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Separation of the C_7F_{16} isomers by gas chromatography

Fluorocarbons are difficult to prepare and are even more difficult to purify. Gas chromatography seems the most practical approach to purifying fluorocarbons. GREENE AND WACHI[1] have separated low-molecular-weight fluorocarbons on a silica gel column and REED *et al.*[2,3] have evaluated several liquid phases for the chromatographic separation of fluorocarbons. REED has separated the isomers of C_6F_{14} on a *n*-hexadecane substrate[4] and has done quantity purification of fluorocarbons on a preparative scale *n*-hexadecane column[5]. This paper describes the gas–liquid chromatographic separation of the perfluoroheptane isomers.

Experimental

Analytical. Gas chromatographic analysis of all samples was done with a Perkin-Elmer Model 154 vapor fractometer. The recording instrument was a 1-mV full scale range Honeywell strip chart recorder. Peak areas were measured by a Perkin-Elmer Model 194B printing integrator which gave 6000 c.p.m. at full scale deflection on the recorder. Gaseous samples were injected from a glass vacuum system through a gas sample valve.

The analytical column was a 1/4 in. × 50 ft. *n*-hexadecane column, as described in Table I. Appearance times and retention volumes of fluorocarbon compounds through the C_6F_{14} isomers were determined by injecting known samples.

Preparation of the C_7F_{16} isomers. Radiolysis studies on fluorocarbons[6–8] show that products from irradiating a saturated perfluoroalkane are saturated perfluoroalkane products with molecular weights above and below the parent compound. All of these products can be explained by a radical formation, radical propagation, and radical recombination mechanism involving abstraction reactions[8]. Because there are only certain radicals possible from a given parent the kind and distribution of radiolysis products from a given perfluoroalkane parent may be predicted[6–8].

Using $n\text{-}C_5F_{12}$ as an example, the following scheme illustrates the most probable C_7F_{16} isomers obtainable from $n\text{-}C_5F_{12}$.

Rupture to produce radicals

$$\begin{array}{rl} n\text{-}C_5F_{12} \rightsquigarrow CF_3\cdot & + \; CF_3CF_2CF_2CF_2\cdot \\ C_2F_5\cdot & + \; CF_3CF_2CF_2\cdot \\ F\cdot & + \; CF_3CF_2CF_2CF_2CF_2\cdot \\ F\cdot & + \; CF_3\dot{C}FCF_2CF_2CF_3 \\ F\cdot & + \; (C_2F_5)_2CF\cdot \end{array}$$

F-Abstraction to produce radicals

$$\begin{array}{l} R\cdot + n\text{-}C_5F_{12} \rightarrow R\text{–}F + CF_3CF_2CF_2CF_2CF_2\cdot \\ R\cdot + n\text{-}C_5F_{12} \rightarrow R\text{–}F + CF_3\dot{C}FCF_2CF_2CF_3 \\ R\cdot + n\text{-}C_5F_{12} \rightarrow R\text{–}F + (C_2F_5)_2CF\cdot \end{array}$$

Recombination to yield C_7F_{16} isomers

$$\begin{array}{lll}
CF_3CF_2CF_2CF_2\cdot & +\ CF_3CF_2CF_2\cdot \rightarrow & n\text{-}C_7F_{16} \\
CF_3CF_2CF_2CF_2CF_2\cdot & +\ CF_3CF_2\cdot \longrightarrow & n\text{-}C_7F_{16} \\
CF_3\dot{C}FCF_2CF_2CF_3 & +\ CF_3CF_2\cdot \longrightarrow & 3\text{-}CF_3C_6F_{13} \\
(C_2F_5)_2CF\cdot & +\ CF_3CF_2\cdot \longrightarrow & 3\text{-}C_2F_5C_5F_{11}
\end{array}$$

The recombination of radicals is expected to form mostly these three C_7F_{16} isomers as perfluoroheptane products from n-C_5F_{12}. The amount of each perfluoroheptane isomer produced will depend on stearic factors, radical diffusion, "cage effects", etc.

Seven pure perfluoroalkanes, n-C_4F_{10}, i-C_4F_{10}, n-C_5F_{12}, n-C_6F_{14}, 2-$CF_3C_5F_{11}$, 3-$CF_3C_5F_{11}$ and 2,3-$(CF_3)_2C_4F_8$ were sealed in aluminum tubing and were irradiated in a cobalt-60 source to produce the nine C_7F_{16} isomers[6,7].

Results and discussion

The radiolysis products obtained from the seven starting compounds are fully tabulated and described elsewhere[6,7]. All radiolysis products through the C_6F_{14} isomers were identified by comparison with appearance times of known samples.

Since the logarithm of the retention volume *versus* carbon number gives a straight line for saturated normal hydrocarbons[9,10], a plot of the logarithm of the retention volume *versus* carbon number was made for the saturated normal perfluoroalkanes and this plot resulted in a straight line, as shown in Fig. 1. The retention volumes for n-C_7F_{16} (427.8 cm^3) and n-C_8F_{18} (760.7 cm^3) were found by extrapolating this plot.

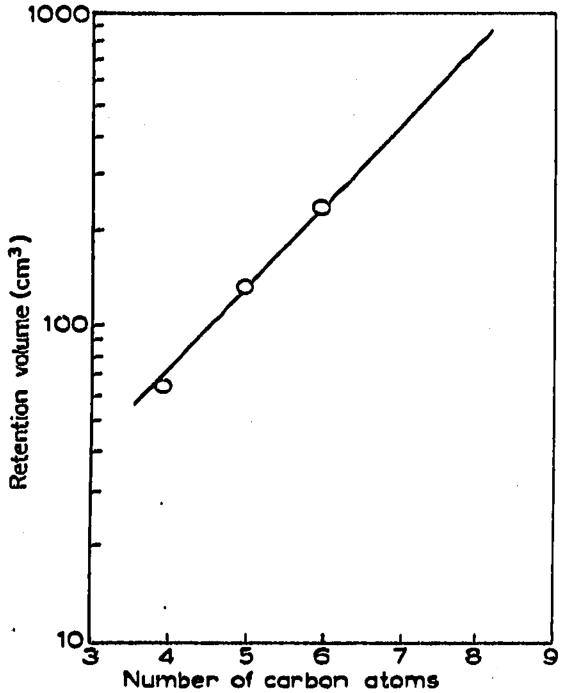

Fig. 1. Logarithm of retention volume *versus* number of carbon atoms in normal saturated fluorocarbons.

TABLE I

STANDARD RETENTION VOLUMES IN *n*-HEXADECANE

Description of the *n*-hexadecane column: 50 ft. × 0.197 in. I.D.; volume of *n*-hexadecane, 63.7 cm³; packing ratio, 0.4 g *n*-hexadecane/g of 30–80 mesh Chromosorb P; column temperature, 44°; carrier gas inlet pressure, 34.7 p.s.i.a.; carrier gas outlet pressure, 14.7 p.s.i.a.; helium gas flow rate at column exit, 18.1 cm³/min at 24°.

Compound	*Appearance time (min)*	*Retention volume (cm³)*
Air and CF_4	18.7	
C_2F_6	19.7	10.2
C_2F_6O	20.5	18.4
C_3F_8	21.6	29.6
C_3F_8O	21.6	29.6
$(C_2F_5)_2O$	23.1	45.0
CO_2	24.8	62.3
n-C_4F_{10}	25.0	64.4
i-C_4F_{10}	26.0	74.6
n-C_5F_{12}	31.4	129.7
i-C_5F_{12}	33.8	154.2
n-C_6F_{14}	42.1	238.9
2-$CF_3C_5F_{11}$	45.2	270.6
3-$CF_3C_5F_{11}$	47.5	294.1
2,3-$(CF_3)_2C_4F_8$	52.8	348.2

For the perfluorobutanes, perfluoropentanes, and perfluorohexanes, retention volumes on the *n*-hexadecane column for the isomers of each molecular weight class were found to lie between the retention volume of the normal isomer of that class and the retention volume of the normal isomer of the next higher molecular weight class (see Table I). This behavior was assumed for the perfluoroheptane isomers and thus the range of retention volumes was established for the perfluoroheptane isomers, *i.e.*, the retention volumes for the perfluoroheptane isomers come between the retention volumes of n-C_7F_{16} and n-C_8F_{18}.

Actual chromatographic peaks obtained in the perfluoroheptane range from analyzing the radiolysis products from the parent compounds were compared to the predicted perfluoroheptane products and the retention volumes for the perfluoroheptane isomers were determined and they are given in Table II.

TABLE II

APPEARANCE TIMES AND RETENTION VOLUMES FOR THE C_7F_{16} ISOMERS ON THE *n*-HEXADECANE COLUMN

Compound	*Appearance time (min)*	*Retention volume (cm³)*
n-C_7F_{16}	60.6	427.8
2-$CF_3C_6F_{13}$	64.7	469.7
3-$CF_3C_6F_{13}$	66.4	487.0
2,2,3-$(CF_3)_3C_4F_7$	66.4	487.0
3-$C_2F_5C_5F_{11}$	70.7	530.9
2,4-$(CF_3)_2C_5F_{10}$	74.2	566.7
2,3-$(CF_3)_2C_5F_{10}$	76.8	593.2
3,3-$(CF_3)_2C_5F_{10}$	88.0	707.6
n-C_8F_{18}	93.2	760.7

For example, radiolysis products of n-C_4F_{10} should yield only two peaks in the perfluoroheptane range, *viz.* n-C_7F_{16} and 3-$CF_3C_6F_{13}$. Since the retention volume for n-C_7F_{16} is known, the retention volume for 3-$CF_3C_5F_{11}$ is established.

None of the expected isomer 2,2-$(CF_3)_2C_5F_{10}$ was found in the radiolysis products from 2-$CF_3C_5F_{11}$. Its absence corresponds to the absence of $(CF_3)_4C$ and 2,2-$(CF_3)_2C_4F_8$ in any of the radiolysis products. Apparently the neo structure cannot be made by radiolysis of perfluoroalkanes.

^{19}F NMR spectra of n-C_6F_{14} and n-C_7F_{16} which had been purified on a 50-ft. n-hexadecane preparative scale column and ^{19}F NMR spectra of a C_5F_{12} mixture, a C_6F_{14} mixture, a C_7F_{16} mixture and a C_8F_{18} mixture have been recorded and support the assignment of retention volumes for the perfluoroheptane isomers[11].

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