

CHROM. 9116

LIQUID CHROMATOGRAPHY OF *tert.*-BUTYL PER-ESTERS OF SILYL-SUBSTITUTED CARBOXYLIC ACIDS ON MODIFIED ADSORBENTS

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(Received February 10th, 1976)

SUMMARY

Liquid chromatography on silica of high specific surface area, the surface of which has been modified by a monolayer, has been used for the separation and analysis of *tert.*-butyl per-esters of silyl- and germyl-substituted carboxylic acids; with increase in the amount of modifier, the elution time of the peroxides decreases. Optimal conditions for separating such compounds from impurities formed during a synthetic process have been established. Selectivity coefficients and separation factors for the peroxides $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ show that the best separation is achieved on a column packed with 30% of β,β' -oxydipropionitrile deposited on C-3 silica gel, *i.e.*, on a dense monolayer of this modifier with a high specific surface area. Compounds of the type $\text{R}_3\text{Si}(\text{CH}_2)_n\text{-C}_9\text{H}_{19}$ formed by thermal decomposition of peroxides in nonane solution, have been separated by a preparative method.

INTRODUCTION

Peroxide compounds are widely used as polymerization initiators and catalysts for various syntheses¹. However, the explosive nature and instability of many compounds of this class necessitate special methods for their analysis and purification. A method of liquid-solid molecular chromatography on thin layers deposited on adsorbents of high specific surface area (*s*) appeared to be particularly suitable for this purpose, and permitted the analysis of peroxides (with a suitable eluent) at room temperature². Also, this method provided the possibility of characterising the impurities and collecting the pure peroxides on the preparative scale. This paper describes the

use of liquid chromatography for the separation and analysis of eight *tert.*-butyl per-esters of silyl-substituted carboxylic acids with the general formula $(\text{CH}_3)_2\text{-RSi}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$, where $\text{R} = \text{CH}_3$ or C_6H_5 and $n = 1, 2, 3$ or 4 .

EXPERIMENTAL

The investigations were performed on a liquid chromatograph (Tsvet 301) equipped with a dielectric-constant detector and a stainless-steel column (67 cm \times 4 mm I.D.). The support materials used were C-3 silica gel³ ($s = 250 \text{ m}^2/\text{g}$; grain size 35–50 μm) and Woelm silica gel ($s = 260 \text{ m}^2/\text{g}$; grain size 100 μm), each coated with a layer of a strongly polar substance [β, β' -oxydipropionitrile (BOP)] or a less polar substance [Carbowax 600 (see ref. 4)] deposited from chloroform solution. Elution was carried out with *n*-hexane at room temperature, and samples were injected with a 10- μl syringe.

RESULTS AND DISCUSSION

It is known that unmodified silica adsorbents strongly retain complex organic substances; this complicates the use of liquid-solid chromatography on such adsorbents. However, liquid-liquid chromatography has poor selectivity for compounds of similar structure and also exhibits many procedural difficulties. Therefore, for use in liquid molecular chromatography, we studied methods of modifying the adsorbent in order to decrease retention values while maintaining good selectivity.

For the liquid chromatography of *tert.*-butyl per-esters of silyl-substituted carboxylic acids, C-3 silica gel coated with different amounts (5, 10, 20 or 30%) of BOP was used. With 5% of BOP, the selectivity was good but the retention time was almost 2 h. In this case, molecules of the test substances interacted not only with the BOP molecules, but also with uncoated active sites on the gel, and this sharply increased the elution times. The best separation of peroxides from impurities was attained on a column of C-3 silica gel coated with 30% of BOP (see Fig. 1); this coating ($1.2 \text{ mg}/\text{m}^2$) corresponds to a dense monolayer of the modifier⁵. In this instance,

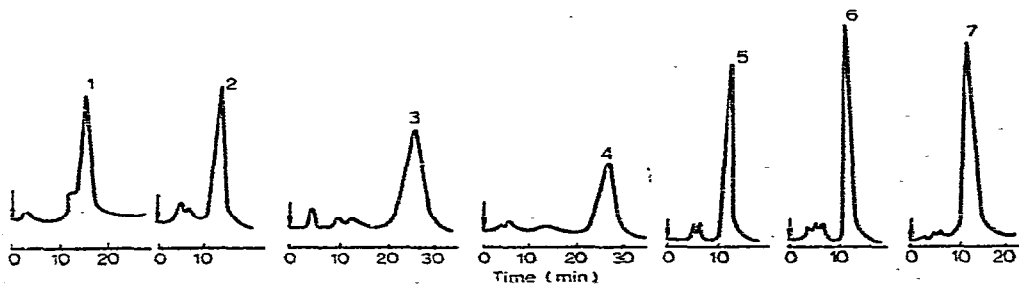


Fig. 1. Chromatogram of *tert.*-butyl per-esters of silyl-substituted carboxylic acids on C-3 silica gel with a modifying layer of BOP ($1.2 \text{ mg}/\text{m}^2$). Chromatograph: Tsvet-301, with a dielectric-constant detector and stainless-steel column (67 cm \times 4 mm I.D.). Eluents: *n*-hexane (2.0 ml/min). Temperature: ambient. Peaks: 1 = $(\text{C}_2\text{H}_5)_2\text{SiCH}_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 2 = $(\text{C}_2\text{H}_5)_2\text{Si}(\text{CH}_2)_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 3 = $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 4 = $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 5 = $\text{CH}_3(\textit{n}\text{-C}_4\text{H}_7)_2\text{Si}(\text{CH}_2)_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 6 = $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 7 = $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$.

the analysis time for peroxides of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ was 12.5 min and that of peroxides of the type $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ was 25 min. The deposited BOP molecules completely screened the active sites on the silica gel surface and also filled the fine pores (the specific areas of C-3 silica gel coated with 5 and 30% of BOP are 203 and 173 m^2/g respectively; the corresponding values for 20% of Carbowax 600 on the C-3 gel and for 30% of BOP on Woelm silica gel are 204 and 99 m^2/g , respectively). Since the solubility of the test substances in BOP is small, separation in this instance occurs mainly through differences in adsorption, *i.e.*, by LSC.

When separating peroxides on a column of Woelm silica gel coated with 30% of BOP (a coating of about 1.1 mg/m^2), with the other conditions being similar, the analysis time is reduced to 17 min for $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ and to 8 min for $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ (see Fig. 2); obviously, this is attributable to the lower specific surface area of the modifier film in comparison with the film on C-3 silica gel.

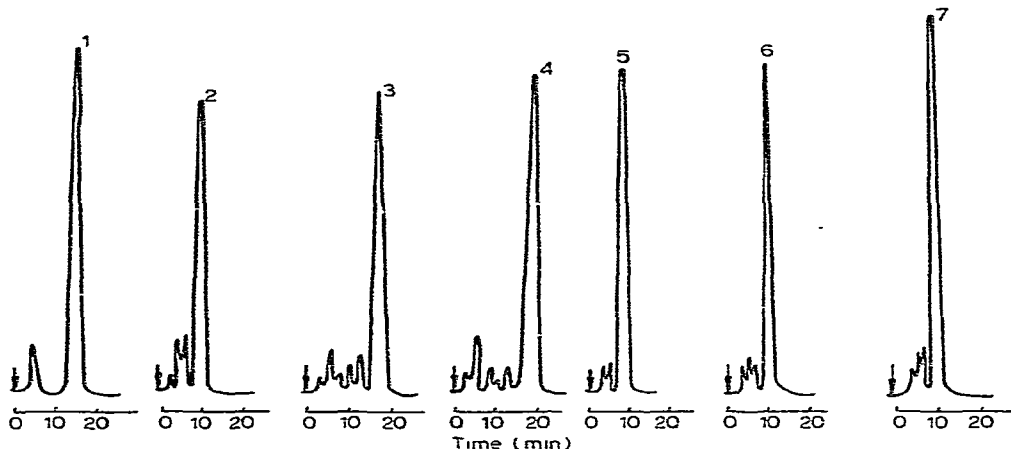


Fig. 2. Chromatogram of *tert.*-butyl per-esters of silyl-substituted carboxylic acids on Woelm silica gel with modifying layer of BOP (1.1 mg/m^2). Peaks and operating conditions as in Fig. 1.

Fig. 3 shows that, with separation on a 20% film of the less polar Carbowax 600 on C-3 silica gel (mean surface concentration $\approx 0.8 \text{ mg}/\text{m}^2$), the retention time is shorter than on the BOP film and the separation selectivity is diminished. The latter phenomenon is due to a decrease in the adsorbate-adsorbent interaction.

The separation of *tert.*-butyl per-esters of silyl-substituted carboxylic acids on these coated adsorbents was unsuccessful. Thus, when a mixture of eight peroxides was applied to such a column, only two peaks emerged (see Fig. 4); the first was due to peroxides of the type $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$, and the second to those of the type $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_n\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$.

By comparing the selectivity coefficients (r) and separation factors (R) (ref. 6) for peroxides of the type $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ obtained on the three columns specified in Table I, it can be seen

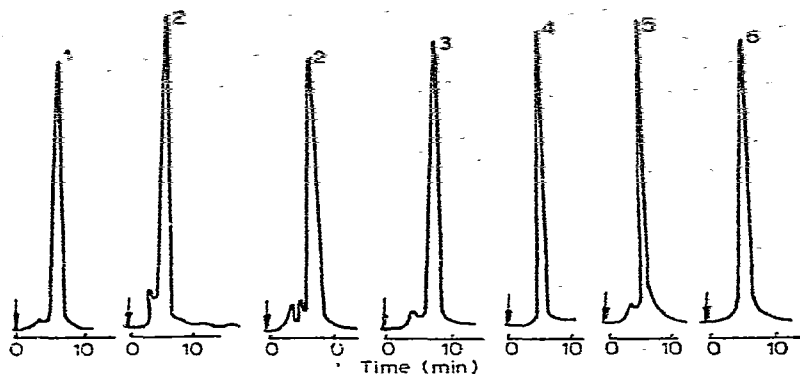


Fig. 3. Chromatogram of *tert.*-butyl per-esters of silyl-substituted carboxylic acids on C-3 silica gel coated with Carbowax 600 (0.8 mg/m²). Peaks and operating conditions as in Fig. 1.

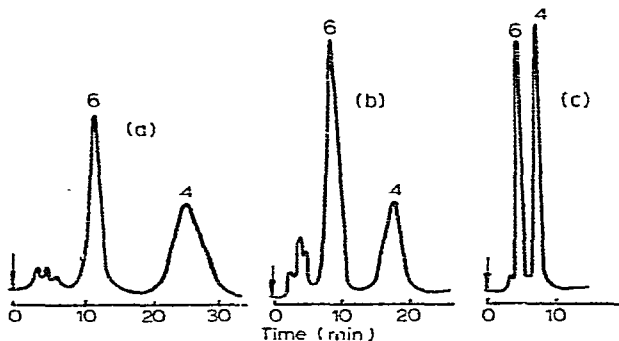


Fig. 4. Chromatogram of peroxides on different adsorbents: (a) on C-3 silica gel with modifying layer of BOP (1.2 mg/m²); (b) on Woelm silica gel with modifying layer of BOP (1.1 mg/m²); (c) on C-3 silica gel with modifying layer of Carbowax 600 (0.8 mg/m²). Peaks 4 and 6 and operating conditions as in Fig. 1.

TABLE I

COMPARISON OF SELECTIVITY COEFFICIENTS (r) AND SEPARATION FACTORS (R) FOR PEROXIDES $(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ AND $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_3\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$

Adsorbent	r	R
BOP on C-3 silica gel (30%, or 1.2 mg/m ²)	0.34	2.53
BOP on Woelm silica gel (30%, or 1.1 mg/m ²)	0.33	2.33
Carbowax 600 on C-3 silica gel (20% or 0.8 mg/m ²)	0.24	1.71

that the best separation was achieved on the column with 30% of BOP on C-3 silica gel, *i.e.*, on a dense monolayer with a rather large specific surface area.

The separation of thermal-decomposition products of the per-esters $(\text{CH}_3)_3\text{SiCH}_2(\text{CH}_3)\text{CHC}(\text{O})\text{OOC}(\text{CH}_3)_3$ and $(\text{CH}_3)_3\text{Si}(\text{CH}_2)_4\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$ in nonane solution was also investigated. Thermal decomposition of these compounds involves a free-radical mechanism and results in formation of a complex mixture of products; complete separation of these compounds by fractional distillation was not possible.

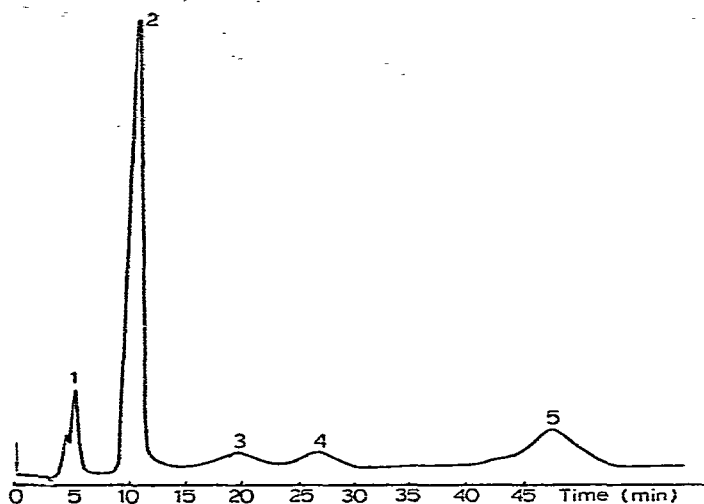


Fig. 5. Chromatogram of *tert.*-butyl per-esters of a germyl-substituted carboxylic acid, and related compounds, on C-3 silica gel with modifying layer of BOP (1.2 mg/m²). Peaks: 1 = (C₂H₅)₃Ge(CH₂)₂C(O)Cl; 2 = (C₂H₅)₃Ge(CH₂)₂C(O)OOC(CH₃)₃; 3 = unidentified; 4 = (C₂H₅)₃Ge(CH₂)₂-C(O)OH; 5 = (CH₃)₃COOH.

However, qualitative and quantitative analysis of the volatile products of thermal decomposition of the peroxides studied was achieved by the liquid chromatographic method described here. Pure (CH₃)₃SiCH₂(CH₃)CHC₉H₁₉ and (CH₃)₃Si(CH₂)₄C₉H₁₉ obtained through radical re-combination were separated from high-boiling decomposition products by preparative liquid chromatography. Thus, liquid chromatography on a dense monolayer deposited on an adsorbent can aid in elucidating the mechanism of complex reactions.

The proposed method has also been useful in separating the *tert.*-butyl per-esters of (triethylgermyl)propionic acid from impurities (see Fig. 5).

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