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A COMPLETE FLUORINE-19 NMR CHARACTERIZATION OF A COMMERCIAL GRADE SAMPLE OF PERFLUOROHEXANES

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SUMMARY

The complete qualitative and quantitative chemical characterization of a complex, commercial grade sample of 'perfluorohexanes' has been accomplished with the use of a single instrumental analytical method: fluorine-19 nuclear magnetic resonance (F-nmr) spectroscopy. With the combination of routine one dimensional (1D) and two dimensional (2D) F-nmr data acquisition techniques, the commercial grade sample was found to be composed of all five acyclic perfluorohexane isomers and two cyclic perfluorinated alkanes. The F-nmr spectra yielded information about chemical shifts, spin-spin fluorine-fluorine (F-F) coupling constants, and relative intensities for fluorine nuclei in all components. The qualitative and quantitative specificity of the F-nmr analysis method circumvented the need to use other instrumental analytical methods for compositional evaluations.

INTRODUCTION

Fluorine-19 nmr spectroscopic investigations of a commercial grade sample of 'perfluorohexanes' have yielded complete qualitative and quantitative compositional data for seven perfluorinated alkanes. Specifically, F-nmr data have provided information about the identities and absolute quantities of the five acyclic perfluorohexane isomers and the two cyclic C_6F_{12} isomers shown in Table 1.

F-nmr data for many of the 'pure' perfluorohexane (C_6F_{14}) acyclic isomers and for many of the 'pure' C_6F_{12} cyclic isomers have been assigned and reported previously. For example, Alley [1] and Tiers [2,3] have

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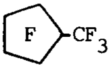
reported data for perfluoro(n-hexane) (1), Dresdner [4] has reported data for perfluoro(2-methylpentane) (2) and perfluoro(2,3-dimethylbutane) (4), and several independent sources [5, 6, 7, 8, 9] have reported data for perfluorocyclohexane (6). However, no F-nmr data have yet been published for the complete characterization of a single, complex perfluorinated alkane mixture composed of the five perfluorohexane acyclic isomers (1∿5) and two of the C_6F_{12} perfluorinated cyclic alkanes (6, 7). This paper will report F-F spin-spin coupling constant data and complete chemical shift data for fluorine nuclei in all components. In addition, complete quantitative compositional data will be reported for the seven-component mixture.

TABLE 1

Seven perfluoroalkanes in a commerical grade sample of 'perfluorohexanes'

No.	Structure	Name
1	$CF_3-CF_2-CF_2-CF_2-CF_2-CF_3$	perfluoro(n-hexane)
2	$(CF_3)_2CF-CF_2-CF_2-CF_3$	perfluoro(2-methylpentane)
3	$CF_3-CF_2-CF(CF_3)CF_2-CF_3$	perfluoro(3-methylpentane)
4	$(CF_3)_2CF-CF(CF_3)_2$	perfluoro(2,3-dimethylbutane)
5	$(CF_3)_3C-CF_2-CF_3$	perfluoro(2,2-dimethylbutane)
6		perfluoro(cyclohexane)
7		perfluoro(methylcyclopentane)

RESULTS AND DISCUSSION

A commercial grade sample of 'perfluorohexanes' was subjected to F-nmr spectroscopic analyses at the 94.2 MHz observation frequency. The sample, a clear and colorless fluorocarbon fluid product of 3M which is used in the electronics industry as a coolant and test bath medium, was produced by the electrochemical fluorination (ecf) of a 'hexane' hydrocarbon mixture. Vendor data indicated the 'hexane' cell feed was actually composed of about 86 wt.% n-hexane, with branched chain C_6H_{14} isomers, cyclohexane, and methylcyclopentane comprising the remaining 14 wt.%.

Routine high resolution one dimensional (1D) F-nmr data were combined with two dimensional (2D) F-F homonuclear correlated spectroscopic (COSY) F-nmr data for the complete and unambiguous qualitative and quantitative characterization of the perfluorinated acyclic and cyclic alkanes in the complex mixture. The 1D F-nmr data yielded information about the chemical shifts, spin-spin F-F coupling constants, and relative intensities for the numerous fluorine absorptions. In contrast, the 2D-COSY technique yielded connectivity information for the fluorine nuclei interacting via spin-spin coupling mechanisms. The combination of the two acquisition techniques greatly facilitated assignment of the fluorine spectra.

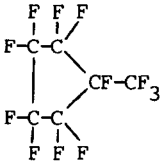
A complete summary of F-nmr spectral assignments and the corresponding compositional data for the five F-acyclic alkanes and the two F-cyclic alkanes is given in Table 2. The data in Table 2 clearly illustrate the versatility of the F-nmr technique for the complete characterization of a mixture of this type. Even at the 94.2 MHz observation frequency, the dispersion of F-19 absorptions over the chemical shift range of interest is more than adequate for the complete and unambiguous assignment of all component identities. The high degree of specificity in these spectral assignments circumvented the need to use other characterization tools such as infrared spectroscopy, gas chromatography (gc), gc combined with mass spectrometry, or other variations of chromatographic and spectroscopic analyses for the identification of the various components.

As a consequence of the complete assignment of the F-nmr spectra, the concentrations of the individual components can be confidently and accurately assigned. A propagation-of-errors analysis method indicates that errors associated with measurement of fluorine peak area integrations (1D F-nmr spectrum) propagate to yield relative errors of $\pm 1 \sim 2\%$ in the concentrations of 1 and 2, and relative errors of $\pm 3 \sim 5\%$ in the concentrations of $3 \sim 7$. Considering the relatively high degree of quantitative precision and accuracy attainable using this method, the compositional data show a significant and real reduction in the amount of n-hexane isomer. The change from about 86 wt.% $CH_3(CH_2)_4CH_3$ in the hydrocarbon cell feed to about 70 wt.% $CF_3(CF_2)_4CF_3$ in the ecf product mixture is attributable to bond cleavage, rearrangement, and isomerization reactions associated with the ecf process [10, 11].

Some other noteworthy features of Table 2 include the spectral data for 5, 6, and 7. The data for 5 allow observation and measurement of the five bond F-F coupling between fluorines o and q [$^5J(o\text{-}q)=9.0$ Hz]. The

TABLE 2

F-nmr spectral assignments and compositional data for the seven perfluoroalkanes in a commercial grade sample of 'perfluorohexanes'

Cpd. No.	Structure	Wt. % Composition	Chemical[a] Shifts	Peak[b] Patterns	Coupling[c] Constants (Hz)
1	$CF_3-CF_2-CF_2-CF_2-CF_2-CF_3$ a b c	69.9%	a - 81.2	triplet	a-c=10
			b -125.9		
			c -122.4		
2	$(CF_3)_2CF-CF_2-CF_2-CF_3$ d e f g h	16.8%	d - 72.0		
			e -185.8		
			f -115.0		
			g -124.8		
			h - 80.8	triplet	f-h=12.2
3	$CF_3-CF_2-CF(CF_3)CF_2-CF_3$ i j k l	7.5%	i - 80.3		
			j -116.7		
			k -184.4		
			l - 71.0		
4	$(CF_3)_2CF-CF(CF_3)_2$ m n	1.3%	m - 70.4	doublet	m-n=7.9
			n -178.8		
5	$(CF_3)_3C-CF_2-CF_3$ o p q	1.2%	o - 62.0	sextet	o-p=11.1
			p -108.7	decade	o-q=9.0
			q - 78.6	decade	
6	 r	0.6%	r -132.7	broad singlet Δν 1/2=210 Hz	
7	 s t u v w x	2.7%	s -133.0	AB quartet	s-t=260
			t -129.0		
			u -130.7	AB quartet	u-v=275
			v ca.-126		
			w -186.4		
			x - 72.6		

[a] Chemical shifts expressed (-) ppm upfield of internal $CFCl_3$.

[b] Multiplets when not specifically stated.

[c] Only obvious coupling constants were measured.

large five bond F-F coupling is probably attributable to a 'through-space' spin-spin coupling mechanism (as compared to a 'through-bond' mechanism) which becomes operative when the geometry of the molecule dictates close spatial arrangements of the interacting fluorines [12, 13]. Ng [13] also postulates that the 'through-space' mechanism is a consequence of direct overlap of electronic clouds of the interacting fluorine atoms, such that the distance between fluorine atoms is less than twice the Van der Waals' radius for fluorine (i.e., less than 2.72 Å). As the F-F orbital overlap increases (i.e., the F-F distance decreases), the coupling constant increases monotonically. Therefore, the spin-spin coupling interaction between fluorines o and q in 5 is more likely a result of a 'through-space' mechanism since a 'through-bond' coupling between fluorines o and q can be regarded as insignificant over five bonds.

The F-nmr data of the commercial 'perfluorohexanes' mixture also show a broad, unresolved singlet ($\Delta\nu$ 1/2=210 Hz) for perfluorocyclohexane (6). This spectral phenomenon indicates that 6 exists as a rapidly interconverting chair structure at the 22°C experimental temperature [14]. The resonance is very broad because the rate of ring inversion (ring flip) and, consequently, the rate of exchange between axial and equatorial fluorines is comparable to the time scale of the nmr measurement. In contrast to the rapidly interconverting chair structure of 6, the perfluoromethyl group in perfluoro(methylcyclopentane) (7) locks the ring into a fixed conformation. Therefore, the perfluoromethylene fluorines in 7 show geminal inequivalence and they appear as easily recognized second-order AB quartet patterns, typical of cyclic compounds. The low field half of the u-v AB pattern is partially obscured by the resonances due to fluorines b, c, and g.

EXPERIMENTAL

High resolution 1D and COSY 2D F-nmr data were acquired on an IBM NR-100/AF FT-NMR spectrometer system operating at 94.2 MHz in the fluorine-19 observation mode. The ambient probe temperature was ca. 22°C for all measurements. For the high resolution 1D nmr work, the commercial grade sample of 'perfluorohexanes' inert liquid was diluted about 50% in Freon-11® ($CFCl_3$). These data were acquired in an unlocked mode of operation using a 32K word data size over a sweep width of 28,000 Hz. All chemical shifts are expressed as negative ppm upfield of Freon-11.

For the COSY-2D nmr experiment, the sample was sealed in a capillary tube which was subsequently inserted into a standard 5 mm nmr tube containing $CDCl_3$. Deuterium lock was maintained throughout the 2D nmr experiment which involved acquisition of 512 (2048 word) spectra over a sweep width of about 12,100 Hz. The 2D data matrix was then zero-filled to 1024 x 2048 words before transformation to the frequency domain (absorption mode) spectral format.

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