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ARPA ORDER No. 184-62

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THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research and Advanced Technology

United Technology Center

DIVISION OF UNITED AIRCRAFT CORPORATION

P.O. BOX 358, SUNNYVALE, CALIFORNIA

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**FINAL TECHNICAL SUMMARY REPORT
1 MARCH 1961 THROUGH 28 FEBRUARY 1963
CONTRACT No. Nonr 3433(00)**
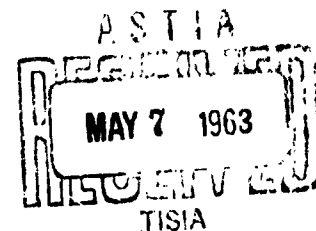
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**DEPARTMENT OF THE NAVY
OFFICE OF NAVAL RESEARCH
WASHINGTON 25, D. C.**

United Technology Center

DIVISION OF UNITED AIRCRAFT CORPORATION

SUNNYVALE, CALIFORNIA   739-4880

30 April 1963
MC 167-63

Director
Advanced Research Projects Agency
Washington 25, D. C.

        VIA: Office of Naval Research
              Washington 25, D. C.
              Attention: Code 426

Subject: Transmittal of Final Technical Summary Report

Reference: Contract Nonr 3433(00)

Gentlemen:

United Technology Center submits the subject report UTC 2002-FR in accordance
with requirement set forth in Section D, Paragraph (3) of the referenced
contract.

This report covers the period, 1 March 1961 to 28 February 1963.

                    Very truly yours,

                    UNITED TECHNOLOGY CENTER

                    M. Cohen, Director
                    Contract Management

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Enclosure

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Issued 29 March 1963

THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING

Research and Advanced Technology
UNITED TECHNOLOGY CENTER
Division of United Aircraft Corporation
Sunnyvale, California

FINAL TECHNICAL SUMMARY REPORT
FOR PERIOD 1 MARCH 1961 THROUGH 28 FEBRUARY 1963
Under Contract No. Nonr 3433(00)

Propulsion Chemistry Branch
Materials Sciences Division
Office of Naval Research
ARPA Order No. 184-62

(This project is financially supported by the
Advanced Research Project Agency)

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ABSTRACT

The objectives of the work reported herein have been the determination of the strengths of oxygen-fluorine bonds in chemical species from thermo-chemical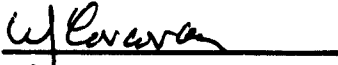 data and the correlation of the variations of the bond strength to the molecular structure. The ultimate purpose has been the definition of a sufficiently general O-F bond energy to permit a valid theoretical evaluation of the potential of species containing this grouping as rocket propellant oxidizers.

The heat of formation of fluorine nitrate, NO_3F, has been determined to be +2.5 ±0.6 kcal/mole. This highly accurate value was obtained from the heat release from the synthesis reaction involving the direct fluorination of sodium nitrate.

The heat of formation of fluorine perchlorate, ClO_4F, has been determined to be +37.5 ±9 kcal/mole from the measured value of the heat of hydrolysis. An essentially corroborating value of +37 ±15 kcal/mole for the heat of formation was obtained from the heat release from the reaction of fluorine perchlorate with hydrogen; however, experimental limitations contribute to the large uncertainty associated with the value.

The direct synthesis reaction for nitryl fluoride, NO_2F, has yielded a heat of formation value of -25.8 ±0.5 kcal/mole. The heat released from the fluorination of nitrogen dioxide corresponds to the existing value for the heat of formation.

Procedures which will yield thermochemical information leading to the heat of formation of the compounds fluorine fluorosulfonate (FSO_3F) and pentafluorosulfur hypofluorite (F_5SOF) have been specified. Well-defined reactions with thermodynamically known products are available for evalu-ation of the thermochemical properties of these O-F bonded species.

As a consequence of this work a reasonable heat of formation for O-F bonded species may be generated, employing a single representative value for the strength of this bond. A narrow range of values (37 to 47 kcal/mole) for the O-F bond energy was obtained from the heat of formation and normal assumptions for the other bonds present in the molecule for the species for which data was obtained or available. The average value for the energy of the O-F bond for all O-F bonded species was found to be 43 kcal/mole which corresponds very closely to the value of 45 kcal/mole derived from the heat of formation of oxygen difluoride. The variation found in the O-F bond energies for the species is less than is observed for other bonds.

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1.0 INTRODUCTION

This report is the Final Technical Summary Report on the thermochemistry of O-F bonded compounds. The work accomplished under Contract Nonr 3433(00) in the synthesis, thermochemical and analytical evaluation of O-F bonded compounds, and in the determination of the O-F bond energy is summarized. The report covers the achievements of the program since its inception, 1 March 1961, and is issued in lieu of the Eighth Quarterly Technical Report, covering the period 1 December 1962 through 28 February 1963.

The program for the determination of the thermochemistry of oxygen-fluorine bonding was undertaken to provide a background of technical data to evaluate more accurately the potential of chemical species possessing O-F bonds as oxidizing agents in high performance propellant systems. An essential parameter in evaluation of the potential of a new or hypothetical compound is an accurate estimate of the heat of formation. Entirely satisfactory theoretical analyses of the performance of propellants may be obtained provided the energy content is known within several kilocalories per mole. Estimates of the heat of formation can generally be made on the basis of bond energy summations. However, lack of an adequate general value for the energy of the O-F bond to be used in the calculations has led to this program to obtain this datum.

As a consequence of the relatively low average O-F bond energy inferred from thermochemical data on OF_2, liquid and solid species containing O-F bonding were expected to exhibit performance capabilities approaching that of cryogenic oxidizers. However, the O-F bond energies derived from published data on other O-F-containing species have exhibited a wide range of values from approximately 25 to 60 kcal/mole depending upon the assumed values for the bond energies of the other bonds in the molecule. The result

of the possible wide range of O-F bond energies in chemical species generally negates the value of theoretical analysis unless the variation is predictable. From the published information, the effect of substituent groups on the O-F bond apparently produces major variations in the O-F bond strength. While this variation is a reciprocal effect, no loss in validity is suffered in the analysis of the performance potential of a specific compound in ascribing the perturbation to the O-F bond alone. A low O-F bond energy, whether real or apparent, is a desirable characteristic because, in either event, a a more endothermic species is involved. Therefore, the basic problem no longer is simply the definition of a representative value for the O-F bond energy but must also include the evaluation of the effect of the substituent groups. Since this effect is not readily predicted on theoretical grounds, an empirical correlation of the O-F bond energies with molecular structure and chemical substituent is required.

The objective of the research effort under Contract Nonr 3433(00) has been the determination of reliable thermochemical data for O-F bonded species from which valid heat of formation values and appropriate O-F bond energies could be defined. Among the species possessing O-F bonded structures which were considered for evaluation were NO_3F, ClO_4F, CF_3OF, FSO_3F, and F_5SOF. Consideration was also given to the N-F bonded species, NO_2F. From the derived data, a representative value for the O-F bond energy can be obtained; in addition, the perturbing effect of substituent groups can be evaluated, leading to a generalized statement of the O-F bond energy in terms of molecular structure. From this understanding of the effect of neighboring groups on the stability of the O-F bond stems the capability of predicting, with reasonable accuracy, the performance potential of hypothetical species possessing structures containing O-F bonds without resorting to lengthy synthesis and thermochemical evaluation of each individual compound.

2.0 TECHNICAL ACHIEVEMENTS

The technical achievements of the program to elucidate the thermochemistry of oxygen-fluorine bonding include the preparation of high purity samples of species containing the bonding under discussion, the development of reliable analytical procedures for the assay of the materials used in thermochemical evaluation, the quantitative determination of the products obtained during the evaluation, and the definition of the reaction systems most amenable to practical calorimetric techniques. The specific materials which have been evaluated are fluorine nitrate (NO_3F), fluorine perchlorate (ClO_4F), nitryl fluoride (NO_2F), and fluorine fluorosulfonate (FSO_3F). Preliminary studies of the species trifluoromethyl hypofluorite (CF_3OF) and pentafluorosulfur hypofluorite (F_5SOF) were also conducted.

As a result of the effort reported herein, a value for the heat of formation of NO_3F accurate to ± 0.6 kcal/mole has been obtained from calorimetric investigation of the synthesis reaction while the synthesis, combustion and hydrolysis reactions of ClO_4F have yielded a reasonable value for its heat of formation. A procedure has been established to permit evaluation of the heat of formation of FSO_3F and the heat of formation of NO_2F has been obtained from the synthesis reaction which corroborates the value obtained by others. Despite evidence for considerable dissociation of NO_2F, the measurement of the dissociation pressure as a function of temperature gave results which could not be directly interpreted in terms of the heat of formation.

The report is organized into separate sections related to the achievements on each compound studied and discussions related to the specific species. A discussion follows which generalizes the results obtained in terms of the thermochemistry of the O-F bond.

2.1 HEAT OF FORMATION OF FLUORINE NITRATE

The physical and chemical properties of NO_3F have been studied extensively by numerous workers; however, thermochemical data with regard to the heat of formation of NO_3F and the related O-F bond energy have not been obtained from the previously reported research efforts. (During the course of this investigation, a heat of formation of -4.2 ± 0.9 kcal/mole for NO_3F was reported elsewhere[1]*. On the basis of bond energy estimates, this value was more exothermic than expected.) Therefore, a program was instituted to evaluate the thermochemical properties of this O-F bonded species.

Several reaction systems involving NO_3F have been reported which are potentially applicable to the determination of the heat of formation of fluorine nitrate by calorimetric methods. A preliminary investigation was conducted to ascertain the applicability of several types of reactions to calorimetric investigation and to permit the selection of the most effective procedure. Combustion, decomposition, and synthesis reactions were among those considered for this study.

2.1.1 Evaluation of NO_3F Reactions for Calorimetric Study

Since NO_3F is a potent chemical oxidizer, combustion reactions with simple fuels were evaluated for thermochemical application. Upon gas phase mixing in a modified combustion bomb system, NO_3F reacted hypergolically with NH_3, NO, and H_2S, and to varying extents, after spark initiation, with H_2, HCl, CO, and BF_3. No reaction could be induced in a NO_3F-CH_4 mixture. However, a varying distribution of solid and gaseous products was noted in each of these reactions. No combustion system was observed which consistently yielded well-defined products.

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* Superscript numbers denote references appearing on page 37.

Others[2] have reported that the spark-induced decomposition of fluorine nitrate yields only nitrosyl fluoride and oxygen. The stoichiometry of this decomposition was reported to be

$$NO_3F \rightarrow NOF + O_2. \tag{1}$$
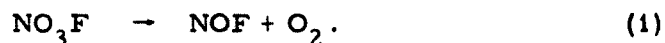
Because of the simple products, this reaction appeared promising from a calorimetric standpoint. However, in this laboratory, studies employing fuse wire to initiate gas phase decomposition have shown the reaction to be more complex than represented above with variable formation of NO_2, NO, and NO_2F in conjunction with NOF and O_2.

Fluorine nitrate has been found by others[3] and by this laboratory to react quantitatively with an aqueous potassium iodide solution. As the results of a calorimetric study of the aqueous system would be difficult to interpret because of the ill-defined final state of the products, the reaction of fluorine nitrate with solid anhydrous potassium iodide was evaluated. The results of several solid phase studies indicate that the reaction between solid potassium iodide and NO_3F proceeds to a maximum conversion of only five percent. This low conversion precludes further calorimetric study.

The original preparation of fluorine nitrate [4] involved the fluorination of nitric acid according to the following equation:

$$HNO_3 \ (\ell) + F_2 \ (g) \rightarrow NO_3F \ (g) + HF \ (g) \tag{2}$$
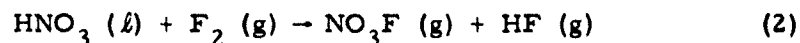
In principle, this reaction is ideally suited for calorimetric study; however, experimental difficulties associated with the degree of solubility of fluorine and generated fluorine nitrate in the nitric acid were found to reduce the over-all material balance accuracy.

The reaction of fluorine with solid anhydrous sodium nitrate has been reported[5] to yield fluorine nitrate as the only gaseous product:

$$NaNO_3 \text{ (s)} + F_2 \text{ (g)} \rightarrow NO_3F \text{ (g)} + NaF \text{ (s)} \qquad (3)$$
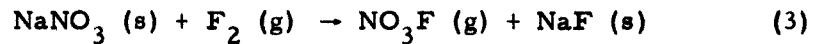
Synthesis of fluorine nitrate through Equation 3 was found by this laboratory to give essentially theoretical yields. With an excess of finely divided sodium nitrate and undiluted fluorine, yields up to about 98 percent were realized. This system, because of its high yields, simplicity, and the absence of detectible side reactions, was chosen for the thermochemical evaluation of the heat of formation of fluorine nitrate.

2.1.2 Experimental

The basic apparatus used in the measurement of the heat evolved by reaction of fluorine and sodium nitrate was an adiabatic flow calorimeter operated at 25° C. The main calorimetric system consisted of a U-tube reactor constructed from 12 inches of 3/8-inch O.D. copper tubing. The reactor was packed with a weighed quantity (approximately 6 g.) of finely divided anhydrous reagent grade sodium nitrate (ca. 50 microns in diameter) and connected to a supply cylinder of fluorine (98 percent purity, Allied Chemical Corporation) through a feed line. The temperature of the calorimetric fluid was measured continuously with a precision platinum resistance thermometer and a Mueller bridge before, during, and after the reaction. The heat capacity of the calorimetric system was evaluated by supplying a known quantity of energy from a heater to the system and by measuring the over-all temperature rise with the platinum resistance thermometer. The data for the initial and final drift rate periods were fitted to straight lines by the method of least squares, and the true temperature rise was determined by subtracting a heat leak correction employing the average slope of the two drift lines from the observed equilibrium temperature rise. A typical time-temperature curve is shown in Figure 1.
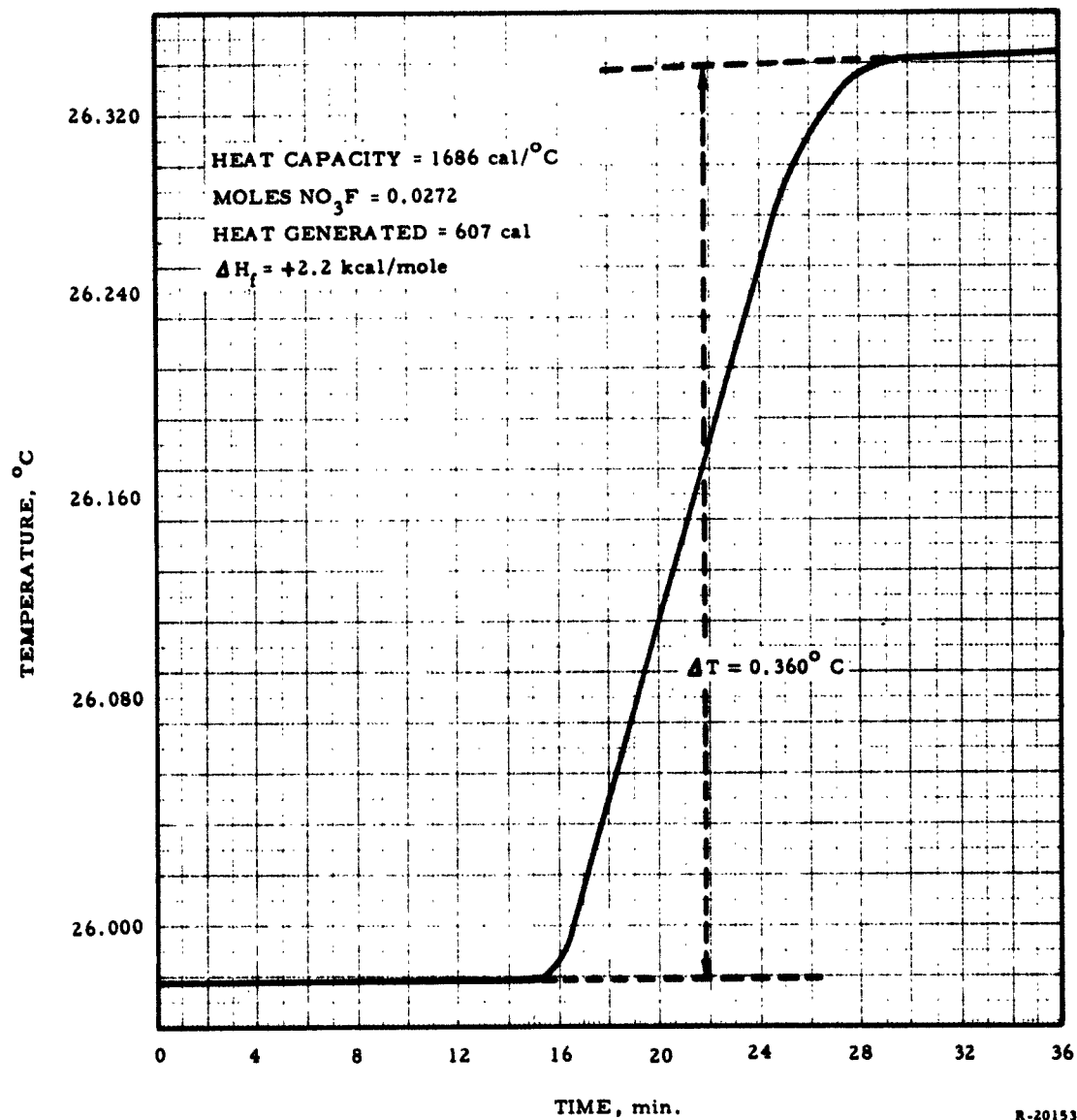
Figure 1. Calorimeter Temperature versus Time
for NO_3F Formation Reaction

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The products from the reactor, with the exception of unreacted fluorine, were trapped directly in a collecting vessel by freezing with liquid oxygen. Upon completion of the reaction, the products were allowed to gasify and the pressure accurately determined. From the known volume and pressure of the measuring system the number of moles of product was computed. The weight of the products was determined by condensing and weighing the gaseous material in the collecting vessel, thereby giving the average molecular weight of the product.

The contents of the collecting vessel were then quantitatively divided, one portion being transferred to an infrared cell for spectral analysis, and the second portion hydrolyzed in a caustic solution for chemical analysis. The infrared spectra of the fluorine nitrate synthesized during several calorimetric runs agreed well with the reported spectra[6] with prominent absorption bands at 920, 1030, 1430, 1950, and 3060 cm^{-1}; these bands are characteristic of fluorine nitrate.

Fluorine nitrate was originally reported to undergo the following hydrolysis reaction[6]:

$$NO_3F \ (g) + 2NaOH \ (aq) \rightarrow NaNO_3 \ (aq) + NaF(aq) + H_2O(\ell) + 1/2 \ O_2(g) \quad (4)$$
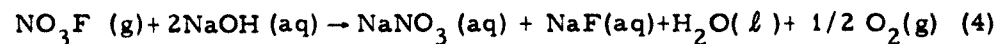
The analyses of the NO_3F-NaOH reaction product for nitrate, fluoride, and decrease in hydroxide for several fluorine nitrate samples from calorimetric runs agreed well with the stoichiometry defined by Equation 4.

The fluorine that did not react with sodium nitrate to form fluorine nitrate and sodium fluoride was reacted with an aqueous solution of potassium iodide in the trap in the exit line of the calorimetric system, and the amount of iodine released was titrated according to the conventional starch-thiosulfate method, thus obtaining an additional fluorine balance.

Upon completion of each calorimetric determination, the U-tube reactor was again weighed and the contents accurately analyzed for the remaining nitrate and fluoride content generated from the fluorine nitrate synthesis reaction. According to the stoichiometry demanded by Equation 3, a solid phase weight loss of one gram should be equivalent to 23.3 m moles of fluorine nitrate and sodium fluoride. Good agreement was achieved between each of the independent checks on the quantity and purity of the fluorine nitrate generated in the several calorimetric studies. The derived data are summarized in Table I.

2.1.3 Discussion

The heat of formation per mole of fluorine nitrate was derived from the experimental heat of reaction and reported standard heats of formation of $NaNO_3(s)$ and $NaF(s)$ of -111.5 and -136.0 kcal/mole, respectively[7]. Using these values, the standard heat of formation per mole of fluorine nitrate becomes

$$\Delta H_{f\ 298}^{o} \quad NO_3F(g) = 24.5 + \Delta H_{r\ 298} \quad . \tag{6}$$

Using the average heat of reaction for the determinations of -22.0 kcal/mole (Table I), the derived heat of formation value of fluorine nitrate from Equation 6 is $+2.5 \pm 0.5$ kcal/mole.

Analytical, material balance, gas density, and hydrolysis measurements result in similar percent yields of fluorine nitrate and serve as independent checks of the derived heat of formation value for fluorine nitrate for each experiment. The validity of the results is substantiated by the essentially constant value obtained in the several experimental determinations, which would be sensitive to side reactions, resulting in an observed positive or negative trend in the heat of formation values as a function of fluorine nitrate yield.

TABLE I

SYNTHESIS AND CALORIMETRIC DATA FOR NO$_3$F

	Run Number						
	3.[*]	5.[*]	6.[*]	7.[**]	9.[**]	10.[**]	12.[**]
Moles F$_2$ used	0.0576	0.0455	0.0489	0.0363	0.0139	0.0139	0.0134
Flow Rate, ml/min	107	120	107	96	50	54	43
Moles NO$_3$F (wt. loss)	0.0284	0.0212	0.0271	0.0337	0.0130	0.0131	0.0126
Percent yield (wt. loss)	49.3	46.6	55.4	92.8	93.5	94.2	94.0
Moles NO$_3$F (analysis)	0.0231	0.0226	0.0274	0.0336	0.0136	0.0135	0.0131
Percent yield (analysis)	40.1	49.7	56.0	92.6	97.8	97.1	97.8
Moles NO$_3$F (weighing)	-	-	-	-	-	0.0134	0.0124
Percent yield (weighing)	-	-	-	-	-	96.4	92.5
Moles NO$_3$F (pressure)	-	0.0216	0.0272	0.0344	-	0.0131	0.0122
Percent yield (pressure)	-	47.5	55.6	94.8	-	94.2	91.0
Avg. No. Moles NO$_3$F	0.0258	0.0218	0.0272	0.0339	0.0133	0.0133	0.0126
Avg. percent yield	44.8	47.9	55.6	93.4	95.7	95.7	94.0
Calc hydrolysis: F$^-$ (millimoles)	-	21.6	20.8	-	-	7.26	7.27
NO$_3^-$ (millimoles)	-	21.6	20.8	-	-	7.26	7.27
H$^+$ (millimoles)	-	-	-	-	-	-	14.54
Found hydrolysis: F$^-$ (millimoles)	-	15.1[***]	14.2[***]	-	-	7.20	7.14
NO$_3^-$ (millimoles)	-	16.5	15.1	-	-	5.84	6.43
H$^+$ (millimoles)	-	-	-	-	-	-	14.65
ΔT ($^\circ$C)	0.324	0.287	0.360	0.434	0.179	0.172	0.166
C$_p$ calorimeter (cal/deg)	1671	1672	1686	1675	1675	1716	1688
Q generated (cal)	542	480	607	727	300	295	280
ΔH$_{r\ avg}$ (kcal/mole)	-21.0	-22.0	-22.3	-21.4	-22.6	-22.2	-22.2
ΔH$_{f\ avg}$ (kcal/mole)	+3.5	+2.5	+2.2	+3.1	+1.9	+2.3	+2.3

NOTE:
  [*] stoichiometric amounts of F$_2$ and NaNO$_3$
  [**] excess amount of NaNO$_3$
  [***] insufficient NaOH

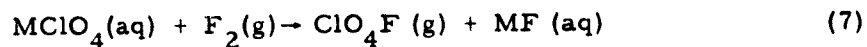## 2.2 THE HEAT OF FORMATION OF FLUORINE PERCHLORATE

2.2.1 Evaluation of ClO_4F Reactions for Calorimetric Study

Four general types of reactions involving fluorine perchlorate were investigated in order to select the most suitable approach to the thermochemical evaluation of the heat of formation of fluorine perchlorate. The types of reactions which were considered for this purpose were (1) the direct fluorination of metal perchlorates yielding ClO_4F, (2) the combustion of ClO_4F with hydrogen, (3) synthesis of ClO_4F by fluorination of 70 percent perchloric acid, and (4) hydrolysis of ClO_4F in aqueous sodium hydroxide.

The direct fluorination of either solid metal perchlorates or their aqueous solutions resulted in formation of ClO_4F:

$$MClO_4(aq) + F_2(g) \rightarrow ClO_4F(g) + MF(aq) \tag{7}$$

where M = Li, Na, K, NH_4, Ag, Mg, Ba, Al, and Fe.
The major difficulty in the derivation of the heat of formation of fluorine perchlorate from the measurement of the heat evolved during synthesis (Equation 7) was the very low rate of fluorine perchlorate formation under conditions amenable to normal calorimetric techniques. Even at very low flow rates of fluorine, conversion of the fluorine to ClO_4F was limited to less than six percent. Furthermore, the temperatures at which many of the reactions of Equation 7 proceeded at a suitable rate were considerably higher than the temperature which was feasible for direct measurement of the heat of reaction. Therefore, this approach was not pursued.

In the presence of excess hydrogen, fluorine perchlorate was expected to undergo the combustion reaction represented by Equation 8:

$$ClO_4F(g) + 5H_2(g) \rightarrow HCl(aq) + HF(aq) + 4H_2O(\ell) \tag{8}$$
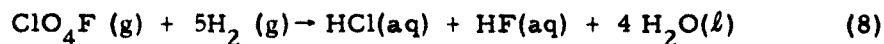
The reaction between hydrogen and ClO_4F was found to be hypergolic, thus eliminating the need for an auxiliary igniter in the calorimeter. Several combustion experiments which led to effectively complete re- action of the fluorine perchlorate were conducted. Selection of the most representative calorimetric results of several of the hypergolic reactions of fluorine perchlorate with hydrogen yielded a preliminary heat of form- ation value of $+37 \pm 15$ kcal/mole.

Calorimetric studies of the heat evolved by direct synthesis of ClO_4F were made using 70 percent perchloric acid and fluorine. The reaction, first reported by Cady[8], results in reasonable yields of ClO_4F:

$$HClO_4 \cdot 2H_2O(\ell) + F_2(g) \rightarrow ClO_4F(g) + HF(g) + 2H_2O(\ell) \qquad (9)$$
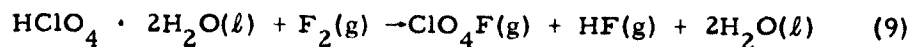
To minimize side reactions, these studies were conducted in a Kel-F reactor shown in Figure 2.

Based on a selection of experimental values derived from the measurement of heat evolved in the above reaction system, using statistical consider- ations, the heat of formation was found to be $+18.5$ kcal/mole. However, the heat of formation values retain a considerable degree of uncertainty, estimated to be ± 10 kcal/mole; this uncertainty is due to a heat transfer problem of the Kel-F reactor which results in a long equilibration period following reaction, and the large quantity of water required to cover the reactor which gives the system a large heat capacity.

Cady[8] reported that OF_2 and O_2 are side products of the reaction of 70 percent $HClO_4$ with F_2, presumably due to the following reactions:

$$2 \ F_2 + H_2O \rightarrow OF_2 + 2 \ HF \qquad (10)$$

$$F_2 + H_2O \rightarrow 1/2 \ O_2 + 2 \ HF \qquad (11)$$
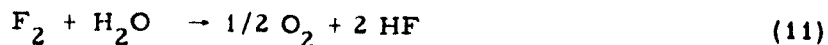
Although these highly volatile materials were not detected in the direct synthesis, their formation would introduce additional uncertainty in the derived heat of formation value of fluorine perchlorate from direct synthesis calorimetry.
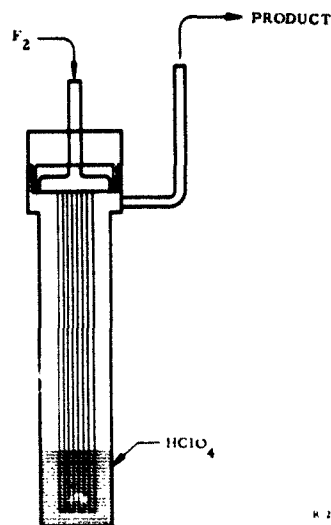
Figure 2. Kel-F Reactor

Cady[8] has reported that fluorine perchlorate undergoes hydrolysis with aqueous sodium hydroxide according to Equation 12:

$$ClO_4F(g) + 2\ NaOH(aq) \rightarrow NaClO_4(aq) + NaF(aq) + H_2O(\ell) + 1/2\ O_2(g) \quad (12)$$
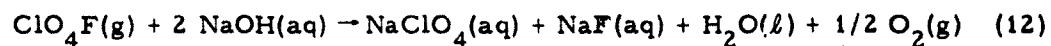
In several preliminary static hydrolyses of fluorine perchlorate by this method, chemical analyses for perchlorate ion, fluoride ion, and decrease in hydroxide ion agreed well with the stoichiometry of Equation 12.

An investigation of a flow system employing the hydrolysis reaction yielded preliminary evidence that fluorine perchlorate was hydrolyzed to greater than 80 percent under flow conditions. Therefore, a flow calorimeter seemed suited to the thermochemical evaluation of fluorine perchlorate by hydrolysis. Heat of formation values obtained by this method were in good agreement with a calculated heat of formation value based on estimated bond energies.

From chemical analyses of samples of hydrolyzed fluorine per-
chlorate from the flow calorimeter it was apparent that OF_2 was
generated by a side reaction of the hydrolysis according to the
following equation:

$$ClO_4F(g) + NaOH(aq) \rightarrow NaClO_4(aq) + 1/2\ OF_2(g) + 1/2\ H_2O(\ell) \qquad (13)$$
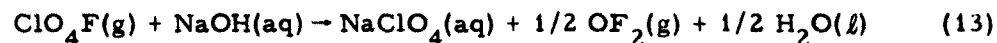
The presence of OF_2 in the exit gases of the calorimeter was estab-
lished by infrared spectra, and a correction factor was applied to the
thermochemical data based on the chemical analysis of the hydrolysis
liquid.

2.2.2 Experimental

A schematic diagram of the flow calorimeter used to measure the heat
generated by the reaction of fluorine perchlorate with aqueous sodium
hydroxide is shown in Figure 3. The main calorimetric system
consisted of a stainless steel reactor (A) immersed in the heat sink
fluid (B) in a Dewar flask; the reactor contained teflon dip spouts
extending into 25.0 ml of 0.75 N sodium hydroxide solution. Fluorine
perchlorate, prepared from fluorination of 70 percent perhcloric acid,
was transferred to a 3/8-inch O.D. copper coil (C) with a volume of
295 ml. The coil was attached to the flow calorimeter at feed line (D).
The chemical reaction was initiated by sweeping the fluorine per-
chlorate sample through the copper coil and into the hydrolysis reactor
by a positive pressure (2 psig) of dried nitrogen supplied at (E) at a
flow rate of approximately 19 ml/min. The temperature of the heat
sink fluid was determined with a precision platinum resistance
thermometer and a Mueller bridge. The temperature of the calori-
metric fluid was measured continuously before, during, and after
the reaction. The heat capacity of the calorimetric system was
evaluated by supplying a known quantity of energy from a heater
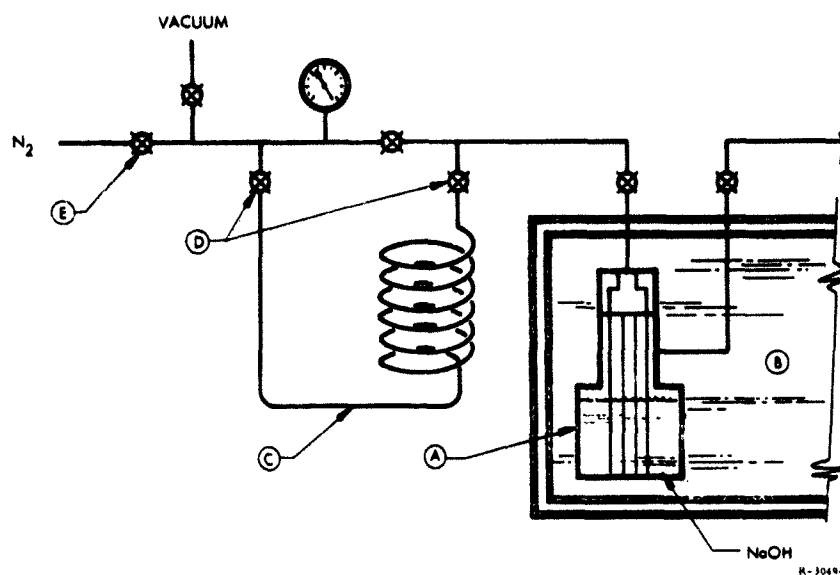
Figure 3. Schematic Diagram of Flow Calorimeter

to the system and measuring the over-all temperature rise of the
system with the platinum resistance thermometer. The data for the
initial and final drift rate periods were fitted to straight lines by the
method of least squares, and the true temperature rise was determined
by subtracting a heat leak correction employing the average slope of
the two drift lines from the observed equilibrium temperature rise.

The exit gases from the reactor were passed through three stainless
steel traps, and upon completion of the reaction, the trapped products
were allowed to vaporize and the pressure in the known volume was
determined with a calibrated Heise gage, permitting determination of
the number of moles of trapped product. During a series of
10 calorimetric runs, the traps had an efficiency ranging from
78 to 91 percent under flow conditions varying as a function of the trap
packing and temperature. The highest recovery of 91 percent was

accomplished by packing the traps with stainless steel helices and cooling to liquid nitrogen temperature. Hence, material balance from trapping methods was an insufficient measure of the extent of the reaction under the experimental conditions.

A portion of the trapped product was vaporized and transferred to an infrared cell for spectral analysis. In addition to unreacted fluorine perchlorate, a varying low percentage of perchloryl fluoride was detected. Previous synthesis studies of fluorine perchlorate prepared from Equation 9 had occasionally generated perchloryl fluoride as an impurity.

Spectral analyses of fluorine perchlorate samples used in the flow calorimeter did not reveal the presence of perchloryl fluoride; however, the impurity could be present in a concentration below the limit of infrared detectability. Perchloryl fluoride in perchloryl fluoride-fluorine perchlorate mixtures, hydrolyzed under static conditions of several days duration, was found to be essentially non-reacting with aqueous sodium hydroxide. Therefore, it was assumed that no correction for such an effect would be required. The increase in concentration of the unreacted impurity as a consequence of the reactivity of fluorine perchlorate would reveal the presence of per-chloryl fluoride in the exit gases.

Upon completion of the calorimetric determination, the reactor was disconnected and a 20.0 ml aliquot of the sodium hydroxide solution was analyzed for the generated fluoride and perchlorate contents and for the decrease in the number of moles of sodium hydroxide.

As material balance was an insufficient measure of the extent of the reaction under flow conditions, emphasis was placed on chemical analysis to determine the amount of fluorine perchlorate which had reacted. Chemical analyses for fluorine perchlorate samples hydrolyzed in the flow calorimeter did not agree as well with the stoichiometry demanded by Equation 12 as did static hydrolyses. The fluoride analysis in all but two of the ten thermochemical investigations of the reaction between fluorine perchlorate and aqueous sodium hydroxide was lower than the perchlorate analysis by an amount approximately equal to the difference between one-half the decrease in sodium hydroxide (or generated H^+) and the analyzed fluoride content; that is, the average of the fluoride and perchlorate analyses is approximately equal to one-half the H^+ analysis. (See Table II.)

The generation of OF_2 as a side reaction of the hydrolysis (Equation 13) can be rationalized from the observed analytical results. Assuming that x moles of fluorine perchlorate reacts with aqueous sodium hydroxide by the alternate OF_2 producing path, and the remaining (1-x) moles of fluorine perchlorate proceed according to the usual reaction path (Equation 12), Equations 12 and 13 may be combined as follows:

$$ClO_4F(g) + (2-x)NaOH(aq) \rightarrow NaClO_4(aq) + (1-x)NaF(aq) + \frac{x}{2}OF_2(g) + \left(1-\frac{x}{2}\right)H_2O(l) + \left(\frac{1-x}{2}\right)O_2(g) \quad (14)$$
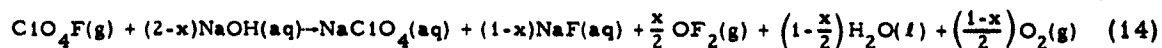
A sample of fluorine perchlorate was passed through aqueous sodium hydroxide in the reactor into an evacuated volume. The exit gases were transferred to one of the traps by condensing with liquid nitrogen and allowed to vaporize into the infrared cell. The presence of OF_2 was verified from infrared analysis.

TABLE II

CALORIMETRIC DATA FOR ClO$_4$F

	_1_	_2_	_3_	_4_	_5_	_6_	_7_	_8_	_9_	_10_	Avg.
						Run Number					
ClO$_4$F in coil, m moles	2.11	2.76	3.51	3.69	5.52	3.49	5.15	3.99	4.10	4.43	
Flow rate, cc/min	38	21	23	20	13	17	15	15	12	14	
Analyses:											
F$^-$, m moles	1.06	2.01	2.50	2.74	4.28	2.54	3.67	2.91	4.12	3.67	
ClO$_4^-$, m moles	1.56	2.36	2.80	3.14	3.53	2.74	4.53	3.34	3.62	3.98	
H$^+$, m moles	2.66	4.44	5.44	6.02	8.35	5.45	8.48	6.66	7.25	7.87	
Avg. F$^-$, ClO$_4^-$	1.31	2.19	2.65	2.94	3.92	2.64	4.10	3.13	3.88	3.83	
Δt, °C	0.066	0.113	0.131	0.141	0.170	0.117	0.202	0.151	0.163	0.180	
kcal liberated	0.144	0.254	0.289	0.317	0.380	0.252	0.448	0.334	0.358	0.396	
x *	0.54	0.42	0.44	0.54	—	0.36	1.12	0.84	—	0.52	
Corr. ClO$_4^-$, m moles	1.60	2.43	2.94	3.28	—	2.90	4.79	3.75	—	4.19	
x	0.34	0.17	0.16	0.16	—	0.12	0.23	0.22	—	0.12	0.19
ΔH$_r$ (avg), kcal/mole	-110.1	-116.0	-109.1	-107.7	(-96.9)	-99.3	-109.3	-106.7	(92.3)	-103.5	-107.7
ΔH$_r$ (x), kcal/mole	-90.0	-104.5	-98.3	-96.5	—	-90.3	-93.5	-89.1	—	-94.5	-94.6
ΔH$_f$ (avg), kcal/mole	+41.4	+47.3	+40.4	+39.0	(+28.2)	+30.6	+40.6	+38.0	(+23.6)	+34.8	+39.0
ΔH$_f$ (x), kcal/mole	+42.1	+46.6	+39.4	+37.6	—	+28.7	+39.3	+33.9	—	+33.2	+37.6

Increased OF_2-NaOH contact time in static hydrolyses of fluorine perchlorate samples would theoretically result in the further hydrolysis of OF_2[9] according to the following equation:

$$OF_2(g) + 2 \text{ NaOH(aq)} \rightarrow 2\text{NaF(aq)} + H_2O(\ell) + O_2(g) \qquad (15)$$
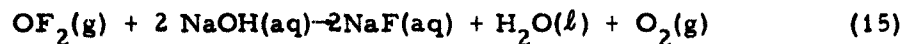
The summation of Equations 13 and 15 results in the commonly observed static hydrolysis, Reaction 12.

2.2.3 Discussion

Several similar approaches to correlate the consistent discrepancy in the analytical results of the thermochemical evaluations of the heat of formation of fluorine perchlorate resulted in corrections of less than 2 kcal/mole to the heat of formation values obtained, disregarding the formation of OF_2. To ascertain the magnitude of the correction factor, a preliminary heat of formation value for fluorine perchlorate was obtained from Reaction 12, assuming that the average result of the fluoride and perchlorate analysis corresponded to the amount of fluorine perchlorate which had been hydrolyzed. The reported standard heats of formation of NaOH (1 mole/100 mole H_2O), $NaClO_4$ (in 400 mole H_2O), NaF (in 100 mole H_2O), and liquid H_2O which are -112.1, -88.76, -135.74, and -68.32 kcal/mole, respectively, were used[7]. With the insertion of the appropriate values of the above terms in Equation 12, the heat of formation per mole of fluorine perchlorate becomes:

$$\Delta H^o_{f\ 298} \cdot ClO_4F(g) = -68.6 - \Delta H_{r\ 298} \qquad (16)$$

Using Equation 16, the average heat of formation value of fluorine perchlorate, measured at 21.5° C and inferred from the data in Table II, is +39.0 ± 3.4 kcal/mole. Run Nos. 5 and 9 were excluded on the basis of statistical correlation.

Assuming that Equation 14 represents the correct reaction path of fluorine perchlorate with aqueous sodium hydroxide under flow conditions, it was necessary to evaluate the x coefficients relating to the extent of OF_2 formation to obtain a corrected heat of formation value for fluorine perchlorate. Since the discrepancies in the analytical results do not correspond exactly to the stoichiometry of Equation 14, the relative accuracy of analytical results for fluoride, perchlorate, and hydrogen ion were employed. The most accurate analytical procedure from the analysis of synthetic samples containing varying amounts of fluoride, perchlorate, and hydrogen ion was found to be the fluoride detection, based on a null-point potentiometric method[10]; the next most accurate procedure was the standard acid-base titration for hydrogen ion; the least accurate was the volumetric reduction of perchlorate using titanous chloride[11].

Basing the evaluation of the x coefficients of Equation 14 on the fluoride and hydrogen ion analyses, the heat of formation of fluorine perchlorate from this equation can be obtained by correcting the perchlorate analysis result from the data shown in Table II and by employing the corrected value in the following calculation.

The stoichiometry of Equation 14 states that the difference between the generated hydrogen ion and fluoride is equal to 1/2 x*, while the difference between the perchlorate and fluoride is equal to x*. Solving for x* from the difference between half of the hydrogen ion analysis and the fluoride

analysis and adding this factor to the observed fluoride analysis, the corrected perchlorate value was obtained. The value of x partici-pating in the formation of OF_2 was determined by normalizing the values of x* to the corrected perchlorate values. Excluding run Nos. 5 and 9 because of the reversed order in the results of chemical analyses, an average value for the extent of the side reaction producing OF_2 was found to be 19 percent.

With the insertion of the appropriate values for the standard heats of formation of NaOH (1 mole/100 mole H_2O), $NaClO_4$ (in 400 mole H_2O), NaF (in 100 mole H_2O), H_2O, O_2, and OF_2 (heat of formation OF_2 = 7.6 ± 2.0 kcal/mole[12]) in Equation 14, the heat of formation per mole of fluorine perchlorate becomes

$$\Delta H_f^o = (61.8)(x) - 68.6 - \Delta H_r \qquad (17)$$

Using Equation 17 with the appropriate values of x inferred in Table II, the average value for the heat of formation of fluorine perchlorate, measured at 21.5° C, is +37.6 kcal/mole.

2.3 THE HEAT OF FORMATION OF NITRYL FLUORIDE

The heat of formation of nitryl fluoride, NO_2F, has been of considerable question in past investigations. Estimated values have ranged from +15 to -20 kcal/mole depending upon the assumed bond energies and structure employed in these estimates. The definition of a more precise heat of formation consistent with the reported structure of NO_2F would permit an inference of the N-F bond energy in the molecule.

Two approaches were taken in an attempt to establish the thermochemical properties of NO_2F: (1) the measurement of the heat of reaction associated with the synthesis reaction, and (2) the measurement of the dissociation pressure as a function of the temperature. Of primary importance was the study of the heat effect generated from the direct combination

of nitrogen dioxide and fluorine according to the equation:

$$NO_2(g) + 1/2\ F_2(g) \rightarrow NO_2F(g) \qquad (18)$$
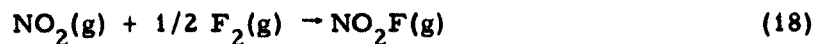
Of the several reactions considered for study, this synthesis was deemed to be the most amenable to accurate calorimetric evaluation.

Calculations of the dissociation constant of NO_2F based on the heat of formation derived from the experimentally determined heat of synthesis indicate that the degree of dissociation should be infinitesimal. However, visual and infrared spectral evidence strongly suggests a reversible equilibrium dissociation of NO_2F of considerable magnitude at, or slightly above, ambient temperature, indicating that a more endothermic heat of formation would be appropriate. In view of these contradictions, a second attempt was made to obtain a precise value of the heat of formation of NO_2F by an alternative method, by the measurement of the variation of the dissociation pressure as a function of temperature.

2.3.1 Experimental Calorimetry

A gas-flow calorimeter system operated at 25° C was employed in this study where a one-fourth inch outside diameter copper coil (about 20 cc internal volume) served as the reactor. Incoming gases were admitted at constant pressure, which was maintained by two Grove precision reducing regulators, while a Grove back pressure regulator controlled the gas exit flow of the calorimeter.

The amount of fluorine (Allied Chemical Co., 98 percent) discharged into the calorimeter was determined by the pressure drop in a calibrated supply cylinder and monitered to a flow rate of about 160 cc/min at atmospheric pressure and ambient temperature. Nitrogen dioxide

(Matheson Co., 99 percent), in equilibrium with the tetroxide, was
fed to the reactor at the same flow rate by a calibrated constant-drive
piston pump.

A one-gallon Dewar flask served to enclose the water heatsink fluid
in which the reactor was completely immersed. The temperature
change of the system occasioned by the formation of NO_2F was
measured with a calibrated precision resistance thermometer and
Mueller bridge assembly. The heat capacity of the system was
determined independently by an electrical calibration heater.

Downstream of the reactor two stainless steel traps held at appropriate
temperatures served as a fractionation means and separated the nitryl
fluoride formed from any unreacted nitrogen dioxide. Excess fluorine
was led into a bubble tower containing aqueous KI from which the
amount of iodine liberated was determined by standard methods. The
actual weight of NO_2F collected was determined by difference of
the weight of the traps before and after the reaction.

2.3.2 Experimental Dissociation Pressures

The reaction studied was assumed to be the reverse of Equation 18 and
was followed in a Kel-F system by an absolute pressure transducer
calibrated for both temperature and pressure variations. The sample
weight (mostly NO_2F) was obtained from the difference in weight of
the cell before and after loading. The variation in volume of the cell
as a function of temperature was also determined as Kel-F was known
to have a large coefficient of cubic expansion. Defining the coefficient
of cubic expansion as the change in volume per unit volume per degree
Centigrade, a value of $5.38 \times 10^{-4} \cdot C^{-1}$ was obtained for Kel-F. The
volume thus follows the relation (in cc and $^\circ C$) $V_t = V_o + (0.07 \Delta t)$

where Δt is the difference in temperature between the working temperature and the reference temperature, over the temperature range 25-75° C. For the measurements under consideration, V_o equals 128.2 cc at 22.0° C, the reference temperature. All temperature measurements were made using a precision grade mercury thermometer which could be read easily to the nearest 0.05 degree.

2.3.3 Results and Discussion

Shown in Table III are the results of three calorimetric experiments for which reliable analysis of the nitryl fluoride product was possible.

TABLE III

CALORIMETRIC DATA FOR NO_2F FORMATION

Run No.	F_2 Used, moles	NO_2F Formed, moles	Yield (Based on F_2) percent	Δt, ° C	C_p of Calorimeter, cal/deg	Q Generated, cal	N_2O_4 Correction, cal	ΔH_r, kcal/mole	ΔH_f, kcal/mole
7	0.0355	0.0522	73.8	0.891	1585	1412	358	-33.9	-25.8
8	0.0353	0.0442	62.8	0.741	1585	1174	303	-33.4	-25.3
10	0.0345	0.0560	81.3	0.974	1585	1543	384	-34.4	-26.3

A correction for the amount of nitrogen tetroxide present in the incoming gas has been applied[12] and the heat of reaction listed is for Equation 18. The average value of -33.9 kcal/mole for this reaction leads to a heat of formation of nitryl fluoride of -25.8 kcal/mole. While the precision of both of the average values is ±0.5 kcal/mole, the considered uncertainty is ±2 kcal/mole.

According to Nichols and Robinson[14], the heat of formation of nitryl fluoride is -26 kcal/mole derived from their hydrolysis experiments. The excellent agreement with the results of this research is remarkable. However, as pointed out earlier, nitryl fluoride may dissociate

appreciably, altering the values listed. Pressure measurements indicate the heat of formation of nitryl fluoride may be nearer to zero.

Listed in Table IV are the final results of two out of the six series of dissociation pressure measurements conducted.

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TABLE IV

DISSOCIATION PRESSURE DATA FOR NO_2F

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	$T, °K$	P_{mm}	K_p atm^{-1}	$-\log K_p$
Run No. 4: 0.255 g. sample	303.2	589.7	6.63×10^{-5}	4.178
	318.2	623.0	2.73×10^{-4}	3.564
	333.2	658.4	8.98×10^{-4}	3.047
	348.2	705.4	4.58×10^{-3}	2.339
Run No. 6: 0.180 g. sample	298.2	417.6	3.21×10^{-4}	3.494
	308.2	429.4	2.53×10^{-4}	3.596
	318.2	443.4	3.48×10^{-4}	3.458

These are the only series that would allow direct calculation. The K_p listed in Table III is only for the reaction

$$2\ NO_2F(g) = 2\ NO_2(g) + F_2(g) \qquad (19)$$
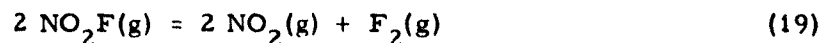
where corrections have been applied for the separate nitrogen tetroxide equilibrium using the data of Bodenstein and Böes[15] as corrected by Giauque and Kemp[13].

A plot of log K_p versus $1/T$ has as its slope a function of the heat of reaction, which can be solved giving average values of +18.1 and +6.9 kcal as written, respectively, for run numbers 4 and 6. From these values the heat of formation of nitryl fluoride was calculated, yielding -1.0 and +4.6 kcal/mole, respectively. The heat of formation

of nitrogen dioxide was taken as +8.06 kcal/mole[16] while that of fluorine was zero by definition.

The agreement between runs 4 and 6 is less than desired. However, in all cases studied, the degree of dissociation lies in the range of 2 to 9 percent and is very difficult to detect. A deviation of ± 2 mg in the sample weight and 0.5 mm in the total pressure (the estimated limits of error) leads to nearly an order of magnitude change in K_p. In the series of runs not reported here it was found that the average molecular weight was apparently either greater than that of nitryl fluoride, which implied some unknown quantity of heavy species being present, or so small as to lead to the impossible situation where the degree of dissociation was greater than 100 percent.

The lack of reproducibility of the pressure measurements may be due to the extreme reactivity of nitryl fluoride. The infra-red spectra obtained with the sample in a metal cell showed many species not present when the sample was in an all Kel-F system. A spectral study of the NO_2 absorption as a function of time was not conclusive but indicated that the NO_2 concentration may be growing. The reaction of NO_2F with metals is well known[14], and in many cases NO_2 is a prime product. Although very little metal was present in the Kel-F pressure measuring cell, the loading valve and pressure transducer were brass and steel, respectively. Further support to the calorimetric heat of formation is given by Perrine and Johnston[17] who have studied the kinetics of Reaction 18. From their data and reasonable approximations they stated that nitryl fluoride is stable by at least 10 or 11 kcal.

From these considerations, the results of the dissociation pressure determinations are considered suspect and emphasis is placed on the calorimetric results.

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2.4 THERMOCHEMISTRY OF FSO_3F, F_5SOF, AND CF_3OF

To extend the evaluation of O-F bond energies to molecules exhibiting a different substituent grouping, the applicability to calorimetric evaluation of the heats of formation of fluorine fluorosulfonate, FSO_3F, pentafluorosulfur hypofluorite, F_5SOF, and trifluoromethyl hypofluorite, CF_3OF, were determined. From the studies conducted on the sulfur-based compounds, only FSO_3F was found to be amenable to evaluation. Lesser effort was applied to the study of CF_3OF because a heat of formation of this material has been reported.

2.4.1 Fluorine Fluorosulfonate

To establish the feasibility of employing FSO_3F in a calorimetric study, synthesis, combustion and hydrolysis reactions were investigated. Side reactions leading to formation of SO_2F_2 could not be completely eliminated by varying the experimental conditions during synthesis of FSO_3F from SO_3 and F_2, thus eliminating this reaction from direct applicability to thermochemical analysis. The combustion reaction with fuels, primarily hydrogen, also resulted in a complex series of products. Therefore, the primary effort for heat of formation determination was directed to the hydrolysis reaction.

Fluorine fluorosulfonate was prepared from SO_3 and F_2 at 200° C as described by Cady[18]. The removal of the major impurity, SO_2F_2, was accomplished by vacuum distillation. Infrared analysis of the purified material indicated no impurities while fractional co-distillation and hydrolysis techniques indicated a purity of greater than 97 percent.

The analysis of the results of the hydrolysis reaction obtained from a preliminary study corroborated Cady's observance of a two-step

reaction with aqueous NaOH. A rapid hydrolysis of the O-F bond occurs as the first reaction; under more severe conditions of temperature and extended digestion, the S-F bond can be made to undergo hydrolysis. As the former reaction can be treated readily in a flow hydrolysis calorimeter, and, as thermochemical data for fluorosulfonic acid and sodium fluorosulfonate have been published recently[19], the initial hydrolysis reaction will be a sufficient measure of the heat of formation of FSO_3F without resorting to complete hydrolysis. A procedure has therefore been defined by which the thermochemical measurements can be made, yielding a heat of formation for this O-F bonded species.

2.4.2 Pentafluorosulfur Hypofluorite

Several reactions to produce F_5SOF from SOF_2 and F_2 at approximately 220° C have been conducted using the procedures of Dudley, Cady, and Eggers[20]. SOF_2 was prepared from $SOCl_2$ and SbF_3, using $SbCl_5$ as a catalyst according to the method of Smith and Muetterties[21]. Preliminary fractional co-distillations of the F_5SOF product, followed by infrared analysis of the various fractions, indicated the principal impurities to be SOF_4, SO_2F_2, SF_6, and SiF_4.

Successive distillations of the impure F_5SOF material using a 30-60 mesh Kel-F packed column on the fractional co-distillation apparatus reduced the several impurity peaks to the detection limit of the thermoconductivity apparatus. The one remaining impurity peak had an area of 0.5 percent of the total product peak area. Infrared analysis of this material, however, indicated the presence of some SO_2F_2 and SOF_4, while mass spectrographic analysis indicated a purity of 92 to 94 percent.

The combustion and synthesis reactions are not amenable to straight-forward thermochemical evaluations as a consequence of the multiplicity of products possible in the former case and the high temperature involved in the latter. Cady has reported the reaction of F_5SOF with a potassium hydroxide solution to proceed rapidly according to the following equation:

$$F_5SOF + 6\ OH^- \rightarrow 5\ F^- + 1/2\ O_2 + FSO_3^- + 3\ H_2O \qquad (20)$$
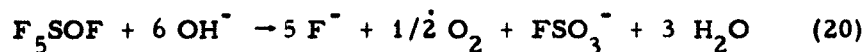
Since information on the heat of formation of sodium fluorosulfonate has been published[19], this reaction provides a potential means for the derivation of the heat of formation of F_5SOF.

2.4.3 Trifluoromethyl Hypofluorite

Trifluoromethyl hypofluorite was prepared from the reaction of CO and F_2 in a 1/4 inch O.D. copper coil at approximately 400° C as described by Cady, et. al[22]. The removal of the major impurity, COF_2, was accomplished by filtering the liquid CF_3OF from the solid COF_2 at -183° C. Mass spectrographic analysis of the purified material indicated a 97.4+ percentage purity.

In an effort to define a reaction system which would be appropriate for the evaluation of the thermochemical properties of CF_3OF, several potential reactions have been screened. The results obtained from the hydrolysis with aqueous NaOH during the development of the analytical procedure indicated that the reaction was not sufficiently quantitative to permit reliable thermochemical evaluation. Experiments performed in this laboratory corroborated the observation by Cady[23] that CF_3OF and H_2 did not react. Trifluoromethyl hypofluorite had been reported to react quantitatively with mercury and semi-quantitatively with sulfur[24]. The characteristics of these

reactions in a flow system were investigated to establish possible applicability to calorimetric study. However, although some evidence of reaction was detected, neither reaction proceeded at a sufficient rate to warrant further consideration.

3.0 DISCUSSION AND CONCLUSIONS

Until recently the bond strength between oxygen and fluorine atoms has been derived solely from the heat of formation of oxygen difluoride, OF_2. At present, the accepted value for the heat of formation of oxygen difluoride is +7.5 ± 2.0 kcal/mole[27] which leads to an average O-F bond energy of 44.8 kcal using the supporting data of Table V. An average bond dissociation energy of 45 kcal is obtained from electron impact studies[25] which gives bond dissociation energies of 64.6 kcal for D (FO-F) and 25.4 kcal for D (O-F). More recently, however, inconsistencies have been noted in bond energy summations using only the O-F bond energy derived from OF_2. When this average bond energy is compared with the value of 25 kcal/mole reported by Stewart and Cady[26] for the O-F bond of trifluoroacetyl hypofluorite, the serious consequences of the use of a single representation bond energy is obvious.

The only unambiguous value of the O-F bond energy has been ascribed to the value derived from the thermochemical data of OF_2. While the energy content of the molecule can be related to the strengths of the O-F bonds, and because no other bonds are present, the average bond energy may be determined uniquely, the mutually perturbing influence of the adjacent O-F bonds cannot be eliminated. Several other oxygen fluorides, O_2F_2 and O_3F_2, have been prepared and may be cited as sources of the O-F bond energy data. However, the O-F bond is no longer isolated and will be dependent on the value assigned to the O-O bonds. The O-O bonds meanwhile will be subject to perturbation as a result of the inductive effect of the terminal fluorine atoms. The solution of the dilemma lies in the accumulation of sufficient thermochemical data to permit a tabulation of a parameter for chemical moieties equivalent to the electronegativity table for atoms.

The heats of formation of fluorine perchlorate and fluorine nitrate have been determined by this laboratory in the course of this investigation and the values obtained are +37.6 ± 9 and +2.5 ± 0.5 kcal/mole, respectively. To calculate bond energies from these values the data of Table V were used.

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TABLE V

AUXILIARY THERMOCHEMICAL DATA

</div>

Species	ΔH_f°, kcal/mole
F(g)	+18.86 ± 0.2 [28]
O(g)	+59.56 ± 0.03 [28]
H(g)	+52.10 ± 0.1 [29]
H_2O(g)	-57.7979

The O-F bond energy, symbolized as E(O-F), for fluorine nitrate is most easily calculated by reference to a Born-Haber cycle in which a fluorine atom is substituted for the hydrogen atom in nitric acid. This calculation involves breaking of an O-H bond requiring 110.78 kcal/mole, assuming that the bond is the same as in water vapor, and the formation of molecular hydrogen gas followed by the formation of an O-F bond after atomizing fluorine gas. A heat of formation value for liquid nitric acid of -41.40 kcal/mole[30] and the heat of vaporization value of +9.43 kcal/mole[30] was used. Combining all these effects and their uncertainties (where known) yields E(O-F) = 43.1 kcal/mole, which corresponds very closely to the value obtained from oxygen difluoride.

In the case of fluorine perchlorate, the calculations are identical in method to that used for fluorine nitrate. The heat of formation of liquid perchloric acid was taken as -11.1 kcal/mole[30] while the heat of vaporization was estimated to be +9.55 ± 0.7 kcal/mole from available data[31]. The E(O-F) is computed to be 38.4 kcal/mole and falls near the values derived from fluorine nitrate and oxygen difluoride.

It has been reported by Porter and Cady[32] that trifluoromethyl hypofluorite, CF_3OF, decomposes to carbonyl fluoride and fluorine. From their dissociation measurements they report a heat of reaction at 298° K of +26.9 ± 1.5 kcal/mole, which leads to a heat of formation for CF_3OF of -177.9 ± 5 kcal/mole using a value of -151 ± 3 kcal/mole[28] for the heat of formation of carbonyl fluoride.

Cady's reported value for E(O-F) of 47 kcal/mole was based on a bond energy summation and a calculated molar heat of formation value of -481.4 kcal/mole for CF_3OF from gaseous atoms at 298° K. The E(C-F) strength of 116.3 kcal/mole was calculated from the heat of formation of CF_4 of -229.4 kcal/mole while the E(C-O) was assumed to be the same as in simple alcohols and ethers and a value of 85 kcal/mole was used.

A recalculation of the E(O-F) from a consideration of the bonds broken and formed during the dissociation reaction using Cady's heat of formation data for CF_3OF yields a value for E(O-F) of +37.6 ± 5 kcal/mole. This latter calculation used -218 ± 1 kcal/mole for the heat of formation of carbon tetra-fluoride[18], yielding an average E(C-F) of 116.1 kcal/mole. It was assumed that E(C-O) and E(C=O) differed by 89.1 ± 2 kcal/mole[33] as an average value. The 9 kcal/mole discrepancy between the two calculation, while not excessive, points out the difficulty encountered in this type of evaluation.

The heats of formation of two other simple compounds containing O-F bonds have been reported[34]; for O_2F_2 the value is +4.73 ± 0.30 kcal/mole and for O_3F_2 the value is +6.24 ± 0.75 kcal/mole. By assuming that the O-O and O-F bond strengths are the same in both molecules and that both are simple, non-branched chains of atoms, the bond energies may be solved unambiguously. The E(O-F) obtained is 74.0 ± 1 kcal/mole while the E(O-O) is 58.0 ± 1 kcal/mole.

The heat of formation for molecular HOF has been reported as -26.1 ± 15 kcal/mole[35]. This value leads to E(O-F) of 45.8 ± 16 kcal/mole. This bond

energy value is in remarkable agreement with other values, considering the degree of uncertainty involved in the heat of formation value.

A summary tabulation of calculated bond energies for the O-F bond is shown in Table VI. The average value for these seven compounds is 43.4 ± 6 kcal/mole, which indicates that, generally, the bond energy of O-F bonds is not affected markedly by the substituents attached and the effect is not immediately predictable.

TABLE VI

BOND ENERGIES FOR O-F BONDS

Species	E(O-F) kcal/mole	ν, cm^{-1}	Species	E(O-F) kcal/mole	ν, cm^{-1}
NO_3F	43.1	806	OF_2	44.8	830
ClO_4F	38.4	887	O_2F_2	47.0	-
CF_3OF	37.4	886	O_3F_2	47.0	-
			HOF	45.8	836

The development of a pseudo-electronegativity treatment involving group contributions suffers from the same uncertainty encountered in evaluation of the O-F bond energy because the bond energy is a necessary parameter in the determination of the bond energy enhancement. The values derived for the O-F bond energy are all more exothermic than the value indicated by Pauling[36] for the purely covalent bond on the basis of the arithmetic mean of the single bond energies. However, the O-O single bond energy depends on an estimate of the partition of the energy among the bonds of hydrogen peroxide. Use of the O-O bond energy derived above would yield a bond energy of 45 kcal for the purely covalent O-F bond, implying a negative ionic character for the bond in the species listed in Table VI. Therefore, the interpretation of the difference in derived O-F bond energy from the bond energy based on the arithmetic mean of the O-O and F-F bonds, assuming additivity, is tenuous.

Perhaps the most valid correlation of structure can be expected to be shown by variations in the characteristic frequency of the O-F bond. The frequency, assuming that the vibration is an independent stretching mode, should be a function of the valence bond force constant and therefore related to bond energy. A set of frequency assignments for the O-F stretching vibrations for several of the species of interest is also presented in Table VI. The development of this concept suffers, however, from a lack of experimental data and from the small variation observed in the frequencies of a majority of the compounds for which data are available.

The several spectroscopic investigations of the structure of NO_2F have shown the structure to be

$$\begin{array}{c} O \\ \diagdown\diagdown \\ \diagup\diagup \quad N - F \\ O \end{array}$$
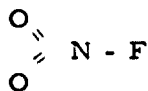
With this structure, an evaluation of the N-F bond energy is readily carried out, using the heat of formation obtained from this research. Assuming an average N-O bond energy of 103.9 kcal/mole[33] as in the nitroparaffins, an N-F bond energy value of 69.0 kcal/mole is calculated in nitryl fluoride. The summation of heat terms includes values of 18.86, 112.96, and 59.559 kcal/mole for the heats of formation of monatomic fluorine, nitrogen, and oxygen, respectively[28]. The bond energy value of 69.0 kcal/mole lies within experimental error of the N-F values for such other gas phase species as NF(73.2 kcal/mole), NF_2(70.9 kcal/mole), NF_3(66.4 kcal/mole)and N_2F_4(65.2 kcal/mole).

As a consequence of the narrow range of bond energies derived for the O-F bond for a variety of hypofluorites, it is concluded that the average value (43 kcal/mole) may be used as a representative bond energy in the

estimation of heats of formation by bond energy summations. The
variations in the O-F bond energy which were observed are less than the
observed bond energy variations for the other types of bonds present in
the molecule. In view of the uncertainty in the other bond energies, the
variations of the O-F bond energy are hardly significant and the validity of
an attempt to correlate the small variations to molecular structure effects
is questionable. Use of the value E(O-F) of 43 kcal/mole will yield
satisfactory heats of formation to permit theoretical evaluation of perform-
ance capabilities of species containing this functional group. Similarly,
the value for the N-F bond of NO_2F has been found to be adequately
represented by the average of the other values for the bond.

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