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## Note

### High-performance liquid chromatography of bis(2-ethylhexyl)-peroxydicarbonate on spherical silica gel

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Organic peroxides are used as initiators of radical polymerization reactions and as synthetic intermediates in industrial processes. They are relatively involatile but are thermally unstable. The most routine analysis of peroxides is concerned with the non-selective determination of total peroxide oxygen, as most organic peroxides are readily reduced by iodide ions in acidic solution<sup>1</sup>.

Gas chromatography (GC) of organic peroxides is complicated primarily by their thermolability and high reactivity<sup>2-4</sup>. However, some information has been given<sup>5-7</sup> about the applicability of GC to the separation of hydroperoxides. Paper chromatography<sup>8</sup> and thin-layer chromatography (TLC)<sup>9</sup> have also been used for the separation of organic peroxides. More recently, high-performance liquid chromatography (HPLC) with ultraviolet (UV)<sup>1,10</sup> and amperometric<sup>11</sup> detection has been successfully applied to the determination of organic peroxides. However, there is no information in the literature on the determination of bis(2-ethylhexyl)peroxydicarbonate (BEHPDC), which is produced by oxidation of 2-ethylhexyl chloroformate (EHCF)<sup>12</sup> and is used as an active initiator of the radical polymerization of vinyl chloride.

The objective of this work was to find suitable HPLC conditions for the rapid resolution and determination of BEHPDC and EHCF.

#### EXPERIMENTAL

##### *Apparatus and column*

Investigations were carried out using a Liquochrom Model OE-307 liquid chromatograph equipped with a stopped-flow injector and a Model OE-308 variable-wavelength UV detector (Labor MIM, Budapest, Hungary), connected to an OH-814/1 recorder (Radelkis, Budapest, Hungary) with a chart speed of 1 cm/min.

The column (250 × 4.6 mm I.D.), made of stainless steel with a polished inner surface, was pre-packed with 9- $\mu$ m Chromspher-Sil spherical silica gel (Labor MIM).

##### *Mobile phase*

The mobile phase was prepared by mixing *n*-hexane (analytical-reagent grade) obtained from Reachim (U.S.S.R.) or VEB Jenapharm (Apolda, G.D.R.) with 1,4-dioxane (analytical-reagent grade) obtained from P.P.H. POCh (Gliwice, Poland).

The solvent mixture was degassed under vacuum and was filtered through a 5- $\mu$ m stainless-steel sieve-filter before use.

### Standards

2-Ethylhexyl chloroformate (98%) supplied by Z.Ch. (Bydgoszcz, Poland), bis(2-ethylhexyl)peroxydicarbonate (95%) synthesized in this Institute, 2-ethylhexanol-1 (purum) obtained from Loba-Chemie (Vienna, Austria), 2-ethylhexanal-1 (purum) from Fluka (Buchs, Switzerland), *n*-octanal (puriss) from PolyScience (Niles, IL, U.S.A.), diphenyl carbonate (98%) from Merck-Schuchardt (Hohenbrunn, G.F.R.) and toluene (puriss) supplied by P.P.H. POCh were used as standards.

### Procedure

The samples of BEHPDC mixed with toluene (3:1, w/w) were dissolved in the mobile phase at a concentration of 4–10 mg/ml and 0.1–0.2 mg of diphenyl carbonate as an internal standard was added to 1 ml of the solution. Aliquot samples (10  $\mu$ l) were injected using a microsyringe (S.G.E., Melbourne, Australia) into the HPLC column.

The flow-rate of mobile phase was 0.9 ml/min and the inlet pressure was about 25 bar. In all instances the column effluents were monitored with a UV spectrophotometric detector at 225 nm. All measurements were made at  $21 \pm 2^\circ\text{C}$ .

### RESULTS AND DISCUSSION

To investigate the separation of EHCF, BEHPDC, their impurities and toluene (which extracts the BEHPDC from the reaction medium and stabilizes it at the same time), spherical silica gel as the column packing material and *n*-hexane with

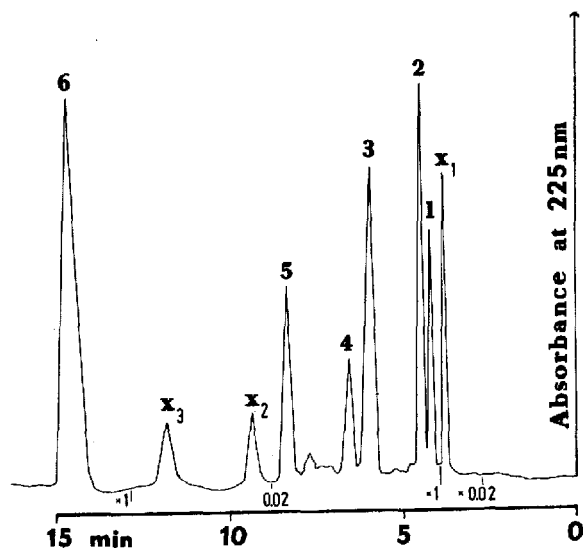


Fig. 1. HPLC separation of the mixture of standards. Column: 250  $\times$  4.6 mm I.D., stainless steel, packed with Chromspher-Sil (9  $\mu$ m). Mobile phase: *n*-hexane-1,4-dioxane (98.5:1.5, v/v). Flow-rate: 0.9 ml/min. Pressure: 25 bar. Temperature: ambient. Detection: UV, 225 nm. Sample size: 10  $\mu$ l. For peak identification, see Table I.

TABLE I  
RETENTION DATA

Peak No.*	Compound	Retention time (min)	Elution volume, $V_e$ (ml)
x <sub>1</sub>	Impurity from 2-ethylhexyl chloroformate	3.85	3.5
1	Toluene	4.20	3.8
2	2-Ethylhexyl chloroformate (EHCF)	4.50	4.0
3	Bis(2-ethylhexyl)peroxydicarbonate (BEHPDC)	5.95	5.3
4	<i>n</i> -Octanal	6.55	5.9
5	2-Ethylhexanal-1	8.35	7.5
x <sub>2</sub>	Impurity from BEHPDC	9.35	8.4
x <sub>3</sub>	Impurity from BEHPDC	11.80	10.6
6	Diphenyl carbonate**	14.70	13.2

\* See Fig. 1.

\*\* Internal standard.

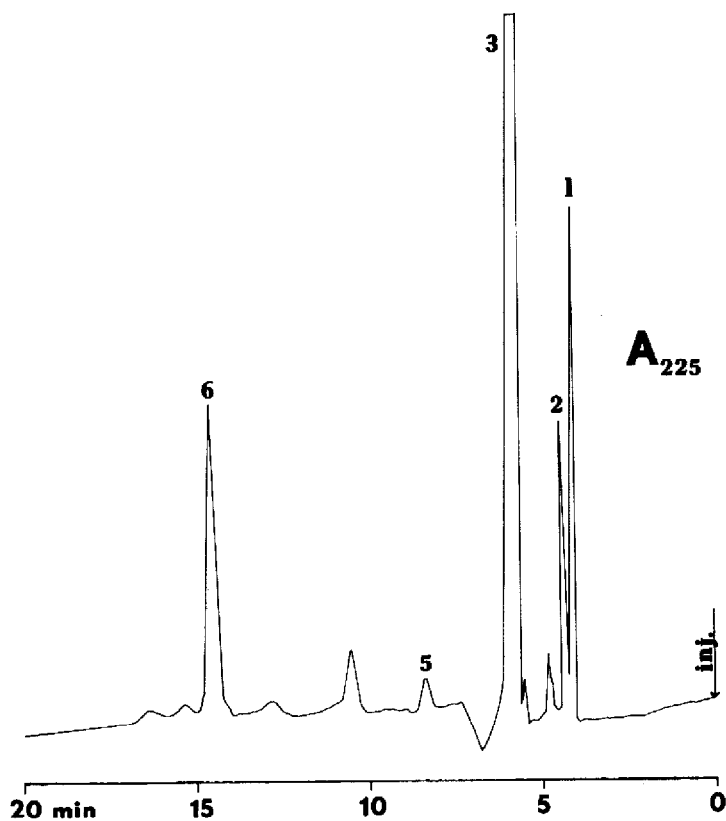


Fig. 2. HPLC trace of a sample taken from the EHCF oxidation process. Conditions as in Fig. 1. For peak identification, see Table I.

TABLE II

THERMAL STABILITY OF BEHPDC AT AMBIENT TEMPERATURE ( $21 \pm 2^\circ\text{C}$ )

Time after synthesis (h)	Concentration of BEHPDC (% w/w)	
	Sample I mixed with toluene, 75:25 (w/w)	Sample II without toluene
0	70.00	95.00
2	70.02	94.15
4	69.95	92.45
6	69.60	89.00

1,4-dioxane as the eluent were chosen. Satisfactory resolution of the mixture of standards was achieved by isocratic elution with *n*-hexane-1,4-dioxane (98.5:1.5, v/v). A typical chromatogram is shown in Fig. 1. Retention data of the compounds are given in Table I.

Fig. 2 shows the chromatogram of a sample taken from the EHCF oxidation

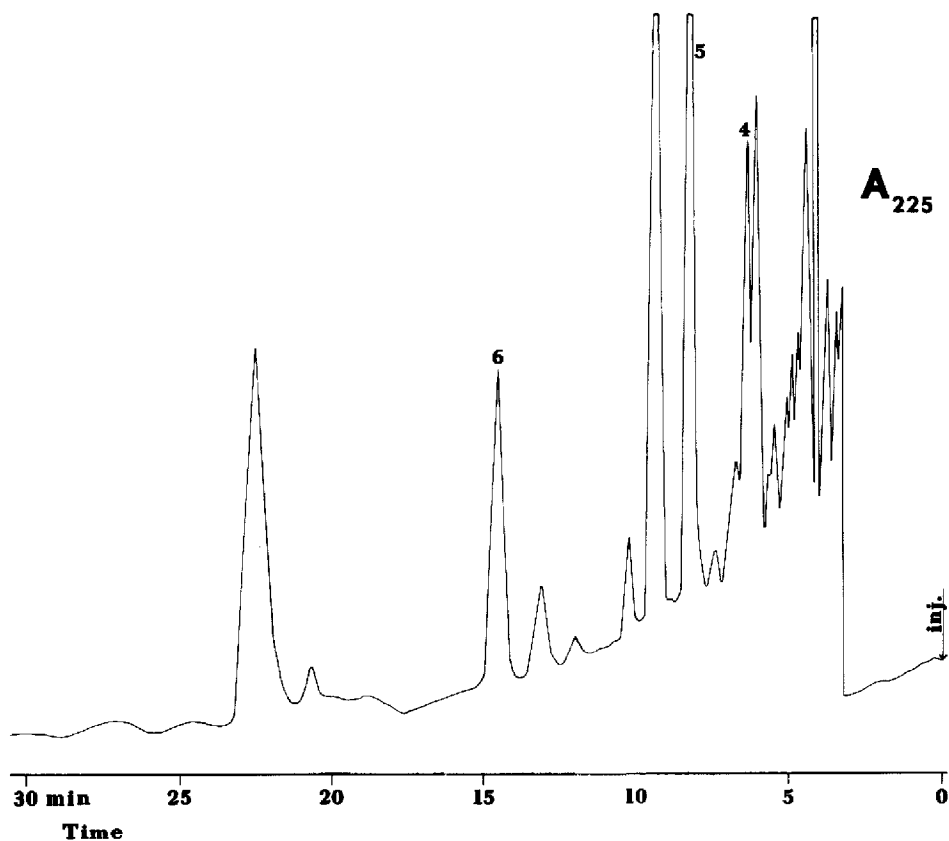


Fig. 3. HPLC trace obtained after thermal decomposition of BEHPDC at  $60\text{--}70^\circ\text{C}$ . Conditions as in Fig. 1. For peak identification, see Table I; other peaks unidentified.

process. Because the self-accelerating decomposition temperature (SADT) of BEHPDC was found<sup>13</sup> to be 5°C, the samples were stored at 0–5°C in toluene (3:1, w/w).

The thermal stability of BEHPDC at ambient temperature is shown in Table II. It can be seen that samples mixed with toluene do not decompose at ambient temperature for at least 2 h after the synthesis.

Fig. 3 shows a chromatogram obtained after thermal decomposition of pure BEHPDC at 60–70°C. Thermal degradation of BEHPDC resulted in liberation mostly of 2-ethylhexanal-1 and 2-ethylhexanol-1<sup>14</sup>. Silica can be used as a stationary phase to determine underivatized aliphatic alcohols by HPLC, but the low UV absorptivity of these compounds makes the detection of small amounts difficult<sup>15</sup>. In our work, 2-ethylhexanol-1 was not detected because of the conditions used (UV, 225 nm). Therefore, for the quantitative determination of BEHPDC an internal standard method was used. The results are given in Table III.

TABLE III  
RESULTS OF BEHPDC ANALYSES

Sample No.	Concentration of BEHPDC (mg/ml)		Standard deviation (mg/ml)	Mean recovery (%)
	Actual	Experimental*		
1	4.49	4.67	0.01	104
2	6.80	7.00	0.01	103
3	8.99	9.48	0.02	105

\* Means of three replicate injections.

## CONCLUSIONS

HPLC on spherical silica gel with isocratic elution at ambient temperature using *n*-hexane–1,4-dioxane (98.5:1.5, v/v) as the mobile phase and UV detection at 225 nm can be used to control the analysis of BEHPDC (stabilized with toluene) without decomposition of the sample. The method described is easy to perform and can be proposed for routine analysis in the industrial synthesis of bis(2-ethylhexyl) peroxydicarbonate.

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