Characteristic features of cyclotrimerization of perfluoroalkyl- and perfluorooxaalkylacetylenes

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Cyclotrimerization of perfluoroalkyl- and perfluorooxaalkylacetylenes has been studied under various conditions. A scheme of the reaction mechanim has been suggested.

Key words: perfluoroalkylacetylene, perfluorooxaalkylacetylene, tridecafluoro-1-hydrooct-1-yne, tridecafluoro-4,7,10-trioxa-1-hydroundec-1-yne, pentacosafluoro-4,7,10,16,19-hexaoxa-1-hydroeicos-1-yne, perfluorohexyl peroxide, tris(perfluoroalkyl)benzene; cyclotrimerization, perfluoroalkylbenzene.

The introduction of perfluorinated substituents into an aromatic ring is known to be a complex nonselective process.[1] In the present work we have studied cyclotrimerization of perfluoroalkylacetylenes under various conditions as a method for the synthesis of tris(perfluoroalkyl)benzenes.

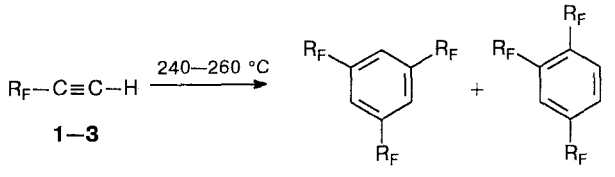
Cyclotrimerization of various perfluoroalkylacetylenes and diacetylenes at 225 °C to give both tris(perfluoroalkyl)benzenes and oligomers and polymers has been previously reported.[2—4]

We studied the peculiarities of cyclotrimerization of perfluoroalkylacetylenes under various conditions depending on the temperature and the structure of the fluorinated radical.

Thermal cyclotrimerization of perfluoroalkylacetylenes (**1**)—(**3**) was carried out in evacuated glass tubes (see Experimental). We found that the reaction starts at ~235 °C (the conversion is ~25 % over a period of 1 h); at 260 °C it takes ~15 min, and the ratio between the symmetric and asymmetric isomers is ~ 6 : 1 (the conversion and the yields were determined by ^{19}F NMR).

† Deceased.

Scheme 1



1: $R_F = C_6F_{13}$
2: $R_F = CF_3(OCF_2CF_2)_2OCF_2$
3: $R_F = CF_3(OCF_2CF_2)_5OCF_2$

Hydrogen-containing admixtures retard cyclotrimerization and increase the amount of side products. For example, when the proportion of hydrogen-containing impurities is 3—4 mol. % (determined by ^1H NMR), the reaction yields >30 % polyfluorinated polyenes. Their formation is accompanied by coloring of the mixture, an increase in the molecular weight (determined by ebullioscopy), and the appearance of broadened signals at 5—6 ppm in the ^1H NMR spectrum. These effects are observed even when an inert compound, such as benzene, is added.

When the purity of the starting compounds is increased to 99.5 % and more, the time of the reaction substantially decreases, and in this case, it affords tris(perfluoroalkyl)benzenes containing almost no impurities.

Cyclotrimerization of compounds **2** and **3** occurs much more slowly than that of **1** and is accompanied by blackening of the reaction mixture and the formation of gaseous thermodestruction products (fluorides of perfluorocarboxylic acids and HF, which were determined by ^1H NMR), and at a conversion above 40 %, the glass tube is destroyed by the action of the large amounts of gas including HF.

When approximately 2—4 mol. % of acetylene **1** is added to compound **2** or **3**, the reaction occurs with a quantitative yield, like the reaction of individual **1**.

Figure 1 presents the plots of the conversion of **1**, **2**, and their mixture *vs* time. Compound **1** is the most reactive, a mixture of **1** and **2** is slightly less reactive, and pure compound **2** reacts most slowly. Similar results were obtained for compound **3** and its mixture with **1**.

In our opinion, this result attests that the reaction is a chain reaction. In fact, if compound **1** acted as a comonomer, its content in a mixture with **2** required for

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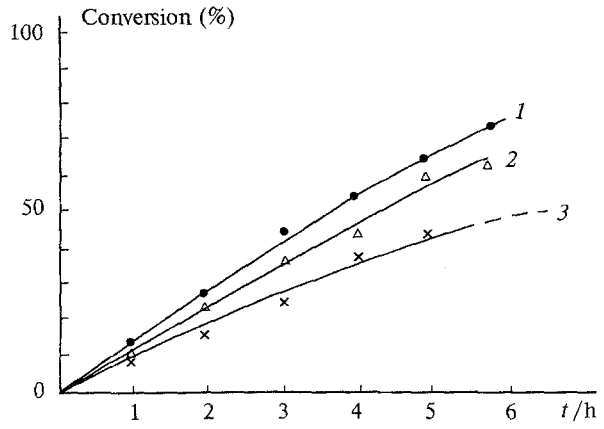


Fig. 1. The dependence of the conversion of acetylenes and their mixture at 245 °C *vs* time: cyclotrimerization of **1** (*1*); cyclotrimerization of **2** with 2 % **1** added (*2*); cyclotrimerization of **2** (*3*).

completion of the reaction and preparation of the corresponding perfluoroalkylbenzene would be ~1/3. The other possibility, *i.e.*, catalysis of the reaction by acetylene **1** is unlikely.

Since the use of metallocomplex catalysts for cyclotrimerization of nonfluorinated acetylenes has been described in the literature,[5] we carried out a number of experiments with some of them (Table 1). As can be seen from Table 1, these compounds act as catalysts, but the selectivity of cyclotrimerization is low, and polyacetylenes are formed as by-products in all cases.

It has been noted[6] that UV-irradiation of trifluoromethylacetylene results in the formation of 1,3,5-tris(perfuoromethyl)benzene in a low yield. The reaction was carried out in the presence of various additives (NO, C_3H_8) that, in our opinion, prevented the formation of substituted benzenes, the yield of which did not exceed several percent.

We studied cyclotrimerization of fluorine-containing acetylenes under UV-irradiation. The experiments were carried out with samples sealed in a quartz cell *in vacuo* and irradiated with high-pressure and medium-pressure Hg-lamps at 20—25 °C. The cyclotrimerization of compound **1** gave tris(perfluoroalkyl)benzene in a quantitative yield. However, the individual oxygen-containing acetylenes, as in the thermal process, exhibited low reactivities, which can be increased by introducing 2—4 mol. % of compound **1** into reaction mixture. The reaction yields the symmetric and asymmetric isomers at the same ratio as in the thermal process. Based on the hypothesis of the chain character of the reaction and assuming that it occurs by a radical mechanism, we decided to study cyclotrimerization of these acetylenes in the presence of peroxides.

Table 1. Cyclotrimerization of **1** in the presence of various catalysts at 110 °C

Catalyst	Conversion **1**, (%)	Yield of tris(perfluorohexyl)-benzenes (%)
$Mo(CO)_6$	100	72
$CoCp(CO)_2$	82	24
$Co_2(CO)_8$	63	32
$IrHCl_2(Ph_3P)_3$	55	15

In the presence of benzoyl or azoisobutyronitrile peroxides, the fluorine-containing acetylenes do not react below 120 °C. This may be due either to insolubility of these peroxides in organofluorine acetylenes or to the fact that hydrogen-containing compounds were found to retard cyclotrimerization.

Therefore, we used the perfluoroacyl peroxide $C_6F_{13}COOOOC_6F_{13}$, which is readily soluble in fluorine-containing acetylenes and decomposes at ~20 °C. The cyclotrimerization was carried out at 20—25 °C in tubes sealed *in vacuo*. Acetylene **1** yielded a mixture of isomers of tris(perfluorohexyl)benzenes in 100 % overall yield. The ratio between the symmetrical and asymmetrical isomers was the same as in the previous experiments. Acetylenes **2** and **3** possess much lower reactivities, as in the case of thermal cyclotrimerization.

Figure 2 presents the dependence of the conversion on the amount of the peroxide for acetylenes **1** and **2**, which indicates that at a given peroxide : acetylene ratio, the conversion of compound **2** is lower by a factor of ~5.

Figure 3 shows the time dependences of the decomposition of perfluoroacyl peroxide (curve *1*) and of the yield of tris(perfluorohexyl)benzene (curve *2*). The reaction was carried out in an NMR tube, and ^{19}F NMR spectra were periodically recorded. From these data it follows that at the initial stage of the reaction, the decomposition of one molecule of peroxide results in

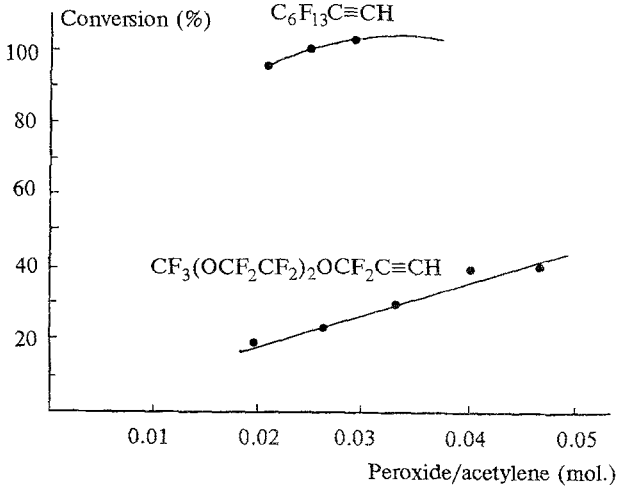


Fig. 2. The dependence of the degree of conversion on the peroxide : acetylene ratio.

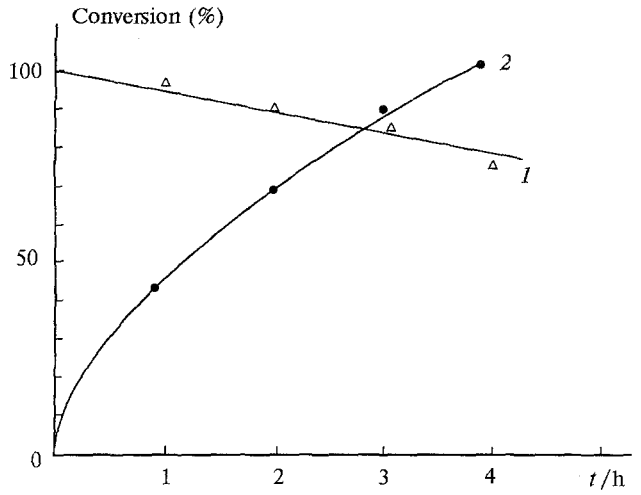


Fig. 3. Decomposition of perfluoroacyl peroxide in the presence of fluorine-containing acetylene: decomposition of the peroxide (*1*); formation of tris(perfluoroalkyl)benzene (*2*).

the formation of ~20 molecules of tris(perfluorohexyl)benzene. Of course, this value gives only the lower limit of the length of the kinetic chain. Due to the high rate of recombination of the radicals, decomposition of perfluoroacyl peroxide cannot be detected by ESR, however, in a mixture of the peroxide and acetylenes **1** and **2**, stable radicals exist for ~40 h.

During the decomposition of a large amount (~10 mol. %) of the perfluoroacyl peroxide in **2**, we did not detect perfluorohexyl substituted benzenes (with an accuracy of less than 0.5 %).

Based on the results obtained, a scheme for the reaction mechanism can be suggested (Scheme 2).

The decrease in the rate of the cyclotrimerization of acetylenes and the formation of fluorine-containing polyenes that occur when hydrogen-containing admixtures are introduced in the system can also be readily explained. Under the action of an initiator, a great number of primary radicals are generated from the hydrogen-containing compounds. When such a radical adds two or three acetylene molecules, the ring closure (at least of the benzene ring) becomes impossible. The possibility that the impurities may add to the growing chain at the second or third stage of the process should also be taken into account. The resulting fluorine-containing polymers may undergo further transformations, especially at high temperatures.

Experimental

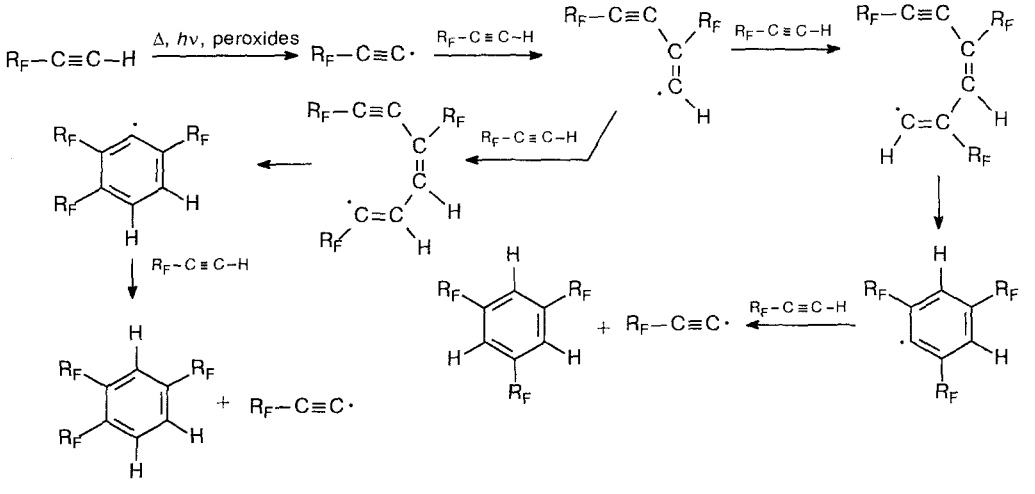
The NMR spectra were recorded on a Bruker AC-200P spectrometer in perfluorobenzene. HMDS and $CFCl_3$ were used as the standards. Perfluoroacyl peroxide was prepared by the previously suggested method,[7] and the fluorine-containing acetylenes were synthesized by the known procedure.[3] We used acetylenes with the following boiling points: n-$C_6F_{13}C{\equiv}CH$ (**1**) 98—98.5 °C; $CF_3(OCF_2CF_2)_2OCF_2C{\equiv}CH$ (**2**) 101—101.5 °C; $CF_3(OCF_2CF_2)_5OCF_2C{\equiv}CH$ (**3**) 163—164.5 °C.

All of the experiments were carried out in sealed glass tubes. The samples were prepared as follows. A tube with the reagents was frozen with liquid nitrogen and evacuated to 0.01 Torr. The vacuum system was valved off, and the sample was warmed to ambient temperature. Then it was once again frozen and evacuated. This procedure was repeated until there was no more evolution of dissolved air after thawing of a sample.

General procedure of cyclotrimerization. A weighed sample of a fluorine-containing acetylene and a catalyst if needed were placed in a tube (no more than 1/3 of its volume), and the tube was degassed and kept at a specified temperature.

In the case of acetylene **1** a viscous yellow liquid is formed in a yield of more than 97 %. Freezing point −47 °C, $M_n^- = 1020$ (ebullioscopy in C_6F_6).

Scheme 2



The ^{1}H NMR spectrum of 1,3,5-tris(perfluorohexyl)-benzene: signals in the δ 7.9—8.3 region (the benzene ring protons).

The ^{19}F NMR spectrum of 1,3,5-tris(perfluorohexyl)-benzene, δ: 110.4 (α-CF_2), 121.7 (β-CF_2), 121.9 (γ-CF_2), 123.0 (δ-CF_2), 128.3 (ε-CF_2, 81.4 (CF_3).

The ^{19}F NMR spectrum of 1,2,4-tris(perfluorohexyl)benzene, δ: 103.4 (1 and 2 α-CF_2), 111.8 (4 α-CF_2), 117.8 (1 and 2 β-CF_2), 121.1 (4 β-CF_2), 121.5 (γ-CF_2), 123.0 (δ-CF_2), 128.3 (ε-CF_2), 81.4 (CF_3).

The ^{1}H NMR spectra of the isomers of perfluorooxalkyl substituted benzenes prepared by cyclotrimerization of compound **2** exhibit signals at δ 8.0—8.3.

^{19}F NMR, δ: 67.9 (OCF_2Ar in the 1,3,5 isomer), 64.5 and 68.2 (OCF_2Ar in the 1,2,4 isomer), 90.3 (OCF_2CF_2), 92.3 ($CF_3OCF_2^-$), 57.8 (OCF_3).

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