IR MATRIX ISOLATION SPECTRA OF SOME PERFLUORO ORGANIC FREE RADICALS

PART III.   n-C$_3$F$_7$ and iso-C$_3$F$_7$

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SUMMARY

The perfluoro radicals n-C$_3$F$_7$ and iso-C$_3$F$_7$ have been prepared by pyro-
lyzing the corresponding iodides in a platinum effusion tube at temperatures
between 450-550°C and isolated in argon matrices. By eliminating absorption
bands attributed to known fluorine compounds and applying relative absorption
band intensity correlations, several absorption bands have been assigned, some
30 to n-C$_3$F$_7$ and 29 to iso-C$_3$F$_7$, in the spectral range 2000-200 cm^{-1}. A ten-
tative vibrational assignment is presented for both species on the assumption
of C$_s$ symmetry. Some thermodynamic implications of the findings are also
discussed.

INTRODUCTION

Previous papers in this series have described the results of studies in
which the pyrolyses of perfluoro-organic iodides have been used as radical
sources for the characterization of CF$_3$O$_2$ [1] and C$_2$F$_5$ [2] via IR matrix
isolation spectroscopy. These studies have been further extended, and the
pyrolyses of n-C$_3$F$_7$I and iso-C$_3$F$_7$I have been used as sources of the corre-
sponding perfluoro-radicals for matrix IR characterization. To date, the
only structural data on these radicals have come from EPR studies [3], which
show the radical centers to be nonplanar. No IR spectral data have been
reported.

EXPERIMENTAL

The experimental arrangement used in this study has been described pre-
viously, therefore only those details pertinent to the present conditions
will be noted. The two perfluoro-propyl iodides were obtained from PCR Re-
search Chemicals, Inc.; purities were not stated. Both materials were puri-
fied before use by trap-to-trap distillation in the vacuum line. The IR
spectra of the individual compounds indicated isomeric purity, though a
small amount of C_2F_5I (less than 1%) was present in the n-C_3F_7I. Pyrolysis
temperatures of 530-455°C and 550-475°C were used for the n- and iso- com-
pounds, respectively. Matrix deposition times varied 1.5-45 hr. The iodides
were leaked into the pyrolysis tube at rates of $8 \times 10^{-7} - 5 \times 10^{-5}$ mole hr^{-1}.
Argon matrix gas flow rates varied 50-150 cm^3 NTP hr^{-1}. The perfluorocar-
bons CF_4, C_2F_4, C_2F_6, C_3F_6, cyclo-C_3F_6, C_3F_8, and n-C_6F_{14} were obtained from
PCR Research Chemicals, Inc., or from Matheson, at stated purities of 97-
99.7%. All the perfluorocarbons were subjected to vacuum line purification
procedures before use. Spectra were recorded on a Perkin Elmer IR spectro-
photometer (Model 283). Reported frequencies are accurate to 1.5 cm^{-1} in
the 2000-200 cm^{-1} region.

RESULTS

The general experimental approach sought to (1) obtain matrix spectra
of n-C_3F_7I, iso-C_3F_7I, and their possible stable pyrolysis products (the
fluorocarbons listed above); (2) obtain matrix spectra of the products from
pyrolyses of C_3F_7I; (3) identify known stable and unstable (CF_2, CF_3, and
C_2F_5) halocarbons in the resulting spectra; and (4) make relative intensity
measurements on the remaining unknown absorption bands to identify common
precursor species.

Preliminary experiments were conducted with each iodide to determine
the best temperature ranges for pyrolysis. The temperatures chosen struck
a balance between maximizing carbon-iodine bond fission and minimizing sub-
sequent radical decomposition. Iodide decomposition varied about 30-60%.
In addition to the obvious production of a new species in the n- and iso-C_3F_7I
systems, the pyrolyses of n-C_3F_7I gave fairly substantial amounts of C_2F_4,
CF_3, and CF_2 and minor amounts of C_3F_6; similarly, the pyrolyses of iso-C_3F_7I
produced fairly large amounts of C_3F_6, C_2F_4, CF_3, and CF_2 and minor amounts
of C_3F_8. In both systems, the appearance of these 'unwanted' species was
minimized by using lower temperatures.

Spectral data were recorded from 12 pyrolysis experiments for n-C_3F_7I and 11 experiments for iso-C_3F_7I. Typical spectra are shown in Figures 1 through 6. It was apparent from the spectra that the absorption bands of the parent iodide and its decomposition products overlapped frequently. This behavior, particularly severe in the n-C_3F_7I pyrolysis spectra, considerably complicated the measurement of absorption band intensities. Despite these difficulties, however, measurement of absorption band intensities was attempted, though in the pyrolyzed n-C_3F_7I spectra the overlapping with many of the absorption bands was too severe for meaningful quantitation. The measurements of absorption band intensities for the unknown absorption features obtained in the pyrolysis of iso-C_3F_7I and n-C_3F_7I are presented in Tables 1 and 2. The relative absorption band intensity ratios based on these measurements are shown in Tables 3 and 4.

TABLE 1

Intensity measurements (absorbance units) of probable iso-C_3F_7 bands

Band	a	b	c	d	e	f	g	h	i	j	k	l	m	n
Expt. Frequency (cm⁻¹)	1365	1362	1249	1242	1206	1192	1157	1152	1141	1138	986	968	874	842
17	0.096	0.090	0.121	0.136	0.156	0.039	0.134	0.106	0.007	0.029	0.137	0	0	0
22	0.411	0.391	0.458	0.564	0.597	0.167	0.519	0.396	0.027	0.111	0.533	0.0073	0.0044	0
23	I	I	I	I	I	0.678	I	I	0.215	0.454	I	0.0142	0.0118	weak
24	I	I	I	I	I	I	I	I	0.182	I	I	0.0398	0.0289	0.0066
25	0.331	0.330	0.381	0.438	0.491	0.132	0.417	0.301	0.018	0.034	0.420	0.0063	0	0
26	0.428	0.404	0.537	0.562	0.638	0.181	0.551	0.421	0.031	0.121	0.559	0.0056	0.0033	0
27	0.340	0.350	0.630	0.465	0.543	0.129	0.429	0.316	0.025	0.0367	0.433	0.0070	weak	0
28	I	I	I	I	I	I	I	I	I	I	I	0.0647	0.0537	0.0106
29	I	I	I	I	I	I	I	I	I	I	I	0.0908	0.102	0.0206
30	I	I	I	I	I	I	I	I	I	I	I	0.149	0.149	0.0306
33	-	-	-	-	-	-	-	-	-	-	I	0.239	0.265	0.061

o	p	q	r	s	t	u	v	w	x	y	z	aa	bb	cc
821	775	731	703	684	613	543	499	489	456	347	321	293	255	207
0	0	weak	0.062	0	0	0	0	0	0	0	0	0	-	-
0	0.0051	0.0080	0.239	0.0075	0.033	0.0233	-	0	0.0123	-	-	0.0056	-	-
0.0044	0.0287	0.0412	I	0.0346	0.0125	0.0782	0.0231	0.022	0.0538	0	0	0.0229	0	0
0.0095	0.0555	0.0877	I	0.0676	0.0211	0.168	0.0335	0.035	0.101	-	-	0.0363	-	-
0	0.0065	0.0075	0.188	0.0040	0.019	0.0162	0	weak	0.0101	0	0	0.0041	-	-
0	0.0051	0.0091	0.258	0.0069	0.026	0.0181	weak	weak	0.0131	0	0	0	0	0
0	0	0.0091	0.213	0.0080	weak	0.0161	0	0	0.0106	-	-	-	-	-
0.0106	0.104	0.158	I	0.143	0.0514	0.486	0.0486	0.047	0.167	0.0162	0.017	0.0540	0.056	-
0.0327	0.171	0.317	I	0.243	0.118	I	0.0870	0.082	0.286	0.0316	0.0251	0.104	0.070	0.049
0.0496	0.268	0.552	I	0.361	0.152	I	0.129	0.120	0.412	0.0409	0.0403	0.148	0.098	0.111
0.085	0.426	I	I	0.806	0.347	I	0.176	0.176	0.703	0.075	0.060	0.239	0.215	0.187

I - too intense to measure

TABLE 2

Intensity measurements (absorbance units) of probable n-C$_3$F$_7$ bands

Band	b	c	k	l	n	o	s	u	v	w	x	y	z	aa	bb	cc	dd
Frequency (cm^{-1})	1287	1285	1116	1114	1016	958	638	608	572	549	520	472	465	401	395	306	273
Expt.																	
35	0.510	0.552	0.139	0.176	0.254	0.008	0.034	0.014	weak	0.010	0.014	0	0	0	0	0	0
36	0.371	0.339	0.105	0.128	0.182	weak	0.0251	0.0070	0.0034	0.0064	0.0065	0	0	0	0	0	0
37	0.405	0.437	0.109	0.136	0.200	weak	0.0272	0.0108	0.0049	0.0097	0.0108	0	0	0	0	0	0
38	0.385	0.417	0.099	0.123	0.189	0.008	0.024	0.009	weak	weak	0.011	0	0	0	0	0	0
39	0.566	0.617	weak	0.135	0.262	0.009	0.034	0.009	0.006	0.011	0.013	0	0	0	0	0.012	0.024
40	0.098	0.112	0.025	0.029	0.044	0	weak	weak	0	0	0	0	0	0	0	0	0
41	0.179	0.190	0.050	0.056	0.076	0	weak	weak	0	weak	weak	0	0	0	0	0	0
42	0.279	0.311	0.078	0.090	0.136	0	weak	weak	weak	weak	0.009	0	0	0	0	0	0
43	0.205	0.222	-	weak	0.091	0	weak	0.005	weak	weak	weak	0	0	0	0	0	0
44	0.964	I	-	weak	0.394	0.008	0.051	0.017	0.008	0.012	0.016	0.0091	0.0117	0	0	0	0.035
45	I	I	-	weak	I	0.023	0.156	0.053	0.025	0.040	0.042	0.031	0.037	0.005	0.008	0.046	0.084
46	I	I	-	-	I	0.055	0.408	0.121	0.056	0.097	0.106	0.062	0.072	0.010	0.020	0.085	0.199

I - too intense to measure

Fig. 1. Matrix isolation spectrum of pyrolysis products of iso-C₃F₇I.
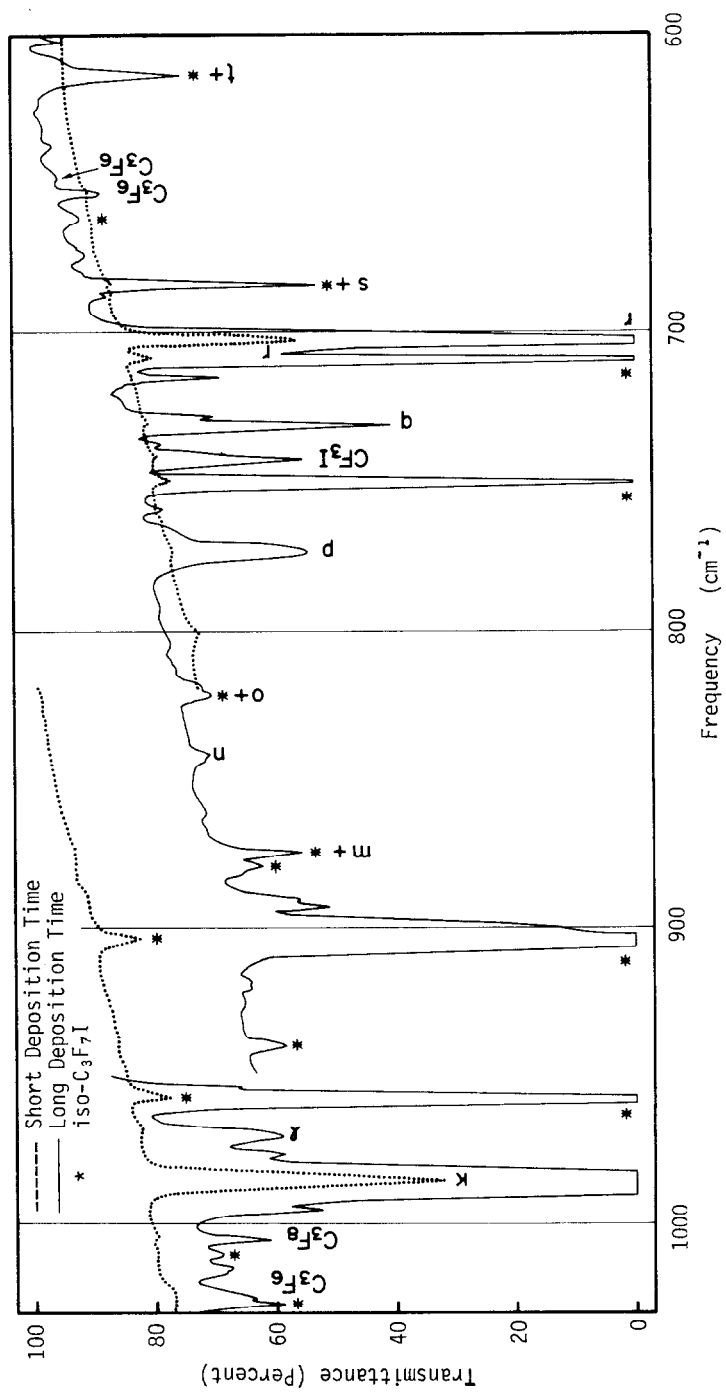
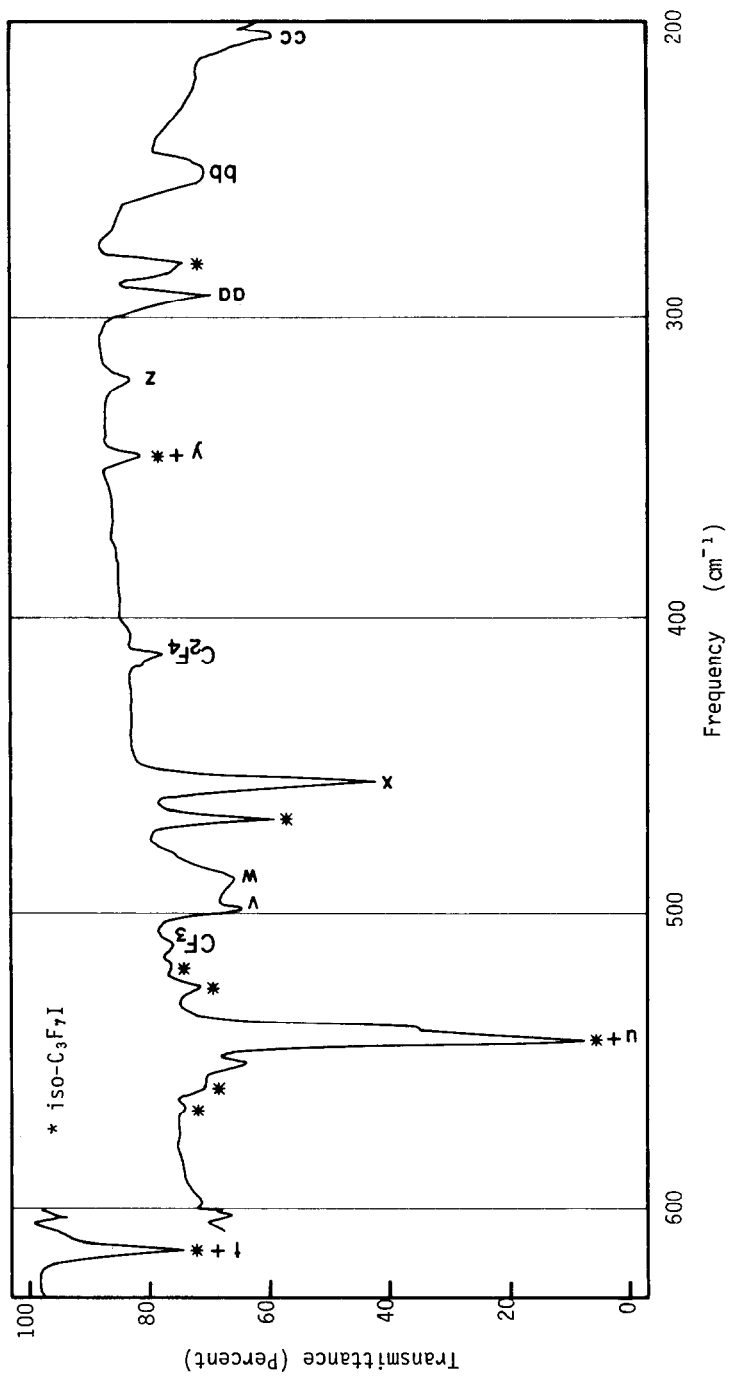Fig. 2. Matrix isolation spectrum of pyrolysis products of iso-C_3F_7I.

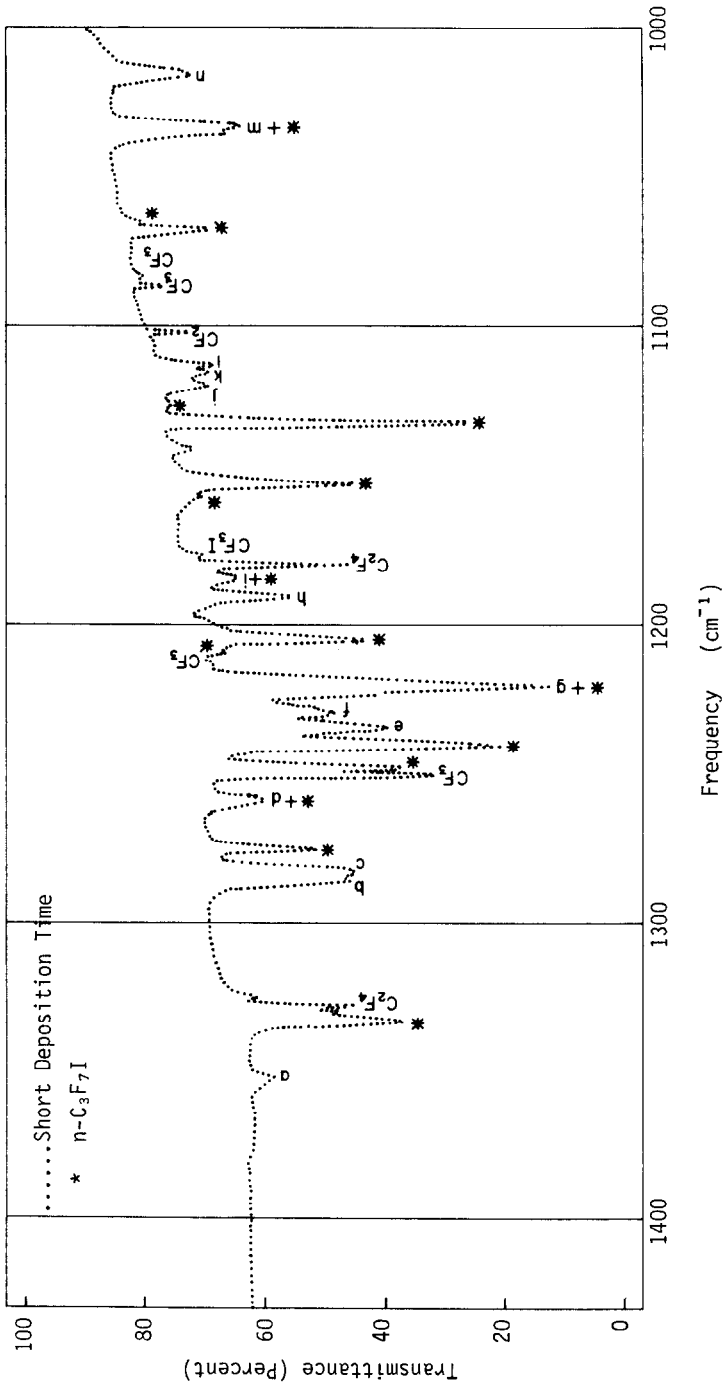Fig. 3. Matrix isolation spectrum of pyrolysis products of iso-C_3F_7I.

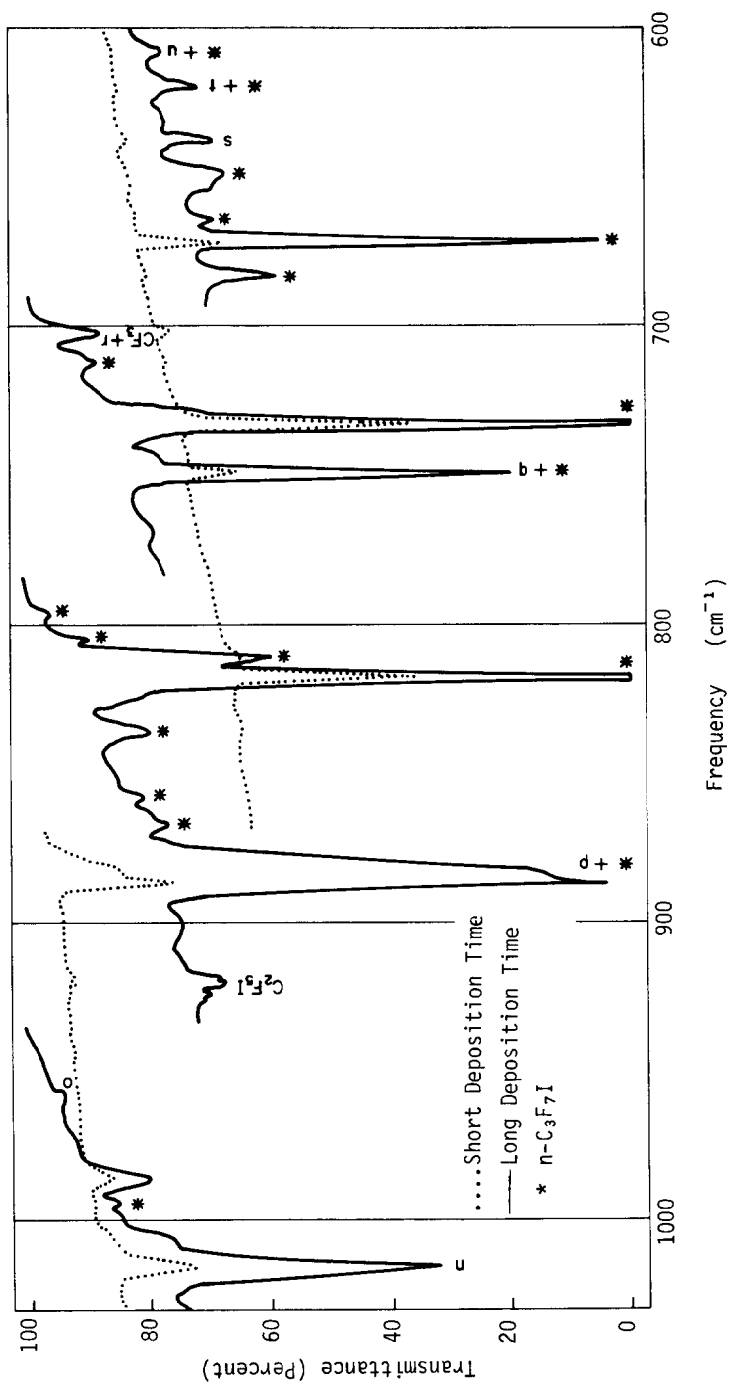Fig. 4. Matrix isolation spectrum of pyrolysis products of n-C₃F₇I.

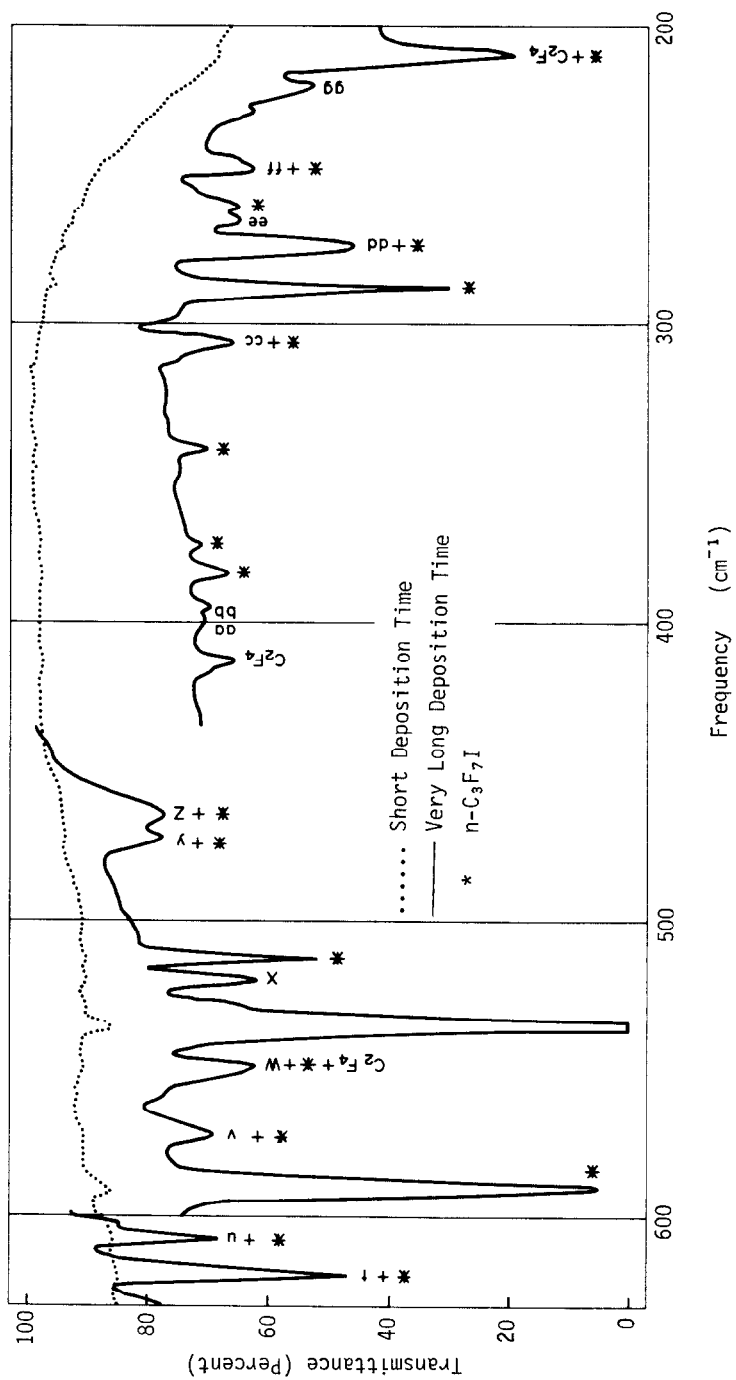Fig. 5. Matrix isolation spectrum of pyrolysis products of $n-C_3F_7I$.

Fig. 6. Matrix isolation spectrum of pyrolysis products of n-C₃F₇I.

DISCUSSION

Details of the mechanisms of the low-pressure pyrolysis of $n-C_3F_7I$ and $iso-C_3F_7I$ are not available. A recent determination [4] showed the C—I bond energy to be the same in both compounds at 206 kJ mol^{-1}, only slightly less than in CF_3I (220 kJ mol^{-1}) and C_2F_5I (212 kJ mol^{-1}). By analogy with the pyrolysis behavior of CF_3I and C_2F_5I [1,2], simple C—I bond fission appears to be the predominant primary process in the C_3F_7I compounds. This assumption is so made here. Little is known of the stability of the resulting perfluoro radicals. Kinetic data on the two reactions

$$CF_3CF_2\dot{C}F_2 \rightarrow \dot{C}F_3 + CF_2\!\!=\!\!CF_2 \quad or \quad CF_3\dot{C}F_2 + \dot{C}F_2$$
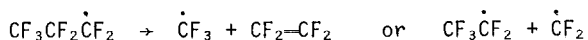
have recently been reviewed [5], indicating that both channels are of equal importance at $\simeq700$ K, with higher temperatures favoring the latter mode. Kinetic data on the decomposition of $iso-C_3F_7$ are not available.

In the present study, both CF_3 and C_2F_4 were identified as major side products in the pyrolysis of $n-C_3F_7I$; no CF_3CF_2 was formed, as the above kinetic data suggest. Although CF_2 was found, which could be taken as evidence for the second reaction, it should be noted that under these experimental conditions the pyrolysis of CF_3I always resulted in the formation of some CF_2, presumably due to partial decomposition of CF_3 [1,2]. C_3F_6 was a minor product in the pyrolysis and presumably could be formed by eliminating the fluorine atom from the radical on the effusion tube surface. The present finding that C_3F_6, C_2F_4, CF_3, and CF_2 are major side products in the pyrolysis of $iso-C_3F_7I$ suggests that both fluorine atom elimination and migration must occur readily if these products are to be accounted for. It is possible that, on pyrolysis, a concerted elimination reaction could take place in addition to simple C—I fission, with IF being eliminated and C_3F_6 formed. This type of behavior is known to occur in the pyrolysis of some alkyl halides, with hydrogen halide being eliminated [6]. However, in the present study no evidence for the formation of IF was obtained from the recorded spectra [7], ν (IF) $\simeq 604$ cm^{-1}.

In light of the above, it appears reasonable to conclude that the majority of the unknown absorption bands listed in Tables 3 and 4 may be assigned to the perfluoro n- and iso-propyl radicals. As noted in a previous paper [1], in view of the experimental difficulties, the errors in the intensity correlations given in Table 4 are consistent with the assignment of all the absorption bands to a single species, $iso-C_3F_7$. The intensity correlation data for $n-C_3F_7$ in Table 3 are not nearly so comprehensive because of the

TABLE 3

Relative intensity ratios for probable n-C_3F_7 bands

Band	Frequency (cm^{-1})	Intensity Correlation With Band at 1016 cm^{-1}	Intensity Correlation With Band at 638 cm^{-1}	Remarks
a	1354 (m)	?	?	overlapped with C_3F_7I band
b	1287 (vs)	± 7.2%	+ 9.9%	partially overlapped with band c
c	1285 (vs)	± 9.2%	+ 10.8%	partially overlapped with band b
d	1260 (m)	?	?	overlapped with C_3F_7I band
e	1236 (s)	?	?	partially overlapped with C_3F_7I band and band f
f	1231 (s)	?	?	partially overlapped with C_3F_7I band and band e
g	1222 (vs)	?	?	overlapped with C_3F_7I band
h	1191 (s)	?	?	overlapped with C_3F_7I band
i	1185 (w)	?	?	overlapped with C_3F_7I band
j	1121 (m)	?	?	overlapped with C_3F_7I band
k	1116 (s)	± 7.7%	± 1.8%	partially overlapped with bands j and l
l	1114 (s)	± 9.7%	± 10.5%	partially overlapped with band k
m	1034 (w)	?	?	overlapped with C_3F_7I band
n	1016 (m)	reference	+ 3.3%	
o	958 (vw)	± 28.7%	± 36.7%	overlapped with weak C_3F_7I band
p	888 (m)	?	?	overlapped with C_3F_7I band
q	750 (m)	?	?	overlapped with C_3F_7I band
r	703 (w)	?	?	overlapped with CF_3 band
s	638 (m)	± 3.3%	reference	
t	621 (w)	?	?	overlapped with C_3F_7I band
u	608 (vw)	+ 18.4%	+ 16.5%	
v	562 (vw)	+ 12.7%	+ 32.1%	overlapped with weak C_3F_7I band
w	549 (w)	± 23.6%	± 16.4%	overlapped with weak C_3F_7I band
x	520 (w)	+ 20.5%	± 22.8%	
y	472 (vw)	too weak to correlate	± 13.4%	overlapped with weak C_3F_7I band
z	465 (vw)	too weak to correlate	+ 16.0%	overlapped with weak C_3F_7I band
aa	401 (vvw)	too weak to correlate	± 17.4%	
bb	395 (vvw)	too weak to correlate	± 2.8%	
cc	306 (w)	± 2.3%	± 24.8%	overlapped with weak C_3F_7I band
dd	273 (w)	?	± 18.0%	overlapped with weak C_3F_7I band
ee	265 (vvw)	?	?	insufficient information for correlation test
ff	248 (vw)	?	?	insufficient information for correlation test

TABLE 4

Relative intensity ratios for probable iso-C_3F_7 bands

Band	Frequency (cm^{-1})	Intensity Correlation With Band at 986 cm^{-1}	Intensity Correlation With Band at 456 cm^{-1}	Remarks
a	1365 (s)	± 5.0%	± 1.7%	partially overlapped with band b
b	1362 (s)	± 7.6%	± 3.0%	partially overlapped with band a
c	1249 (vs)	± 18.7%	± 24.0%	partially overlapped with CF$_3$ band, iso-C$_3$F$_7$I band and band d
d	1242 (vs)	± 3.3%	± 3.0%	partially overlapped with band c
e	1206 (vs)	± 4.2%	± 2.7%	
f	1192 (m)	± 5.1%	± 5.2%	
g	1157 (vs)	± 0.9%	± 1.7%	partially overlapped with band h
h	1152 (s)	± 3.1%	± 4.4%	partially overlapped with band g
i	1141 (w)	± 11.9%	± 33.8%	partially overlapped with band j
j	1138 (m)	± 3.5%	± 5.4%	partially overlapped with band i
k	986 (vs)	reference	± 2.6%	reference band for intensity correlation
l	968 (vw)	± 22.5%	± 31.7%	
m	874 (vw)	± 23.5%	± 18.5%	overlapped with iso-C$_3$F$_7$I band
n	842 (vvw)	too weak to correlate	± 13.1%	
o	821 (vvw)	too weak to correlate	± 23.7%	overlapped with iso-C$_3$F$_7$I band
p	775 (w)	± 26.5%	± 17.3%	
q	731 (w)	± 14.1%	± 24.9%	overlapped with iso-C$_3$F$_7$I band
r	703 (m)	± 3.9%	± 3.2%	
s	684 (w)	± 27.3%	± 28.9%	overlapped with iso-C$_3$F$_7$I band
t	613 (vw)	± 16.5%	large	overlapped with iso-C$_3$F$_7$I band
u	543 (w)	± 10.9%	± 29.8%	overlapped with iso-C$_3$F$_7$I band
v	499 (vw)	too weak	± 19.1%	
w	489 (vw)	too weak	± 18.6%	
x	456 (w)	± 2.6%	reference	reference band for intensity correlation
y	347 (vvw)	too weak	± 6.0%	overlapped with iso-C$_3$F$_7$I band
z	321 (vvw)	too weak	± 8.6%	
aa	293 (vw)	± 5.2%	± 12.7%	
bb	255 (vw)	too weak	± 17.9%	
cc	207 (vw)	too weak	± 6.7%	

problems with absorption band overlapping. Where values were calculated, however, the agreement is acceptable.

Tentative frequency assignments for n-C_3F_7 and iso-C_3F_7 are presented in Tables 5 and 6 using the frequencies listed in Tables 3 and 4, respectively. In making these frequency assignments, comparable vibrational assignments for C_3F_8 [8,9] and C_3F_7I [8,10] were used as models. Both n- and iso-C_3F_7 radicals could exist with either C_1 or C_S symmetry. In the C_S configuration, two rotational conformers are possible for both radicals. In the C_1 configuration for n-C_3F_7 only, two rotational conformers are possible. Obviously the present data do not permit resolution of any of these possibilities. In all cases, a total of 24 IR active frequencies would be expected. Two torsional modes and C-C-C skeletal bend [9] for both radicals almost certainly lie above 50 μ, the long wavelength limit of the present study leaving a total of 21 frequencies which potentially could be observed. C_S symmetry was arbitrarily assumed for the purpose of making the assignments given in Tables 5 and 6. For the iso-radical, frequencies of similar vibrational modes in C_3F_8 [9] are presented for comparison.

For both radical species it was necessary to assume that some of the high-frequency C–F stretching mode absorption bands in the 1100-1400 cm^{-1} region occurred as doublets. Only seven frequencies in this region are expected, yet for both radicals, ten maxima were identified. The appearance of some of these bands as doublets could be due to matrix site effects or could be a manifestation of the existence of two different structural forms, C_S or C_1 or their rotational conformers. In either case it would be reasonable to expect that some of the lower frequency modes might also occur as doublets; although not specifically indicated in Tables 1 and 3, some indeed did. Thus, in the iso-C_3F_7 spectrum the bands labelled p and bb are quite broad, possibly indicating the presence of closely lying doublets, whilst the band g appears to have a doublet structure.

Only one CF_3 stretching frequency above 1300 cm^{-1} occurs in CF_3CF_2 [2], suggesting that a similar situation in n-C_3F_7 is not unreasonable. The situation for iso-C_3F_7 is not so clear-cut. In C_3F_8 [9], three CF_3 stretching vibrations over 1300 cm^{-1} were assigned, whilst in CF_3COCF_3 [8], only one. In the assignment presented in Table 6 for iso-C_3F_7, a probable doublet at 1365-1362 cm^{-1} is the only frequency greater than 1300 cm^{-1} assigned to a CF_3 stretching mode. It is entirely possible that the doublet is in reality two distinct frequencies assignable to two different CF_3 stretching modes, perhaps ν_1 and ν_{16}, and that ν_2 appears as a doublet at 1242-1249 cm^{-1}.

TABLE 5

Tentative frequency assignment for n-C_3F_7 of C_s symmetry

α' Modes	Observed Frequency (cm^{-1})	Approximate Mode Description
ν_1	1354	ν_s CF$_3$
ν_2	1287-1285	ν_{as} CF$_3$
ν_3	1236-1231	ν_s CF$_2$
ν_4	1222	ν_{as} CF$_2$
ν_5	1016	ν_{as} CC$_2$
ν_6	750	δ_s CF$_3$
ν_7	683	δ_{as} CF$_3$
ν_8	608	δ CF$_2$
ν_9	548	δ CF$_2$
ν_{10}	520	δ CF$_2$
ν_{11}	465	δ CF$_2$
ν_{12}	273	δ CF$_2$
ν_{13}	306	ν_s CC$_2$
ν_{14}	220	ρ CF$_3$
ν_{15}	--	δ CC$_2$
α'' Modes		
ν_{15}	1260	ν_{as} CF$_3$
ν_{16}	1191	ν_{as} CF$_3$
ν_{17}	1116-1114	ν_{as} CF$_2$
ν_{18}	703	ν_{as} CF$_2$
ν_{19}	621	ν_{as} CF$_3$
ν_{20}	472	ρ CF$_2$
ν_{21}	248	ρ CF$_2$
ν_{22}	--	ρ CF$_3$
ν_{23}	--	torsion
ν_{24}	--	torsion

ν_s = Symmetric stretching ν_{as} = Asymmetric stretching
ν_s = Symmetric deformation δ_{as} = Asymmetric deformation
ν = Stretching ρ = rocking δ = bending

TABLE 6

Tentative frequency assignment for iso-C_3F_7 of C_s symmetry

	Observed Frequency (cm^{-1})	Approximate Mode Description	
α' Modes			
ν_1	1365-1362	ν_s CF$_3$	1370[a]
ν_2	1242	ν_s CF$_3$	1350
ν_3	1192	ν_{as} CF$_3$	1262
ν_4	1157-1152	ν_{as} CF$_3$	1210
ν_5	1141-1138	ν_s CF	
ν_6	986	ν_{as} CC$_2$	1007
ν_7	775	δ_s CF$_3$	781
ν_8	731	δ_s CF$_3$	731
ν_9	703	δ CCF	337
ν_{10}	499	δ_{as} CF$_3$	548
ν_{11}	489	δ_{as} CF$_3$	507
ν_{12}	347	ρ CF$_3$	383
ν_{13}	321	ν_s CC$_2$	318
ν_{14}	293	ρ CF$_3$	278
ν_{15}	--	δ CC$_2$	151
α'' Modes			
ν_{16}	1249	ν_{as} CF$_3$	1370
ν_{17}	1206	ν_{as} CF$_3$	1268
ν_{18}	684	δ_{as} CF$_3$	618
ν_{19}	543	δ_{as} CF$_3$	537
ν_{20}	456	ρ CF$_3$	461
ν_{21}	255	ρ CF$_3$	276
ν_{22}	207	δ CCF	219
ν_{23}	--	torsion	--
ν_{24}	--	torsion	--

ν_s = Symmetric stretching ν_{as} = Asymmetric stretching
δ_s = Symmetric deformation δ_{as} = asymmetric deformation
ν = stretching ρ = rocking δ = bending

[a] Analogous frequencies of $CF_3CF_2CF_3$.

The asymmetric carbon skeletal stretching mode is expected with moderate intensity at about 1000 cm^{-1} [8,9]. Bands at 986 and 1016 cm^{-1} appearing in Figures 2 and 4 are thus assigned to carbon skeletal stretching modes in iso-C_3F_7 and n-C_3F_7, respectively. Assignment of the remaining absorption bands to the various bending deformation and rocking modes for both radicals is at best somewhat arbitrary, though reasonable by comparison with other assignments in similar molecules. Obviously, not all the frequencies listed in Tables 3 and 4 have been used in the present vibrational assignments for each of the radicals. The 'excess' frequencies can be accounted for in terms of combination, difference, or overtone modes, but the possibility that some of these frequencies could be assigned more properly to different con- formers of the radicals cannot be eliminated.

In the present study the spectral region below 200 cm^{-1} was not examined and hence two expected torsional modes and a carbon skeletal bend for each radical in this region were not observed. In C_3F_8 the magnitude of torsional modes is also not known. Excluding torsional modes, the vibrational assign- ments now available for the fluorine radicals CF_2 [11], CF_3 [12], C_2F_5 [2], n-C_3F_7, and iso-C_3F_7 strongly suggest that the magnitudes of the radical vibration frequencies could be estimated [4] without serious error from the values of those occurring in analogous saturated compounds. EPR studies on perfluoro radicals indicate that the tetrahedral geometry of the carbon atom at the radical center is maintained. These two findings suggest that fairly good confidence can be placed in thermodynamic data, $S°$, and $C°$ estimated[13] for the perfluoro alkane radicals based on structural and energy level data [4] derived from saturated analogues. Two areas of uncertainty remain in such estimations for the larger radicals: (1) Are the torsional modes much more different in the perfluoro radicals than in the saturated compounds? (2) Do the radicals exist in more than one structural form?

By extending the present matrix method to longer wavelengths, the tor- sional modes could be observed, but it appears unlikely that differentiation of structural conformers could be achieved.

REFERENCES

1 R. Butler and A. Snelson, paper submitted for publication in J. Phys. Chem., 1979.

2 R. Butler and A. Snelson, paper submitted for publication in J. Fluorine Chem., 1979.

3 K.S. Chen, P.J. Krusic, P. Meakin, and J.K. Kochi, J. Phys. Chem., <u>78</u> (1974), 2014.

4 E.N. Okafo and E. Whittle, Int. J. Chem. Kinetics, <u>7</u> (1975), 287.

5 A.S. Rogers, in J.W. Root (Editor), A.C.S. Symposium Series No. 66, 1978, p. 296.

6 S.W. Benson, Thermochemical Kinetics, John Wiley and Sons, Inc., New York, 1968.

7 W.H. Evans, T.R. Munson, and D.D. Wagman, J. Res. Natl. Bur. Stands., <u>55</u> (1955), 147.

8 E.L. Pace, A.C. Plaush, and H.V. Samuelson, Spectrochim. Acta, <u>22</u> (1966), 993.

9 H. Burger and G. Pawelke, Spectrochim. Acta, <u>35A</u> (1979), 525.

10 C.V. Barney, Spectrochim. Acta, <u>21</u> (1965), 1809.

11 D.E. Milligan, D.E. Mann, M.E. Jacox, and R.A. Mitsch, J. Chem. Phys., <u>41</u> (1964), 1199 and <u>48</u> (1968), 2265.

12 D.E. Milligan, M.E. Jacox, and J.J. Comeford, J. Chem. Phys., <u>44</u> (1966), 4058.

13 H.E. O'Neal and S.W. Benson, in J. Kochi (Editor), Free Radicals, John Wiley and Sons, New York, 1973, p. 275.