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ANALYSIS OF ORGANOMETALLIC COMPOUNDS BY LIQUID CHROMATOGRAPHY

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SUMMARY

Liquid chromatography has been used for the separation and analysis of some classes of thermally unstable organometallic peroxides and low-volatile polynuclear organometallic compounds. The optimal conditions for the separation of oxidation products of silicon-substituted phenols, *tert.*-butyl esters of silicon-, germanium- and tin-substituted peroxy-carboxylic acids have been determined. The compounds are separated on modifier monolayers applied to silica adsorbent supports having a large specific surface area. The method has also been applied to the separation and analysis of pentafluorophenyl polynuclear organometallic compounds. It enables an investigation of their reactivity, relative stability and the detection of intermediates and by-products.

INTRODUCTION

The development of the chemistry of organometallic compounds (OMCs), including organometallic peroxides which have great theoretical and practical significance¹, has necessitated thorough investigations of their compositions, structures, reactivities and physico-chemical properties. This cannot be done without quick and reliable methods of analysis. However, many OMCs are thermally unstable or have low volatility which makes difficult or even rules out the use of classical instrumental methods of analysis.

In the literature there are some data on the utilization of liquid chromatography (LC) for the analysis of complex metal compounds²⁻⁴. We have therefore investigated the application of modern LC to the separation and analysis of thermally unstable peroxides and low-volatile polynuclear OMCs.

EXPERIMENTAL

The investigations were carried out on Tsvet-303 and -304 liquid chromatographs equipped with a permeability detector and a UV detector (254 nm). Stainless-steel columns (25, 35 and 67 cm × 2, 3 and 4 mm I.D.) were used. The silica gels KCK-2 and C-3 with specific surface areas of 338 m²/g and 346 m²/g respectively and

Silochrom C-80 adsorbent with a specific surface area of $80 \text{ m}^2/\text{g}$ were used as supports⁵. These were coated with layers of highly polar β, β' -oxydipropionitrile (BOP) and less polar Carbowax 600 deposited from chloroform solution. The column was packed with the sorbent (grain size $10 \mu\text{m}$) by the balanced density method. *n*-Hexane and *n*-hexane-diethyl ether (32:1, 28:1 and 24:1, v/v) were used as eluents. Analyses were carried out at room temperature and at 45°C . Samples were injected with a $10\text{-}\mu\text{l}$ syringe.

The absolute calibration method was used for quantitative calculations. The error in the determination of concentrations was $\pm 7\%$.

The sensitivity of the detectors to the substances under study was calculated from the threshold sensitivity formula. It ranged from $1 \cdot 10^{-2}$ to $5 \cdot 10^{-5} \text{ mg/ml}$ for various classes of substances.

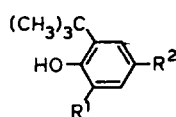
RESULTS AND DISCUSSION

On the basis of the obtained results, the most suitable method for the separation and analysis of the compounds studied (Table I) is liquid chromatography using silica gel supports with rather large specific surface areas and coated with a polar liquid which is strongly adsorbed. The latter strongly absorbs the components to be separated and is only slightly soluble in the eluent. This mode of LC meets the requirements for the separation of thermally unstable peroxide OMCs, and enables us to control the process by varying the quantity of the polar phase applied to the adsorbent.

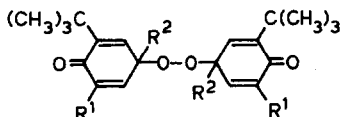
The compounds of the first class (see Table I) —silicon-substituted sterically hindered phenols, are thermally unstable and under migration of substituent in the *ortho*-position at high temperatures; this presents a problem for their analysis by gas chromatography⁶. The use of LC ruled out the possibility of these migrations and allowed a study of the synthesis and reactivity of such compounds.

TABLE I

CLASSES OF THERMALLY UNSTABLE PEROXIDE AND LOW-VOLATILE ORGANOMETALLIC COMPOUNDS INVESTIGATED



I a-d



II a-d

where a: $\text{R}^1 = \text{Si}(\text{CH}_3)_3$, $\text{R}^2 = \text{C}(\text{CH}_3)_3$; b: $\text{R}^1 = \text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5$, $\text{R}^2 = \text{C}(\text{CH}_3)_3$; c: $\text{R}^1 = \text{R}^2 = \text{Si}(\text{CH}_3)_3$; d: $\text{R}^1 = \text{R}^2 = \text{C}(\text{CH}_3)_3$.

III $\text{R}_3\text{M}-\text{O}-\text{O}-\text{M}'(\text{C}_6\text{H}_5)_3$

where $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, $n\text{-C}_5\text{H}_{11}$; $\text{M} = \text{M}' = \text{Si}$; $\text{M} = \text{Si}$, $\text{M}' = \text{Ge}$

IV $\text{R}^1\text{R}_2^2\text{M}(\text{CH}_2)_n\text{C}(\text{O})-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$

where $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{CH}_3$; $\text{R}^1 = \text{R}^2 = \text{CH}_3$; $\text{R}^1 = \text{R}^2 = \text{C}_2\text{H}_5$; $\text{M} = \text{Si}$, Ge ; $n = 1-4$

V $\text{ROC}(\text{O})\text{R}^1\text{C}(\text{O})-\text{O}-\text{O}-\text{C}(\text{CH}_3)_3$

where $\text{R} = \text{R}_3^2\text{M}$, R_3^2MCH_2 ; $\text{M} = \text{Si}$, Ge , Sn ; $\text{R}^2 = \text{CH}_3$, C_2H_5 , C_6H_5 ; $\text{R}^1 = \text{C}_2\text{H}_4$, C_6H_4

VI $(\text{C}_6\text{F}_5)_3\text{M}-\text{M}'-\text{PtL}_2-\text{M}(\text{C}_6\text{F}_5)_3$

where $\text{M} = \text{Ge}$, Sn ; $\text{M}' = \text{Cd}$, Hg ; $\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$

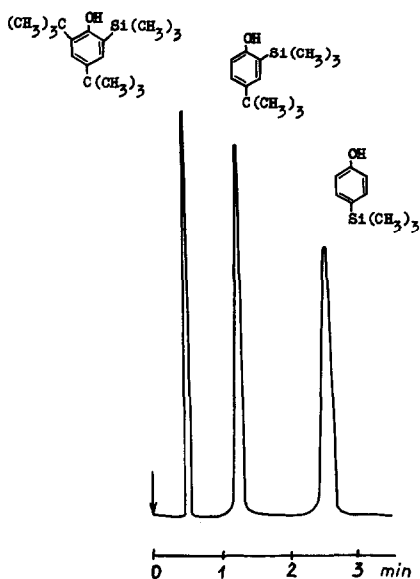


Fig. 1. Chromatogram of the separation of 2-trimethylsilyl-4,6-di-*tert.*-butylphenol, 2-trimethylsilyl-4-*tert.*-butylphenol and 4-trimethylsilylphenol. Chromatograph: Tsvet-304 with a UV detector (254 nm) and stainless-steel column (35 cm \times 4 mm I.D.). Adsorbent: Silochrom C-80 (grain size \approx 15 μ m). Eluent: *n*-hexane–diethyl ether (28:1), flow-rate 1.8 cm³/min. Temperature: 23°C.

The optimal conditions for the separation and analysis of mono-, di- and trisubstituted phenols were attained on the adsorbent of lower specific surface area, *i.e.*, macroporous Silochrom C-80, and with *n*-hexane–diethyl ether (28:1) as eluent at 23°C. The retention times for the phenols increased in the following order: tri-, di- and monosubstituted phenols (Fig. 1). This is accounted for by the fact that the substituents in the *ortho*-position screen the phenol OH group, decreasing the energy of intermolecular interaction with the adsorbent surface.

The above optimization of the conditions for the separation sterically hindered phenols enabled us to carry out the analysis of synthesized phenols to study their relative stability and the migration of substituents in the *ortho*-position to the phenol hydroxyl group, and to determine quantitatively the percentage conversion of germyl-substituted phenols into the corresponding ethers in the presence of various bases⁷.

Thus the LC method was successfully used for the analysis of oxidation products of thermally unstable silyl-substituted phenols (Table I, compounds of class II). The results show that these compounds are best separated on columns with 5% BOP on C-3 silica gel. When the amount of stationary phase was increased to 10, 20 and 30% the separation selectivity decreased due to the increase in adsorption energy of the studied molecules on the modifier film. The LC analysis revealed the presence of multicomponent mixtures after the oxidation of the studied phenols (Fig. 2).

The identification of the components of the oxidation mixture was difficult, since there were no authentic samples of the substances to confirm the structures of the products. To solve this problem we have developed a LC technique for prepara-

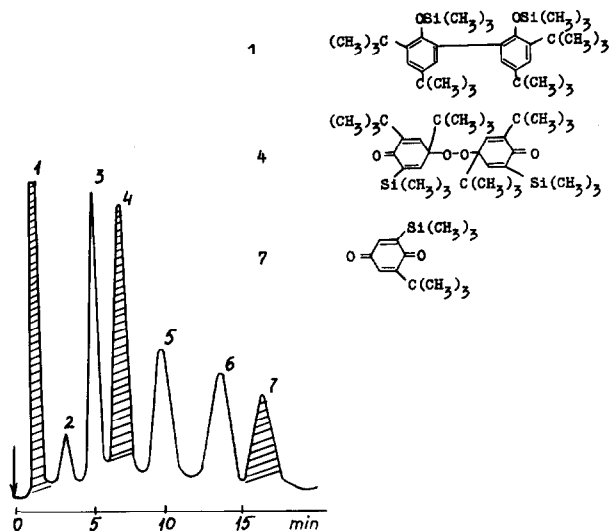


Fig. 2. Chromatogram of the separation of the products of oxidation of 2-trimethylsilyl-4,6-di-*tert.*-butylphenol with oxygen in the presence of $\text{K}_3\text{Fe}(\text{CN})_6$. Chromatograph: Tsvet-303 with a dielectric constant detector and stainless-steel column (35 cm \times 4 mm I.D.). Adsorbent: C-3 silica gel (5% BOP) with a grain size of $\approx 15 \mu\text{m}$. Eluent: *n*-hexane, flow-rate $1.2 \text{ cm}^3/\text{min}$. Temperature: 23°C .

tive extraction of the main oxidation products⁸, *i.e.*, thermally unstable silicon-substituted peroxides, substituted benzoquinones-1,4 and migration products.

Compounds of class III (Table I) —peroxides with $\text{M}-\text{O}-\text{O}-\text{M}'$ bonds— are easily isomerized at higher temperatures⁹, which prevents the use of gas chromatography for their analysis. We used C-3 and KCK-2 silica gels modified with 2% ethylene glycol mono- β -cyanoethyl ether and β,β' -oxydipropionitrile, and *n*-hexane as the eluent. The analysis was performed at 23°C . The analysis of bis(diphenylmethylsilyl) peroxide under the chosen optimal conditions (Fig. 3) showed the presence of silox-

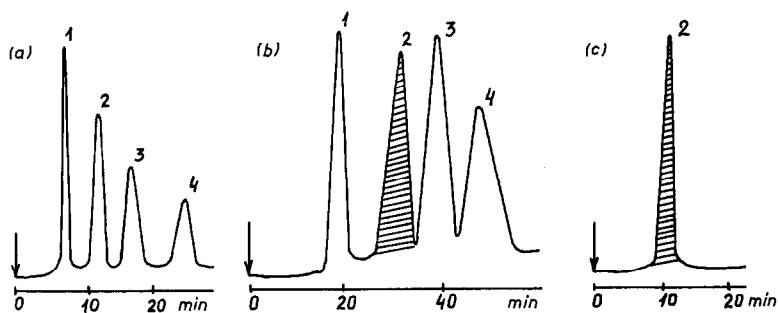


Fig. 3. Chromatograms of the separation of bis(diphenylmethylsilyl) peroxide under different conditions. a, Analytical column (35 cm \times 3 mm); adsorbent, KCK-2 silica gel (grain size $\approx 10 \mu\text{m}$) modified with 5% BOP; eluent, *n*-hexane (flow-rate $1.0 \text{ cm}^3/\text{min}$). b, Preparative column (80 cm \times 15 mm); eluent, *n*-hexane flow-rate $2.5 \text{ cm}^3/\text{min}$; sample volume, $50 \mu\text{l}$. c, Repeated analysis of the peroxide after preparative extraction. Peaks: 1 = $(\text{C}_6\text{H}_5\text{O})(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{Si}-\text{O}-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$; 2 = $(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{Si}-\text{O}-\text{O}-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$; 3 = unknown; 4 = $(\text{C}_6\text{H}_5)_2(\text{CH}_3)\text{SiOOH}$.

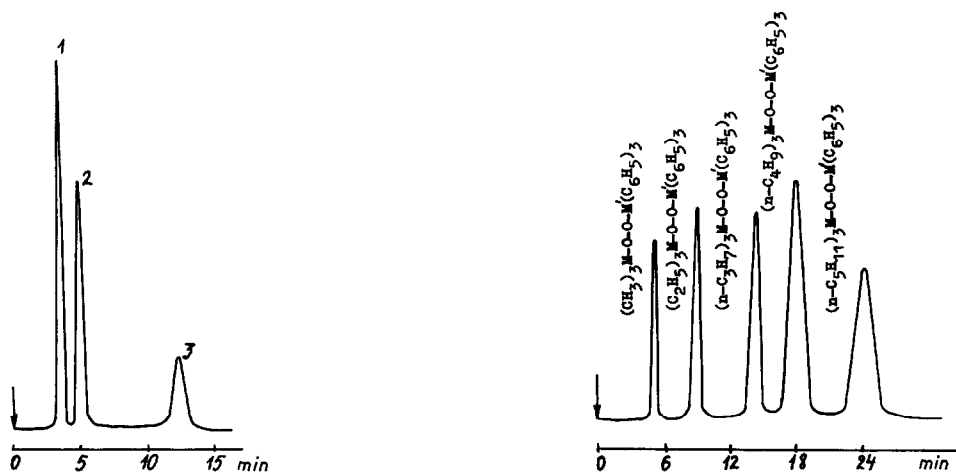


Fig. 4. Chromatogram of the group separation of a mixture of peroxides with M-O-O-M' bonds from impurities. Stainless-steel column: 25 cm \times 3 mm. Adsorbent: silica gel KCK-2 modified with 2% mono- β -cyanoethyl ether of ethylene glycol. Eluent: *n*-hexane (flow-rate 1.5 cm³/min). Peaks: 1 = mixture of migration products of structure R₃M-O-M'(OC₆H₅)(C₆H₅)₂ (ten compounds); 2 = mixture of peroxides of structure R₃M-O-O-M'(C₆H₅)₃ (Table I, class II) (ten compounds); 3 = (C₆H₅)₃MOOH, where M = Si, Ge; the first product of synthesis (two compounds).

Fig. 5. Chromatogram of the separation of ten peroxides with M-O-O-M' bonds. Chromatograph: Tsvet-304 with a UV detector and column of 25 cm \times 4 mm I.D.. Adsorbent: C-3 silica gel (grain size \approx 10 μ m). Stationary phase: squalane (50%). Eluent: water-methanol (70:30), flow-rate of 1.2 cm³/min. Temperature: 55°C. M = M' = Si; M = Si, M' = Ge.

anes (the products of peroxide migration) and hydroperoxides (the first products in the synthesis of organometallic peroxides with M-O-O-M' bonds¹⁰). The LC results were confirmed by IR spectroscopy, and peroxide purity was verified by repeated analysis on an analytical column.

We could not separate homologues by normal-phase LC (Fig. 4). However, the use of reversed-phase LC enabled the separation of the mixture of ten peroxides into five peaks, each corresponding to two organometallic peroxides, Si-O-O-Si and Si-O-O-Ge possessing the same alkyl substituents. In this case the components of the mixture were eluted in the order of increasing chain length of the alkyl substituents from methyl to amyl (Fig. 5).

We have also successfully used the LC method to study compounds of class IV (Table I) —*tert.*-butyl esters of silyl- and germyl-substituted peroxycarboxylic acids¹¹. Thermal decomposition of such peroxides is rapid even at 110–130°C^{12,13}. As in the case of triphenyl(trialkylsilylperoxy)-silanes and -germanes, LC on the modified adsorbents was optimal for the analysis of the *tert.*-butyl esters. However, in this case we used even greater amounts of the modifier to decrease the sorbent activity and retention time, while preserving sufficient separation. Thirteen new peroxides were investigated by the LC method on C-3 silica gel and Woelm silica gel modified with 30% BOP, using *n*-hexane as the eluent. Fig. 6 shows chromatograms of the products of synthesis of esters β -(triethylgermyl)peroxypropionic acid.

A new type of peroxides has recently been synthesized —*tert.*-butyl esters of

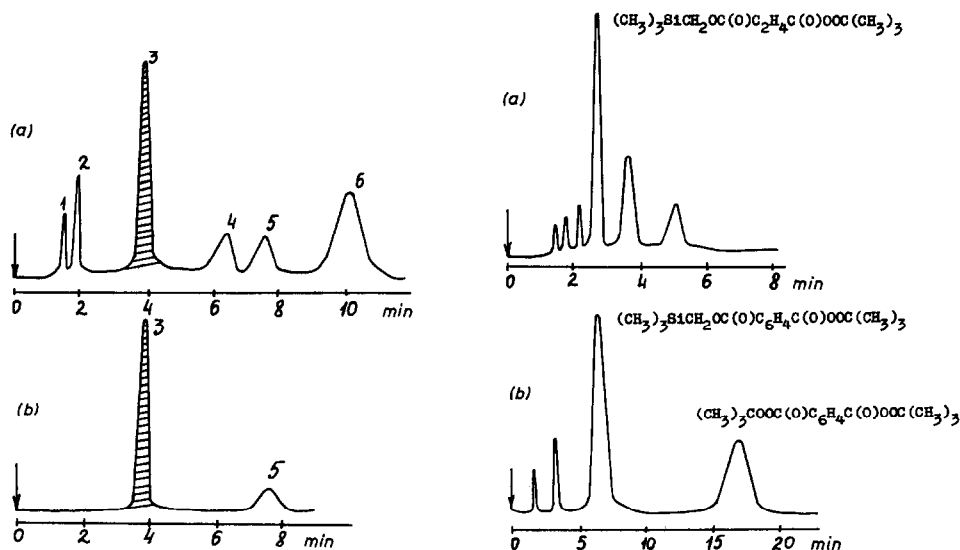


Fig. 6. Chromatographic analysis of the products of synthesis of the *tert.*-butyl ester of β -(triethylgermyl)peroxypropionic acid from unpurified materials (a) and from purified materials (b). Chromatograph: Tsvet-303 with a dielectric constant detector. Adsorbent: Woelm silica gel (grain size $\approx 15 \mu\text{m}$). Eluent: *n*-hexane (flow-rate $1.5 \text{ cm}^3/\text{min}$). Peaks: 1,2 = impurities in original $(\text{C}_2\text{H}_5)_3\text{Ge}(\text{CH}_2)_2\text{C}(\text{O})\text{OH}$; 3 = $(\text{C}_2\text{H}_5)_3\text{Ge}(\text{CH}_2)_2\text{C}(\text{O})\text{OOC}(\text{CH}_3)_3$; 4 = unknown; 5 = $(\text{C}_2\text{H}_5)_3\text{Ge}(\text{CH}_2)_2\text{C}(\text{O})\text{OH}$; 6 = $(\text{CH}_3)_3\text{COOH}$.

Fig. 7. Chromatogram of the separation of *tert.*-butyl esters of peroxysuccinic (a) and peroxyphtalic (b) acids. Chromatograph: Tsvet-304 with a UV detector (254 nm) and stainless-steel column of $35 \text{ cm} \times 2 \text{ mm}$. Adsorbent: Silochrom C-80 (grain size $\approx 15 \mu\text{m}$). Eluent: *n*-hexane (flow-rate $1.0 \text{ cm}^3/\text{min}$). Temperature: 23°C .

peroxysuccinic and -phtalic acids (Table I, class V). The analysis of these compounds by other methods presents the same problems as in the case of peroxide OMCs of classes II–IV (Table I). The best separation of these esters was attained on macroporous Silochrom C-80 and also on C-3 silica gel modified with 20% of Carbowax 600, a less polar modifier than BOP. The main impurities in the synthesized peroxide OMCs, among which there are peroxide compounds, were identified by the LC method. The iodometric titration method does not indicate the real purity of these peroxide OMCs (Fig. 7). The LC analysis of *tert.*-butyl esters of peroxy-succinic and -phtalic acids containing $(\text{CH}_3)_3\text{Si}$ fragments has shown that such peroxides are easily hydrolyzed in the course of chromatographic separation and require thorough predrying of eluents. The LC analysis of the OMCs of classes II–IV has revealed the trends in their retentions. Thus, the retention times for thermally unstable peroxide OMCs depend on the number and polarity of the substituent groups and increase in the following order: triphenyl(trialkylsilylperoxy)silanes (class III); silicon-substituted 4,4'-bis(cyclohexadienone) peroxides (class II); *tert.*-butyl esters of silyl- and germyl-substituted peroxy-carboxylic acids (class IV); *tert.*-butyl esters of peroxy-succinic and -phtalic acids containing organometallic fragments (class V).

The problem of the analysis and separation of OMCs containing three or more elements has recently arisen in connection with the synthesis of polynuclear OMCs,

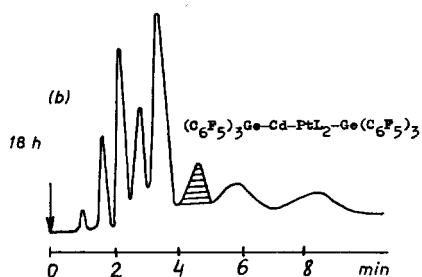
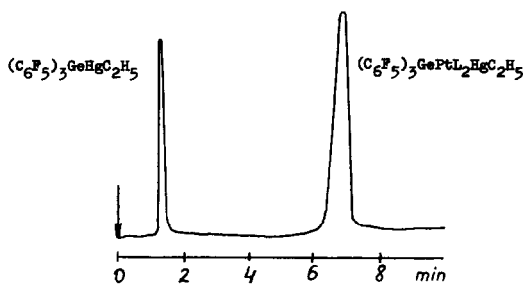
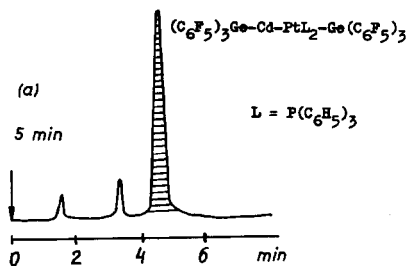
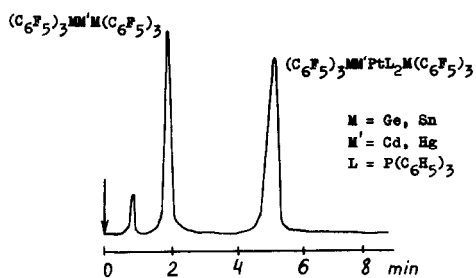


Fig. 8. Chromatograms of the separation of the products of synthesis of polynuclear OMCs. Chromatograph: Tsvet-304 with a UV detector and column of 35 cm × 4 mm. Adsorbent: Silochrom C-80 (grain size ≈ 10 μm). Eluent: *n*-hexane–diethyl ether (24:1), flow-rate 1.85 cm³/min. Temperature: 45°C.

Fig. 9. Chromatogram of the separation of products of synthesis of (C₆F₅)₃GeCdPtL₂Ge(C₆F₅)₃ after exposure to air. Conditions as in Fig. 8.

which are potential high temperature superconductors^{14,15}. We have studied the separation and analysis of pentafluorophenyl polynuclear OMCs (Table 1, class VI). The optimal conditions for these low-volatile compounds were attained on stainless-steel columns packed with macroporous Silochrom C-80 (grain sizes 5, 10 and 15 μm) using *n*-hexane–diethyl ether (24:1, 32:1) as the eluent at 45°C. The use of

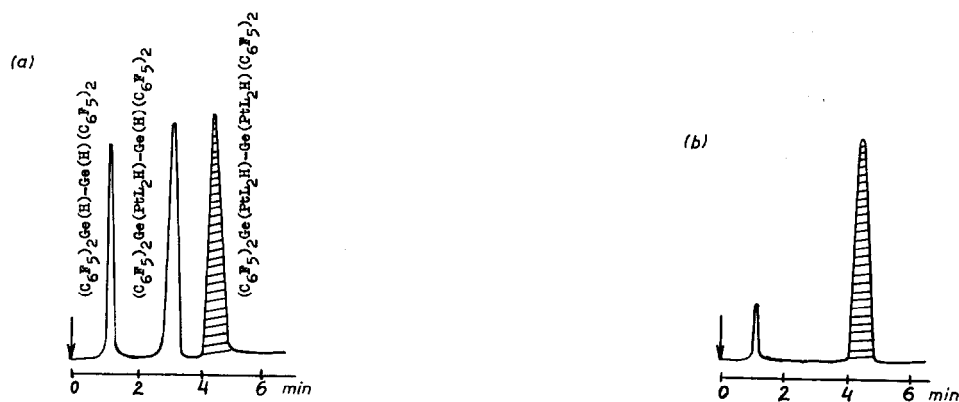


Fig. 10. Chromatogram of the products of synthesis of (C₆F₅)₂Ge(PtL₂H)–Ge(PtL₂H)(C₆F₅)₂. a, Untreated mixture; b, after double recrystallization from benzene–hexane solution. Chromatograph: Tsvet-304 with a UV detector and column of 15 cm × 4 mm. Adsorbent: Silochrom C-80. Eluent: *n*-hexane–diethyl ether (32:1), flow-rate 1.7 cm³/min. Temperature: 45°C.

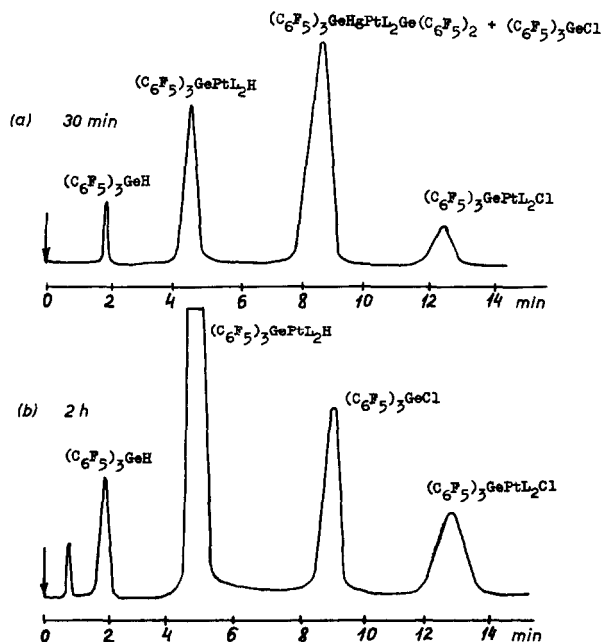


Fig. 11. Chromatogram of the products of the reaction of $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$ with HCl. Conditions as in Fig. 8.

stainless-steel columns does not result in the decomposition of compounds with M-M'-Pt-M bonds.

The qualitative and quantitative composition of the products of synthesis of polynuclear OMCs was monitored by the changes in the peak areas of the original and final components (Fig. 8). The experimental results show that the retention times of the formed polynuclear OMCs differ sharply from those of the original products. The increase in intermolecular interaction energy for platinum- and palladium-substituted polynuclear OMCs can be attributed to the change in molecular configuration after introduction of the PtL_2 fragment and consequently the appearance of new electron-donor and -acceptor properties.

Our LC techniques for qualitative and quantitative analysis of polynuclear OMCs and germylated platinum and palladium hydrides enabled us to investigate 30 synthesis reactions, and the reactivity and relative stability of compounds obtained for the first time¹⁶. For example, Fig. 9 shows that a compound with Ge-Cd-Pt-Ge bonds is unstable and undergoes transformations after exposure to air for 18 h.

Apart from the expected diplatinum derivative, a further component was identified on the chromatogram (Fig. 10) in the course of LC analysis of the products of reaction of tetraoxy(pentafluorophenyl)-1,2-dihydrogermane) with zerovalent platinum complexes. Its identity and purity were determined by the same method after recrystallization from the reaction mixture, and its structure was determined by IR spectroscopy.

The use of our LC technique for the analysis of the products of reaction of a complex with Ge-Hg-Pt-Ge bonds with hydrogen chloride (Fig. 11) has enabled us

to identify the main components of the reaction mixture and to propose mechanisms for the processes involved¹⁶.

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