

## Short Communication

### The chemistry of trifluorovinylsulfur pentafluoride.

#### Preparation and characterization of 1-iodotetrafluoroethylsulfur pentafluoride

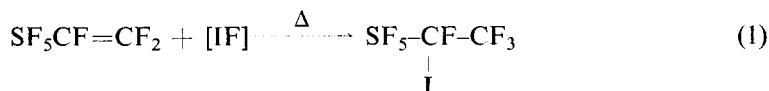
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Roberts *et al.*<sup>1</sup> reported the preparation of  $\text{SF}_5\text{CF}=\text{CF}_2$  via the dehydrohalogenation of 2-chloro-1,2,2-trifluoroethylsulfur pentafluoride. The olefin is a clear colorless liquid with a b.p. (extrapolated) of  $19^\circ$  and a normal Trouton constant of 20.5<sup>1</sup>. Other than the photochemical reaction of  $\text{SF}_5\text{CF}=\text{CF}_2$  with  $\text{Cl}_2$  to yield  $\text{SF}_5\text{CFClCF}_2\text{Cl}^1$ , its reaction with tetrafluoroethylene to yield a co-polymer<sup>2</sup> and its reaction with  $\text{CF}_3\text{COCF}_3$ <sup>3</sup>, no other work has appeared.

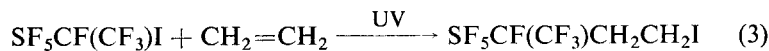
It has now been found that under proper conditions iodine monofluoride adds across the double bond in  $\text{SF}_5\text{CF}=\text{CF}_2$  according to the following equation:



Although iodine monofluoride has not been isolated, it is believed to be formed *in situ* from a mixture of iodine and iodine pentafluoride according to the equation<sup>4</sup>:



1-Iodotetrafluoroethylsulfur pentafluoride is a white solid at  $-78^\circ$  and a colorless liquid at room temperature having a pungent and irritating odor. Under ultraviolet irradiation the iodide will add across the  $\pi$ -bond in ethylene giving:



The iodide is a white solid at  $-78^\circ$  and a colorless liquid at room temperature.

The two new iodides have been characterized *via* their infrared spectra, ultraviolet spectra, NMR spectra and mass spectra.

The infrared spectra are tabulated in Table 1. Both iodides show the strong C-F symmetric and asymmetric stretching bands at  $1100\text{--}1280\text{ cm}^{-1}$ , and the  $\text{CF}_3$  deformation band<sup>5</sup> (sym)  $795\text{--}730\text{ cm}^{-1}$ .

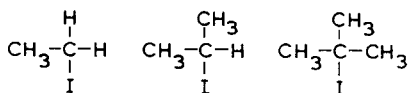
TABLE 1

INFRARED SPECTRA OF SF<sub>5</sub> IODIDES (cm<sup>-1</sup>)

SF <sub>5</sub> CF(CF <sub>3</sub> )I	SF <sub>5</sub> CF(CF <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> I
1252 (s)	1449 (w); 962 (w)
1233 (vs)	1274 (s); 935 (w)
1205 (s)	1220 (s); 870 (vs)
1112 (m)	1183 (s); 833 (s)
926 (m)	1163 (m); 820 (s)
889 (vs)	1143 (m); 752 (w)
793 (vs)	1064 (w); 746 (w)
714 (m)	1020 (w); 725 (w)
678 (w)	1000 (w); 671 (w)

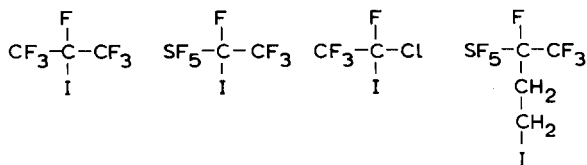
The assignments of S-F vibrations in many SF<sub>5</sub> compounds<sup>6-11</sup> make it possible to assign similar absorptions in the iodides. The intense bands found for SF<sub>5</sub>CF(CF<sub>3</sub>)I at 926 and 889 cm<sup>-1</sup> are assigned, respectively, to the planar SF<sub>4</sub> stretching vibration and the axial S-F stretching vibration. The very intense broad band centered 870 cm<sup>-1</sup> in SF<sub>5</sub>CF(CF<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>I is assigned the S-F stretching vibrations. Haszeldine<sup>12</sup> has assigned the carbon-iodine stretching frequency for perfluorinated iodides in the range 740-690 cm<sup>-1</sup>. Thus, for SF<sub>5</sub>CF(CF<sub>3</sub>)I the C-I stretching is probably the 714 cm<sup>-1</sup> absorption.

Kimura and Nagakura<sup>13</sup> found in the ultraviolet spectra of organic iodides a red shift in the longest wavelength band caused by alkyl substitution. They attributed this shift to the lower electronegativity of the alkyl substituent. If an alkyl group is replaced by another substituent with lower electronegativity, an electron transfer due to an inductive effect will increase the electron density around the iodine atom causing greater repulsion and thus raising the energy of the lone-pair orbital. If it is further assumed that the excited states of these bands remain unaltered by various alkyl substituents, then the relationship between the electronegativity of the substituent group and the wavenumber of iodide absorption is found (as the wavenumber decreases so does the electronegativity). The following (methyl replacement of H) further illustrates this relationship:



Wavenumber (cm<sup>-1</sup>)      38,730      38,095      37,202

It is rather interesting to compare the above iodides with the following fluorinated ones:



Wavenumber (cm<sup>-1</sup>)      36,232<sup>3</sup>      35,336      35,461<sup>3</sup>      38,168

It can no longer be assumed in the fluorinated hydrocarbon iodides that the excited states are unaffected. Due to the large inductive effect of the perfluoroalkyl substituent the excited state (in particular  $\sigma^*$ ) is lowered in energy, causing a red shift from hydrocarbon iodides. The (CF<sub>3</sub>)<sub>2</sub>CF group is more electronegative than the SF<sub>5</sub>C(CF<sub>3</sub>)F group and this is reflected in a greater blue shift of the former. Of particular interest is the almost exact absorption value for the SF<sub>5</sub>C(CF<sub>3</sub>)F and ClC(CF<sub>3</sub>)F iodides. This would strongly suggest a very similar electronegative value for SF<sub>5</sub> and chlorine. It is also found that the further the perfluoro group is removed from the carbon-iodine bond (separated by methylene groups) the more the absorption spectrum resembles the corresponding hydrocarbon iodide [*i.e.* in SF<sub>5</sub>C(CH<sub>2</sub>CH<sub>2</sub>I)FCF<sub>3</sub>].

In reaction (1) the formation of large amounts of CF<sub>3</sub>CF<sub>2</sub>I accounts for the low yield of SF<sub>5</sub>CF(CF<sub>3</sub>)I. Its formation could result directly from the [IF] reaction:



or possibly from the decomposition of SF<sub>5</sub>CF=CF<sub>2</sub> and/or SF<sub>5</sub>CF(CF<sub>3</sub>)I in the presence of electrophilic reagents such as I<sup>+</sup> or AlCl<sub>3</sub>. It has been reported that compounds containing SF<sub>5</sub> groups are unstable in the presence of electrophilic reagents<sup>14,15</sup>.

We have found, qualitatively, that SF<sub>5</sub>CF=CF<sub>2</sub> and AlCl<sub>3</sub> react in a sealed Pyrex glass ampoule with prolonged heating at 100–125°. Very little SF<sub>5</sub>CF=CF<sub>2</sub> was recovered, while products such as S<sub>2</sub>Cl<sub>2</sub>, Cl<sub>2</sub>, C<sub>2</sub>F<sub>6</sub> and SF<sub>4</sub> were found to be present. This substantiates that SF<sub>5</sub>CF=CF<sub>2</sub> is attacked by electrophilic reagents and probably is partly responsible for the low yields of SF<sub>5</sub>CF(I)CF<sub>3</sub>\*.

#### EXPERIMENTAL

SF<sub>5</sub>CF=CF<sub>2</sub> was prepared by the method of Case, Ray and Roberts<sup>1</sup>. The IF<sub>5</sub> and CH<sub>2</sub>=CH<sub>2</sub> were used as received and the aluminum was of high purity (greater than 99.99%). The infrared spectra of the chemicals were taken where possible and they agreed with the published spectra.

\* *Special Note:* In preparing SF<sub>5</sub>CF(I)CF<sub>3</sub> it was found that if the reaction temperature was quickly raised from room temperature to 110° over 3 h period an explosive exothermic reaction occurred. It is important, therefore, that the reaction temperature be carefully controlled in order to avoid a runaway decomposition reaction.

The IR spectra were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. The IR cell was made of Monel metal and equipped with a Monel valve. The path length of the cell was 5.0 cm.

Gas chromatographic separations were carried out with either a di-n-butylmaleate column or a fluorolube column. An Aerograph Autoprep (Model A-700) was used.

The ultraviolet spectra were recorded using a Cary Model 14 recording spectrophotometer. The liquid spectra were taken with a cell having a path length of 1.00 cm.

The NMR spectra were recorded with a Varian A-56-60 spectrometer with TMS ( $^1\text{H}$ ) or  $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ) as internal standards. The mass spectrum was taken on a spectrometer from Consolidated Electrodynamics Corp., Model 21-103 (modified) at an ionizing current of  $52.5 \mu\text{A}$  and an inlet system (stainless steel) temperature of  $150^\circ$ .

#### *Preparation of $\text{SF}_5\text{CF}(\text{I})\text{CF}_3$*

To a 300 ml nickel pressure vessel, 0.099 mole of iodine,  $1.23 \times 10^{-3}$  mole of aluminum triiodide, and  $1.9 \times 10^{-2}$  mole of pure aluminum turnings were added. The vessel was cooled to  $-78^\circ$ , evacuated and 0.045 mole of iodine pentafluoride was added. The mixture was heated at  $140-150^\circ$  for about 3 h. The vessel was cooled at  $-78^\circ$ , 0.178 mole of  $\text{SF}_5\text{CF}=\text{CF}_2$  was added, and nitrogen was then added until the pressure was 30 psi. The vessel was heated with shaking at  $50^\circ$  for 18 h,  $70^\circ$  for 26 h,  $90-95^\circ$  for 41 h and at  $100^\circ$  for 19.5 h. The volatile products at  $-78^\circ$  were separated on a fluorolube column. The major products were identified as  $\text{CF}_3\text{CF}_2\text{I}$  (60%),  $\text{SF}_4 + \text{SOF}_2$  (23%),  $\text{SF}_5\text{CF}=\text{CF}_2 + ?$  (10%). The non-volatile products were distilled through an all-glass distillation set-up when  $3.9 \times 10^{-2}$  mole of product (nc) was produced (yield 21.9%): b.p.  $80-82^\circ$  (759.7 mmHg);  $\lambda_{\text{max}}$ . (iso-octane) 283  $\text{m}\mu$ .  $^{19}\text{F}$  NMR band centers (in ppm) F,  $-65.5$ ;  $\text{SF}_4$ ,  $-49.8$ ; CF,  $+96.8$ ;  $\text{CF}_3$ ,  $+83.1$ . Calcd. for  $\text{C}_2\text{F}_9\text{SI}$ : C, 6.78; F, 48.31; S, 9.07; I, 35.85%; mol. wt., 354. Found: C, 6.9; F, 47.1; S, 8.7; I, 32%; mol. wt., 352.

#### *Preparation of $\text{SF}_5\text{CF}(\text{CF}_3)\text{CH}_2\text{CH}_2\text{I}$*

0.28 g of mercury was added to an approximate 5 l static Pyrex glass reactor equipped with a quartz finger. The vessel was evacuated and  $6.8 \times 10^{-3}$  mole of  $\text{SF}_5\text{CF}(\text{CF}_3)\text{I}$  and excess  $\text{H}_2\text{C}=\text{CH}_2$  was added. The mixture was irradiated for 3 h with a 450 W Hanovia lamp surrounded by a Pyrex glass filter. Distillation of the mixture gave  $4.3 \times 10^{-3}$  mole of product (nc) (63% yield): b.p.  $98^\circ$  (164 mmHg);  $\lambda_{\text{max}}$ . (iso-octane) 262  $\text{m}\mu$ .  $^{19}\text{F}$  NMR band centers (in ppm) F,  $-73.3$  and  $-66.5$ ;  $\text{SF}_4$ ,  $-51.3$  and  $-48.8$ ; CF,  $+140.3$ ;  $\text{CF}_3$ ,  $+75.1$ .  $^1\text{H}$  NMR spectroscopy showed the existence of a complex band at 3 ppm. Calcd. for  $\text{C}_4\text{H}_4\text{F}_9\text{SI}$ : C, 12.57; H, 1.05%. Found: C, 12.78; H, 1.10%.

TABLE 2

MASS SPECTRA OF SF<sub>5</sub>CF(CF<sub>3</sub>)I

<i>m/e</i>	Abundance*	Species
69	m-s	CF <sub>3</sub> <sup>+</sup>
70	w-m	SF <sub>2</sub> <sup>+</sup>
89	m-s	SF <sub>3</sub> <sup>+</sup>
100	m-s	CF <sub>3</sub> CF <sup>+</sup>
119	m	C <sub>2</sub> F <sub>5</sub> <sup>+</sup>
127	s	SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup>
158	w-m	CFI <sup>+</sup>
208	w-m	C <sub>2</sub> F <sub>3</sub> I <sup>+</sup>
227	vs	CF <sub>3</sub> CFI <sup>+</sup>
354	s	SF <sub>5</sub> CF(CF <sub>3</sub> )I <sup>+</sup> (molecule-ion)

\* w = weak, m = medium, s = strong, vs = very strong

TABLE 3

MASS SPECTRA OF SF<sub>5</sub>CF(CF<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>I

<i>m/e</i>	Abundance*	Species
39	w-m	C <sub>3</sub> H <sub>3</sub> <sup>+</sup>
40	vw	C <sub>3</sub> H <sub>4</sub> <sup>+</sup>
51	m	SF <sup>+</sup>
59	m	CFCH <sub>2</sub> CH <sub>2</sub> <sup>+</sup>
65	s	CF <sub>2</sub> CH <sub>3</sub> <sup>+</sup>
69	w-m	CF <sub>3</sub> <sup>+</sup>
70	w	SF <sub>2</sub> <sup>+</sup>
77	vs	C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup>
89	s	SF <sub>3</sub> <sup>+</sup>
100	vs	CF(CF <sub>3</sub> ) <sup>+</sup>
127	vs	SF <sub>5</sub> <sup>+</sup> , I <sup>+</sup>
141	s	CH <sub>2</sub> I <sup>+</sup>
155	vw	CH <sub>2</sub> CH <sub>2</sub> I <sup>+</sup>
255	w	C(CF <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> I <sup>+</sup>
382	vs	SF <sub>5</sub> CF(CF <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> I <sup>+</sup> (molecule-ion)

\* w = weak, m = medium, s = strong, vs = very strong

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