

The results obtained at 198° with the OV-17 stationary phase are comparable with those obtained at lower temperatures with the mixed phase QF-1 + DC-200; however OV-17 often permits one to obtain better separations. For example, it is superior for the four BHC isomers, for the methyl ester of some herbicides, and for compounds of the DDT series; however, the dieldrin/*p,p'*-DDE separation is not satisfactory at 198° whereas it is at 175° (Table I).

The use of OV-17 as a stationary phase has contributed to the solution of some of the problems in pesticide residue analysis, for example, the systematic analysis of pesticides in water (to be published). The pesticides are first separated into four groups, and the components of the first two groups are separated very well on the column with OV-17 (Figs. 1 and 2).

In addition, excepting for dimethoate, paraoxon and methylparaoxon, all the compounds listed in Table I are regularly eluted and give symmetrical peaks. There is, however, some disadvantage to this column since larger amounts of substances are necessary to obtain detector responses equivalent to those obtained when using other stationary phases such as the mixed QF-1 + DC-200 phase.

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- 1 B. J. GUDZINOWICZ, *The Analysis of Pesticides, Herbicides and Related Compounds using the Electron Affinity Detector*, Jarrel-Ash Co., Waltham, Mass., 1965.
- 2 J. A. BURKE AND W. HOLSWADE, *J. Assoc. Offic. Agr. Chem.*, 49 (1966) 374.
- 3 R. E. DUGGAN, *Pesticide Analytical Manual*, Vol. I. U.S. Department of Health, Education and Welfare, Food and Drug Administration, 1968.
- 4 R. S. HENLY, R. F. KRUPPA AND W. R. SUPINA, *J. Agr. Food Chem.*, 14 (1966) 667.
- 5 C. M. MENZIE AND R. M. PROUTY, *J. Gas Chromatog.*, 6 (1968) 64.
- 6 C. A. BACHE AND D. J. LISK, *J. Assoc. Offic. Anal. Chem.*, 51 (1968) 1270.
- 7 J. ROBINSON, A. RICHARDSON, B. BUSH AND K. E. ELGAR, *Bull. Environ. Contam. Toxicol.*, 1 (1966) 127.

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Thermal decomposition of some methyl substituted benzhydrols

Recently pyrolysis gas chromatography has been developed as a valuable method of analysis^{1,2}, suitable for a wide variety of volatile³⁻⁷ and non-volatile substances⁸⁻¹², especially polymers¹³. This method was chosen for a study of the thermal decomposition of some methyl substituted benzhydrols. The pyrolysis was performed by means of an electrically heated gold tube (Fig. 1), constructed in such a way that this furnace could easily be attached to the injection port of a Varian-Aerograph 1521-1B gas chromatograph. The pyrolysis temperature was $600 \pm 5^\circ$.

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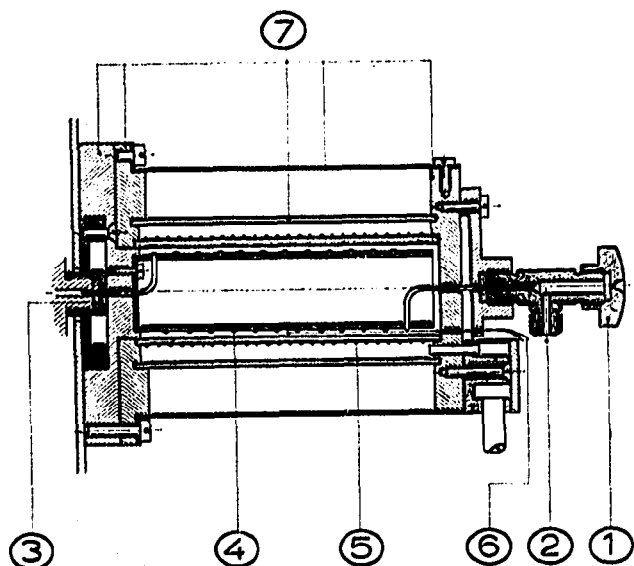


Fig. 1. 1 = injection port; 2 = carrier gas inlet; 3 = carrier gas outlet; 4 = gold tube (length 90 cm; I.D. 1 mm) in the form of a spiral around a steel cylinder; 5 = heating filament on ceramic support; 6 = thermocouple Ni/Cr-Ni; 7 = isolation material.

The benzhydrols were dissolved in either benzene or toluene; a 10% solution was used, of which 2 μ l was injected. No decomposition of benzene or toluene was observed at 600°.

The other chromatographic conditions were: column, 5% SE-30 on Chromosorb W (not acid washed; 60–80 mesh¹⁴); carrier gas, helium (99.99%); flow rate, 60 ml/min; oven temperature, 65°, after the appearance of the toluene peak the oven temperature was raised to 175°. A typical pyrogram is given in Fig. 2.

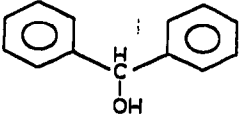
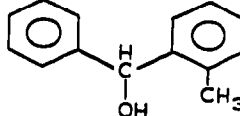
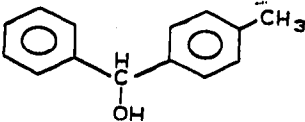
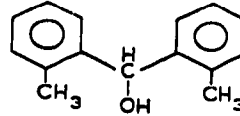
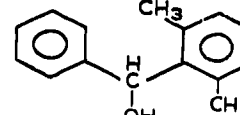
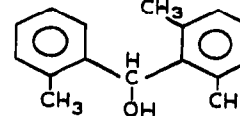
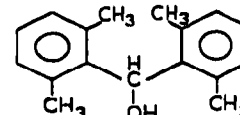
Among the benzhydrols studied the 2-methyl compound was pyrolysed repeatedly and the decomposition products sampled in cold traps. These products were analysed by means of their IR absorption spectra between 2–25 μ m, with a Grubb-Parsons Spectromaster.

The results were checked by injection of a quantity of the supposed pyrolysis product together with the benzhydrol into the gold tube. Increase of the peak height was taken as an indication that the IR spectrum had been interpreted correctly.

The pyrograms of the other benzhydrols were identified analogously and confirmation of the supposed compounds was performed in the same way. The results are summarised in Table I. The retention times of the various decomposition products remained constant after repeated runs, but the percentage of decomposition varied. Mean values are given in Table I for the percentage of decomposition.

The variation in the quantity of the decomposition products can be explained by the deposition of carbon on the wall of the gold tube during pyrolysis¹⁵. The extent of decomposition of benzhydrols is very low with a clean gold tube, but it increases when a carbon layer has been formed. It is possible to increase the extent of decomposition considerably by activation of this carbon layer with a stream of oxygen at 600° (ref. 16). It can be concluded therefore that a carbon layer promotes the decomposition of the benzhydrols, but the extent of this decomposition is related to the activity of the carbon, which diminishes after successive runs, but can be restored by oxygen treatment.

TABLE I

Benzhydrol	Decomposition products	% Decomposition product ^a	Relative retention time (toluene = 1)
	1 Methane 2 Benzene 3 Diphenylmethane 4 Benzhydrol	6 1 14 79	0.30 0.65 4.80 6.20
	1 Methane 2 Benzene 3 Toluene 4 2-Methyldiphenylmethane 5 2-Methylbenzophenone 6 2-Methylbenzhydrol	4 5 2 6 8 75	0.30 0.65 1.00 5.40 6.60 7.00
	1 Methane 2 Benzene 3 Toluene 4 4-Methyldiphenylmethane 5 4-Methylbenzophenone 6 4-Methylbenzhydrol	9 6 6 14 < 1 65	0.30 0.65 1.00 5.40 6.60 7.35
	1 Methane 2 Benzene 3 Toluene 4 Xylenes 5 2-Methyldiphenylmethane 6 2-Methylbenzophenone 7 2-Methylbenzhydrol 8 2,2'-Dimethylbenzhydrol	9 6 2 2 6 10 12 53	0.30 0.65 1.00 1.90 5.40 6.60 7.10 8.10
	1 Methane 2 Benzene 3 Toluene 4 Xylenes 5 2-Methyldiphenylmethane 6 2-Methylbenzophenone 7 2-Methylbenzhydrol 8 2,6-Dimethylbenzhydrol	10 4 12 2 9 10 10 43	0.30 0.65 1.00 1.90 5.40 6.60 7.10 8.10
	1 Methane 2 Benzene 3 Toluene 4 Xylenes 5 2-Methyldiphenylmethane 6 2-Methylbenzhydrol 7 2,2',6-Trimethylbenzophenone 8 2,2'-Dimethylbenzhydrol 9 2,2',6-Trimethylbenzhydrol	10 3 8 5 5 < 1 5 5 59	0.30 0.65 1.00 1.90 5.40 6.90 7.60 8.00 9.50
	1 Methane 2 Benzene 3 Toluene 4 Xylenes 5 A diphenylmethane 6 2,2',6-Trimethylbenzhydrol 7 ? 8 2,2',6,6'-Tetramethylbenzhydrol	10 6 2 6 27 4 6 39	0.30 0.65 1.00 1.90 5.40 9.20 10.10 11.30

^a Calculated from the peak heights.

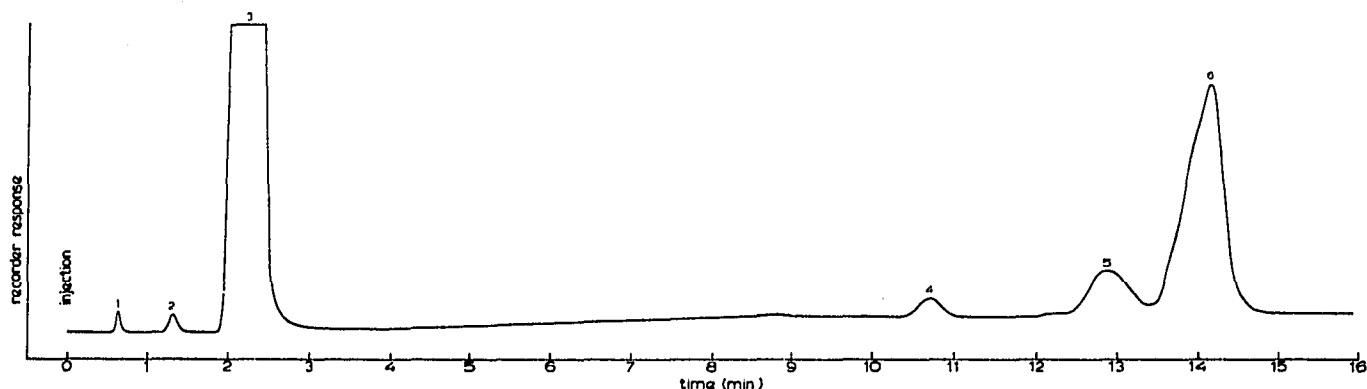


Fig. 2. Pyrogram of 2-methylbenzhydrol under standard conditions. Decomposition products 1-6 as in Table I.

It can be seen from Table I that several benzhydrols were decomposed into a diphenylmethane and a benzophenone in almost equal amounts. This disproportionation is interesting and will be studied in more detail. It is believed that radical mechanisms are responsible for the formation of these and many other decomposition products, formed during pyrolysis of the benzhydrols.

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- 1 M. BEROZA AND R. A. COAD, *J. Gas Chromatog.*, 4 (1966) 199.
- 2 R. L. LEVY, *J. Gas Chromatog.*, 5 (1967) 107.
- 3 J. H. DHONT, *Nature*, 192 (1961) 747.
- 4 J. H. DHONT, *Nature*, 200 (1963) 882.
- 5 J. H. DHONT, *Analyst*, 89 (1964) 71.
- 6 J. Q. WALKER AND C. J. WOLF, *Anal. Chem.*, 40 (1968) 711.
- 7 D. L. FANTER, J. Q. WALKER AND C. J. WOLF, *Anal. Chem.*, 40 (1968) 2168.
- 8 D. R. DILL AND R. L. MCKINLEY, *J. Gas Chromatog.*, 6 (1968) 68.
- 9 D. NOFFZ, W. BENZ AND W. PFAB, *Z. Anal. Chem.*, 235 (1968) 121.
- 10 F. FARRÉ-RIUS AND G. GUIOCHON, *Anal. Chem.*, 40 (1968) 998.
- 11 P. I. A. SZILAGYI, D. E. SCHMIDT AND J. P. GREEN, *Anal. Chem.*, 40 (1968) 2009.
- 12 S. K. YASUDA, *J. Chromatog.*, 35 (1968) 323.
- 13 G. M. BRAUER, *J. Polymer Sci.*, 8 (1965) 3.
- 14 A. M. AVEDIKAN, J. CHAPUT, S. COFFI N'KETSIA, J. DAUSQUE, A. KERGOMARD, J. M. RONDIER AND H. TOUTOU, *Bull. Soc. Chim. (France)*, (1966) 95.
- 15 M. DYSON AND A. B. LITTLEWOOD, *J. Gas Chromatog.*, 6 (1968) 451.
- 16 C. L. MANTELL, *Adsorption*, Chem. Eng. Series, McGraw-Hill, New York-London, 1951, p. 154.

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