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THE SYNTHESES AND MASS SPECTRA OF $P[C{\equiv}C{-}CF_3]_3$, $As[C{\equiv}C{-}CF_3]_3$, and $Sb[C{\equiv}C{-}CF_3]_3$

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SUMMARY

The syntheses of $P[C{\equiv}C{-}CF_3]_3$, $As[C{\equiv}C{-}CF_3]_3$, and $Sb[C{\equiv}C{-}CF_3]_3$ are reported. The compounds are colorless and volatile, with melting points of -20° to -25°, 23-24°, and 55-56°C, respectively. The mass spectra show the molecular ion of each compound. The rearrangement ion $[F_3C{-}C{\equiv}C{-}C{\equiv}C{-}CF_2]^+$ gives the strongest peak in each spectrum.

INTRODUCTION

This paper reports the first syntheses of these compounds. They were prepared as part of a study of fluoropolymers. Our detailed study of their infrared, Raman, and F^{19} NMR spectra has shown that the compounds have a C_{3v} [trigonal pyramid] framework with freely-rotating $-CF_3$ groups [1]. No other CF_3-substituted metalloid acetylenes of such high symmetry have had their geometrical structures confirmed.

The synthesis and mass spectrum of $Si[C{\equiv}C{-}CF_3]_4$ have been reported [2]. A partial study of the infrared and Raman spectra of $Si[C{\equiv}C{-}CF_3]_4$, $Ge[C{\equiv}C{-}CF_3]_4$, and $Sn[C{\equiv}C{-}CF_3]_4$ has been made [3].

To our knowledge, no mass spectra of trifluoropropynyl derivatives, other than the data of [2], have been reported.

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SYNTHESES

The overall reaction scheme was:

$$H\text{-}C{\equiv}C\text{-}CF_3 + C_4H_9\text{-}Li \text{ (in hexane)} \xrightarrow[-30°]{\text{diethyl ether}} Li\text{-}C{\equiv}C\text{-}CF_3 + C_4H_{10}\uparrow$$

$$3Li\text{-}C{\equiv}C\text{-}CF_3 + MCl_3 \xrightarrow[-78°;\ -30°]{\text{diethyl ether}} M[C{\equiv}C\text{-}CF_3]_3 + 3LiCl\downarrow$$

where M = P, As, or Sb. All of the reactions were carried out in a dry nitrogen atmosphere.

The $H\text{-}C{\equiv}C\text{-}CF_3$ gas was purchased from PCR, Inc. and was transferred via a vacuum line and frozen (using liquid nitrogen) into a three-necked 250 ml round-bottom flask; the amount transferred was monitored by the pressure in the filling system, and by a final weighing. The n-butyl lithium was a 22% solution in n-hexane, purchased from Alfa Products. The diethyl ether was the anhydrous grade (sealed in metal) of Fischer Scientific Co. The MCl_3 were Fischer Reagent compounds.

Due to the possibly explosive nature of the starting materials and the reaction products, only small scale reactions were used and great care was taken to employ protective shielding at all stages of the work. No mishaps occurred.

The general procedure employed the quantities of reagents needed to give a theoretical yield of 0.003 mole of $M[C{\equiv}C\text{-}CF_3]_3$. The actual yields were approximately 50% of the theoretical, and no effort was made to maximize this, due to the suspected inherent instability of acetylide by-products in the final purification step.

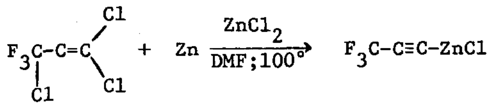
The general procedure was to freeze out 0.009 mole of $H\text{-}C{\equiv}C\text{-}CF_3$ gas into the 250-ml flask containing a teflon-covered stirring magnet. After the addition of dry nitrogen gas to one atmosphere of pressure, 20 ml of diethyl ether was added dropwise via a separatory funnel and frozen on top of the $H\text{-}C{\equiv}C\text{-}CF_3$. A slow purge of nitrogen was maintained, and the flask's temperature was slowly raised to -30° in a dry ice bath. Then the ether solution was stirred via a magnetic stirrer and the n-butyl lithium solution (0.009 mole) was added dropwise over a thirty minute period. The reaction was immediate and exothermic, but its temperature was kept at -30°. (The flask was fitted with a thermometer, and the separatory funnels were the pressure-equalizing type which thus permitted them to be purged.) A solution of 0.003 mole of MCl_3 in 15 ml of ether, under nitrogen, was prepared in a separatory funnel and this funnel was used to replace the previous one on the reaction flask. The reaction medium was cooled to -78°

and the MCl_3 solution was then added dropwise over a thirty minute interval while maintaining the -78° temperature. The reaction was exothermic, and the reaction medium remained colorless with a white precipitate of LiCl being formed. After the addition, the reaction temperature was increased to -30° and the stirring continued for an additional thirty minutes. The $M[C\equiv C\text{-}CF_3]_3$ was then isolated by connecting the reaction flask to a vacuum line trapping system and pumping the volatiles through in-series traps at 0°, -20°, and at liquid nitrogen temperature. The $M[C\equiv C\text{-}CF_3]_3$ was the dominant component in the 0° trap. Subsequent vacuum transfers and trapping were used for the final purification; the separations were monitored by their vapor phase IR spectra. No MCl_3 was encountered in the purification steps.

At room temperature, $P[C\equiv C\text{-}CF_3]_3$ is a colorless liquid and the As and Sb compounds form colorless crystals; the evacuated sealed-tube melting points are -20° to -25°, 23-24°, and 55-56°, respectively. $Sb[C\equiv C\text{-}CF_3]_3$ melts with apparent decomposition or polymerization, forming a white powder which does not dissolve in the melt. $P[C\equiv C\text{-}CF_3]_3$ in an evacuated glass tube turns slowly to an amber color at room temperature in the absence of light; fluorescent room lights cause a rapid darkening; a non-volatile amber-colored residue remains when the $P[C\equiv C\text{-}CF_3]_3$ is then pumped away. The As and Sb compounds showed no color change when left at room temperature for several hours in evacuated glass tubes, whether in darkness or under fluorescent room lights; however, both situations left a white residue when the compounds were pumped away. All three compounds have been stored at liquid nitrogen temperature for many months without apparent change.

Several attempts were made to prepare $Bi[C\equiv C\text{-}CF_3]_3$ by this method, but with uncertain results. The IR spectra used to monitor the workups indicated that we did prepare it in minute quantities, but we were unable to purify a sufficient quantity to characterize.

We first prepared $P[C\equiv C\text{-}CF_3]_3$ by another method. The yield was low and purification from the necessary solvents and unreacted PCl_3 was tedious, and we therefore developed the much easier method reported above. Briefly, the first method was:



$$F_3C\text{-}C\equiv C\text{-}ZnCl + PCl_3 \xrightarrow[DMF]{} P[C\equiv C\text{-}CF_3]_3 + ZnCl_2$$

DMF was dimethyl formamide. The preparation of $F_3C{-}C{\equiv}C{-}ZnCl$ was essentially that of Norris and Finnegan [4]. A Lewis base must be used as a solvent; pyridine was also tried, but the yield was very low and the purification was again difficult.

INSTRUMENTATION

The mass spectra were recorded on a Perkin-Elmer Model 270 spectrometer, using a gas inlet system and 80 eV ionization. The ion source temperature was 180°C, the target was at 120 volts, and the accelerating voltage was 2000. The scanning rate was linear and approximately 50 mass units/sec. Resolution was 0.5 mass unit or better throughout the range.

MASS SPECTRA

Tables 1, 2, and 3 tabulate the mass spectra for the Sb, As, and P compounds, respectively. The possible C_yF_z and possible MC_vF_w values are listed for each peak. Probable assignments for some of the spectral peaks are given in these tables. [Several samples, from different purifications, were used for each $M[C{\equiv}C{-}CF_3]_3$ to obtain its mass spectrum. A comparison then pinpointed several impurity peaks and these are not listed in the tables; in a few cases this has deleted some true C^{13} peaks and may have deleted a few very weak sample peaks.]

Bar graphs of the spectra are shown in Figures 1a and 1b.

Combined tables for the three compounds listing the observed possible MC_vF_w and C_yF_z are useful for detailed comparison of the spectra. Such tables are available from the authors, or may be compiled from Tables 1, 2, and 3. It is useful to note that only one C_yF_z combination is mathematically possible for a mass number _if_ one is possible.

For the spectrum of $Sb[C{\equiv}C{-}CF_3]_3$, a doublet occurs for each SbC_vF_w entity due to the natural abundance of the Sb^{123} and Sb^{121} isotopes (42.75 and 57.25%, respectively). _All_ of the peaks due to SbC_vF_w entities can be distinguished from C_yF_z possibilities. In only four cases can _both_ members of such doublets be also accounted for by C_yF_z values; one member would have to contain ten or more F atoms, so that each case is infeasible.

TABLE 1. Mass spectrum of $Sb[C{\equiv}C\text{-}CF_3]_3$

m/e	Relative Intensity	Possible C_yF_z	Possible SbC_vF_w	Other Possibility
402	1.7	-	$Sb^{123}C_9F_9$	
400	2.2	-	$Sb^{121}C_9F_9$	
309	0.3	-	$Sb^{123}C_6F_6$	
307	0.4	-	$Sb^{121}C_6F_6$	
259	0.6	-	$Sb^{123}C_5F_4$	
257	0.8	-	$Sb^{121}C_5F_4$	
254	1.3	-	$Sb^{123}C_3F_5$	
252	0.9	-	$Sb^{121}C_3F_5$	
241	1.7	C_9F_7	-	
240	0.5	-	$Sb^{123}C_5F_3$	
238	0.7	-	$Sb^{121}C_5F_3$ $Sb^{123}C_8F$	
236	0.4	C_7F_8	$Sb^{121}C_8F$	
235	8.4	-	$Sb^{123}C_3F_4$	
233	10.1	-	$Sb^{121}C_3F_4$	
223	0.6	-	$Sb^{123}C_2F_4$	
222	6.3	C_9F_6	-	
221	0.3	-	$Sb^{121}C_2F_4$ $Sb^{123}C_5F_2$	
219	0.4	C_4F_9	$Sb^{121}C_5F_2$	
217	1.7	C_7F_7	$Sb^{123}C^{*}_{3}F_3$	
216	42.1	-	$Sb^{123}C_3F_3$	
215	2.2	-	$Sb^{121}C^{*}_{3}F_3$	
214	49.9	-	$Sb^{121}C_3F_3$ $Sb^{123}C_6F$	
212	0.4	C_5F_8	$Sb^{121}C_6F$	

TABLE 1 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible SbC_vF_w	Other Possibility
209	0.4	-	$Sb^{123}C_4F_2$	
207	0.4	-	$Sb^{121}C_4F_2$	
204	4.0	-	-	203*
203	34.5	C_9F_5	-	
197	1.6	-	$Sb^{123}C_3F_2$	
195	1.6	C_2F_9	$Sb^{121}C_3F_2$	
191	5.4	C_8F_5	-	
190	1.1	-	$Sb^{123}C_4F$	
188	2.0	C_3F_8	$Sb^{121}C_4F$	
186	3.0	C_6F_6	-	
185	0.5	-	$Sb^{123}C_2F_2$	
183	0.5	-	$Sb^{121}C_2F_2$	
173	0.5	-	$Sb^{123}CF_2$	
172	7.8	C_8F_4	-	
171	0.4	-	$Sb^{121}CF_2$ $Sb^{123}C_4$	
169	0.6	C_3F_7	$Sb^{121}C_4$	
168	7.8	-	-	
167	100.0	C_6F_5	-	
166	1.9	-	$Sb^{123}C_2F$	
165	0.3	C_9F_3	-	
164	3.5	-	$Sb^{121}C_2F$	
163	0.2	-	-	
162	0.1	C_4F_6	-	
161	13.9	-	$Sb^{123}F_2$	
160	0.1	C_7F_4	-	

TABLE 1 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible SbC_vF_w	Other Possibility
159	19.0	-	$Sb^{121}F_2$	
154	0.4	-	-	153*
153	5.8	C_8F_3	-	
149	5.6	-	-	148*
148	54.0	C_6F_4	-	
147	1.2	-	$Sb^{123}C_2$	
145	1.7	-	$Sb^{121}C_2$	
142	15.2	-	$Sb^{123}F$	
141	8.4	C_7F_3	-	
140	20.6	-	$Sb^{121}F$	
136	1.6	C_5F_4	-	
134	0.5	C_8F_2	-	
131	0.2	C_3F_5	-	
130	3.7	-	-	
129	47.3	C_6F_3	-	
123	5.9	-	Sb^{123}	
122	4.6	C_7F_2	-	
121	6.8	-	Sb^{121}	
118	5.2	-	-	
117	52.5	C_5F_3	-	
111	0.4	-	-	
110	2.5	C_6F_2	-	
104	0.5	-	-	103*
103	4.3	C_7F	-	
100	0.5	C_2F_4	-	
99	1.2	-	-	98*

TABLE 1 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible SbC_vF_w	Other Possibility
98	14.7	C_5F_2	-	
93	6.9	C_3F_3	-	
86	1.5	C_4F_2	-	
81	3.6	C_2F_3	-	
80	1.1	-	-	79*
79	14.2	C_5F	-	
74	5.1	C_3F_2	-	
70	0.4	-	-	69*
69	14.7	CF_3	-	
67	0.7	C_4F	-	
62	0.6	C_2F_2	-	
55	3.0	C_3F	-	
50	2.7	CF_2	-	
43	4.2	C_2F	-	
31	16.4	CF	-	
19	0.8	F	-	
12	3.6	C	-	

(*) One C^{13} present (used in table only when needed for clarification).

(-) Not possible.

In the spectrum of $As[C{\equiv}C{-}CF_3]_3$, <u>every</u> peak due to an AsC_vF_w entity can be distinguished from C_yF_z possibilities. There are <u>no</u> peaks observed for which both AsC_vF_w and C_yF_z values are chemically feasible.

As expected, there are many mass peaks in the $P[C{\equiv}C{-}CF_3]_3$ spectrum which could be either due to PC_vF_w or to C_yF_z, within our instrumental resolution. This is because CF is a frequent fragmentation loss in

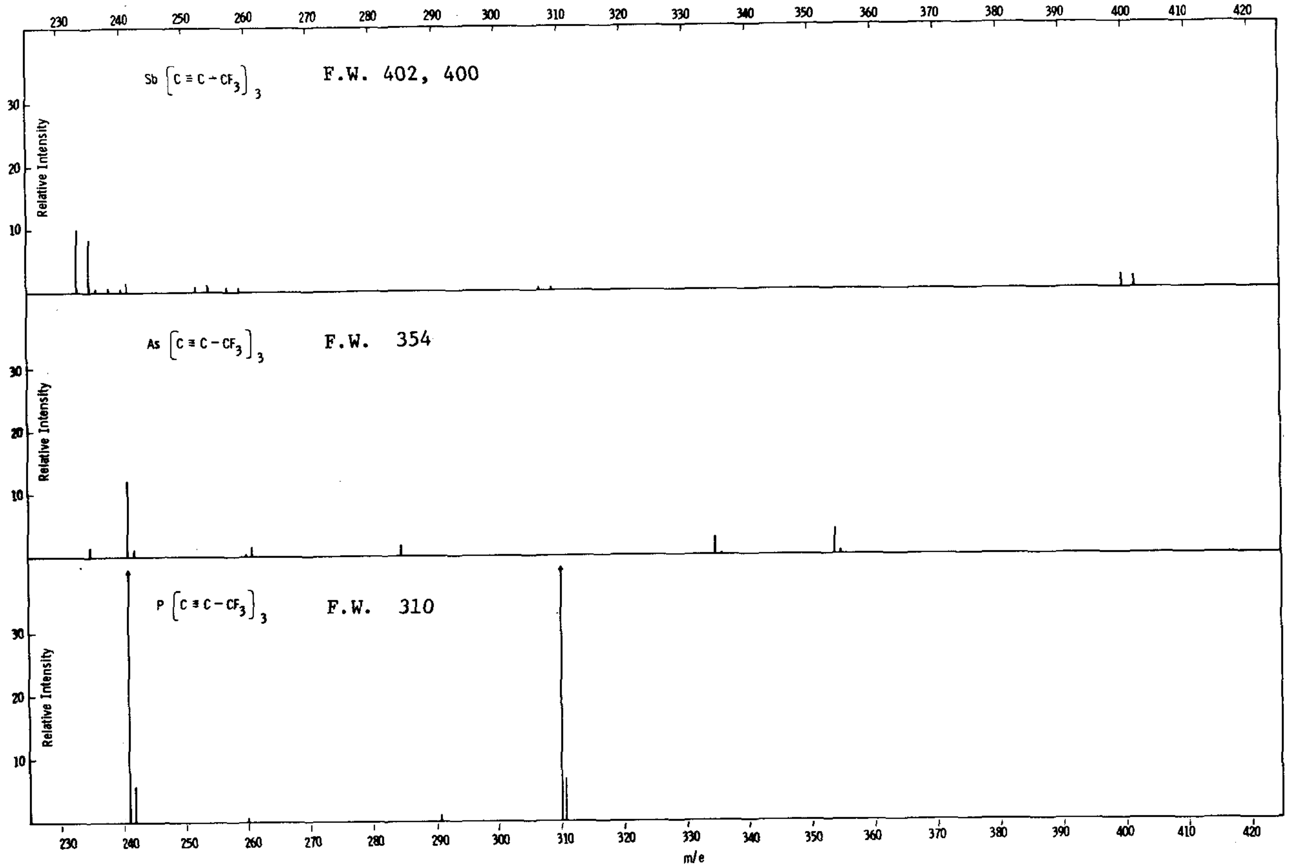


Fig. 1a. Mass spectra, 225 to 425 m/e.

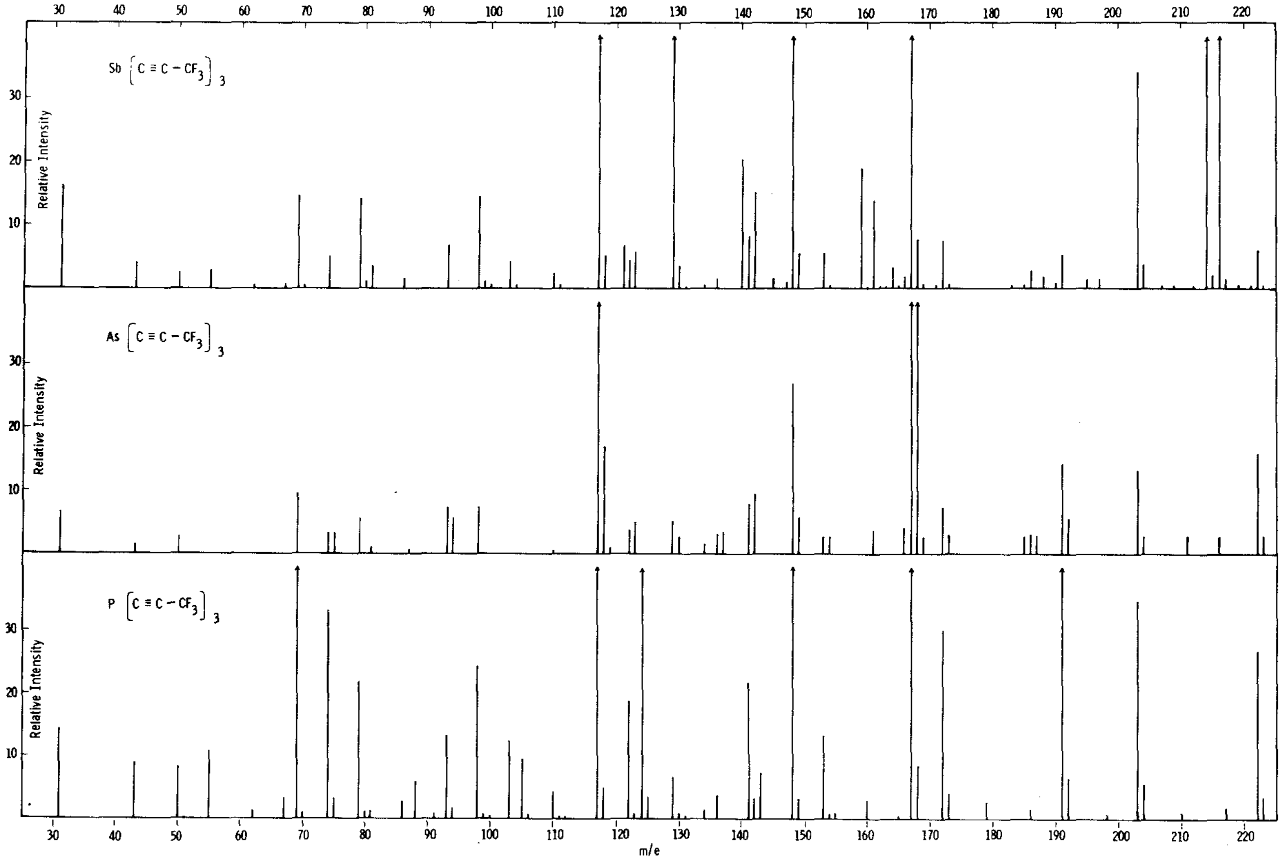


Fig. 1b. Mass spectra, 25 to 225 m/e.

TABLE 2. Mass spectrum of $As[C\equiv C-CF_3]_3$

m/e	Relative Intensity	Possible C_yF_z	Possible AsC_vF_w	Other Possibility
355	0.4	-	-	354*
354	4.1	-	AsC_9F_9	
336	0.2	-	-	335*
335	2.8	-	AsC_9F_8	
285	1.8	-	AsC_9F_6	
261	1.6	-	AsC_6F_6	
260	0.2	C_9F_8	-	
242	1.2	-	AsC_6F_5	
241	12.2	C_9F_7	-	
235	1.6	-	AsC_7F_4	
223	2.9	-	AsC_6F_4	
222	16.0	C_9F_6	-	
216	2.8	-	AsC_7F_3	
211	2.9	-	AsC_5F_4	
204	2.8	-	AsC_6F_3	
203	13.2	C_9F_5	-	
192	5.6	-	AsC_5F_3	
191	14.1	C_8F_5	-	
187	2.9	-	AsC_3F_4	
186	3.1	C_6F_6	-	
185	2.8	-	AsC_6F_2	
173	3.0	-	AsC_5F_2	
172	7.5	C_8F_4	-	
169	2.8	C_3F_7	-	
168	50.9	-	AsC_3F_3	
167	100.0	C_6F_5	-	

TABLE 2 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible AsC_vF_w	Other Possibility
166	4.1	-	AsC_6F	
161	3.8	-	AsC_4F_2	
154	2.8	-	AsC_5F	
153	2.8	C_8F_3	-	
149	5.7	-	AsC_3F_2	
148	27.1	C_6F_4	-	
143	0.6	C_4F_5	-	
142	9.4	-	AsC_4F	
141	8.0	C_7F_3	-	
137	3.3	-	AsC_2F_2	
136	3.0	C_5F_4	-	
134	1.6	C_8F_2	-	
130	2.8	-	AsC_3F	
129	5.1	C_6F_3	-	
123	5.0	-	AsC_4	
122	3.7	C_7F_2	-	
119	1.0	C_2F_2	-	
118	17.0	-	AsC_2F	
117	63.2	C_5F_3	-	
110	0.6	C_6F_2	-	
98	7.4	C_5F_2	-	
94	5.7	-	AsF	
93	7.3	C_3F_3	-	
87	0.7	-	AsC	
81	1.0	C_2F_3	-	
79	5.7	C_5F	-	

TABLE 2 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible AsC_vF_w	Other Possibility
75	3.3	-	As	
74	3.3	C_3F_2	-	
69	9.4	CF_3	-	
50	2.8	CF_2	-	
43	1.6	C_2F	-	
31	6.7	CF	-	

(*) One C^{13} present (used in table only where needed for clarification).

(-) Not possible.

TABLE 3. Mass spectrum of $P[C\equiv C-CF_3]_3$

m/e	Relative Intensity	Possible C_yF_z	Possible PC_vF_w	Other Possibility
311	6.7	-	-	310*
310	51.6	-	PC_9F_9	
291	1.1	-	PC_9F_8	
260	0.4	C_9F_8	PC_8F_7	
242	5.8	-	-	241*
241	45.0	C_9F_7	PC_8F_6	
223	3.5	-	-	222*
222	26.7	C_9F_6	PC_8F_5	
217	1.8	C_7F_7	PC_6F_6	
210	1.0	C_8F_6	PC_7F_5	
204	5.4	-	-	203* + imp.
203	34.7	C_9F_5	PC_8F_4	

TABLE 3 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible PC_vF_w	Other Possibility
198	0.6	C_7F_6	PC_6F_5	
192	6.6	-	-	191*
191	74.0	C_8F_5	PC_7F_4	
186	1.4	C_6F_6	PC_5F_5	
179	2.8	C_7F_5	PC_6F_4	
173	4.2	-	-	172* + imp.
172	30.0	C_8F_4	PC_7F_3	
168	8.3	-	-	167*
167	100.0	C_6F_5	PC_5F_4	
165	0.4	C_9F_3	PC_8F_2	
160	3.1	C_7F_4	PC_6F_3	
155	0.9	C_5F_5	PC_4F_4	
154	0.6	-	-	153*
153	13.1	C_8F_3	PC_7F_2	
149	3.3	-	-	148*
148	43.3	C_6F_4	PC_5F_3	
143	7.2	C_4F_5	PC_3F_4	
142	3.2	-	-	141* + imp.
141	21.7	C_7F_3	PC_6F_2	
136	3.7	C_5F_4	PC_4F_3	
134	1.6	C_8F_2	PC_7F	
131	0.3	C_3F_5	PC_2F_4	
130	0.6	-	-	
129	6.7	C_6F_3	PC_5F_2	
125	3.6	-	-	124*
124	59.6	C_4F_4	PC_3F_3	

TABLE 3 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible PC_vF_w	Other Possibility
123	0.9	-	-	122*
122	18.6	C_7F_2	PC_6F	
118	5.0	-	-	117*
117	93.3	C_5F_3	PC_4F_2	
112	0.3	C_3F_4	PC_2F_3	
111	0.3	-	-	
110	4.2	C_6F_2	PC_5F	
106	0.6	-	-	105*
105	9.5	C_4F_3	PC_3F_2	
104	8.6	-	-	103* + imp.
103	12.3	C_7F	-	
100	0.4	C_2F_4	PCF_3	
99	0.9	-	-	98*
98	24.2	C_5F_2	PC_4F	
94	1.8	-	-	93* + imp.
93	13.2	C_3F_3	PC_2F_2	
91	0.9	C_6F	-	
88	6.0	CF_4	-	
86	2.9	-	PC_3F	
81	1.2	C_2F_3	PCF_2	
80	1.2	-	-	79*
79	21.7	C_5F	PC_4	
75	3.2	-	-	74* + imp.
74	33.0	C_3F_2	PC_2F	
70	0.9	-	-	69*

TABLE 3 (continued)

m/e	Relative Intensity	Possible C_yF_z	Possible PC_vF_w	Other Possibility
69	93.3	CF_3	-	
67	3.2	C_4F	-	
62	1.4	C_2F_2	PCF	
55	10.7	C_3F	PC_2	
51	0.2	-	-	
50	8.2	CF_2	PF	
43	8.9	C_2F	PC	
31	14.2	CF	P	
19	0.6	-	F	
12	1.0	C	-	

(*) One C^{13} present. (-) Not possible. (imp.) Impurity.

fluorocarbon ionization. However, the major MC_vF_w and C_yF_z ions of the Sb and As compounds have their possible counterparts in the $P[C{\equiv}C\text{-}CF_3]_3$ spectrum. Thus the major fragmentation pathways are probably common to the three compounds.

FRAGMENTATION PATHWAYS

Figures 2, 3, and 4 show proposed fragmentation pathways for the major ion decompositions. The ion charge symbolism of Shannon [5] is used. A (+) indicates even-electron ions and (+·) indicates odd-electron ions. A two-electron shift is indicated by an arrow ↷, and a one-electron shift is indicated by a fish-hook ⇀. In the fragmentation pathways some of the ions are depicted with non-bonded electron pairs (:) as a bookkeeping aid. The fragmentations and mechanisms shown are not the only reasonable ones in some cases, and should not be considered as the ultimate refinement. It is likely that some ions are formed by several routes, but to suggest the existence of all such routes is conjecture. No metastable ions were observed; their absence indicates that the precursor ions decomposed before

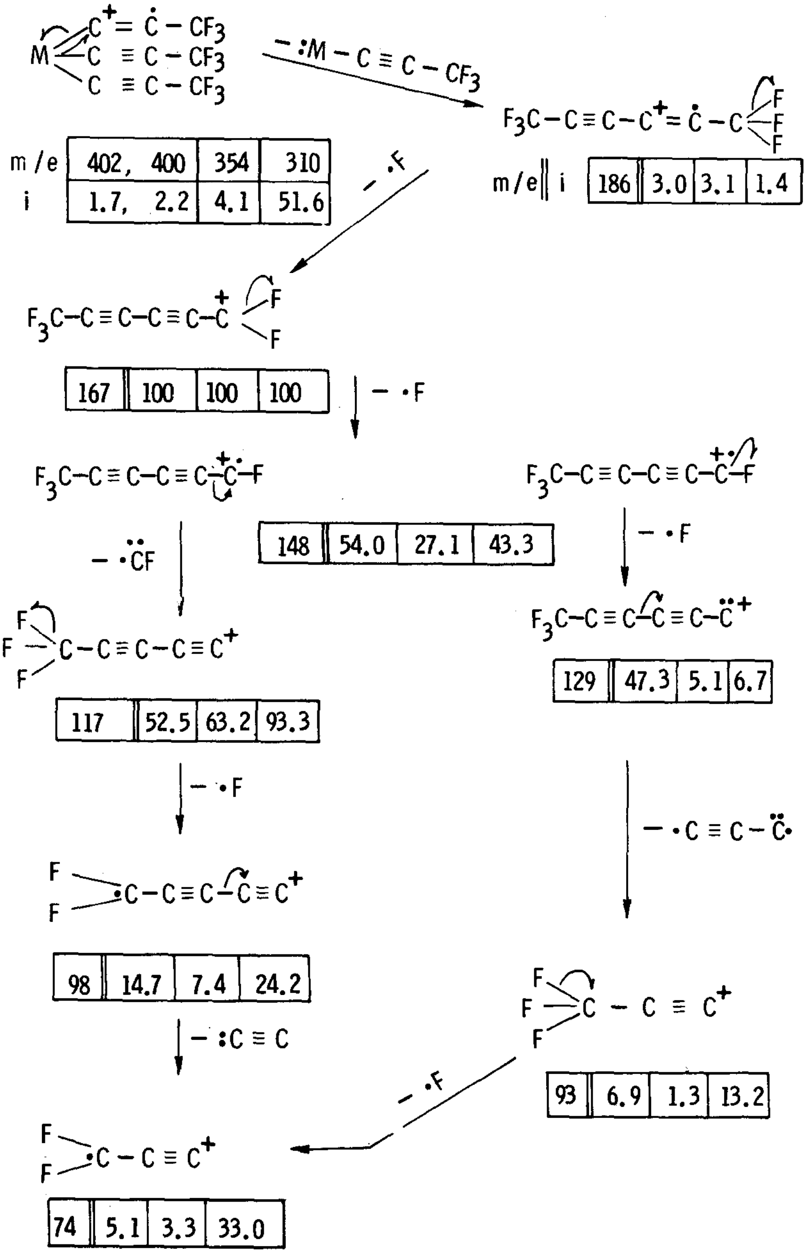


Fig. 2. Proposed fragmentation pathways.

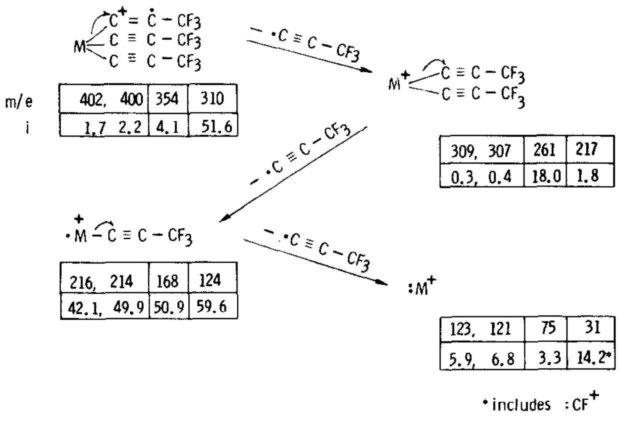


Fig. 3. Proposed fragmentation pathways.

leaving the ion source. The use of metastable ions to confirm proposed mechanisms is unfortunately not possible. Explanations for the weaker mass peaks can also be worked into fragmentation pathways, but this becomes tedious conjecture.

Relative intensities (really peak heights) are indicated in the subsequent discussion by i. The strongest peak was given i 100. Intensities will be listed in the order (Sb^{123}, Sb^{121}; As; P). As examples, the $MC_9F_9^{+\cdot}$ ion has (i 1.7, 2.2; 4.1; 51.6) and $C_9F_7^{+\cdot}$ has (i 1.7; 12.2; 45.0).

The strongest peak (base peak) of all three spectra is the $[F_3C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CF_2]^+$ rearrangement ion, m/e 167. We propose that it is formed by loss of the $M\text{-}C{\equiv}C\text{-}CF_3$ radical from the molecular ion (i 1.7, 2.2; 4.1; 51.6) to give $[F_3C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CF_3]^{+\cdot}$, m/e 186 (i 3.0; 3.1; 1.4), followed by loss of a ·F radical. Subsequent loss of another ·F radical produces $[F_3C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}CF]^{+\cdot}$, m/e 148 (i 54.0, 27.1; 43.3). Loss of a ·CF radical then yields $[F_3C\text{-}C{\equiv}C\text{-}C{\equiv}C]^+$, m/e 117 (i 52.5; 63.2; 93.3). Several other fairly strong peaks can be fitted into this chain, as seen in Figure 2.

Pant and Sacher [2] reported a m/e 186 ion (i 1.0) in their spectrum of $Si[C{\equiv}C\text{-}CF_3]_4$. The base peak was m/e 148. From their Figure 1, peaks at m/e 167 (i ∿69) and m/e 117 (i ∿90) were found.

A $[CF_3]^+$ ion is usually the overwhelmingly strong base peak in fluorocarbon spectra. This peak is observed for the $M[C{\equiv}C\text{-}CF_3]_3$ with (i 14.7; 9.4; 93.3). It occurs [2] in $Si[C{\equiv}C\text{-}CF_3]_4$ with i ∿31. The

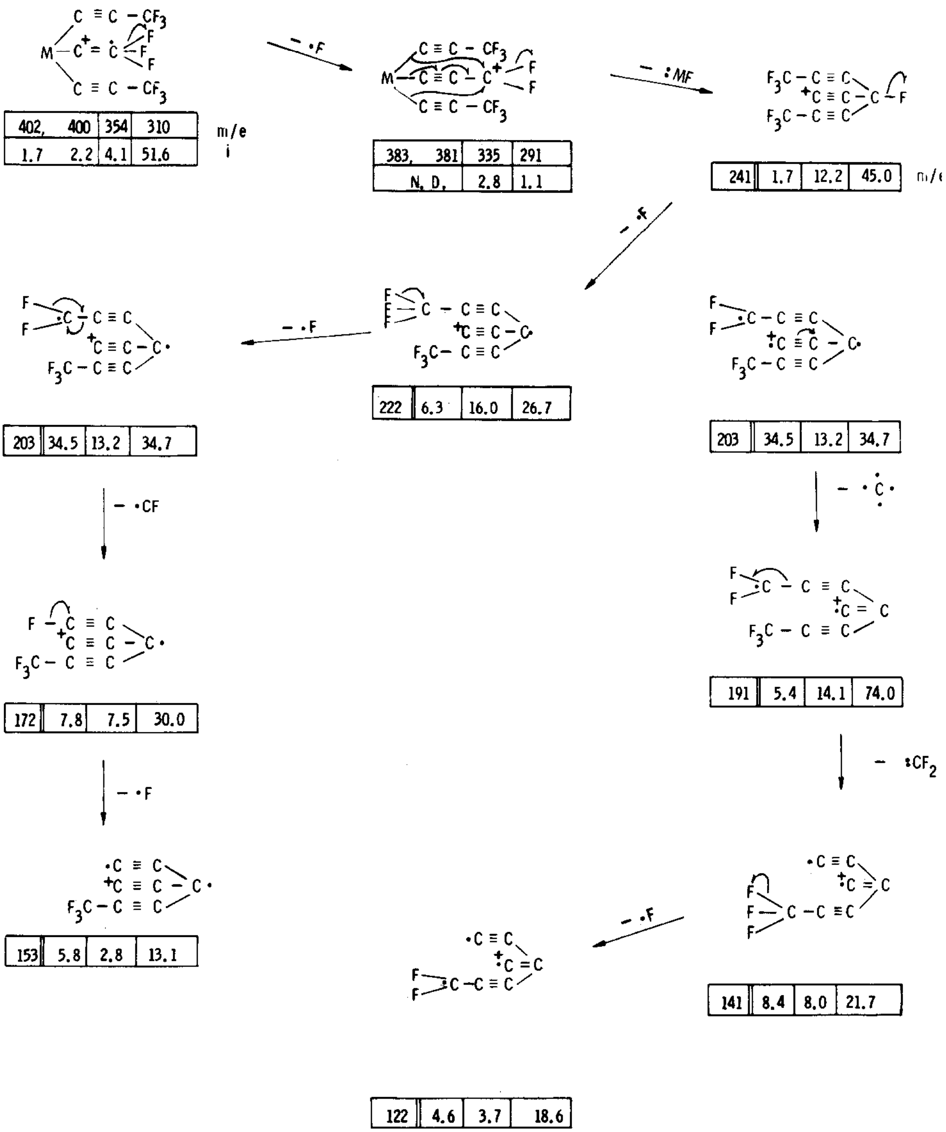


Fig. 4. Proposed fragmentation pathways.

$[CF_3]^+$ ion is undoubtedly formed from these acetylides by numerous pathways.

The $M[C{\equiv}C\text{-}CF_3]_3$ compounds apparently all lose the $\cdot C{\equiv}C\text{-}CF_3$ radical from the molecular ion to yield the $[M(C{\equiv}C\text{-}CF_3)_2]^+$ ion (i 0.3, 0.4; 18.0; 1.8). Loss of another such radical gives the strong $[M\text{-}C{\equiv}C\text{-}CF_3]^{+\cdot}$ ion (i 42.1, 49.9; 50.9; 59.6). Loss of the remaining ·C≡C-CF_3 radical to give the M^+ ion is possible for Sb^+ (i 5.9, 6.8) and As^+ (i 3.3); the appearance of P^+ is uncertain due to the coincidence with CF at m/e 31 (i 14.2) and the occurrence of a background oxygen peak at m/e 32 coincident with $C^{13}F$. Several other strong peaks can be considered for this pattern, as shown in Figure 3.

One of the most interesting rearrangement ions found was m/e 241 (i 1.7; 12.2; 45.0) for $[C_9F_7]^+$, and a possible fragmentation pathway is shown in Figure 4. To form this ion, M and 2F must be lost from the molecular ion, which involves electrons shuffling over the entire bonding framework. Strong fragmentation peaks of $[C_9F_7]^+$ are found in the spectra of all three $M[C{\equiv}C\text{-}CF_3]_3$.

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