Notes

CHROM. 6104

Determination of organic peroxides by gas chromatography

The applications of organic peroxides have considerably increased during the last few years. Most noteworthy are the epoxidation of olefinic bonds and the oxidation of tertiary amines to amine oxides; the well-established production of phenol from cumene hydroperoxide is still in use. Hence a convenient method for the determination of hydroperoxides, especially the industrially important cumene, ethylbenzene and *tert.*-butyl hydroperoxides, is of great value.

The methods most commonly used to date have been chemical, in particular iodimetric, ferrometric, stannometric, arsenometric, etc. The very sensitive methods of paper chromatography are not much used as they are extremely time-consuming. Polarographic, spectral and colorometric methods may also be applied.

Determination by gas chromatography is complicated primarily by the thermolability and high reactivity of organic peroxides[1]. The conditions for the quantitative GLC analysis of the decomposition products of cumene hydroperoxide have been described[2]. RUBAN AND KOROL[3] established the GLC conditions for the determination of cumene hydroperoxide at concentrations of 0.1–20% with a relative accuracy of 4%. They used silanized Chromosorb G with 1.5% tricresyl phosphate as packing at an operating temperature of 100°.

Our method permits the direct quantitative determination by gas chromatography of even less stable organic peroxides. The determination is not affected by the other components in the reaction mixture, which is a problem with several other methods (for example, in the use of certain chemical methods, organic hydroperoxides and epoxides mutually interfere in the determination).

Table I shows the decomposition half-lives of the hydroperoxides[4] studied.

TABLE I

THERMAL STABILITY OF ORGANIC HYDROPEROXIDES

Hydroperoxide	*Half-life at selected temperature*[a]		*10-h half-life (°C)*
	°C	*h*	
tert.-Butyl hydroperoxide	130	520	172
	145	120	
	160	29	
Cumene hydroperoxide	115	470	158
	130	113	
	145	29	
	160	9	

[a] All half-life determinations were made in benzene at concentrations of 0.1–0.2 *M*.

Although basic information is given on the thermal stability of two of the most commonly used organic hydroperoxides, these values are not directly applicable under the conditions of GLC determination. Values are not given for ethylbenzene hydroperoxide but, according to FANČOVIČ AND HRUŠOVSKÝ[5], it is less thermally stable than the other two.

Organic hydroperoxides are highly polar materials that are capable of forming, for example, sodium salts. Their low thermal stability, high reactivity and polarity complicate their chromatographic determination. Hence it is necessary to use a relatively low temperature, an inactive support and a fixed phase of low polarity.

Experimental

Preparation of pure compounds. Cumene hydroperoxide was prepared[6] by the liquid-phase oxidation of cumene with oxygen in an aqueous emulsion without a catalyst. Ethylbenzene hydroperoxide was prepared in the same manner[6] from ethylbenzene at 130–135°. When the oxidation was complete, the concentration of cumene hydroperoxide was 24–27% and that of ethylbenzene hydroperoxide 10–12%. More concentrated solutions were prepared by vacuum distillation (1 Torr) of solvent. *tert.*-Butyl hydroperoxide was prepared by the oxidation of *tert.*-butyl alcohol with hydrogen peroxide in sulphuric acid. The di-*tert.*-butyl peroxide content, after isolation by distillation, was 6%.

Analyses. All GLC analyses were carried out on a Chrom II chromatograph with flame ionization detection. Glass columns of 3 mm I.D. and 2 m or 2.3 m length were used. Column 1 was filled with 15% Silikon für Gaschromatographie (Merck) on Chromaton N-AW HMDS (Lachema, Brno), 100–70 mesh. Silikongummi (Merck) was used to coat the solid support by the rotating evaporator method using acetone as solvent. Column 2, which was obtained complete from Lachema, Brno, was filled with 10% methylvinylsilicone polymer SE-54 on Chromaton N-AW HMDS, 100–70 mesh.

The results given in Table II were obtained by injection of about 1 μl of sample. The concentration of hydroperoxide in these samples was varied in the range 0–90%; the other principal components were hydrocarbons and alcohols of the same basic skeletal structure as well as olefins, the corresponding alkene oxide and, in some cases, acetophenone. The samples were injected directly into the column in order to avoid thermal decomposition at hot metal inlet-ports. Nitrogen was used as the carrier gas

TABLE II

RELATIVE ELUTION TIMES OF ORGANIC HYDROPEROXIDES IN GLC DETERMINATION

Compound	*Operating temperature* (°C)	*Relative elution time* *Column 1*	*Column 2*
Cumene	148	1.00	1.00
Ethylbenzene		0.78	0.77
Dimethylphenyl carbinol		1.75	1.87
Methylphenyl carbinol		1.76	1.86
Cumene hydroperoxide		3.27	3.62
Ethylbenzene hydroperoxide		2.99	3.30
tert.-Butyl alcohol	82	1.00	1.00
tert.-Butyl hydroperoxide		2.96	2.33

at a flow-rate of 15.5 ml/min. The time taken for one analysis was about 25 min; all other parameters are given in Table II.

Results and discussion

Table II shows the relative elution times of the individual hydroperoxides and of the corresponding hydrocarbons (or carbinols) on both columns with respect to cumene (or *tert.*-butyl alcohol) which serves as the internal standard. Under these conditions, it was also possible to determine the other thermally unstable components, especially the corresponding alkene oxide (or carbinol), formed by the epoxidation of double bonds by organic hydroperoxide. Fig. 1 gives an example of the determination of the individual components of the reaction mixture in the epoxidation of cyclohexene with cumene hydroperoxide. The analysis conditions used were as given in Table II.

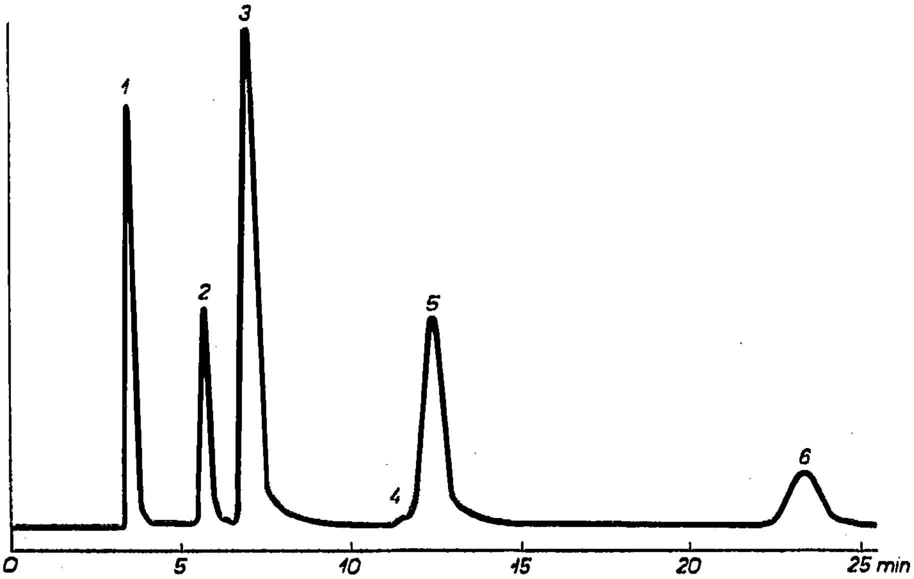

Fig. 1. Chromatogram (column 1) of the reaction mixture from the epoxidation of cyclohexene with cumene hydroperoxide. 1 = Cyclohexene; 2 = cyclohexene oxide; 3 = cumene; 4 = acetophenone; 5 = dimethylphenyl carbinol; 6 = cumene hydroperoxide.

The results of the individual determinations were consistent with those obtained by iodimetric titrations of the same hydroperoxides.

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