CONTRIBUTION FROM THE INSTITUTE FOR MATERIALS RESEARCH,
NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C. 20234

Mass Spectrometric Study of Photoionization. XIV. Nitrogen Trifluoride and Trifluoramine Oxide

BY VERNON H. DIBELER AND JAMES A. WALKER

Received March 4, 1969

Photoionization yield curves for the NF_3^+, NF_2^+, and NF^+ ions of nitrogen trifluoride and the ONF_3^+, ONF_2^+, and NO^+ ions of trifluoramine oxide were obtained from threshold to 600 Å. Ionization energies were used to calculate heats of formation of ions, ionization energies of radicals, and bond dissociation energies. The following bond dissociation energies (in eV) were derived: $D(NF_2\text{–}F) = 2.39$, $D(NF\text{–}F) = 3.4$, and $D(NF) = 2.4$. The heat of formation, $\Delta H_f°_0(ONF_3) = -3.02$ eV (-69.6 kcal mol^{-1}), was derived from ionization threshold data and used to estimate $D(O\text{–}NF_3) = 4.3$ eV, $D(ONF_2\text{–}F) = 1.9$ eV, and related thermodynamic properties.

Introduction

Electron impact studies have been reported[1-4] for a number of nitrogen–fluorine molecules and ionization threshold data used to derive N–F and N–N bond dissociation energies. The thermodynamic values thus obtained are generally in fair agreement for several molecules, although the ordering of some N–F bond strengths is uncertain and rather broad limits of error must be assumed for some values. Furthermore, in the case of at least one molecule, tetrafluorohydrazine, the ambient temperature of the electron impact source affects the equilibrium $N_2F_4 \rightleftarrows 2NF_2$ and results in ambiguous interpretation[5] of the NF_2^+ ion yield of the molecule.

Recently, a new highly stable nitrogen–fluorine molecule, trifluoramine oxide, was discovered and produced independently by several research groups[6] and a thorough investigation of its physical and chemical properties is in progress in at least one laboratory.[7] Elsewhere, a determination of the heat of formation of ONF_3 has been reported[8] as the result of a high-temperature and high-pressure kinetics study. The value $\Delta H_f°(ONF_3) = -34.1 \pm 0.5$ kcal mol^{-1} suggests that the bond dissociation energy $D(O\text{–}NF_3)$ is considerably less than that of nitric oxide and is nearly the same as the first N–F bond in NF_3. This is contrary to conclusions reached by Fox, *et al.*[7] As information on the ionization and dissociation processes in the molecule provides another means of determining $\Delta H_f°_0(ONF_3)$ and is also of interest in relation to other nitrogen–fluorine compounds, we have undertaken a study using the precise method of monoenergetic photon impact. We include a reexamination of nitrogen trifluoride in order to improve the ionization threshold measurements for that molecule and to assist in the evaluation and interpretation of data from trifluoramine oxide.

Experimental Section

The photoionization yield curves and ionization threshold data were obtained by means of the combined vacuum ultraviolet monochromator and mass spectrometer described previously in some detail.[9] The means of sample introduction, the continuum photon sources, the photon and ion detection systems, and the probable uncertainties in measurements of the ion and photon intensities are essentially as reported in the preceding paper[10] of this series.

The nitrogen trifluoride was a commercial sample of research grade material obtained through Dr. G. T. Armstrong of the Thermochemistry Section. After removal of a small amount of impurity not condensable at liquid nitrogen temperature, the mass spectrum of the remainder showed no ions other than those expected of NF_3. Although the manufacturer reported the presence of approximately 1% N_2F_2, the absence of an N_2F^+ ion (a principal ion in the mass spectrum of both *cis*- and *trans*-N_2F_2)[11] indicates an estimated upper limit of 0.1% for this impurity.

The trifluoroamine oxide was very kindly supplied by Dr. W. B. Fox of Allied Chemical Corp., through Dr. Armstrong, and was a portion of the material recently used by Maryott[12] for a determination of the dipole moment of ONF_3. It was purified by repeated low-temperature trap-to-trap distillations in an all-stainless-steel vacuum system. The only impurity observed in the mass spectrum of the product was on the order of 0.2 mol % nitric oxide and nitrogen trifluoride. The former impurity was distinguished from the NO^+ fragment ion of ONF_3 by the appearance of the principal autoionizing line of the nitric oxide molecule ion[13] at 897 Å and the weaker lines at 811 and 783 Å. Although the NF_3^+ ion is a possible fragment ion of ONF_3, it is an extremely weak one, and the observation of an NF_2^+ ion with the same relative intensity as in NF_3 suggested the presence of that impurity. Thus, it is clear that an accurate assessment of these impurities is not possible on this basis. However, the estimate is considered reasonable from the behavior of similarly treated samples for which impurity levels were monitored by infrared spectrophotometry and by vapor-phase chromatography.

---

[1] R. M. Reese and V. H. Dibeler, *J. Chem. Phys.*, **24**, 1175 (1956).

[2] J. T. Herron and V. H. Dibeler, *J. Res. Natl. Bur. Std.*, **65A**, 405 (1961).

[3] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

[4] E. D. Loughran and C. Mader, *J. Chem. Phys.*, **32**, 1578 (1960).

[5] (a) C. B. Colburn and F. A. Johnson, *ibid.*, **33**, 1869 (1960); (b) A. Kennedy and C. B. Colburn, *ibid.*, **35**, 1892 (1961).

[6] (a) W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Am. Chem. Soc.*, **88**, 2604 (1966); (b) N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966); (c) E. C. Curtiss, D. Pilipovich, and W. H. Moberly, *J. Chem. Phys.*, **46**, 2904 (1967).

[7] W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, **7**, 2064 (1968).

[8] R. Bougon, J. Chatelet, J.-P. Desmoulin, and P. Plurien, *Compt. Rend.*, **C266**, 1761 (1968).

[9] V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **46A**, 409 (1964).

[10] V. H. Dibeler and J. A. Walker, *Inorg. Chem.*, **8**, 50 (1969).

[11] J. T. Herron and V. H. Dibeler, unpublished data.

[12] A. A. Maryott, S. T. Kryder, and M. S. Malmberg, private communication.

[13] R. M. Reese and H. M. Rosenstock, *J. Chem. Phys.*, **44**, 2007 (1966).

Results and Discussion

NF_3.—The relative intensities of the positive ions in the mass spectrum of NF_3 produced by 584-Å photons are given in Table I. No negative ions were observed and it is estimated that the relative abundance of any ion-pair process is less than 0.001. These data are consistent with the electron impact mass spectrum[1] obtained at 70 eV. The absence of N^+ and F^+ ions in the photoionization mass spectrum indicates that the thresholds for those ions must be greater than 21.22 eV, a conclusion that is also consistent with the published electron impact data.

TABLE I

MASS SPECTRA OF NITROGEN TRIFLUORIDE AND TRIFLUORAMINE OXIDE BY PHOTON IMPACT

Molecule	Ion	Rel abundance[a]
NF_3	NF_3^+	0.29
	NF_2^+	1.00
	NF^+	0.21
ONF_3	ONF_3^+	0.003
	ONF_2^+	1.00
	ON^+	0.55

[a] Measured at the 584-Å helium resonance line (21.22 eV).

The photoion yield curves for the NF_3^+, NF_2^+, and NF^+ ions of NF_3 are shown in Figure 1. Wavelength in ångströms is plotted on the abscissa with equivalent energy in electron volts given at intervals. The number of ions detected per photon transmitted through the ion source is plotted in arbitary units on the ordinate. For simplicity, the ordinate origin of the NF^+ and NF_3^+ curves is displaced and the scale is one-fourth that of the NF_2^+ ion.

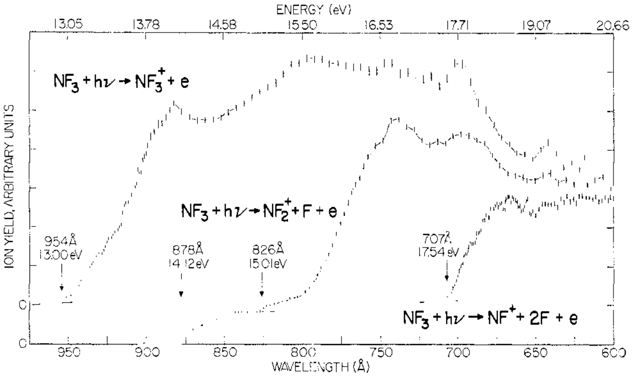

Figure 1.—Photoion-yield curves for the NF_3^+, NF_2^+, and NF^+ ions of nitrogen trifluoride—the arbitrary scale for the NF_2^+ ion is four times the scales for the NF_3^+ and NF^+ ions.

Qualitatively, the shape of the NF_3^+ ion-yield curve is similar to that reported[14] for NH_3. The intensity rises slowly over a wavelength range of about 70 Å, indicating the excitation of many vibrational modes and suggesting an important structural change in the transition from molecule to ion, *e.g.*, from pyramidal structure with nearly 90° valence bonds in the ground-state molecule to very nearly planar structure in the ion.

From about 880 to 700 Å, the ion yield is relatively constant showing no definite evidence for autoionization processes. At about 700 Å a significant reduction in ion yield occurs.

As in the case of ammonia, there is some evidence for steplike structure near threshold (950–900 Å) at intervals of about 8 Å (1000 cm^{-1}). These intervals correspond approximately to the totally symmetric stretching (ν_1) and bending vibrations (ν_2) or combinations of these[15,16] in the molecule.

The definite onset of the NF_3^+ ion occurs at 954 Å (13.00 ± 0.02 eV). This agrees with the electron impact value[1,2] of 13.2 ± 0.2 eV within the estimated uncertainty of that value. Apparently, no Rydberg series converging to an ionization limit of NF_3 has been reported. However, LaPaglia and Duncan[17] have obtained the ultraviolet absorption spectrum and observed a very strong absorption below 960 Å. They ascribe that wavelength limit to the lowest ionization threshold of the molecule and our value of 954 Å clearly supports their interpretation.

Two independent, careful determinations of the heat of formation of NF_3 have been reported recently;[18] their results are in agreement within the experimental uncertainties. We have selected the value[18b] obtained by the combustion of sulfur in NF_3 and, taking the enthalpy difference between 0 and 298.15°K for NF_3 as tabulated by Wagman, *et al.*,[19] we obtain $\Delta H_f{}^\circ{}_0(NF_3) = -30.38 \pm 0.2$ kcal mol^{-1} (-1.3174 ± 0.0087 eV).[20] Adding the threshold energy of the NF_3^+ ion results in 11.683 ± 0.02 eV (269.4 ± 0.5 kcal mol^{-1}) for the heat of formation of the ion. Threshold energies and derived thermodynamic values for this and subsequently treated ions are summarized in Table II.

The principal ion in the mass spectrum, NF_2^+, exhibits a weak but definite onset at 878 Å (14.12 ± 0.01 eV). The ion-yield curve gives evidence of some step structure with intervals of about 8 Å (1000 cm^{-1}) in the wavelength region above 850 Å. A spectroscopic study[21] of the NF_2 radical reports values for the ν_1 and ν_3 stretching fundamentals of 1074 and 935 cm^{-1}, respectively, for the NF_2 molecule. Our present sensitivity and resolution apparently permit only an approximate determination of comparable values for the ion. In the region 845–825 Å, the yield is remarkably constant until a second definite increase occurs at about 826 Å (15.01 ± 0.02 eV). At that point the curve rises sharply to a maximum at about 740 Å and then slowly decreases to 600 Å with some evidence for unresolved autoionization peaks. Some of the latter

---

(14) V. H. Dibeler, J. A. Walker, and H. M. Rosenstock, *J. Res. Natl. Bur. Std.*, **70A**, 459 (1966).

(15) M. K. Wilson and S. R. Polo, *J. Chem. Phys.*, **20**, 1716 (1952).

(16) R. J. L. Popplewell, F. N. Masri, and H. W. Thompson, *Spectrochim. Acta*, **23A**, 2797 (1967).

(17) S. R. LaPaglia and A. B. F. Duncan, *J. Chem. Phys.*, **34**, 1003 (1961).

(18) (a) G. C. Sinke, *J. Phys. Chem.*, **71**, 359 (1967); (b) L. C. Walker, *ibid.*, **71**, 361 (1967).

(19) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, National Bureau of Standards Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., Jan 1968.

(20) The following conversion factors are used throughout: 1 eV $molecule^{-1}$ = 96.4870 kJ mol^{-1}; 1 kcal mol^{-1} = 4.1840 kJ mol^{-1}; 1 eV ≈ 8065.73 cm^{-1}.

(21) M. D. Harmony, R. J. Myers, L. J. Schoen, D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **35**, 1129 (1961).

TABLE II

SUMMARY OF THRESHOLD ENERGIES AND THERMODYNAMIC PROPERTIES OF IONS AND RADICALS FROM NITROGEN TRIFLUORIDE AND TRIFLUORAMINE OXIDE

Ion process	Threshold, eV	Thermodynamic properties
$NF_3 + h\nu \rightarrow NF_3^+ + e$	13.00 ± 0.02^a	$\Delta H_f{}^\circ{}_0(NF_3^+) = 11.68$ eV (269.4 kcal mol^{-1})
$\rightarrow NF_2^+ + F + e$	14.12 ± 0.01	$\Delta H_f{}^\circ{}_0(NF_2^+) = 12.13$ eV (279.7 kcal mol^{-1}) $I(NF_2) = 11.73$ eV
	15.01 ± 0.02	$\Delta H_f(NF_2{}^{*+})^b = 13.02$ eV (300.2 kcal mol^{-1})
$\rightarrow NF^+ + 2F + e$	17.54 ± 0.02	$\Delta H_f{}^\circ{}_0(NF^+) = 14.88$ eV (343.1 kcal mol^{-1})
$ONF_3 + h\nu \rightarrow ONF_3^+ + e$	13.26 ± 0.01	$\Delta H_f{}^\circ{}_0(ONF_3^+) = 10.24$ eV (236.1 kcal mol^{-1})
$\rightarrow ONF_2^+ + F + e$	13.59 ± 0.01	$\Delta H_f{}^\circ{}_0(ONF_2^+) = 9.90$ eV (228.3 kcal mol^{-1}) $\Delta H_f(ONF_2) = -1.8$ eV (-42 kcal mol^{-1}) $D(O{-}NF_3) = 4.26$ eV (98 kcal mol^{-1}) $D(ONF_2{-}F) = 1.9$ eV (44 kcal mol^{-1})
$\rightarrow NO^+ + 3F + e$	15.21 ± 0.02	$\Delta H_f{}^\circ{}_0(ONF_3) = -3.02 \pm 0.05$ eV (-69.6 ± 1.2 kcal mol^{-1})

[a] Estimated uncertainties. [b] The asterisk indicates a probable excited state of the ion.

features can be correlated with similar structure in the molecule-ion curve.

The threshold at 14.12 eV is interpreted as the heat of reaction, ΔH_0, for the process $NF_3 + h\nu \rightarrow NF_2^+ + F + e$. From the ΔH_0 and the heats of formation of NF_3 and F we can calculate the heat of formation of NF_2^+. A recent study of the photoionization of fluorine[22] has resulted in a new, more accurate value of $\Delta H_f{}^\circ{}_0(F) = 0.67 \pm 0.01_5$ eV (15.45 ± 0.35 kcal mol^{-1}). This value, together with the heat of formation of NF_3, results in $\Delta H_f{}^\circ{}_0(NF_2^+) = 12.13 \pm 0.02$ eV (279.7 ± 0.5 kcal mol^{-1}).

Apparently, it is impossible to reduce the uncertainty in $\Delta H_f(NF_2^+)$ by an alternative calculation. For example, direct electron impact measurements[2,4] of $I(NF_2)$ result in a value of about 11.9 eV with an estimated uncertainty of at least ± 0.2 eV (± 5 kcal mol^{-1}). On the other hand, Walker[18b] has combined second- and third-law evaluations[23] of data on the thermal dissociation of N_2F_4[2] with a newly derived value for the heat of N_2F_4 to calculate $\Delta H_f{}^\circ{}_{298.15}(NF_2) = 8.5 \pm 2$ kcal mol^{-1}, or applying the enthalpy difference for temperature,[19] $\Delta H_f{}^\circ{}_0(NF_2) = 9.1 \pm 2$ kcal mol^{-1}. As uncertainties reported for electron impact data generally refer to the reproducibility of measurements rather than to the probable error, we prefer to combine the heats of formation of the ionized and neutral species of NF_2 to redetermine $I(NF_2) = 11.73 \pm 0.09$ eV, or 270.6 ± 2 kcal mol^{-1}. Although more accurate, this is probably within the total range of previously reported electron impact values.

The new heat of formation of NF_2 also permits a more accurate calculation of the bond dissociation energy, $D_0(NF_2{-}F) = 2.39 \pm 0.09$ eV (55.1 ± 2 kcal mol^{-1}). Again, although more accurate, this is essentially in agreement with the results obtained by electron impact[2,5b] and further improvement in derived values must await support from improved thermal or spectral data.

The second onset for NF_2^+ at 15.0 eV is difficult to interpret. Mader and Loughran[24] observed an upward break about 0.7 eV above threshold in their electron impact ionization curve for NF_2^+ under experimental conditions which most likely produced NF_2 radicals from the N_2F_4 introduced into their ion source.[25] Thus they suggested the possibility of an electronically excited state of the NF_2^+ ion 0.7 eV above threshold. Assuming that our somewhat greater energy interval (0.9 eV) results from the more favorable means of determining the photoionization thresholds, the interpretation seems reasonable, particularly as there is no possibility of thermal decomposition in the present experiments and as no known excited state of the product fluorine atom exists within 100,000 cm^{-1} of the ground state. Furthermore, one would expect a low-lying singlet excited state of the ion.

The NF^+ ion curve exhibits a sharp rise at about 707 Å (17.54 ± 0.02 eV) and shows some evidence for step structure in the region 700–675 Å and possibly for unresolved autoionization in the region 675–600 Å. The photoionization threshold, which is just outside the reported range of electron impact values (17.9 ± 0.3 eV), is ascribed to ΔH_0 for the reaction $NF_3 + h\nu \rightarrow NF^+ + 2F + e$. As in the case of NF_2^+, the heat of formation of the ion can be calculated from the ΔH_0 and the heats of formation of NF_3 and F. Thus, assuming the absence of excess energy, we derive $\Delta H_f{}^\circ{}_0(NF^+) = 14.88 \pm 0.03$ eV (343.1 ± 0.7 kcal mol^{-1}).

Although a number of spectroscopic studies of the NF molecule have been made both in matrix[26] and in gas phase,[27] no determination of the ionization threshold or of the dissociation energy (and, thereby, the heat of formation) has been reported. Both properties, however, have been estimated from electron impact data assuming the equality of the two bond dissociation energies, $D(NF{-}F) = D(N{-}F)$. An alternative means is now available. From the recent values of the heats of formation of NF_3 and F we calculate $\Delta H_0 = 8.21$ eV (189.3 ± 1.0 kcal mol^{-1}) for the reaction $NF_3 \rightarrow N + 3F$. Subtracting the first N–F bond dissociation

---

[22] V. H. Dibeler, J. A. Walker, and K. E. McCulloh, *J. Chem. Phys.*, in press.

[23] "JANAF Thermodynamic Data," The Dow Chemical Co., Midland, Mich., March 31, 1964.

[24] See footnote 3 of ref 5a.

[25] On the other hand, Herron and Dibeler[2] did not observe a break in the NF_2^+ ion curve in their study of the thermal decomposition of N_2F_4. However, the threshold law for electron impact is not favorable to the detection of closely spaced sequential processes.

[26] (a) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **40**, 2461 (1964); (b) J. E. Comeford and D. E. Mann, *Spectrochim. Acta*, **21**, 197 (1965).

[27] (a) A. E. Douglas and W. E. Jones, *Can. J. Phys.*, **44**, 2251 (1966); (b) W. E. Jones, *ibid.*, **45**, 21 (1967).

energy of 2.39 eV gives 5.82 ± 0.10 eV (134.2 ± 2.3 kcal mol^{-1}) for the sum of the bond dissociation energies, D(NF–F) + D(N–F). Equally distributed, this would result in an "average" bond dissociation energy of about 67 kcal mol^{-1} which is in good agreement with electron impact values. However, applying the same reasoning used by Kennedy and Colburn for the first and second N–F bonds, it is likely that the second and third bonds are not equal. In fact, Herron and Dibeler[2] determined that the threshold energies for the two processes

$$NF_2 \longrightarrow NF_2^+ + e$$

$$NF_2 \longrightarrow NF^+ + F^-$$

were the same within the reproducibility of the measurements (±0.2 eV). Making the more reasonable assumptions that the *ionization energies* of NF_2 and NF radicals are very nearly the same and that I(NF) is approximately equal to the ionization energy of the isoelectronic molecule O_2 (12.07 eV),[28] the quantity D(NF–F) must be approximately equal to the electron affinity of the fluorine atom, 3.45 eV (79.5 kcal mol^{-1}). Then, by difference, D(N–F) = 2.37 eV (54.6 kcal mol^{-1}) or is equal to the first N–F bond dissociation energy well within the range of estimated uncertainty. This differs considerably from the estimated value of D(N–F) = 4 ± 1 eV recommended by Gaydon.[29] From D(N–F) we calculate the heat of formation[30] ΔH_f(NF) = 3.2 ± 0.2 eV, or 74 ± 5 kcal mol^{-1}. (See Table III for bond dissociation energies of NF_3.)

TABLE III

SUMMARY OF BOND DISSOCIATION ENERGIES IN NF_3

Bond	Dissociation Energy	
	eV	kcal mol^{-1}
NF_2–F	2.39 ± 0.09[a]	55.1 ± 2
NF–F[b]	3.45 ± 0.2	79.5 ± 5
N–F[b]	2.37 ± 0.2	54.6 ± 5

[a] Estimated uncertainties as noted in text. [b] Sum of D(NF–F) and D(N–F) equals heat of atomization of NF_3 (8.21 eV) less D(NF_2–F).

ONF_3.—The relative intensities of the positive ions in the mass spectrum of trifluoramine oxide produced by 584-Å photons (21.22 eV) are listed in Table I. The two principal ions, NO^+ and ONF_2^+, and the very weak molecule ion are consistent with the relative abundances in the 70-V electron impact spectrum reported by Fox, *et al.*[7] The higher energy of the latter spectrum produced additional fragment ions, including NF_2^+. As indicated in the Experimental Section, our observation of NF_3^+ and NF_2^+ ions by photon impact is ascribed to impurity. No negative ions have been reported and we estimate the abundance of any ion-pair process to be less than 0.001 relative to the ONF_2^+ ion. The fact that the principal ions result from the dissociation of N–F bonds rather than from the N–O bond is of interest in judging the reliability of the heat of formation of ONF_3 determined below. This behavior is also consistent with mass spectra of analogous oxytrihalide molecules such as were reported by Kiser.[31]

In spite of the low relative abundance, we have succeeded in obtaining an ion-yield curve for the molecule ion. Thus, curves for the three ions are plotted in Figure 2 in the same manner as in Figure 1. Again, for simplicity, the origins of the ordinates are displaced and the ordinate scales for the ONF_2^+ and NO^+ ions are 100 times the scale for the molecule ion.

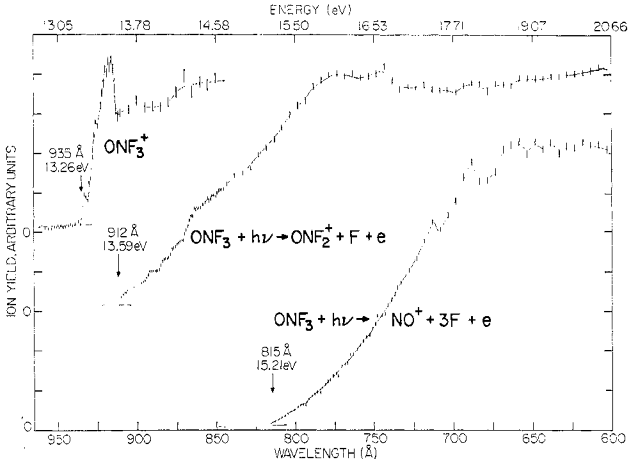

Figure 2.—Photoion-yield curves for the ONF_3^+, ONF_2^+, and NO^+ ions of trifluoramine oxide. Arbitrary scales for the ONF_2^+ and NO^+ ions are 100 times that for the ONF_3^+ ion.

As the NO^+ ion provides a means of determining the heat of formation of the ONF_3 molecule, it is convenient to discuss first the results for that ion. The NO^+ curve shown in Figure 2 differs in minor respects from the original curve as small corrections have been made for contributions due to a trace of nitric oxide as noted in the Experimental Section. The only contributions of possible significance were the strong autoionizing Rydberg levels of the nitric oxide molecule[13] occurring in the wavelength region 900–775 Å. The photoionization curve of nitric oxide was remeasured in that region and the impurity contributions were subtracted on the basis of the intensity of the 897-Å line observed (before threshold) in the NO^+ ion yield from ONF_3. It will be noted that some deviations from an otherwise smooth curve appear in the vicinity of the corrections at 794, 773, and 771 Å. These inaccuracies no doubt result from the difficulty of comparing the intensities of very narrow lines but have no effect on the threshold determination.

The definite and rapidly rising onset of the NO^+ ion of ONF_3 first appears at 815 Å (15.21 ± 0.02 eV). The curve exhibits some evidence for unresolved autoionization in the region 715–650 Å and then a nearly constant yield to 600 Å. Aside from the questionable interpretation of autoionization, there is

---

(28) V. H. Dibeler and J. A. Walker, *J. Opt. Soc. Am.*, **57**, 1007 (1967).

(29) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 3rd ed, Chapman and Hall, Ltd., London, 1968.

(30) Enthalpy differences due to temperature change are not considered here.

(31) R. W. Kiser, J. G. Dillard, and D. L. Dugger, Chapter in "Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, No. 72, American Chemical Society, Washington, D. C., 1968.

no evidence for thresholds of electronically excited states of the ion and we can make no contribution to the recent discussions[32] on that matter.

Assuming negligible excess energy in the process, the threshold of 15.21 eV is the ΔH_0 for the reaction $ONF_3 + h\nu \rightarrow NO^+ + 3F + e$. The complexity of the reaction makes such an assumption questionable. However, the ion-yield curve gives no indication that the ion is formed with significant excess energy. On the other hand, the possibility of molecular fluorine as a neutral product is discarded by analogy with NF_3 and on the basis of the calculations given below and there is no evidence for any other ionization process that can contribute to this threshold. The heat of formation[19] $\Delta H_f{}^\circ{}_0(NO^+) = 234.8$ kcal mol^{-1}, or 10.18_2 eV, is probably established within ±0.01 eV. From that value, ΔH_0, and the $\Delta H_f{}^\circ{}_0(F)$, we calculate $\Delta H_f{}^\circ{}_0$ $(ONF_3) = -3.02 \pm 0.05$ eV (-69.6 ± 1.2 kcal mol^{-1}). This is considerably more negative than -34.1 kcal mol^{-1} determined by Bougon, *et al.*[8] However, our value is supported by the following considerations. From the appropriate heats of formation, we derive the bond dissociation energy $D(O\text{–}NF_3) = 4.26$ eV (98 kcal mol^{-1}). Compared with a dissociation energy of 63 kcal mol^{-1} derived from the experimental results of Bougon, *et al.*, our value indicates a much stronger O–N bond and is quite consistent with the observations by Fox, *et al.*,[7] on the relative chemical and thermal stabilities of the N–O and N–F bonds. Furthermore, Fox estimated that the N–O bond has a slightly greater than 70% double-bond character in ONF_3. Our calculated $D(O\text{–}NF_3)$ is about 65% of the bond dissociation energy of nitric oxide and nearly 85% of the dissociation energy of the N═O double bond in nitroxyl.[33]

We should emphasize that the contribution of excess kinetic energy to dissociative ionization has been determined to be an important consideration in some polyatomic molecules.[34,35] Furthermore, a reaction calorimetry study of the heat of formation of ONF_3 has been made recently by Mrs. Reatha King.[36] Preliminary calculations indicate a heat of formation for ONF_3 about 20 kcal mol^{-1} less negative than that reported herein. If correct, this would indicate that the NO^+ ion is formed with about 1 eV of excess energy. However, as indicated above, there is no evidence for appreciable excess energy in that process.

The molecule ion (Figure 2) has an abrupt onset at 935 Å (13.26 ± 0.01 eV). No other determination of the ionization energy has been reported. However, this is very similar to the threshold energy for NF_3 and *trans*-N_2F_2.[2] The rapidly rising curve shows some evidence for unresolved autoionization structure in the region from onset to about 910 Å and then a relatively constant ion yield to 850 Å. The remainder of the curve was not obtained in detail because of the very low signal. However, a cursory examination indicated quite uniform ion intensity to 600 Å. It is interesting to note that the very rapid decrease in ion yield at about 912 Å corresponds with the onset of the curve for the ONF_2^+ ion. Further discussion on that point is deferred to the section on the ONF_2^+ ion.

The value $\Delta H_0 = 13.26$ eV for the reaction $ONF_3 + h\nu \rightarrow ONF_3^+ + e$ added to the heat of formation of the molecule results in $\Delta H_f{}^\circ{}_0(ONF_3^+) = 10.24 \pm 0.05$ eV, or 236.1 ± 1.2 kcal mol^{-1}. The summation of the appropriate heats of formation indicates that $D(O\text{–}N^+F_3) = 4.00$ eV, or about 92 kcal mol^{-1}. Thus the O–N bond dissociation energies in the ion and the molecule are very similar. On the other hand, the first N–F bond dissociation energy for the ion is calculated from data given below to be about 0.4 eV, *i.e.*, considerably less than the first N–F bond in NF_3 and probably in ONF_3. These conclusions are quite consistent with the mass spectrum and with the chemical and physical properties of ONF_3 as noted above.

The ONF_2^+ ion, the second principal ion of ONF_3, has a definite onset at 912 Å (13.59 ± 0.01 eV). This is closely related in wavelength to the short-wavelength edge of the broad peak-like structure and the beginning of the constant-yield region in the molecule-ion curve. We may speculate that the broad peak represents autoionization of unresolved Rydberg levels of the molecule converging to the threshold of an electronically excited state of the molecule ion at about 910 Å. This state undergoes dissociation to produce the ONF_2^+ ion.

Steplike structure of the ONF_2^+ ion in the region from onset to 865 Å is ascribed to vibrationally excited states of the ion. Principal steps appear at 12-Å intervals (1460 cm^{-1}) with intermediate steps at 6-Å intervals (730 cm^{-1}). The former interval is of the order of the NO stretching frequencies for various N–O molecules,[6c] whereas the latter may represent a symmetric NF stretch or a bending frequency. The remainder of the curve below 865 Å is remarkably smooth, rising slowly to a maximum at about 750 Å and then remaining constant to 600 Å. There is no further evidence for autoionization or higher ionization processes.

In the absence of excess energy in the dissociation process, the threshold is assumed to be $\Delta H_0 = 13.59$ eV for the process $ONF_3 + h\nu \rightarrow ONF_2^+ + F + e$. The usual summation of heats of formation results in $\Delta H_f{}^\circ{}_0(ONF_2^+) = 9.90 \pm 0.05$ eV (228.3 ± 1.2 kcal mol^{-1}). Assuming the ionization energies of the ONF_2 and NF_2 radicals are approximately equal, we estimate $\Delta H_f(ONF_2) = -1.8$ eV and, consequently, a bond dissociation energy $D(ONF_2\text{–}F) = 1.9$ eV, or 44 kcal mol^{-1}. Although speculative, this value is quite consistent with conclusions drawn and assumptions made in previous sections and with observations reported by Fox, *et al.*[7]

Acknowledgment.—This work was supported in part by the U. S. Atomic Energy Commission. We also wish to thank Dr. G. T. Armstrong for providing the samples

---

(32) (a) H. Sjogren and I. Szabo, *Arkiv Fysik*, **37**, 551 (1968); (b) K. P. Huber, *Can. J. Phys.*, **46**, 1691 (1968).

(33) S. W. Benson, *J. Chem. Educ.*, **42**, 502 (1965).

(34) M. Krauss, J. A. Walker, and V. H. Dibeler, *J. Res. Natl. Bur. Std.*, **27A**, 281 (1968).

(35) W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

(36) G. T. Armstrong, private communication.

of nitrogen trifluoride and trifluoramine oxide and Dr. F. E. Brinckman for carrying out purification procedures on the latter material. We gratefully acknowledge helpful discussions with Dr. W. H. Evans on the reliability and usefulness of pertinent thermodynamic data.

CONTRIBUTION FROM THE ANORGANISCH-CHEMISCHES INSTITUT DER UNIVERSITÄT,
GÖTTINGEN, GERMANY

Preparation and Reactions of Fluorosulfonyliminosulfuroxy Difluoride. XVII[1]

BY HERBERT W. ROESKY AND DANIEL P. BABB

Received February 10, 1969

FSO_2NSOF_2 was prepared by the direct fluorination of FSO_2NSO. A study of the reactions of FSO_2NSOF_2 with ammonia and several amines has resulted in the preparation and characterization of previously unreported compounds of the general formula FSO_2NSOFX where X = NH_2, $NHCH_3$, $N(CH_3)_2$, and $N(C_2H_5)_2$. Hydrolysis of FSO_2NSOF_2 in the presence of R_4PCl or R_4AsCl where R = C_6H_5 led to salts containing the imidodisulfurylfluoride ion. The compounds have been isolated and identified by infrared, nmr, and elemental analyses.

Introduction

Recently the preparation of FSO_2NSOF_2[2] was reported as resulting from the reaction of FSO_2NH_2 and SOF_4 in the presence of NaF; however, the chemistry of this compound was not discussed.

This investigation reports the preparation of FSO_2NSOF_2 in nearly quantitative yield by the direct fluorination of FSO_2NSO.[3] Additional characterization of this compound was completed. Hydrolysis of FSO_2NSOF_2 with tetraphenylphosphonium chloride and tetraphenylarsonium chloride led to salts containing the imidodisulfuryl fluoride ion. The intermediate ion, $(FSO_2)_2N^{\ominus}$, which can also be obtained from $(FSO_2)_2NH$,[4,5] suggests a probable mechanism for this hydrolysis. Compounds of the general formula FSO_2NSOFX where X = NH_2, CH_3NH, $(CH_3)_2N$, and $(C_2H_5)_2N$ resulted from reaction with NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(C_2H_5)_2NH$.

Experimental Section

Reagents.—Fluorine, tetraphenylphosphonium chloride, tetraphenylarsonium chloride, and the amines were obtained from Kali Chemie, A.G., or Fluka, A.G. These reagents were used without further purification. FSO_2NSO was prepared by the reaction of $SOCl_2$ with FSO_2NH_2.[3]

General Methods.—All reactions of FSO_2NSOF_2 were carried out in Pyrex flasks under an atmosphere of nitrogen. Prior to use the nitrogen was dried over a column of P_4O_{10}. Because the compounds could be extremely toxic, all reactions were performed in a well-ventilated hood.

Infrared spectra (Table I) were recorded using a Leitz infrared spectrophotometer. The spectra of liquids were obtained in the liquid phase as capillary films with potassium bromide windows and in the solid phase as potassium bromide pellets.

Nuclear magnetic resonance spectra (Table II) were recorded using a Varian A-56/60 spectrometer. Tetramethylsilane and trichlorofluoromethane were used as external standards. Vapor pressure data for FSO_2NSOF_2 were measured in a conventional glass vacuum apparatus using a quartz spiral monometer.

Elemental analyses (Table III) were performed by Beller Microanalytical Laboratory, Goettingen, Germany. Boiling points of liquids and melting points of solids are given in Table III.

Preparation of Fluorosulfonyliminosulfuroxy Difluoride, FSO_2NSOF_2.—Fluorine at the rate of 20 cm^3/min was bubbled through 50 ml of FSO_2NSO in a quartz trap at room temperature. The material was simultaneously subjected to ultraviolet radiation from a lamp[6] placed 1–2 cm distant from the trap. Two additional quartz traps at −80° were connected to the trap, the first to collect any products which were carried out of the irradiated trap by the flow of fluorine, and the second to exclude moisture from the air. After 72 hr, distillation of the material in the two traps over a column packed with glass helices of 30-cm length and 1-cm diameter gave a 92% yield of the product, bp 72°. The material was identified by ir and nmr spectra.[2] A boiling point of 71.5° was found by extrapolation of a plot of log P(mm) *vs.* $1/T$. The data are [T (°C), P (mm)]: −15, 7.5; −10, 11; −5, 15.5; 0, 20; 5, 30; 10, 40; 15, 52.5; 19.5, 65.5. The vapor pressure curve from these data was found to be of the form $\log P(\text{mm}) = (-2062/T) + 8.860$. The values for ΔH and ΔS were calculated to be 9.4 kcal/mol and 27.3 cal/mol deg.

Preparation of Fluorosulfonyliminosulfuroxyamino Fluoride, $FSO_2NSOFNH_2$.—The reaction was carried out in a three-neck 2-l. flask equipped with a Dry Ice condenser maintained at −80°, a stirring motor, and a nitrogen T adapter. To 33.3 g (0.181 mol) of FSO_2NSOF_2 dissolved in 1 l. of dry ethyl ether was added 11.6 g (0.683 mol) of ammonia over a period of 30 min through the Dry Ice condenser. The flask was maintained at about −80°. After the addition was complete, the flask was slowly warmed to room temperature. The solid was removed by filtration under dry nitrogen. The solvent of the resulting solution was removed by means of a water pump vacuum and the residue was distilled in oil pump vacuum. Other products formed which were seen by an nmr spectrum of the crude product mixture, could not be isolated; yield, 1.5 g (0.0084 mol).

Preparation of Fluorosulfonyliminosulfuroxymethylamino Fluoride, $FSO_2NSOFNHCH_3$.—To a mixture of 37 g (0.20 mol) of FSO_2NSOF_2 and 500 ml of dry ethyl ether, 12.5 g (0.40 mol) of CH_3NH_2 was added using a dropping flunnel. The addition was carried out over a period of 1 hr. The flask was maintained at

---

[1] Paper XVI: H. W. Roesky, *Inorg. Nucl. Chem. Letters*, **5**, 173 (1969).

[2] O. Glemser, H. W. Roesky, and P. R. Heinze, *Angew. Chem.*, **79**, 723 (1967).

[3] H. W. Roesky, *ibid.*, **79**, 724 (1967).

[4] R. Appel and G. Eisenhauer, *Ber.*, **95**, 246 (1962).

[5] J. K. Ruff, *Inorg. Chem.*, **4**, 1446 (1965); M. Lustig, C. L. Bumgardner, F. A. Johnson, and J. K. Ruff, *ibid.*, **3**, 1165 (1964).

[6] Philips, 500 W, Type 57300 ZB.