

disagrees with a mass spectrometric estimate<sup>8</sup> of the relative bond strengths of OF and OF<sub>2</sub>, it agrees in general with two other theoretical estimates.<sup>9,10</sup> It also agrees in principal with the comparison made by Porter<sup>3a</sup> between Cl<sub>2</sub>O and the ClO radical in which he points out "the influence of the odd electron in strengthening the bond." In the case of the Cl-O bond energy, the increase is 16 kcal./mole over the average Cl-O bond energy in Cl<sub>2</sub>O. In view of this and the relative position of the OF radical absorption, it appears not too

unlikely that the OF radical bond energy will be close to Glockler's first estimate<sup>9</sup> of about 56 kcal./mole. It would seem then that the inability to find the OF radical in past gas phase work may be related to extreme chemical reactivity rather than to instability.

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## Sulfur-Nitrogen and Oxygen-Nitrogen Bond Dissociation Energies of Some N-Fluorinated Amines

Grover S. Paulett and Max Lustig

*Contribution from the Gorgas Laboratory, Rohm and Haas Company, Redstone Arsenal Research Division, Huntsville, Alabama. Received August 28, 1964*

*The mass spectra and appearance potentials for the principal ions of FSO<sub>2</sub>NF<sub>2</sub>, (FSO<sub>2</sub>)<sub>2</sub>NF, SF<sub>5</sub>NF<sub>2</sub>, and FSO<sub>2</sub>ONF<sub>2</sub> were measured. The values for D(S-N) were found to be 39, 48, and 32 kcal./mole, respectively, and D(O-N) for the latter compound was found to be 35 kcal./mole.*

### Introduction

A number of compounds containing sulfur, nitrogen, and fluorine have been reported.<sup>1</sup> However, until recently, no single bonded S-N or O-N N-fluorinated amines were known. The preparation of fluorosulfuryldifluoramine, FSO<sub>2</sub>NF<sub>2</sub>,<sup>2</sup> bis(fluorosulfuryl)fluoramine, (FSO<sub>2</sub>)<sub>2</sub>NF,<sup>3</sup> pentafluorosulfur difluoramine, SF<sub>5</sub>NF<sub>2</sub>,<sup>4-6</sup> and N,N-difluorohydroxylamine O-fluorosulfate, FSO<sub>2</sub>ONF<sub>2</sub>,<sup>7</sup> made it of interest to investigate the mass spectra and appearance potentials of the principal ions in these compounds to determine the S-N and O-N bond dissociation energies.

### Experimental

The compounds were prepared by the methods reported in the literature.<sup>2-7</sup> Samples were purified by vacuum line fractionation followed by gas partition chromatography except for the FSO<sub>2</sub>NF<sub>2</sub>. It was purified only by the literature method<sup>3</sup> and was found to contain 4-5% SO<sub>2</sub>. The FSO<sub>2</sub>ONF<sub>2</sub> contained only a trace of SiF<sub>4</sub> and the (FSO<sub>2</sub>)<sub>2</sub>NF and SF<sub>5</sub>NF<sub>2</sub> showed

no impurities. Gas chromatographic, infrared, and mass spectral analyses were used for detection of impurities. The impurities found are not closely related to the compounds studied and are unlikely to cause interference with the appearance potential measurements. The shape of the ion efficiency curves did not indicate interferences. The mass spectra and appearance potentials were measured using a Consolidated Systems Corporation high speed mass spectrometer. All mass spectra were obtained at an ionization voltage of 70 v. The appearance potentials were obtained by the vanishing current method with argon added as a voltage standard. The repeller voltage was adjusted to its minimum value, the accelerator voltage was maintained constant, and magnetic scanning was used to keep the effects of contact potentials and field penetration the same during measurements. The mass spectra are shown in Table I and the appearance potentials (A.P.) in Table II. The errors shown for the appearance potentials are the estimated errors in the measurements. Table III shows the bond energies and heats of formation with the estimated error in the heats of formation.

### Results and Discussion

The mass spectra obtained for these compounds are given in Table I. The mass spectrum for SF<sub>5</sub>NF<sub>2</sub> differs from that reported by Cady and co-workers,<sup>4</sup> but it is very similar to that reported by Logothetis, *et al.*<sup>5</sup> The reason for this difference is not readily apparent but may be a result of the mass spectrometer source heater being turned off in this research, whereas the source heater was set at 175° when the former group recorded their spectrum.<sup>8</sup> The heated source may cause sample decomposition.<sup>4</sup> Samples generally gave more reproducible spectra if the source was unheated.

(8) G. H. Cady, private communication.

- (1) H. L. Roberts, *Quart. Rev.* (London), **15**, 30 (1961).
- (2) C. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963).
- (3) M. Lustig, C. Bumgardner, F. A. Johnson, and J. K. Ruff, *ibid.*, **3**, 1165 (1964).
- (4) G. H. Cady, D. F. Eggers, and B. Tittle, *Proc. Chem. Soc.*, 65 (1963).
- (5) A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *Inorg. Chem.*, **2**, 173 (1963).
- (6) E. C. Stump, Jr., C. O. Padgett, and W. S. Brey, Jr., *ibid.*, **2**, 648 (1963).
- (7) M. Lustig and G. H. Cady, *ibid.*, **2**, 388 (1963).

**Table I.** Mass Spectra<sup>a</sup>

<i>m/e</i>	Ion <sup>b</sup>	Relative intensity			
		SF <sub>5</sub> NF <sub>2</sub>	FSO <sub>2</sub> <sup>+</sup> NF <sub>2</sub>	(FSO <sub>2</sub> ) <sub>2</sub> <sup>+</sup> NF	FSO <sub>2</sub> <sup>+</sup> ONF <sub>2</sub>
14	N <sup>+</sup>	...	1.1	...	2.1
16	O <sup>+</sup>	...	1.2	...	0.7
19	F <sup>+</sup>	1.1	0.6	...	0.6
20	HF <sup>+</sup>	0.4	0.8	...	0.9
30	NO <sup>+</sup>	...	...	...	25.8
32	S <sup>+</sup>	5.4	5.1	...	2.8
33	NF <sup>+</sup>	3.4	11.2	0.1	14.8
34	i	0.2	...	...	...
35	SF <sub>2</sub> <sup>2+</sup>	0.4	...	...	...
46	SN <sup>+</sup>	0.9	...	1.9	...
48	SO <sup>+</sup>	...	7.6	6.6	4.6
50	i	...	0.2	...	...
51	SF <sup>+</sup>	5.3	1.7	0.1	...
52	NF <sub>2</sub> <sup>+</sup>	20.8	12.0	...	100.0
53	i	0.3	...	...	...
54	SF <sub>4</sub> <sup>2+</sup>	0.8	...	...	...
64	SO <sub>2</sub> <sup>+</sup>	...	9.6	4.4	3.4
67	SOF <sup>+</sup>	...	25.0	17.0	3.1
68	ONF <sub>2</sub> <sup>+</sup>	...	...	...	1.1
69	i	...	1.1	...	0.2
70	SF <sub>2</sub> <sup>+</sup>	8.3	...	...	...
72	i	0.4	...	...	...
80	SO <sub>3</sub> <sup>+</sup>	...	...	...	3.9
83	FSO <sub>2</sub> <sup>+</sup>	...	100.0	100.0	28.0
85	i	...	4.8	5.4	1.5
89	SF <sub>3</sub> <sup>+</sup>	100.0	...	...	...
91	i	4.0	...	...	...
97	FSO <sub>2</sub> N <sup>+</sup>	...	0.2	8.2	...
99	FSO <sub>3</sub> <sup>+</sup> , i	...	...	0.5	1.0
108	SF <sub>4</sub> <sup>+</sup>	12.5	...	...	...
110	i	0.5	...	...	...
116	FSO <sub>2</sub> NF <sup>+</sup>	...	0.1	...	...
127	SF <sub>5</sub> <sup>+</sup>	50.7	...	...	...
129	i	1.9	...	...	...
135	FSO <sub>2</sub> NF <sub>2</sub> <sup>+</sup>	...	0.1	...	...
199	(FSO <sub>2</sub> ) <sub>2</sub> NF <sup>+</sup>	...	...	1.2	...

<sup>a</sup> Spectra obtained with 70-v. electrons. <sup>b</sup> The letter i signifies the <sup>34</sup>S isotope of the immediately preceding sulfur-containing entry.

potentials and assumed processes given in Table II. The ions and radicals are assumed to be formed in their ground states and to have no excess kinetic energy. The work of Reese, Diebler, and Franklin<sup>9</sup> on sulfonyl fluoride, SO<sub>2</sub>F<sub>2</sub>, gives an ionization potential I.P. (FSO<sub>2</sub>) = 11.4 e.v. and Δ*H*<sub>f</sub>(FSO<sub>2</sub><sup>+</sup>) = 5.3 e.v. Using these values the S-N bond energy for FSO<sub>2</sub>NF<sub>2</sub> is calculated to be 39 kcal./mole and that for (FSO<sub>2</sub>)<sub>2</sub>NF to be 48 kcal./mole, and the heat of formation of FSO<sub>2</sub>NF<sub>2</sub> is -170 kcal./mole.

The S-N bond dissociation energy for SF<sub>5</sub>NF<sub>2</sub> can be calculated from the appearance potential for the NF<sub>2</sub><sup>+</sup> ion from the relation

$$D(\text{S-N}) = \text{A.P.}(\text{NF}_2^+) - \text{I.P.}(\text{NF}_2) - D(\text{S-F})$$

The S-F bond energy is 3.1 e.v. from the heat of formation of SF<sub>6</sub><sup>10a</sup> and the ionization potential of NF<sub>2</sub> is 11.8 e.v.<sup>10b</sup> This gives *D*(S-N) = 16.3 - 11.8 - 3.1 = 1.4 e.v. = 32 kcal./mole. A value of Δ*H*<sub>f</sub>(SF<sub>5</sub>NF<sub>2</sub>) = 10.8 e.v. or -249 kcal./mole was obtained using the known Δ*H*<sub>f</sub>(SF<sub>4</sub>) = -171.7 kcal./mole,<sup>11</sup> Δ*H*<sub>f</sub>(NF<sub>2</sub><sup>+</sup>) = 12.2 e.v.,<sup>10b</sup> and Δ*H*<sub>f</sub>(F) = 18.5 kcal./mole.<sup>10a</sup>

The ionization efficiency curve for the SF<sub>5</sub><sup>+</sup> ion from SF<sub>5</sub>NF<sub>2</sub> has a long tail and appears to be due to two different processes, one with an appearance potential at 12.0 v. and another at 14.3 v. The higher appearance potential was obtained by the linear extrapolation method. Diebler and Mohler<sup>12</sup> report the appearance potential of SF<sub>5</sub><sup>+</sup> from SF<sub>6</sub> to be 15.9 e.v. Fox and Curran<sup>13</sup> report 15.85 e.v., and Marriott and Craggs<sup>14</sup> report a value of 15.77 e.v. Ahearn and Hannay<sup>15</sup> have studied the negative ions from SF<sub>6</sub> and find an F<sup>-</sup> ion at 15.7 e.v. formed by an electron-pair process. They suggest that this appearance potential

**Table II.** Appearance Potentials of Selected Fragment Ions from S-NF and O-NF Compounds

Compound	Ion	A.P., e.v.	Assumed process
FSO <sub>2</sub> NF <sub>2</sub>	FSO <sub>2</sub> <sup>+</sup>	13.1 ± 0.1	FSO <sub>2</sub> NF <sub>2</sub> → FSO <sub>2</sub> <sup>+</sup> + NF <sub>2</sub>
	NF <sub>2</sub> <sup>+</sup>	14.6 ± 0.3	→ NF <sub>2</sub> <sup>+</sup> + ?
(FSO <sub>2</sub> ) <sub>2</sub> NF	FSO <sub>2</sub> <sup>+</sup>	13.5 ± 0.1	(FSO <sub>2</sub> ) <sub>2</sub> NF → FSO <sub>2</sub> <sup>+</sup> + FSO <sub>2</sub> NF
SF <sub>5</sub> NF <sub>2</sub>	SF <sub>5</sub> <sup>+</sup>	14.3 ± 0.5	SF <sub>5</sub> NF <sub>2</sub> → SF <sub>5</sub> <sup>+</sup> + ?
	SF <sub>6</sub> <sup>+</sup>	12.0 ± 0.2	→ SF <sub>6</sub> <sup>+</sup> + ?
	SF <sub>4</sub> <sup>+</sup>	15.9 ± 0.2	→ SF <sub>4</sub> <sup>+</sup> + NF <sub>2</sub>
	SF <sub>3</sub> <sup>+</sup>	16.0 ± 0.2	→ SF <sub>3</sub> <sup>+</sup> + NF <sub>2</sub> + F <sub>2</sub>
	NF <sub>2</sub>	16.3 ± 0.2	→ NF <sub>2</sub> <sup>+</sup> + SF <sub>4</sub> + F
	FSO <sub>2</sub> ONF <sub>2</sub>	NF <sub>2</sub> <sup>+</sup>	13.3 ± 0.1
	FSO <sub>2</sub> <sup>+</sup>	13.3 ± 0.2	→ FSO <sub>2</sub> <sup>+</sup> + NO + F <sub>2</sub>

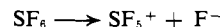
**Table III.** Bond Dissociation Energies in S-N and O-NF Compounds

Compound	Bond	<i>D</i> , kcal./mole	Δ <i>H</i> <sub>f</sub> , kcal./mole
FSO <sub>2</sub> NF <sub>2</sub>	S-N	39	-170 ± 10 <sup>a</sup>
(FSO <sub>2</sub> ) <sub>2</sub> NF	S-N	48	...
SF <sub>5</sub> NF <sub>2</sub>	S-N	32	-249 ± 10
FSO <sub>2</sub> ONF <sub>2</sub>	O-N	35	-163 ± 10
FSO <sub>2</sub> ONF <sub>2</sub>	S-O	~65	-163 ± 10

<sup>a</sup> Estimated uncertainty in the heats of formation.

The bond energies and heats of formation (Table III) were calculated from the measured appearance

value is close to that of SF<sub>5</sub><sup>+</sup> reported by Diebler and Mohler<sup>12</sup> so that the process may be



(9) R. M. Reese, V. H. Diebler, and J. L. Franklin, *J. Chem. Phys.*, **29**, 880 (1958).

(10) (a) National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952; (b) E. D. Loughran and C. Mader, *J. Chem. Phys.*, **32**, 1578 (1960).

(11) J. D. Vaughn and E. L. Muettterties, *J. Phys. Chem.*, **64**, 1787 (1960).

(12) V. H. Diebler and F. L. Mohler, *J. Res. Natl. Bur. Std.*, **40**, 25 (1948).

(13) R. E. Fox and R. K. Curran, *J. Chem. Phys.*, **34**, 1595 (1961).

(14) J. W. Marriott and J. D. Craggs, Electrical Research Associates Technical Report L/T 301, 1953.

(15) A. J. Ahearn and N. B. Hannay, *J. Chem. Phys.*, **21**, 119 (1953).

Using  $D(\text{S-F}) = 3.1$  e.v. and the electron affinity of fluorine,  $E.A.(\text{F}) = 3.62$  e.v.,<sup>16</sup>  $I.P.(\text{SF}_5) = 15.4$  e.v. is calculated. If this value for  $I.P.(\text{SF}_5)$  is used, then a reasonable process cannot be written for the appearance potential of  $\text{SF}_5^+$  from  $\text{SF}_5\text{NF}_2$ .

The O-N bond dissociation energy for  $\text{FSO}_2\text{ONF}_2$  was calculated to be 35 kcal./mole using  $I.P.(\text{NF}_2)$  and  $A.P.(\text{NF}_2^+)$ . Cottrell<sup>17</sup> gives a range varying between 35 and 40 kcal./mole for the bond dissociation energy for alkyl nitrates and nitrites obtained by pyrolysis. The  $D(\text{O-N})$  value found in this research is in good agreement with those results. The sulfur-oxygen bond dissociation energy for  $\text{FSO}_2\text{ONF}_2$

(16) H. O. Pritchard, *Chem. Rev.*, **52**, 529 (1953).

(17) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth, Inc., Washington, D. C., 1958.

was found to be *ca.* 65 kcal./mole from measurement of the appearance potential for the  $\text{FSO}_2^+$  ion.

The substitution of fluorine atoms for other groups bonded to sulfur and/or nitrogen decreases the  $D(\text{S-N})$  value. For the series,  $(\text{FSO}_2)_2\text{NF}$ ,  $\text{FSO}_2\text{NF}_2$ , and  $\text{SF}_5\text{NF}_2$ , there is a successive decrease in the  $D(\text{S-N})$  values (Table III). This decrease might be expected owing to the electron-withdrawing power of the fluorine atoms. In addition, the low S-N bond dissociation energy value for  $\text{SF}_5\text{NF}_2$  is consistent with its chemical behavior.<sup>4</sup>

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