

[CONTRIBUTION FROM NATIONAL BUREAU OF STANDARDS]

Mass Spectra of Some Cyclic and Straight Chain Fluorocarbons¹

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The Mass Spectrometry Section of the Bureau of Standards has measured the mass spectra of some pure fluorocarbons prepared by George H. Cady of the Chemistry Department of the University of Washington.^{1a} This paper presents these measurements in comparison with the mass spectra of the corresponding hydrocarbons. Tables of the detailed mass spectral data have been published in the Catalog of Mass Spectral Data.²

Experimental

Mass spectra were obtained with a 180° Consolidated mass spectrometer which has been described in detail elsewhere.³ Recommended procedures were followed in obtaining the spectra except that it was necessary to use a magnet current in excess of the rated current to record the ions of high molecular weight. A magnet current of 1.3 amperes was used in the range from molecular weight 50 up to a value exceeding the molecular weight of the molecule. Mass spectra were measured with ionizing potentials of 50 volts and 70 volts but only the 70-volt spectra are reported here. The temperature of the ionization chamber was automatically maintained at 245° and the electron current to the collector (catcher) was automatically held at 9 microamperes.

Relative intensities in the mass spectrum are expressed on a scale of the peak of maximum height taken as 100 and peaks as small as 0.01 can be detected. The sensitivity is commonly expressed in terms of the current at the maximum peak in arbitrary units divided by the pressure in the gas reservoir. The ratio of this sensitivity to the sensitivity to normal butane at 43⁺ gives a value independent of the arbitrary units used and it is this relative sensitivity that is given here. The resolving power of our mass spectrometer was not sufficient to resolve completely unit mass differences beyond mass 150. This introduces a little uncertainty in reading the mass peaks of the heavier ions from cyclo-C₆F₉H.

The boiling points of the six fluorocarbons measured are listed in Table I. The first three of these compounds were carefully separated from impurities using an 82 theoretical plate fractionating column. The same column was used for cyclo-C₆F₉H but traces of impurities probably remained. The last two compounds are of good quality but inferior to the first three. The mass spectrometer analysis showed no recognizable impurities in any of the perfluoro compounds. In the spectrum of cyclo-C₆F₉H

there is a small peak, 0.19% of the maximum peak, near mass 250. This could be C₆F₁₀⁺ or C₆F₁₀H⁺. The spectrum shows that it cannot be cyclo-C₆F₁₀ but a trace of a perfluoropentene is possible. Another possibility is that it is C₆F₁₀H⁺ from C₆F₁₁H. This compound makes an unknown but probably small contribution to the pattern recorded in Table III.

TABLE II
MASS SPECTRA OF CYCLOHEXANES
Sensitivity relative to 43⁺ of *n*-butane: C₃F₅⁺, 1.37

Ion	Rel. inten.	Ion	Rel. inten.	Ion	Rel. inten.	Ion	Rel. inten.
C ₆ ⁻		C ₆ ⁻		C ₃ ⁻		C ₃ ⁻	
H ₁₂	73.9	F ₁₂	0.70	H ₇	13.6	F ₇	0.02
H ₁₁	4.55	F ₁₁	3.77	H ₆	29.8	F ₆	.48
				H ₅	64.9	F ₅	100
C ₅ ⁻		C ₅ ⁻		H ₄	6.21	F ₄	2.53
H ₁₀	1.20	F ₁₀	0.05	H ₃	28.4	F ₃	15.0
H ₉	22.2	F ₉	20.9	H ₂	2.53	F ₂	2.96
H ₈	1.69	F ₈	0.16	H	1.05	F	1.07
H ₇	2.95	F ₇	2.71				
				C ₂ ⁻		C ₂ ⁻	
C ₄ ⁻		C ₄ ⁻		H ₅	11.7	F ₅	5.59
H ₈	100	F ₈	0	H ₄	13.2	F ₄	29.2
H ₇	34.9	F ₇	21.4	H ₃	30.4	F ₃	2.14
H ₆	6.82	F ₆	3.96	H ₂	4.74	F ₂	1.23
H ₅	4.80	F ₅	2.06				
H ₄	1.35	F ₄	1.54	C ⁻		C ⁻	
H ₃	3.34	F ₃	0.57	H ₃	5.35	F ₃	70.3
H ₂	2.23	F ₂	.36	H ₂	0.42	F ₂	5.15
				H	.08	F	21.8
				C	.05	C	.03

The hydrocarbon mass spectra given for comparison with the fluorocarbons were obtained with National Bureau of Standards Samples of purity 99.85% and better. The tables omit some smaller peaks of less than 2% of the maximum peak.

Results

When mass spectra of fluorocarbons are tabulated in the order of increasing or decreasing molecular weight the ions with different numbers of carbon atoms and of fluorine atoms alternate in a rather confusing disorder. For convenient comparison with the more familiar hydrocarbon spectra the ions containing the same number of carbon atoms have been grouped together in the following tables.

Cyclohexanes.—Table II gives the mass spectra of cyclohexane and the perfluoro compound. In the hydrocarbon molecule the molecule ion (parent ion) and ions C₆H₉⁺, C₄H₈⁺, C₃H₅⁺ and C₂H₃⁺ are relatively abundant. It is of interest that CH₃⁺ has about the same intensity in cyclics as in molecules containing CH₃ terminal radicals.

In the fluorinated compounds the parent ion peaks are always very small indicating that the more probable ionization process is removal of F⁻

TABLE I

BOILING POINTS OF FLUOROCARBONS

Number	Substance	Boiling point, °C.
1	Cyclo-C ₆ F ₁₀	22.5
2	<i>n</i> -C ₆ F ₁₂	29.3
3	<i>i</i> -C ₆ F ₁₂	30.1
4	Cyclo-C ₆ F ₉ H	37.8 to 38.2
5	Cyclo-C ₆ F ₁₂	51 (sublimes)
6	<i>n</i> -C ₇ F ₁₆	82.4 to 82.6

(1) Paper presented before the Oregon meeting of the American Chemical Society, September 13-17, 1948.

(1a) The fluorinated pentanes used for this research were prepared under contract with the Office of Naval Research, Navy Department.

(2) Catalog of mass spectral data, American Petroleum Institute, Project 44, National Bureau of Standards.

(3) H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, *Ind. and Eng. Chem., Anal. Ed.*, **15**, 54 (1943).

TABLE III
 MASS SPECTRA OF CYCLOPENTANES

 Sensitivity relative to 43^+ of *n*-butane; $C_3F_5^+$ of C_3F_{10} , 1.73; $C_3F_5^+$ of C_5F_9H , 0.61

Cyclo- C_5H_{10}	Rel. inten.	Cyclo- C_5F_{10}	Rel. inten.	Ion	Rel. inten.	Cyclo- C_5F_9H	Rel. inten.
C_5^-		C_5^-		C_5^-		C_5^-	
H_{10}	29.3	F_{10}	0.36			F_9H	0.11
H_1	1.07	F_9	4.45	F_9	0	F_8H	4.26
H_8	0.41	F_8	0.02	F_8	0.13	F_7H	0.33
C_4^-		C_4^-		C_4^-		C_4^-	
H_7	29.0	F_7	14.4	F_7	0	F_6H	20.7
H_6	0.91	F_6	0.93	F_6	0.76	F_5H	1.93
H_5	1.86	F_5	0.53	F_5	0.74	F_4H	1.34
C_3^-		C_3^-		C_3^-		C_3^-	
		F_7		F_7	0.66	F_6H	2.97
H_6	100	F_6	0.39	F_6	0.53	F_5H	^a
H_5	28.9	F_5	100	F_5	100	F_4H	80.4
H_4	7.33	F_4	1.36	F_4	1.06	F_3H	1.62
H_3	20.9	F_3	9.65	F_3	9.40	F_2H	11.0
H_2	3.16	F_2	2.62	F_2	2.87	FH	2.39
H	1.42	F	1.13	F	1.55	H	0.69
C_2^-		C_2^-		C_2^-		C_2^-	
H_5	4.56	F_5	0.24	F_5	5.59	F_4H	0.60
H_4	3.73	F_4	23.8	F_4	29.6	F_3H	23.4
H_3	14.7	F_3	1.88	F_3	1.34	F_2H	2.62
H_2	3.35	F_2	1.28	F_2	1.34	FH	1.64
C^-		C^-		C^-		C^-	
H_3	3.44	F_3	16.2	F_3	56.3	F_2H	14.0
H_2	0.51	F_2	5.11	F_2	6.19	FH	2.24
H	0.11	F	23.3	F	30.9	H	0.13

^a Masked by isotope.

rather than an electron. Studies⁴ of mass spectra and appearance potentials for simpler compounds such as carbon tetrafluoride support this view. Ions $C_5F_{11}^+$, $C_5F_9^+$, $C_4F_7^+$, $C_3F_5^+$, $C_2F_4^+$ and CF_3^+ are the most abundant ions in each carbon group.

Cyclopentanes.—Table III gives mass spectra of three cyclopentanes. There is a marked similarity between cyclo- C_5F_{10} and cyclo- C_5F_{12} . The same ions $C_5F_9^+$, $C_4F_7^+$, $C_3F_5^+$, $C_2F_4^+$ and CF_3^+ are abundant in both spectra although in the cyclopentane CF^+ is greater than CF_3^+ . There is a different type of similarity between the two hydrocarbons. In these the largest peaks in the first four carbon groups are the molecule ion and molecule ions which have lost CH_3 , C_2H_4 and C_3H_7 . As a result the larger peaks in the two spectra are different.

Substituting one hydrogen in the fluoro compound doubles the complexity of the spectrum and it is convenient to list the ions in two columns, one containing perfluoro ions and the other containing ions with one hydrogen (Table III). As noted above there are two sources of experimental uncertainty in the data on cyclo- C_5F_9H . A trace of $C_5F_{10}^+$ gives an unknown contribution and insufficient resolution gives some uncertainty in the

height of peaks containing an H atom when there are seven or more fluorine atoms. The absence of $C_4F_7^+$ in the cyclo- C_5F_9H spectrum shows that the $C_5F_{10}^+$ is not from cyclo- C_5F_{10} .

Table III shows a very close parallelism between ions of C_5F_9H containing H and the corresponding ions of cyclo- C_5F_{10} . The occurrence of $C_3F_6H^+$ but no ion $C_3F_7^+$ from cyclo- C_5F_{10} is an exception. Another exception is the fact that CF^+ is large but CH^+ is small. This is not surprising however as the CH^+ peak is of the same magnitude as is found in all hydrocarbons.

The perfluoro ions of cyclo- C_5F_9H do not correspond closely to the ions of C_5F_{10} . The absence of ions C_5F_9 and C_4F_7 is a striking characteristic of the C_5F_9H spectrum. It is suggestive that the abundance of CF_3^+ from C_5F_9H is almost four times the abundance of CF_2H^+ for this is the *a priori* probability of finding H missing or present on one of the C atoms of cyclo- C_5F_9H . The chance of finding H missing or present on two adjacent carbon atoms is 3 to 2 while the ratio of $C_2F_4^+$ to $C_2F_3H^+$ is 2.52 to 2. In ions with more than two carbon atoms there is no evidence for such a relation.

Normal and Isopentanes.—Table IV shows the mass spectra of the normal pentanes and the isopentanes. In both the perfluoro compounds CF_3^+ is by far the largest peak which is quite unlike the hydrocarbon spectra. The difference in the $C_3F_7^+$ peaks is the most conspicuous difference in the perfluoro spectra while the $C_4H_9^+$ peaks are best for distinguishing the hydrocarbons. The largest peak in each carbon group of perfluoro-*n*-

 TABLE IV
 MASS SPECTRA OF NORMAL PENTANES AND ISOPENTANES
 Sensitivity relative to 43^+ of *n*-butane; CF_3^+ of *n*- C_5F_{12} , 2.59; CF_3^+ of *i*- C_5F_{12} , 2.77.

Ion	Relative intensities of mass peaks			
	<i>n</i> - C_5H_{12}	<i>n</i> - C_5F_{12}	<i>i</i> - C_5H_{12}	<i>i</i> - C_5F_{12}
C_5X_{12}	8.79	0.03	6.19	0.00
C_5X_{11}	0.51	0.77	1.82	1.72
C_4X_9	12.6	0.27	54.0	0.87
C_4X_8	2.20	0.26	16.8	1.04
C_4X_7	2.87	3.25	4.71	4.53
C_3X_7	100	9.73	100	0.19
C_3X_6	57.9	1.10	86.0	1.76
C_3X_5	40.5	6.54	67.3	8.32
C_3X_4	2.37	0.35	3.38	0.51
C_2X_3	14.2	2.06	21.5	2.76
C_2X_2	1.55	0.44	2.40	0.53
C_2X_1	24.4	29.5	45.7	16.4
C_2X_0	6.00	7.18	6.17	3.51
C_2X_{-1}	34.6	0.64	42.2	0.52
C_2X_{-2}	3.30	0.45	4.11	0.38
CX_3	4.65	100	8.40	100
CX_2	0.55	3.12	1.05	2.12
CX	0.12	9.21	0.23	6.54
C	0.06	0.05	0.10	0.06
X	0.72	0.08	1.13	0.14

(4) V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **40**, 25 (1948).

pentane is given by losing F, CF₅, C₂F₅, C₃F₇ and C₄F₉.

Normal Heptane.—Table V gives the mass spectra of the *n*-heptanes. Again as in *n*-pentane the largest peak in each carbon group of the fluorocarbon comes from losing F, CF₅, C₂F₅, C₃F₇, C₄F₉ and in addition C₅F₁₁ and C₆F₁₃. It was noted above that the perfluoro cyclics gave identical ions rather than losing identical masses in the dissociation. The ion C₇F₁₅⁺ of mass 369 is probably the heaviest ion ever recorded on this type of mass spectrometer. The perfluoro-*n*-heptane, like the perfluoropentanes, differs from the hydrocarbon in that ionization by loss of CF₃ is very improbable and production of CF₃⁺ most probable.

TABLE V
MASS SPECTRA OF NORMAL HEPTANES
Sensitivity relative to 43⁺ of *n*-butane; CF₃⁺, 3.30

Ion	Rel. inten.	Ion	Rel. inten.
C ₇ ⁻		C ₇ ⁻	
H ₁₆	13.1	F ₁₆	0
H ₁₅	0.01	F ₁₅	0.09
C ₆ ⁻		C ₆ ⁻	
H ₁₃	1.90	F ₁₃	0.02
H ₁₂	0.16	F ₁₂	0
H ₁₁	.03	F ₁₁	1.08
C ₅ ⁻		C ₅ ⁻	
H ₁₁	44.0	F ₁₁	1.20
H ₁₀	17.2	F ₁₀	.03
C ₄ ⁻		C ₄ ⁻	
H ₉	47.8	F ₉	8.48
H ₈	26.3	F ₈	0.21
H ₇	10.5	F ₇	2.53
C ₃ ⁻		C ₃ ⁻	
H ₇	100	F ₇	20.50
H ₆	24.1	F ₆	0.88
H ₅	51.9	F ₅	13.3
H ₄	3.23	F ₄	0.47
H ₃	18.8	F ₃	2.38
C ₂ ⁻		C ₂ ⁻	
H ₅	46.0	F ₅	27.0
H ₄	7.83	F ₄	7.34
H ₃	39.3	F ₃	0.51
H ₂	3.22	F ₂	.24
C ⁻		C ⁻	
H ₃	4.88	F ₃	100
H ₂	0.42	F ₂	1.86
H	.09	F	6.06

Metastable Transitions.—Mass spectra usually show some small diffuse peaks which are in general at non-integral masses. These arise from ions which dissociate after they have

traversed the ion accelerating field and thus have less than the full kinetic energy of the initial ion before dissociation.⁵ The apparent mass m_a of these ions is related to the initial mass m_i and the final mass m_f by the equation

$$m_a = m_i^2/m_f$$

A survey of metastable ions in hydrocarbon spectra⁶ shows that metastable transition peaks are only observed when both the initial and final ions give relatively large peaks.

The same phenomenon is observed in fluorocarbons and Table VI lists the observed metastable transitions. These are all small peaks amounting to a few tenths of a per cent. of the maximum peak at the most. The table shows that these transitions frequently recur in different compounds and that only two types of transition occur, losing CF and losing CF₂. The three metastable transitions found in cyclo-C₆F₉H correspond to the three found in cyclo-C₆F₁₀ with H substituted for one of the fluorine atoms in both the initial and final ions. There is no correspondence between these transitions and the metastable transitions found in the corresponding hydrocarbons.

TABLE VI METASTABLE TRANSITIONS IN FLUOROCARBONS			
Apparent mass	Transition	Compounds showing transition	
76.3	C ₃ F ₅ ⁺ → C ₂ F ₄ ⁺ + CF	Cyclo-C ₆ F ₁₀ , cyclo-C ₆ F ₁₂ , <i>n</i> -C ₇ F ₁₆	
94.8	C ₄ F ₇ ⁺ → C ₃ F ₅ ⁺ + CF ₂	Cyclo-C ₆ F ₁₀ , cyclo-C ₆ F ₁₂ , <i>n</i> -C ₅ F ₁₂ and <i>n</i> -C ₇ F ₁₄	
141.8	C ₅ F ₉ ⁺ → C ₄ F ₇ ⁺ + CF ₂	Cyclo-C ₆ F ₁₀	
189.9	C ₆ F ₁₁ ⁺ → C ₅ F ₉ ⁺ + CF ₂	Cyclo-C ₆ F ₁₂	
59.5	C ₃ F ₄ H ⁺ → C ₂ F ₃ H ⁺ + CF	Cyclo-C ₅ F ₉ H	
78.3	C ₄ F ₆ H ⁺ → C ₃ F ₄ H ⁺ + CF ₂	Cyclo-C ₅ F ₉ H	
124.7	C ₅ F ₈ H ⁺ → C ₄ F ₆ H ⁺ + CF ₂	Cyclo-C ₅ F ₉ H	

Conclusion

No difficulties were encountered in obtaining spectra of these fluorocarbons and the experiments indicate that the mass spectrometer can be very useful in analysing fluorinated compounds up to and including heptanes. This will require accumulating data on mass spectra of pure fluorocarbons. The Mass Spectrometry Section of the Bureau of Standards will be glad of an opportunity to analyse any new fluorocarbons that may be made. An advantage of this method of analysis is that very small quantities, of the order of a milligram, are sufficient for full sensitivity.

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(5) J. A. Hipple, R. E. Fox and E. U. Condon, *Phys. Rev.*, **69**, 347 (1946).

(6) Evelyn G. Bloom, Fred L. Mohler, J. H. Lengel and C. E. Wise, *J. Research Natl. Bur. Standards*, in press.