl (Polyscience, U.S.A.), *o*-terphenyl (ICN Pharmaceuticals, U.S.A.) and dibenzo[*a,h*]anthracene, benzo[*a*]anthracene, triphenylene, phenanthrene, fluoranthene, benzo[*a*]pyrene, *p*-quaterphenyl, perylene, benzo[*ghi*]perylene and coronene (Fluka, Switzerland). Standards of chrysene, dibenzo[*a,c*]pyrene, benzo[*b*]chrysene and benzo[*c*]phenanthrene were kindly provided by the "Istituto sull'Inquinamento Atmosferico" (CNR), Rome, Italy.

Sample preparation

The apparatus for the pyrolysis of benzene has been described previously³. Benzene samples pyrolysed at 773 and 873°K afford a very small amount of ash, which sediment spontaneously. When the pyrolysis is carried out at 1073°K, ash formation becomes troublesome; they were therefore separated by centrifugation for 30 min, and extracted with 1 ml of cyclohexane in an ultrasonic bath for 30 min.

Cyclohexane was almost completely removed by a gentle stream of argon at room temperature, and the volume was restored to 0.5 ml with tetrahydrofuran (THF). Samples of benzene were diluted 1:2 with acetonitrile and analysed, as for the ash extract, by HPLC.

Chromatography

HPLC analysis was formerly performed by the following chromatographic system: a Spherisorb RP-18 column (particle diameter, $d_p = 5 \mu\text{m}$; 15 cm \times 4 mm I.D.; packed by Violet, Italy) with acetonitrile-water (80%) (20 ml), acetonitrile (12 ml) and THF (8 ml) as eluent at a flow-rate of 1 ml/min. This system provides good resolution of the main reaction products in relatively short times, thus allowing their identification. However it does not resolve the minor components of the mixture very well (especially the lesser retained compounds).

In order to improve the separation, the following chromatographic system was used: a LiChrosorb RP-18 column ($d_p = 5 \mu\text{m}$; 25 cm \times 4 mm I.D. (E. Merck) with isocratic elution with acetonitrile-water (55:45) for 20 min, isocratic elution with acetonitrile-water (60:40) for the next 20 min and then with acetonitrile-water (75%) for 30 min, gradient elution to 100% acetonitrile in a 40-min linear program, isocratic elution with acetonitrile for 8 min, linear gradient elution to THF-acetonitrile (50:50) for 5 min and then isocratic elution to THF-acetonitrile (50:50) for 5 min and then isocratic elution with THF-acetonitrile (50:50) for 10 min, all elution being carried out at a flow-rate of 1.5 ml/min.

Under such conditions, as shown by high-performance thin-layer chromatographic runs, even the more strongly retained compounds are removed from the stationary phase.

RESULTS AND DISCUSSION

The chromatogram of a sample of benzene pyrolysed at 1073°K is shown in Fig. 1. The chromatographic peaks and their fluorescence emission spectra have been compared with the 21 original samples of PAHs and polyphenyls at our disposal.

We were able to identify ten of these compounds in the chromatogram of the benzene sample, *viz.* naphthalene, biphenyl, phenanthrene, *o*-terphenyl, triphenylene, *m*-terphenyl, benzo[*c*]phenanthrene, *p*-terphenyl, benz[*a*]anthracene and *p*-quater-

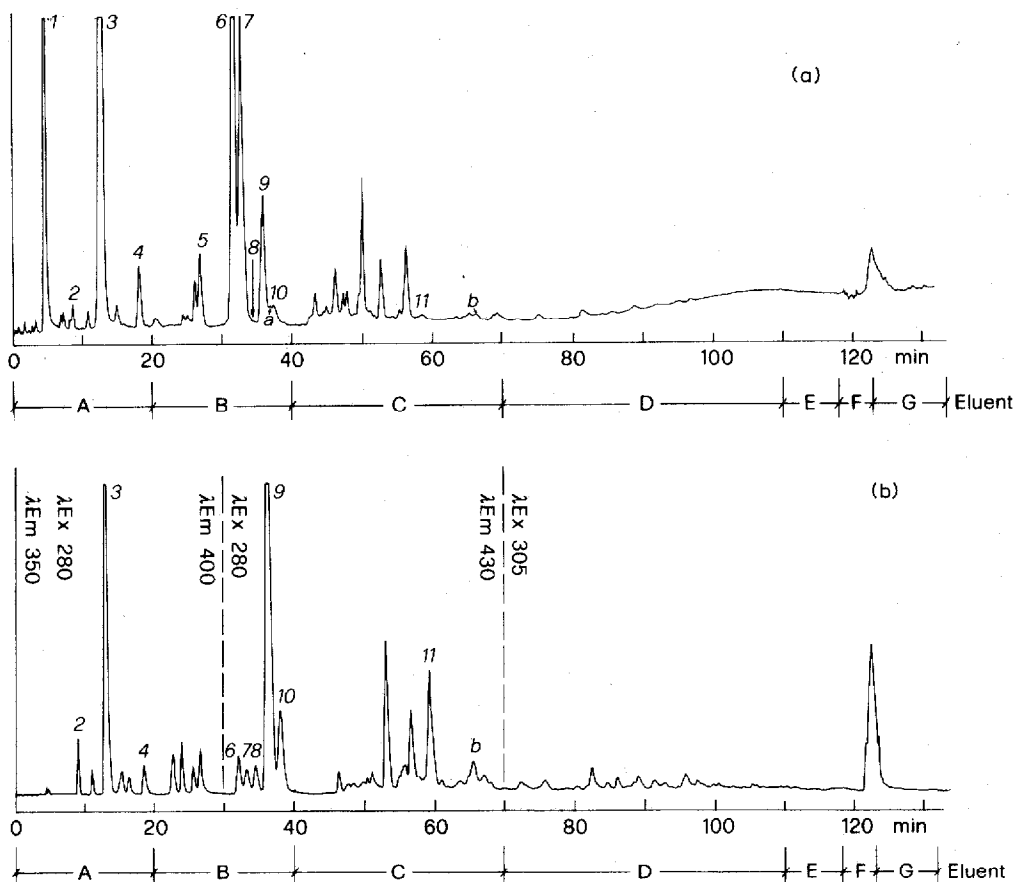


Fig. 1. Elution curves of a benzene sample pyrolyzed at 1073°K (diluted 1:2 with acetonitrile). (a) UV detected at 254 nm (a.u.f.s. 0.064). Solvent program: eluent A = acetonitrile-water (55:45); eluent B = acetonitrile-water (60:40); eluent C = acetonitrile-water (75:25); eluent D = linear gradient to 100% acetonitrile; eluent E = acetonitrile; eluent F = linear gradient to 50% THF in acetonitrile; eluent G = THF-acetonitrile (50:50). Peaks: 1 = benzene; 2 = naphthalene; 3 = biphenyl; 4 = phenanthrene; 5 = *o*-terphenyl; 6 = *m*-terphenyl; 7 = triphenylene; 8 = benzo[*c*]phenanthrene; 9 = *p*-terphenyl; 10 = benzo[*a*]anthracene; 11 = *p*-quaterphenyl. Peak a probably corresponds to chrysene, peak b to dibenzo[*a,c*]pyrene. (b) Fluorescence detected at the excitation and emission wavelength described in the figure. Solvent program and peak numbering as in (a).

phenyl (chromatographic and fluorescence data are listed in Table I).

Chrysene and dibenzo[*a,c*]pyrene are probably also present in the sample, but chrysene is poorly resolved from benzo[*a*]anthracene, which quenches its fluorescence spectrum, and the dibenzo[*a,c*]pyrene peak partially overlaps that of an unidentified compound and so its presence cannot be determined unambiguously.

Apart from the identified compounds, which can account for more than 90% of the pyrolysis products, many peaks are present which we cannot identify at present, either because their chromatographic parameters do not correspond to any of our standards, or because they are present in amounts too small to allow identification by fluorescence spectroscopy. Among these substances there is a group of strongly

TABLE I

CHROMATOGRAPHIC AND FLUORESCENCE DATA OF THE COMPOUNDS INVESTIGATED

 t_R = Retention time; k' = capacity factor.

Compound	Chromatographic data		Fluorescence emission data	
	t_R	k'	λ_{max} (nm)	Excitation wavelength (nm)
Naphthalene	8 min 40 sec	7.8	325, 337	280
Biphenyl	12 min 30 sec	11.6	315	280
Phenanthrene	18 min 10 sec	17.2	349, 366, 385	280
<i>o</i> -Terphenyl	27 min	26	350	280
<i>m</i> -Terphenyl	32 min	31	340	280
Triphenylene	33 min	32	355, 364, 372	280
Benzo[<i>c</i>]phenanthrene	34 min 20 sec	33.4	399	280
<i>p</i> -Terphenyl	36 min	35	327, 340	280
Benzo[<i>a</i>]anthracene	37 min 50 sec	36.8	388, 412, 435	280
<i>p</i> -Quaterphenyl	58 min 50 sec	56.2	355, 367	280

retained, dark yellow compounds, which show a pronounced fluorescence at an excitation wavelength of 305 nm and an emission wavelength of 430 nm.

The chromatogram of benzene pyrolysed at 873°K does not differ significantly from that at 1073°K, while at 773°K, biphenyl, with traces of *m*- and *p*-terphenyl, is formed almost exclusively.

Qualitatively, the chromatogram of the ash extract corresponds to that of the surrounding solution, showing that no preferential adsorption of the higher-molecular-weight compounds on the ash takes place. These results, which seem to be in contrast with a previous report¹, can be ascribed to different pyrolysis conditions.

CONCLUSIONS

HPLC with selective detectors, a technique currently used for the identification of single components of complex mixtures, seems to be particularly useful in determining all the reaction products, since the great versatility of the hydrocarbon reversed phases and the variety of solvents that can be employed provide a complete finger-print of the analysed solutions⁴. Furthermore, use of selective detectors, in our case a spectrofluorimeter, gives good support to the identification of the eluted compounds.

ACKNOWLEDGEMENT

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