age *g* values close to 1.89, it is difficult to establish the existence of any definite correlations of the *g* values with ligand field parameters. However, the distortion of the complexes and the approach of the average *g* values to 2.00 appear to be in the same order as the ligand field strengths of the complexes with the ligands in the order $CH_3CN > C_3H_8O > C_4H_8O_2 \approx C_4H_8O > Cl$, but clearly this order does not hold for all of the types of compounds.

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Nitrodifluoramine and the Mass Spectral and Energetic Characterization of All Known Nitrogen–Oxygen–Flourine Compounds at Cryogenic Temperatures[1]

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In recent years there has been a great interest in nitrogen–oxygen–fluorine compounds because of their possible use as high-energy oxidizer ingredients. Four of the five heretofore known compounds, nitrosyl fluoride (ONF), nitryl fluoride (NO_2F), fluorine nitrate (NO_3F), and trifluoramine oxide (ONF_3), have been well reviewed.[2] The fifth member of this group, nitrosodifluoramine ($ONNF_2$), a dark purple substance which decomposes even below −70°, has been reported by only one laboratory.[3]

The mass spectral and energetic characterization of each of these compounds was undertaken, but those for $ONNF_2$ and a new compound reported herein, O_2NNF_2, were impossible without rather elaborate cryogenic inlet techniques[4] due to the instability of these two compounds.

Experimental Section

Equipment.—Syntheses employed a passivated copper vacuum rack assembly and either Pyrex or Monel reactors. Analyses employed a Bendix Model 14-107 time-of-flight mass spectrometer adapted to include a cryogenic analytical facility which permitted the reaction products to be analyzed without prior warm-up.[4]

N–O–F Compounds.—The known N–O–F compounds were prepared using previously published methods: ONF by the gas phase reaction of F_2 and NO;[5] NO_2F and NO_3F by passing F_2 over solid $NaNO_2$ and KNO_3, respectively;[6,7] $ONNF_2$ in 90–95% yield by passing a 10:1 mixture of NO–N_2F_4 through a glass capillary at 310° followed by a quench at −196°;[3] and ONF_3 in 20–40% yields by electric discharge of NF_3–OF_2–Ar mixtures (1:1:2) at −183° which is similar to earlier techniques[8] but gives much higher yields.

Analytical Procedure.—After the reaction products were condensed at either −196 or −183° and the volatile gases were pumped away, the sample was continuously pumped and slowly warmed whereupon the vaporized fractions were sequentially distilled into the mass spectrometer. All mass spectra and ionization efficiency curves were determined at temperatures which corresponded to a total reactor pressure of 0.1–0.2 Torr. Excess amounts of all components were pumped away before raising the temperature to volatilize the next fraction.

Appearance Potentials.—Appearance potentials were determined from the ionization efficiency curves using the extrapolated voltage difference method[9] with standard argon, $I(\mathrm{Ar}) = 15.76$ eV.

Reactions of N_2F_4.—N_2F_4 and NO_2 react immediately at room temperature yielding complete conversion to NF_3 and other stable products. However, the highly unstable white solid compound, nitrodifluoramine, O_2NNF_2, was formed in 50–75% yield by passing N_2F_4 alone through the capillary furnace at 310°, mixing with NO_2 at the exit of the capillary, and immediately quenching to −196°. Typical conditions were a total flow rate of 0.15 mmol/min and an NO_2:N_2F_4 mole ratio of about 2:1. During the warm-up procedure, small amounts of unreacted N_2F_4 and $ONNF_2$ were pumped away at −160 and −140°, respectively. Mass spectra between −135 and −130, above −105, and above −75° were attributed to O_2NNF_2, N_2O_3, and NO, respectively.

The reaction of N_2F_4 with O_3 was studied by passing N_2F_4 through the glass capillary furnace at 310° and immediately quenching the effluent onto a thin layer of liquid O_3 at −196°. All six N–O–F compounds were produced, but in repeating this experiment to obtain a more detailed characterization of the reaction products, a violent explosion occurred when the pyrolyzed N_2F_4 was initially added to the condensed ozone. The reaction of N_2F_4 with O_3 therefore looks promising, but this has not yet been pursued further due to the dangers of explosions. Similar gas-phase experiments followed by an immediate quench to −196° indicated essentially no reaction.

Results

Mass Spectra.—The data are summarized in Table I wherein small corrections for O_2NNF_2 have been made to account for the presence of varying amounts of N_2F_4 (based upon the mass peak at *m/e* 85, *i.e.*,

TABLE I

POSITIVE ION MASS SPECTRA OF N–O–F COMPOUNDS

		Rel intens at 70 eV, %					
m/e	Ion	ONF	NO_2F	NO_3F	$ONNF_2$	ONF_3	O_2NNF_2
14	N^+	6.0	4.5	2.0	8.0	3.0	6.0
16	O^+	4.0	11.0	10.0	2.5	2.5	8.0
19	F^+	5.0	3.5	2.0	3.0	7.0	2.0
28	N_2^+				3.0		4.0
30	NO^+	100.0	75.0	43.0	100.0	100.0	80.0
33	NF^+	3.5	1.5		28.0	5.5	20.0
35	OF^+			4.0			
44	N_2O^+				<0.2[a]		0.5
46	NO_2^+		100.0	100.0			100.0
47	N_2F^+				<0.1[a]		<0.3[a]
52	NF_2^+				18.0	1.5	15.0
65	NO_2F^+		1.5				
68	ONF_2^+					75.0	
87	ONF_3^+					0.1	
Temp,[b] °C		−140 to −145	−150 to −155	−140 to −145	−148 to −153	−165	−130 to −135

[a] Possibly due to impurities. [b] Temperatures at which spectra were observed correspond to vapor pressures of 0.1–0.2 Torr.

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TABLE II

APPEARANCE POTENTIALS OF N–O–F COMPOUNDS USING THE EXTRAPOLATED DIFFERENCE METHOD AND ARGON AS THE ENERGY STANDARD

Ion source process		Ion	AP_{exptl}, eV	Repetitions	AP_{calcd},[a] eV
$\mathrm{ONF + e^- \rightarrow NO^+ + F^- + e^-}$	(1)	$\mathrm{NO^+}$	8.33 ± 0.10	5	8.11
$\mathrm{NO_2F + e^- \rightarrow NO_2F^+ + 2e^-}$	(2)	$\mathrm{NO_2F^+}$	13.15 ± 0.12	10	...
$\mathrm{NO_2F + e^- \rightarrow NO_2^+ + F + 2e^-}$	(3)	$\mathrm{NO_2^+}$	13.49 ± 0.12	8	13.15
$\mathrm{NO_3F + e^- \rightarrow NO_2^+ + OF + 2e^-}$	(4)	$\mathrm{NO_2^+}$	12.62 ± 0.10	7	12.48
$\mathrm{ONNF_2 + e^- \rightarrow NO^+ + NF_2 + 2e^-}$	(5)	$\mathrm{NO^+}$	10.08 ± 0.13	8	9.74
$\mathrm{ONNF_2 + e^- \rightarrow NF_2^+ + NO + 2e^-}$	(6)	$\mathrm{NF_2^+}$	12.81 ± 0.03	7	12.49
$\mathrm{ONF_3 + e^- \rightarrow ONF_2^+ + F + 2e^-}$	(7)	$\mathrm{ONF_2^+}$	14.15 ± 0.03	9	...
$\mathrm{O_2NNF_2 + e^- \rightarrow NO_2^+ + NF_2 + 2e^-}$	(8)	$\mathrm{NO_2^+}$	11.71 ± 0.11	9	...

[a] Derived using "selected" prior data: $I(\mathrm{NO}) = 9.25$ eV;[10] $I(\mathrm{NO_2}) = 11.0$ (this work); $I(\mathrm{NF_2}) = 12.0$ eV;[10] $\Delta H_f(\mathrm{NO}) = 0.94$ eV;[11] $\Delta H_f(\mathrm{NO_2}) = 0.34$ eV;[11] $\Delta H_f(\mathrm{ONF}) = -0.68$ eV;[12] $\Delta H_f(\mathrm{NO_2F}) = -1.12$ eV;[13] $\Delta H_f(\mathrm{NF_2}) = 0.37$ eV;[14] $\Delta H_f(\mathrm{ONNF_2}) = 0.82$ eV;[3] $\Delta H_f(\mathrm{NO_3})\mathrm{F} = 0.12$ eV;[13,11] $\mathrm{EA(F)} = 3.448$ eV;[15] $\Delta H_f(\mathrm{OF}) = 1.26$ eV;[16] $\Delta H_f(\mathrm{F}) = 0.69$ eV.[11,17]

$\mathrm{N_2F_3^+}$). Since all the unreacted $\mathrm{N_2F_4}$ had been pumped away below −160°, the small amounts of $\mathrm{N_2F_4}$ present at −130° arose from the slight decomposition of $\mathrm{O_2NNF_2}$, even at this temperature. With a conventional room-temperature inlet system rather than the cryogenic system, only the decomposition products of NO and $\mathrm{N_2F_4}$ from $\mathrm{ONNF_2}$ and $\mathrm{NO_2}$ and $\mathrm{N_2F_4}$ from $\mathrm{O_2NNF_2}$ were observed. In the purified cryogenic samples of $\mathrm{ONNF_2}$ and $\mathrm{O_2NNF_2}$, $\mathrm{N_2F_4}$ cannot be present in other than trace amounts since dominant ions in its spectrum, such as m/e 47, $\mathrm{N_2F^+}$, and m/e 85, $\mathrm{N_2F_3^+}$, are here present with only trace intensities. Clearly the data are such that the presence of any compound in any mixture may be readily assessed.

Fragments containing the fluorine atom are reluctant to form a positive ion. Only $\mathrm{ONF_3}$ exhibits a dominant positive ion fragment containing F, but, even here, the major peak is $\mathrm{NO^+}$ which results from the rupture of three bonds, an unusual event for a major fragment. The parent molecular ions were not observed except for very low intensities from $\mathrm{NO_2F}$ and $\mathrm{ONF_3}$.

The $\mathrm{F^-}$ ion is the dominant peak in the negative ion spectrum of each species except for $\mathrm{NO_3^-}$ from $\mathrm{NO_3F}$ and $\mathrm{NO_2^-}$ from $\mathrm{O_2NNF_2}$. $\mathrm{NO_2^-}$ is also a major ion from $\mathrm{NO_3F}$ and a minor ion from $\mathrm{NO_2F}$. $\mathrm{O^-}$ appears as a minor ion from every compound except $\mathrm{ONF_3}$. Other ions include $\mathrm{OF^-}$ from $\mathrm{NO_3F}$, $\mathrm{NF_2^-}$ from $\mathrm{ONNF_2}$ and $\mathrm{O_2NNF_2}$, and $\mathrm{ONF_2^-}$, $\mathrm{ONF^-}$, and $\mathrm{F_2^-}$ from $\mathrm{ONF_3}$. No parent negative ions were observed.

Vapor Pressures.—The temperatures at which the vapor pressures of $\mathrm{ONNF_2}$ and $\mathrm{O_2NNF_2}$ are 1 Torr were estimated to be -141 ± 2 and $-123 \pm 2°$, respectively, from mass spectral intensity comparisons using previous vapor pressure data on the other four compounds.

Appearance Potentials.—These data (see Table II) were developed only for those ionization efficiency curves that were similar to that of the argon calibrating gas and which therefore were well behaved for use of the extrapolated voltage difference method. The ion source processes attributed to each appearance potential and the theoretical appearance potential for these processes calculated from the best previous values of standard heats of formation, ionization potentials, and electron affinities also appear in Table II.[3,10–17] All calculations are referred to reactants and products in their standard states at 298°K.

Derived Thermodynamic Quantities.—Several thermodynamic quantities can be derived from the experimental appearance potentials: $\Delta H_f(\mathrm{ONF}) = \Delta H_f(\mathrm{NO}) + I(\mathrm{NO}) + \Delta H_f(\mathrm{F}) - \mathrm{EA(F)} - A(\mathrm{NO^+, ONF}) = 0.94$[11] $+ 9.25$[10] $+ 0.69$[11,17] $- 3.448$[15] $- 8.33 = -0.90$ eV, which is 0.22 eV lower than the only previous value of −0.68 eV;[12] $\Delta H_f(\mathrm{NO_2F}) = \Delta H_f(\mathrm{NO_2}) + I(\mathrm{NO_2}) + \Delta H_f(\mathrm{F}) - A(\mathrm{NO_2^+, NO_2F}) = 0.34$[11] $+ 11.0 + 0.69 - 13.49 = -1.46$ eV, which is 0.34 eV lower than the previous value of −1.12 eV;[13] and $D(\mathrm{NO_2{-}OF}) = \Delta H_f(\mathrm{NO_2}) + \Delta H_f(\mathrm{OF}) - \Delta H_f(\mathrm{NO_3F}) = A(\mathrm{NO_2^+, NO_3F}) - I(\mathrm{NO_2}) = 12.62 - 11.0 = 1.62$ eV. Since the previous values for $\Delta H_f(\mathrm{OF})$ are probably much less accurate (see Discussion) than those for $\Delta H_f(\mathrm{NO_2})$ and $\Delta H_f(\mathrm{NO_3F})$, $A(\mathrm{NO_2^+, NO_3F})$ leads to $\Delta H_f(\mathrm{OF}) = 1.62 + \Delta H_f(\mathrm{NO_3F}) - \Delta H_f(\mathrm{NO_2}) = 1.62 + 0.12$[11,13] $- 0.34 = 1.40$ eV.

$\Delta H_f(\mathrm{ONNF_2})$ can be calculated from $\Delta H_f(\mathrm{ONNF_2}) = \Delta H_f(\mathrm{NO}) + I(\mathrm{NO}) + \Delta H_f(\mathrm{NF_2}) - A(\mathrm{NO^+, ONNF_2}) = 0.94 + 9.25 + 0.37$[14] $- 10.08 = 0.48$ eV and from $\Delta H_f(\mathrm{ONNF_2}) = \Delta H_f(\mathrm{NF_2}) + I(\mathrm{NF_2}) + \Delta H(\mathrm{NO}) - A(\mathrm{NF_2^+, ONNF_2}) = 0.37 + 12.0$[10] $+ 0.94 - 12.81 = 0.50$ eV, both of which are in excellent agreement but significantly below the only previous value of 0.82 eV.[3]

The heat of formation of $\mathrm{ONF_3}$ cannot be derived from $A(\mathrm{ONF_2^+, ONF_3})$ for comparison with an earlier value[8b] since $\Delta H_f(\mathrm{ONF_2^+})$ is not independently known. Earlier photoionization experiments with $\mathrm{ONF_3}$ yielded $A(\mathrm{ONF_2^+}) = 13.59$ eV.[18] Our value of 14.15 eV is 0.56 eV higher due, most probably, to the difference between the vertical and adiabatic transitions since $\mathrm{ONF_2^+}$ is planar whereas $\mathrm{ONF_3}$ is nearly tetrahedral.[18]

The heat of formation of nitrodifluoramine is $\Delta H_f(\mathrm{O_2NNF_2}) = \Delta H_f(\mathrm{NO_2}) + I(\mathrm{NO_2}) + \Delta H_f(\mathrm{NF_2}) - A(\mathrm{NO_2^+, O_2NNF_2}) = 0.34 + 11.0 + 0.37 - 11.71 = 0.00 \pm 0.11$ eV. Ionization efficiency data of somewhat lower quality yielded $A(\mathrm{NO^+, O_2NNF_2}) = 13.20 \pm 0.01$ eV allowing an independent calculation of $\Delta H_f(\mathrm{O_2NNF_2}) = -0.06$ eV. The measurement of A

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(NF_2^+, O_2NNF_2) was meaningless due to the presence of small amounts of N_2F_4 and/or NF_2 resulting from the slight decomposition of O_2NNF_2 even at about −130°. Since the vapor pressure of NO_2 is exceedingly low at −130°, any NO_2 produced by the decomposition of O_2NNF_2 would be immediately condensed in the mass spectrometer inlet system before being detected.

Discussion

The possibility that the spectrum assigned here as the new compound O_2NNF_2 could be due instead to a mixture of previously known compounds may be ruled out in the following manner. The compound $ONNF_2$ cannot be contributing to the spectrum since $ONNF_2$ is a purple solid which is pumped away below −140° whereas the substance in question is a white solid at −130 to −135°. The peak at NO_2^+ cannot be arising from NO_2F or NO_3F since there are no additional peaks at NO_2F^+ or OF^+. Furthermore, the NO_2^+ peak cannot be arising from either NO_2 or N_2O_3, since from blank experiments the vapor pressures of these compounds are exceedingly low at −130°. The fact that the spectrum in question cannot be attributed to known compounds and the fact that it uniformly increased with increasing temperature and uniformily decreased when the substance was pumped away prove that the spectrum is due to a new compound. Since the preparation of this compound involved the combination of NO_2 and NF_2 radicals, since the mass spectrum suggests that the structure contains NO_2 and NF_2 groups, since the synthesis of the related compound $ONNF_2$ was successfully duplicated and the compound was characterized, and since a stable electronic configuration for O_2NNF_2 is possible,[1b] it was concluded that this new compound was very likely nitrodifluoramine, O_2NNF_2.

The heats of formation of ONF, NO_2F, and $ONNF_2$ derived from the appearance potential data are lower than earlier values suggesting possible excess energy in the ion processes. However, some of the necessary thermodynamic values are not universally accepted. In particular, much controversy has arisen over the values for the heat of formation of OF and the ionization potential of NO_2.

A recent critical discussion of the dissociation energies D(FO–F) and D(O–F) concluded that the most likely value for D(FO–F) was 1.7 ± 0.2 eV which implied D(O–F) = 2.2 ± 0.2 eV. Recalculating D(O–F) using the revised but still controversial value of $\Delta H_f(F) = 0.69^{11,17}$ eV, D(FO–F) = 1.7 ± 0.2 eV leads to $\Delta H_f(OF) = D(FO\text{–}F) + \Delta H_f(OF_2) - \Delta H_f(F) = 1.7 + 0.25^{19} - 0.69 = 1.26 \pm 0.2$ eV and $D(O\text{–}F) = \Delta H_f(O) + \Delta H_f(F) - \Delta H_f(OF) = 2.58 + 0.69 - 1.26 = 2.01 \pm 0.2$ eV. With no evidence of excess energy occurring in the appearance potential of NO_2^+ from NO_3F, our newly derived value of $\Delta H_f(OF) = 1.4 \pm 0.1$ eV is well within experimental uncertainties and seems reasonably well founded. If some excess energy is produced in process 4 of Table II, the derived value of ΔH_f(OF) would be lowered from 1.40 eV accordingly.

The most reliable determinations of $I(NO_2)$ appear to fall into two groups:[10] those centered around 10.0 eV, which may be attributed to the adiabatic ionization potential, and those centered around 11.0 eV, which may correspond to the vertical ionization potential. The large difference between the adiabatic and vertical values is caused by the NO_2 molecule being bent while the NO_2^+ ion is linear. We determined the electron impact value of $I(NO_2) = 11.0 \pm 0.15$ eV from nine independent measurements, and we have used this value in calculations in this work.

The derived heats of formation of $ONNF_2$ and O_2NNF_2 yield respective N–N dissociation energies of $D(ON\text{–}NF_2) = 0.82$ eV and $D(O_2N\text{–}NF_2) = 0.71$ eV which correspond favorably with $D(F_2N\text{–}NF_2) = 0.96$ eV, $D(O_2N\text{–}NO_2) = 0.59$ eV, and $D(O_2N\text{–}NO) = 0.42$ eV.

In summary, this work has demonstrated that the mass spectrometer is a useful tool in studying the synthesis and molecular energetics of nitrogen–oxygen–fluorine compounds. In particular, the cryogenic inlet system used here was shown to be essential for the identification and characterization of the unstable compounds nitrosodifluoramine ($ONNF_2$) and nitrodifluoramine (O_2NNF_2).

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Preparation and Reaction of Allylamine–Rhodium(III) Chloride Complexes

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Allylamine may coordinate with an olefinic double bond and an amino group serving as a bidentate ligand. In the case of allylamine complexes of copper(I)[1] and platinum(II),[2–4] such a bidentate coordination has been reported. However, the reaction of coordinated allylamine has not been reported. In this paper we report the preparation of allylamine complexes of rhodium(III) chloride and their reaction in ethanol solution.

Experimental Section

The infrared spectra were obtained with Japan Spectroscopic Models 102 and 103 spectrometers. The samples were prepared as Nujol mulls or KBr pellets. Glpc analyses were carried out with an Ohkura gas chromatograph, a 3-m Carbowax 20M on Diasolid A column at 70°, and a nitrogen flow rate of 50 cm^3/min.

Preparation of Complexes. (a) **$RhCl_3(C_3H_5NH_2)(H_2O)$.**—Allylamine (75 μl, 1 mmol) was added to a solution of rhodium trichloride trihydrate (264 mg, 1 mmol) in 10 ml of ethanol with stirring by magnetic stirrer. The reaction mixture turned to a light red from a deep red and a reddish brown precipitate appeared. After stirring for several minutes, the precipitate was filtered, washed with ether, and dried under reduced pressure.

(b) **$RhCl_3(C_3H_5NH_2)_2$.**—Bis(allylamine)rhodium(III) chloride was synthesized by the same method as that for $RhCl_3(C_3H_5NH_2)(H_2O)$. One hundred and fifty microliters of allylamine (2 mmol) was added in this case.

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