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STUDY OF THE OXIDATION PRODUCTS OF PHENOLSILICON COMPOUNDS BY MOLECULAR LIQUID CHROMATOGRAPHY*

G. N. BORTNIKOV, L. V. GORBUNOVA, A. V. KISELEV, N. P. MAKARENKO, O. N. MAMYSHEVA and Ya. I. YASHIN

Institute of Chemistry, USSR Academy of Sciences, Gorky (U.S.S.R.)

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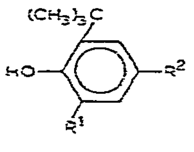
SUMMARY

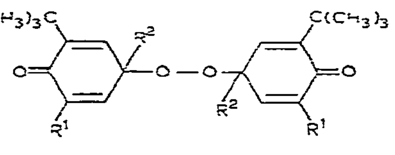
Molecular liquid chromatography was applied to the separation and analysis of thermally unstable organosilicon peroxides. The optimal conditions for the separation of the oxidation products of phenolsilicon compounds were determined and the influence of the amount of β,β'-oxydipropionitrile deposited on silica gel C-3 on the separation of these compounds was studied. By this method, bis(1-trimethylsilyl-3,5-di-*tert.*-butyl-2,5-cyclohexadien-4-one)peroxide was isolated preparatively. The degree of purity of fractions was determined by molecular liquid chromatography and IR spectroscopy.

INTRODUCTION

It was assumed that the oxidation of phenolsilicon compounds (I–III), in a similar manner to their alkyl-substituted analogue (IV), yields 4,4'-biscyclohexadienone peroxides (V–VIII), which can be used as a source of polymerization-initiating radicals.



I–IV



V–VIII

I, V: $R^1 = Si(CH_3)_3$: $R^2 = C(CH_3)_3$: II, VI: $R^1 = Si(CH_3)_2C_6H_5$; $R^2 = C(CH_3)_3$; III, VII: $R^1 = Si(CH_3)_3$; $R^2 = Si(CH_3)_3$: IV, VIII: $R^1 = C(CH_3)_3$: $R^2 = C(CH_3)_3$.

In order to study the mechanism of the thermal decomposition of peroxides of this type and to examine their interactions with different classes of compounds, one must have pure samples. Therefore, it is important to have suitable methods for the

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analysis and purification of 4,4′-biscyclohexadienone peroxides. Preliminary investigations showed that liquid chromatography is the most suitable technique for the separation and analysis of thermally unstable peroxides that decompose comparatively easily. In the literature, there is no evidence of application of this method to the study of the oxidation products of phenolsilicon compounds.

EXPERIMENTAL

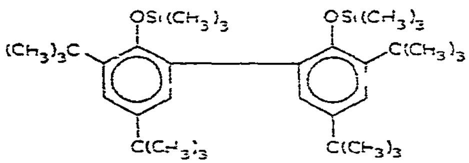
All investigations were carried out on a Tsvet-301 liquid chromatograph with a dielectric constant detector and a stainless-steel column (67 m × 4 mm I.D.). Silica gel C-3[1] with a specific surface area of 250 m^2/g was used as the adsorbent support. A layer of β,β'-oxydipropionitrile was deposited from solution on to this silica gel. After this modification, the new specific surface area was determined. *n*-Hexane was used as the eluent and analyses were carried out at room temperature.

RESULTS AND DISCUSSION

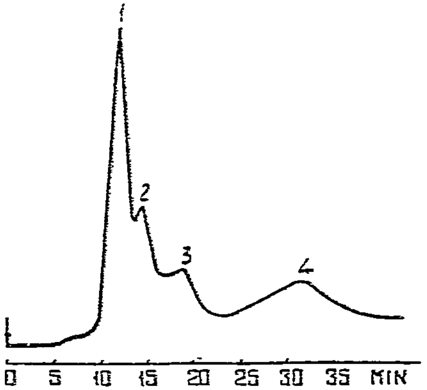
Our investigations showed that the best separation of the oxidation products is achieved on a column with 5% of β,β'-oxydipropionitrile deposited on silica gel C-3. This amount of liquid phase corresponds to a surface coverage of approximately 0.2 mg/m^2, which is much less than the dense monolayer capacity of silica gel surface. It has been shown[2,3] that such an amount is adsorbed fairly well. When the amount of β,β'-oxydipropionitrile on silica gel is increased to 10, 20 and 30% (that is, to 1.2 mg/m^2), the efficiency of column also increases but the selectivity of separation decreases. With 5, 20 and 30% of β,β'-oxydipropionitrile, the specific surface area of the adsorbent decreases to 205, 185 and 175 m^2/g, respectively.

The chromatographic analysis of the reaction mixture after the oxidation of phenol IV in pure oxygen and in the presence of potassium hexacyanoferrate(III) revealed that the mixture consists of four components. The main products were identified and are shown in the chromatogram in Fig. 1. The products of the thermal decomposition of the purified peroxide VIII under vacuum at 140° were also studied. The main product appears to be 2,6-di-*tert.*-butylbenzoquinone-1,4.

Fig. 2 shows a chromatogram of the reaction mixture after the oxidation of phenol I in pure oxygen and in the presence of potassium hexacyanoferrate(III). The main products were identified by using an internal standard. It is difficult to extract peroxides from phenol oxidation reaction mixtures by using conventional methods because of their thermal instability. Therefore, in the present study preparative liquid chromatography was used. The preparatively extracted substance (first peak in Fig. 2) is the product of re-grouping of



IX



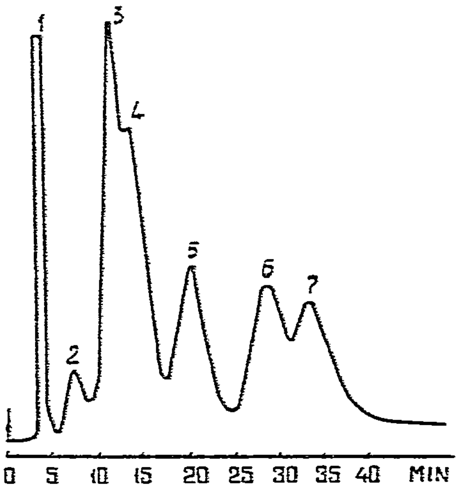
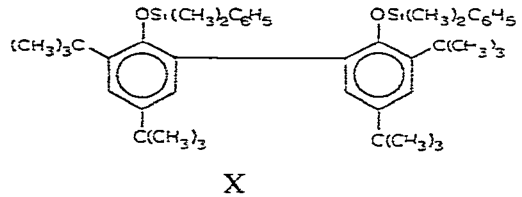


Fig. 1. Chromatogram of the reaction mixture after the oxidation of phenol IV in pure oxygen and in the presence of potassium hexacyanoferrate. Chromatograph: Tsvet-301 with a dielectric constant detector. Adsorbent: β,β'-oxydipropionitrile (5%) deposited on silica gel C-3 (particle size 30–50 μm). Eluent: *n*-hexane. Column: 67 cm × 0.4 cm I.D. Flow-rate: 1.2 cm^3/min; ambient temperature. Peaks: 1 = peroxide VIII; 2 and 3 = unidentified; 4 = 2,6-di-*tert*.-butylbenzoquinone-1,4

Fig. 2. Chromatogram of the reaction mixture after the oxidation of phenol I in pure oxygen and in the presence of potassium hexacyanoferrate. Separation conditions as in Fig. 1 but with flow-rate 2.07 cm^3/min. Peaks: 1 = IX; 2, 3, 5, 6 = unidentified, 4 = peroxide V; 7 = 2-trimethylsilyl-6-*tert*.-butylbenzoquinone-1,4.

and the fourth peak on this chromatogram corresponds to peroxide V. After recrystallization of the prepared peroxide from methanol, the pure peroxide V was extracted, the presence and purity of which were confirmed chromatographically by using an internal standard and by IR spectroscopy.

Examination of the thermal decomposition products of peroxide V showed that the main product appears to be 2-trimethylsilyl-6-*tert*.-butylbenzoqinone-1,4. the presence of potassium hexacyanoferrate, as in the oxidation of the above phenols, the following compounds were identified (under the same conditions): peroxide VI, 2-dimethylphenylsilyl-6-*tert*.-butylbenzoqinone-1,4 and the product of re-grouping of



X

Fig. 3 shows a chromatogram of the products of oxidation of phenol III. The

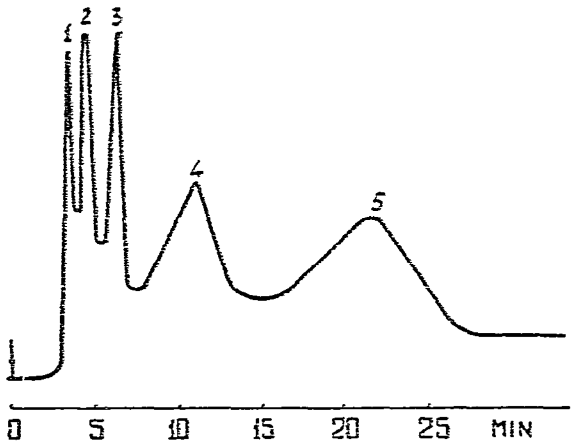
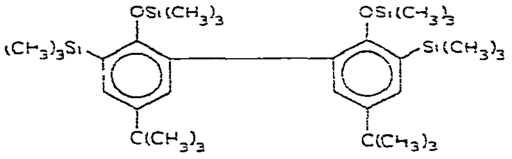


Fig. 3. Chromatogram of the reaction mixture after the oxidation of phenol III in pure oxygen and in the presence of potassium hexacyanoferrate(III). Separation conditions as in Fig. 2. Peaks: 1 = XI: 2, 3 = unidentified; 4 = peroxide VII; 5 = 2-trimethylsilyl-6-*tert.*-butylbenzoquinone-1,4

main products of this oxidation are peroxide VII, 2-trimethylsilyl-6-*tert.*-butylbenzoquinone-1,4 and the products of re-grouping of



XI

The chromatograms of the phenol oxidation products show that the smallest retention times are those of products of re-grouping while quinones have the greatest retention times; peroxides have intermediate values. This order can be attributed to the fact that specific intermolecular interactions with the adsorbent weaken with a transition from substituted quinones (whose active groups are not all screened with *tert.*-butyl radicals or other substituents) to peroxides (the active groups of which are all screened by the corresponding substitutes).

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