Fluorinated Aliphatic Nitriles—Mass Spectra and Fragmentation

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The mass spectra of three fluorinated nitriles of structure CF_3CH_2CHRCN (R = H, CH_3, F) have been determined. The chief mode of fragmentation of $CF_3CH_2CH_2CN$ is cleavage at the γ-position, while in the latter two nitriles, simple β-cleavage without rearrangement is predominant. The major ion degradation paths differ from those for aliphatic hydrocarbon nitriles, depending primarily on the influence of the terminal CF_3 group and the substituent R.

INVESTIGATIONS in progress in this laboratory of the kinetics and mechanism of the free-radical gas phase addition reaction of perfluoroacetonitrile with monoölefins (*5, 7, 8*) have made available a new class of fluorinated nitriles. In particular, sufficient amounts of $CF_3CH_2CH_2CN$ (I), $CF_3CH_2CH(CH_3)CN$ (II) and CF_3CH_2CHFCN (III) have been obtained in purity suitable for study of the effect of substituents on the molecular structure and properties of nitriles. This paper reports the mass spectra of these compounds; the results are examined for the major ion degradation paths, particularly relative to the influence of a terminal CF_3 group on the fragmentation.

EXPERIMENTAL

Mass spectra were obtained with a Consolidated Electrodynamics Model 21-620 Mass Spectrometer, at an ionizing potential and current of 70 electron volts and 20 μamp., respectively. All compounds were degassed three times under high vacuum prior to use.

Materials:

I. 4,4,4-Trifluorobutyronitrile. This laboratory; >99% by preparative scale vapor phase chromatography
II. 2-Methyl-4,4,4-Trifluorobutyronitrile. This laboratory; obtained by preparative v.p.c.; F^{19} NMR showed about 10% of chromatographically inseparable isomer 3-Methyl-4,4,4,-trifluorobutyronitrile
III. 2,4,4,4-Tetrafluorobutyronitrile. This laboratory; >99% by preparative v.p.c.; analysis confirmed by H^1 and F^{19} NMR
IV. *n*-Butyronitrile. Eastman Organic Chemicals, >99% by v.p.c.
V. Isobutyronitrile. Eastman Organic Chemical, > 99% by v.p.c.

RESULTS

Mass spectra for the nitriles investigated are presented in Tables I to V, and shown as bar graphs in Figure 1. All peaks of greater than 0.5% relative intensity are tabulated. Assignments of particular (*m/e*) values are rendered ambiguous by indistinguishability of fragments of empirical formula CH_2 and N. The spectra exhibit some characteristics

Table I. Mass Spectrum of *n*-Butyronitrile

m/e	$I_{Rel.}$	$\sum_{12}$, %	Assignment
12	0.8	0.25	C^+
13	1.2	0.40	CH^+
14	2.4	0.78	CH_2^+, N^+
15	6.2	2.00	CH_3^+, NH^+
25	0.8	0.27	. . .
26	8.8	2.85	CN^+, $C_2H_2^+$
27	43.6	14.16	HCN^+, $C_2H_3^+$
28	11.3	3.66	$C_2H_4^+$
29	90.0	29.23	$CH_3CH_2^+$
30	2.2	0.70	. . .
32	0.6	0.18	. . .
32.5	1.3	0.42	. . .
37	3.2	1.05	. . .
38	4.0	1.30	CCN^+
39	9.7	3.15	$CHCN^+$
40	4.6	1.50	CH_2CN^+
41	100.0	32.47	CH_3CN^+
42	5.1	1.66	$C_3H_6^+$
51	1.5	0.50	. . .
52	2.8	0.90	. . .
53	0.6	0.18	. . .
54	1.3	0.42	$CH_2CH_2CN^+$
63	0.5	0.17	. . .
64	1.2	0.38	. . .
66	0.5	0.17	. . .
68	0.7	0.22	$C_4H_6N^+$
69	0.05	0.02	$C_4H_7N^+$
70	0.09	0.03	$C_4H_8N^+$

Table II. Mass Spectrum of Isobutyronitrile

m/e	$I_{Rel.}$	$\sum_{12}$, %	Assignment
12	0.9	0.24	C^+
13	1.1	0.28	CH^+
14	3.5	0.89	CH_2^+, N^+
15	12.8	3.28	CH_3^+, NH^+
25	1.1	0.29	. . .
26	14.9	3.83	CN^+, $C_2H_2^+$
27	26.2	6.75	HCN^+, C_2H_3
28	44.7	11.50	$C_2H_4^+$
29	24.8	6.39	$C_2H_5^+$
36	0.5	0.13	. . .
37	4.0	1.02	. . .
38	4.7	1.20	CCN^+
39	12.8	3.28	$CHCN^+$
40	6.2	1.59	CH_2CN^+
41	26.2	6.75	CH_3CN^+, $C_3H_5^+$
42	100.0	25.73	$C_3H_6^+$
43	3.4	0.88	. . .
50	0.7	0.19	. . .
51	4.3	1.11	. . .
52	8.7	2.24	. . .
53	8.7	2.24	. . .
54	25.5	6.57	CH_3CHCN^+
55	1.0	0.26	. . .
64	1.0	0.26	. . .
66	0.7	0.18	. . .
67	0.7	0.19	. . .
68	44.7	11.50	$C_4H_6N^+$
69	1.4	0.36	$C_4H_7N^+$
70	0.1	0.04	$C_4H_8N^+$

Table III. Mass Spectrum of 4,4,4-Trifluorobutyronitrile

m/e	$I_{\text{Rel.}}$	$\sum_{12}$, %	Assignment	m/e	$I_{\text{Rel.}}$	$\sum_{12}$, %	Assignment
12	4.5	0.74	C^+	55	4.6	0.75	. . .
13	3.4	0.56	CH^+	56	1.2	0.20	. . .
14	4.6	0.76	CH_2^+, N^+	57	1.4	0.23	. . .
15	2.4	0.39	CH_3^+, NH^+	58	2.5	0.41	. . .
20	1.4	0.22	. . .	59	1.0	0.16	CH_2CNF^+
24	0.9	0.15	. . .	60	0.6	0.10	. . .
25	3.7	0.60	. . .	63	1.7	0.28	. . .
26	27.0	4.43	CN^+, $C_2H_2^+$	64	9.8	1.61	$CF_2CH_2^+$
27	47.4	7.78	HCN^+, $C_2H_3^+$	65	0.7	0.12	. . .
28	78.0	12.80	$C_2H_4^+$	66	0.6	0.10	. . .
29	8.8	1.44	$C_2H_5^+$	68	1.0	0.16	. . .
31	16.4	2.69	CF^+	69	58.8	9.65	CF_3^+
32	1.5	0.24	. . .	70	1.3	0.21	. . .
33	20.4	3.35	CH_2F^+, NF^+	71	3.1	0.50	. . .
36	0.7	0.12	. . .	72	1.2	0.20	. . .
37	3.4	0.55	. . .	77	9.2	1.51	CF_2HCN^+
38	6.2	1.02	. . .	78	0.8	0.13	. . .
39	7.4	1.21	$CHCN^+$	82	0.5	0.09	. . .
40	16.2	2.66	CH_2CN^+	83	3.8	0.62	$CF_3CH_2^+$
41	19.6	3.22	CH_3CN^+	94	0.5	0.08	. . .
42	1.1	0.18	. . .	95	4.0	0.66	CF_3CN^+
43	0.7	0.11	. . .	96	2.0	0.33	$C_3H_3F_3^+$
44	3.9	0.64	. . .	97	0.6	0.10	$C_3H_4F_3^+$
45	3.7	0.60	. . .	100	0.6	0.11	. . .
46	4.0	0.65	. . .	102	4.3	0.70	$C_4F_2H_2N^+$
47	0.7	0.12	. . .	103	25.2	4.14	$C_4F_2H_3N^+$
50	5.8	0.95	CF_2^+	104	9.0	1.48	$C_4F_2H_4N^+$
51	34.2	5.61	CF_2H^+	121	0.2	0.03	. . .
52	16.0	2.63	. . .	122	18.0	2.95	$C_4F_3H_3N^+$
53	6.4	1.05	. . .	123	0.2	0.03	$C_4F_3H_4N^+$
54	100.0	16.41	$C_2H_4CN^+$				

Table IV. Mass Spectrum of 2-Methyl-4,4,4-Trifluorobutyronitrile

m/e	$I_{\text{Rel.}}$	$\sum_{12}$, %	Assignment	m/e	$I_{\text{Rel.}}$	$\sum_{12}$ %	Assignment
12	1.9	0.22	C^+	65	7.6	0.87	. . .
13	2.0	0.22	CH^+	66	5.1	0.59	. . .
14	6.1	0.70	CH_2^+, N^+	67	1.4	0.16	. . .
15	27.6	3.17	CH_3^+, NH^+	68	69.4	7.98	$C_4H_6N^+$
20	1.0	0.12	HF^+	69	46.9	5.40	CF_3^+
25	2.0	0.22	. . .	70	1.4	0.16	. . .
26	21.4	2.46	CN^+, $C_2H_2^+$	71	3.2	0.37	. . .
27	46.7	5.38	HCN^+, $C_2H_3^+$	72	3.4	0.39	. . .
28	77.6	8.92	$C_2H_4^+$	73	2.6	0.30	CH_3CHCNF^+
29	1.8	0.21	$C_2H_5^+$	74	0.5	0.06	. . .
31	9.4	1.08	CF^+	75	2.6	0.30	. . .
32	0.9	0.10	. . .	76	4.3	0.49	CF_2CN^+
33	12.6	1.46	CH_2F^+, NF^+	77	12.2	1.41	CHF_2CN^+
36	0.6	0.06	. . .	78	0.8	0.09	. . .
37	6.5	0.75	. . .	82	0.6	0.07	. . .
38	9.8	1.13	. . .	83	0.9	0.10	$CF_3CH_2^+$
39	31.8	3.66	$CHCN^+$	84	0.5	0.06	. . .
40	9.4	1.08	CH_2CN^+	88	0.5	0.06	. . .
41	97.96	11.27	$C_3H_5^+$, CH_3CN	89	2.0	0.23	. . .
42	23.3	2.68	$C_3H_6^+$	90	12.4	1.43	. . .
43	1.8	0.21	. . .	91	1.2	0.14	. . .
44	2.8	0.32	. . .	94	0.9	0.11	. . .
45	4.3	0.49	. . .	95	4.5	0.52	CF_3CN^+
46	6.1	0.70	. . .	96	0.7	0.08	. . .
47	4.8	0.55	. . .	97	1.3	0.15	. . .
49	0.5	0.06	. . .	98	1.5	0.17	. . .
50	2.2	0.26	CF_2^+	100	0.6	0.07	. . .
51	19.8	2.28	C_2HCN^+	102	15.3	1.76	. . .
52	19.6	2.25	$C_2H_2CN^+$	103	1.8	0.21	. . .
53	7.8	0.90	. . .	109	0.6	0.06	. . .
54	100.0	11.51	CH_3CHCN^+	110	4.9	0.56	$C_4H_5F_3^+$
55	4.7	0.54	. . .	111	0.4	0.05	$C_4H_6F_3^+$
56	0.6	0.07	. . .	116	2.3	0.26	. . .
57	2.2	0.25	. . .	117	10.4	1.20	$C_5H_5F_2N^+$
58	2.2	0.25	. . .	118	4.3	0.49	$C_5H_6F_2N^+$
59	3.1	0.35	CH_2CNF^+	121	0.5	0.06	. . .
60	0.7	0.08	. . .	122	2.3	0.27	$C_4H_3F_3N^+$
63	1.6	0.19	. . .	135	0.5	0.06	$C_5H_4F_3N^+$
64	47.8	5.50	$CF_2CH_2^+$	136	2.4	0.28	$C_5H_5F_3N^+$

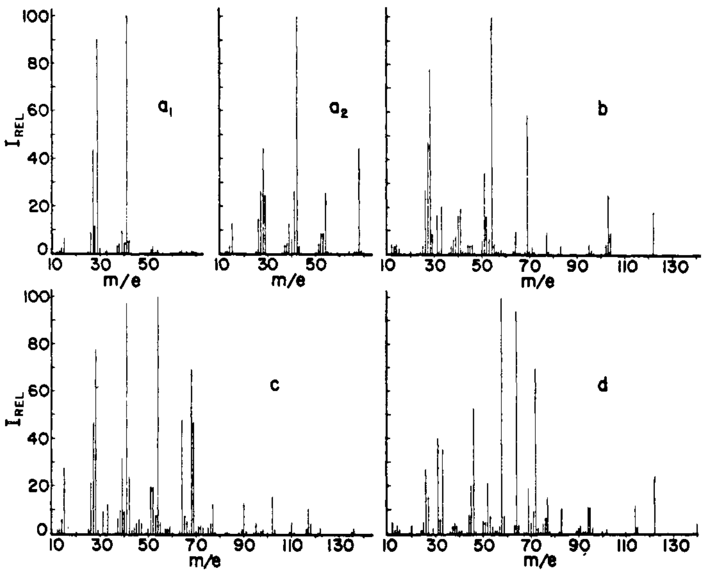


Figure 1. Mass spectra: α_1, α_2, *n*-butyronitrile and iso-butyronitrile, respectively; *b*, 4,4,4-trifluorobutyronitrile; *c*, 2-methyl-4,4,4-trifluorobutyronitrile; *d*, 2,4,4,4,-tetrafluorobutyronitrile

previously reported (*9*) for unsubstituted aliphatic nitriles. The effect of fluorine α-substitution in III is marked, causing departure from nitrile fragmentation patterns, consistent with those reported (*10*) for aliphatic monofluorides. Evidence has been found for an influence by the α-methyl substituent in II.

The mass spectra of IV and V have been redetermined to provide a basis for comparison with reported (*9*) spectra; since some differences were observed in relative peak magnitudes at the ionizing potential used in this work, these spectra are recorded.

For comparison of spectra, the relationship between a given peak intensity and the total spectrum intensity above (m/e) 12 has been calculated and tabulated as the ratio $100I_i/\sum_{i=12} I_i$, i = peak (m/e) number. While total spectrum intensity varied widely with the compounds studied, the contribution of all peaks of greater than 10% relative intensity was essentially constant, ranging from 81 to 85%. However, the number of peaks over 10% relative intensity depends directly on the degree and type of substitution, ranging from four for IV, to eighteen for II. In subsequent discussion, comparisons are based on the intensity ratio $100I_i/\sum_{i=12} I_i$.

DISCUSSION

The fragmentation patterns for this new series of nitriles were examined in light of the data for aliphatic hydrocarbon analogs.

In the spectra of I, the major ion, $(M - CF_3)^+$, confirms the ease of γ-cleavage. The high intensity of (m/e) 69, $[CF_3]^+$, indicates a competing process, possibly caused by the mesomeric effect of fluorine on carbon, as noted elsewhere (*2, 4, 11*). The high intensities of (m/e) 68 and 69 in the spectrum of II, substantiate γ-cleavage. In II, β-cleavage apparently dominates—i.e., the major peak is (m/e) 54, $[CH_3CHCN]^+$. In III, γ-cleavage first appears significant, but as in II, δ-cleavage remains the primary mode. The maximum intensity at (m/e) 58, corresponds to the elements of $[CHFCN]^+$.

In aliphatic nitriles β-cleavage likely involves rearrangement of γ-hydrogen through a six-membered transition state of the molecular ion (*1, 9*). Absence of γ-hydrogen in the CF_3-terminated nitrile precludes rearrangement via such a mechanism. The low $[F{-}N{=}C{=}CHR]^+$ intensities, compared with the analog $[H{-}N{=}C{=}CH_2]^+$ in aliphatic nitriles, is consistent with the greater C—F bond energy over that of C—H, and with the tendency of fluorine to retain both electrons in a bond cleavage. The intensity of this peak increases with R = H, CH_3, F, respectively as would be expected for hyperconjugative stabilization of the

Table V. Mass Spectrum of 2,4,4,4-Tetrafluorobutyronitrile

m/e	$I_{\text{Rel.}}$	$\sum_{12}$, %	Assignment
12	4.82	0.66	C^-
13	1.96	0.27	CH^+
14	3.36	0.46	CH_2^-, N^-
15	1.42	0.20	NH^+
19	0.62	0.08	F^-
20	3.54	0.49	HF^+
24	1.28	0.18	C_2^+
25	4.56	0.63	C_2H^-
26	27.0	3.71	CN^-, $C_2H_2^-$
27	15.4	2.12	HCN^-, $C_2H_3^+$
29	2.34	0.32	...
31	40.1	5.52	CF^+
32	6.00	0.82	CHF^+
33	35.4	4.87	CH_2F^+, NF^-
36	0.94	0.13	...
37	3.06	0.13	...
38	4.56	0.63	CCN^-, $C_3H_2^-$
39	3.24	0.45	$CHCN^+$, $C_3H_3^-$
40	1.40	0.19	CH_2CN^-
41	1.54	0.27	CH_3CN^+
43	0.58	0.12	C_2F^-
44	8.20	1.13	C_2HF^-
45	20.0	2.75	$CHFCH^+$, FCN^+
46	52.8	7.26	$CHFCH_2^+$
47	1.40	0.19	...
50	5.20	0.72	CF_2^+
51	5.00	0.69	...
52	21.0	2.89	$C_3H_2N^+$
53	7.20	0.99	CH_2CHCN^+
54	2.80	0.38	...
55	1.20	0.16	...
56	1.20	0.16	...
57	3.00	0.41	...
58	100.0	13.76	$CHFCN^+$
59	7.60	1.04	CH_2FCN^-
63	3.20	0.44	...
64	94.0	12.93	$CF_2CH_2^+$
65	3.70	0.51	...
67	0.50	0.07	...
68	0.60	0.08	...
69	19.0	2.61	CF_3^+
70	4.40	0.61	...
71	9.40	1.29	...
72	70.0	9.63	CH_2CHFCN^+
73	2.60	0.36	...
74	0.60	0.08	...
75	4.00	0.55	...
76	6.40	0.88	CF_2CN^+
77	15.0	2.06	CF_2HCN^-
78	1.00	0.14	...
82	0.84	0.12	...
83	10.6	1.46	$CF_3CH_2^+$
89	1.20	0.16	...
90	2.40	0.33	...
91	3.18	0.44	$C_3F_2H_3N^-$
92	0.60	0.08	...
93	0.78	0.11	...
94	11.2	1.54	...
95	11.1	1.51	...
96	2.40	0.33	...
100	0.90	0.12	...
102	1.80	0.24	$C_4F_2H_2N^+$
110	0.56	0.07	...
114	11.6	1.60	...
115	2.80	0.38	$C_3F_4H_2^+$
122	24.0	3.30	$C_4F_3H_3N^-$
140	3.14	0.43	$C_4F_4H_2N^+$

ion by a methyl substituent, and mesomeric stabilization when R = F—i.e.,

$$[\mathrm{F{=}\dot{N}{-}C{=}CH{-}F}]^+ \leftrightarrow [\mathrm{F{-}\dot{N}{=}C{=}CH{-}F}]^+ \leftrightarrow [\mathrm{F{-}\dot{N}{=}C{-}CH{=}F}]^+$$

The $[CF_2CH_2]^+$ intensities are consistent with the above trends.

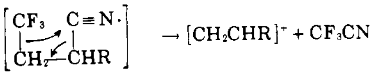
The fragment $[NF]^+$, mass peak 33, likely arises from an electron-capture process involving the F—N = C = CHR molecule. This is significant in I, II, and III, and is support for a F-migration mechanism.

Simple β-cleavage without H-transfer is reported (*9*) to be insignificant in aliphatic nitriles, even with branching at the β-carbon. These results indicate that α-substitution has a pronounced effect on the $[CHRCN]^+$ intensity. Intensities found for various β-cleavages in the present series are:

Nitrile	(*m*/*e*)	Σ_{12}, %	Assignment
$CF_3CH_2CH_2CN$ (I)	40	2.66	M-(CF_3CH_2)
$CF_3CH_2CH(CH_3)CN$ (II)	54	11.51	M-(CF_3CH_2)
	39	3.66	M-(CF_3CH_2)-(CH_3)
	122	0.27	M-(CH_3)
CF_3CH_2CHFCN (III)	58	13.76	M-(CF_3CH_2)
$CH_3CH_2CH_2CN$ (IV)	40	1.50	M-(CH_3CH_2)
$(CH_3)_2CHCN$ (V)	54	6.57	M-(CH_3)
	39	3.28	M-2(CH_3)

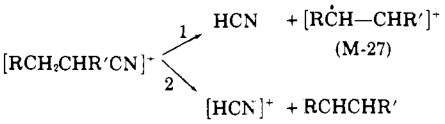
The major ions in the spectra of II and III are $[CH(CH_3)CN]^+$, 54, and $[CHFCN]^+$, 58 respectively. While β-cleavage is of secondary importance in I, IV, and V, α-substitution serves to make this the primary process. Rylander and Meyerson (*12*) report that loss of the largest alkyl group is favored at a branched carbon. This observation is substantiated in the spectra of II and V.

The relatively high $[CH_2CHR]^+$ intensities strongly support a concerted one-electron, two-electron shift for the fluorinated nitriles:



The intensities of the 95 peak, $[CF_3CN]^+$, are low. Moreover, the threefold increase in the 95 peak in III over that in I and II indicates competition between one- and two-electron shifts at the α-position. This is consistent with the high electronegativity of the α-fluoro substituent. The electronegativity of the CF_3 group is close to that of the fluorine atom (*6*). In fragmentation of aliphatic fluorides, the fragment containing the electronegative fluorine tends to retain the extra electron from bond cleavage (*3*, *10*). Thus, cleavage at the CF_3 group is expected to follow a similar course.

Formation of the (*m*/*e*) 27 and (M-27) ions can be understood by two competitive processes—i.e.,



Inspection of the intensities for these two peaks shows that, while in I, II, and IV, step 2 appears favored, in V the reverse is true. The two processes must be almost equally competitive in III.

Relative to the loss of F and HF, reference to the data (*10*) for the fluorinated alkanes is helpful. Electron impact studies have shown loss of HF to be predominant. In the present series, loss of HF from I and II is preferred over loss of F. The peak intensities are in the approximate ratio (M-HF)/(M-F) of 3 to 1. On the other hand, the relatively high intensity of (M-F) relative to zero intensity for (M-HF) in III indicates that the stability of HF is not process controlling.

Consistent with previous reports (*1*, *9*), the molecular ion and (M-1) peaks are low, the latter being more abundant. V is an exception. The high (M-1) intensity in the spectrum of V apparently arises by loss of a hydrogen atom from the molecular ion with the formation of a resonance-stabilized radical ion. An analogous process for IV demands formation of a less stable primary radical-ion; hence, the low (M-1) intensity for this nitrile. The higher (M-1) intensity in I is support for a transmitted inductive effect, even though the CF_3 is one removed from the α-carbon. The formation of the primary radical ion is thus favored, and this increases the (M-1) intensity to more than thirteen times that in IV. In III, the low (M-1) intensity can be attributed to the α-fluoro substituent. However, in II an (M-1) intensity comparable with IV is found, as would be the case if the α-methyl substituent counteracts the inductive effect.

The major ion degradation paths clearly differ in this new class of nitriles from those of aliphatic analogs. High resolution studies, and isotopic labeling, would contribute greatly to a firmer interpretation of the spectra for the new series of nitriles.

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