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# THERMOCHEMISTRY OF OXYGEN-FLUORINE BONDING



Research Division

UNITED TECHNOLOGY CORPORATION
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## SECOND QUARTERLY TECHNICAL SUMMARY REPORT
## CONTRACT NO. NONR 3433(00)

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SECOND QUARTERLY TECHNICAL SUMMARY REPORT
FOR THE PERIOD OF 1 JULY THROUGH 30 SEPTEMBER 1961
Under Contract No. Nonr 3433 (00)

Propulsion Chemistry Branch
Material Sciences Division
Office of Naval Research

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# 1.0 INTRODUCTION

This report is the Second Quarterly Technical Summary Report issued in partial fulfillment of Contract Nonr 3433 (00). This report covers the work accomplished during the months of July, August, and September.

# 2.0 TECHNICAL ACTIVITY

## 2.1 OBJECTIVES OF THE PERIOD REPORTED

The specific objectives of the experimental work performed during this second report period have been the following:

A. Modification of existing experimental equipment for a more detailed study of the synthesis of $NO_2F$ and $NO_3F$.

B. Further development of consistent and accurate analytical techniques for determination of reaction products in the synthesis of $NO_2F$ and $NO_3F$. These techniques include mass spectroscopy, gas chromatography, hydrolysis, purification by fractional distillation, and infrared spectrophotometry.

C. Assembly and calibration of a suitable flow calorimeter for measurement of the heats of formation of $NO_2F$, $NO_3F$, and $ClO_4F$.

D. Synthesis and purification of $NO_2F$ from elemental fluorine and nitrogen dioxide and $NO_3F$ from concentrated nitric acid and elemental fluorine.

E. Preliminary evaluation of the heat of formation of $NO_2F$ from measurement of the heat evolved during reaction of elemental fluorine and nitrogen dioxide.

## 2.2 STUDY OF $NO_2F$

### 2.2.1 Synthesis

The reaction involved in synthesizing $NO_2F$ from $F_2$ and $NO_2$ appears

not to be as clear cut as heretofore believed. To date, the concentration of the by-products in the reaction $1/2F_2 + NO_2 = NO_2F$ is not known with sufficient precision and accuracy to define an absolute value of the heat of formation of $NO_2F$ from the calorimetric studies.

2. 2. 2 Analyses

A. The mass spectrometric studies show an abnormally large percentage of hydrogen fluoride in purified samples of $NO_2F$ prepared via the $NO_2$ and $F_2$ reaction.

The source of HF has not been completely established. The introduction of $NO_2F$ into the mass spectrometer may produce HF since introduction of $F_2$ into the mass spectrometer system generates excessive amounts of HF. This might be expected also with $NO_2F$ since $NO_2F$ is essentially as reactive as $F_2$. On the other hand, $NO_2F$ appears to be stable at extremely low pressures in the mass spectrometer.

B. An infrared spectrum of the synthesized and purified $NO_2F$ is shown in Figure 1. The spectrum agrees well with the published spectra of $NO_2F$.* The peaks at 822, 1312, and 1793 $cm^{-1}$ are characteristic of $NO_2F$.

C. The hydrolysis system fabricated of glass and the coating of inert wax were found to give insufficiently precise results for analysis of $NO_2F$. A reaction of $NO_2F$ with the glass and wax system gives spurious results. To circumvent many of the inherent problems of using glass and wax with fluorine-containing

* Dodd, R.E., J.A. Rolfe, and L.A. Woodward, "Infrared and Raman Spectra of Nitryl Fluoride, "Trans. Faraday Soc., 52, 1956.

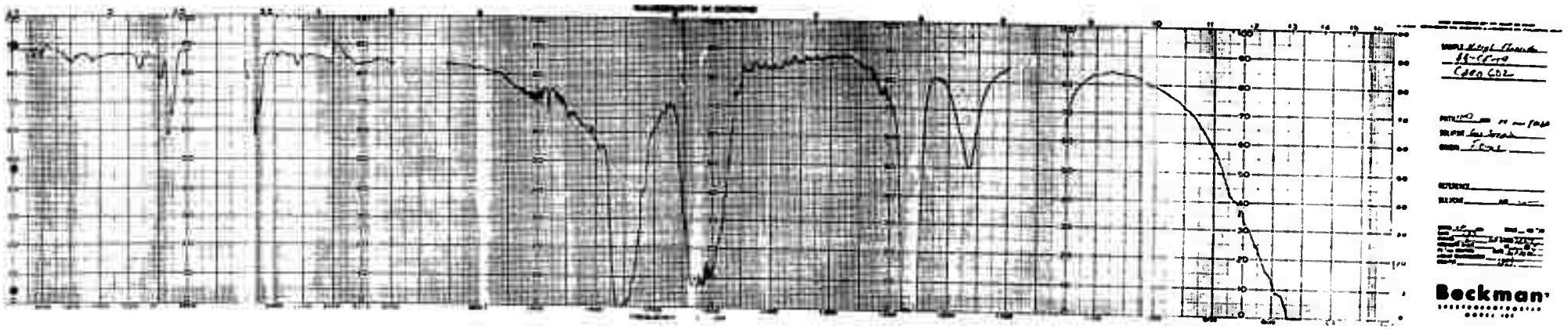


FIGURE 1. INFRARED SPECTRUM OF NITRYL FLUORIDE ($NO_2F$)

materials, a special hydrolysis system fabricated completely of Kel-F has been assembled. This system is ready for operation.

Monel and other metals cannot be used in the fabrication of fluoride hydrolysis systems since the hydrolyzing medium readily dissolves the protective metal-fluoride coatings. The dissolved metal fluorides in turn interfere with the hydrolysis reaction. The use of Kel-F or Teflon for fabrication circumvents this problem.

The hydrolysis analyses obtained in the original glass and wax system are insufficiently precise for reporting at this time.

D. The gas chromatography results are inconclusive. The retention volumes of $F_2$, $NO_2F$, and HF are essentially the same on a 25 foot column packed with Kel-F oil and Kel-F powder. Thus, a reasonable resolution of characteristic peaks for a mixture of $F_2$, $NO_2F$, and HF has not been possible with chromatographic analysis. Attempts will be made to evaluate other packing materials in the chromatography column.

2.2.3 Heat of Formation - Calorimetry

As discussed in the preceding quarterly report, the heat of formation of $NO_2F$ will be measured directly from its synthesis by the $NO_2$ - $F_2$ reaction in a flow calorimeter. Figure 2 is a photograph of the assembled calorimetric system and support equipment. The calorimeter is complete and has been calibrated for heat capacity. The heat capacity of the system is 1.585 kcal/$^{o}$C.

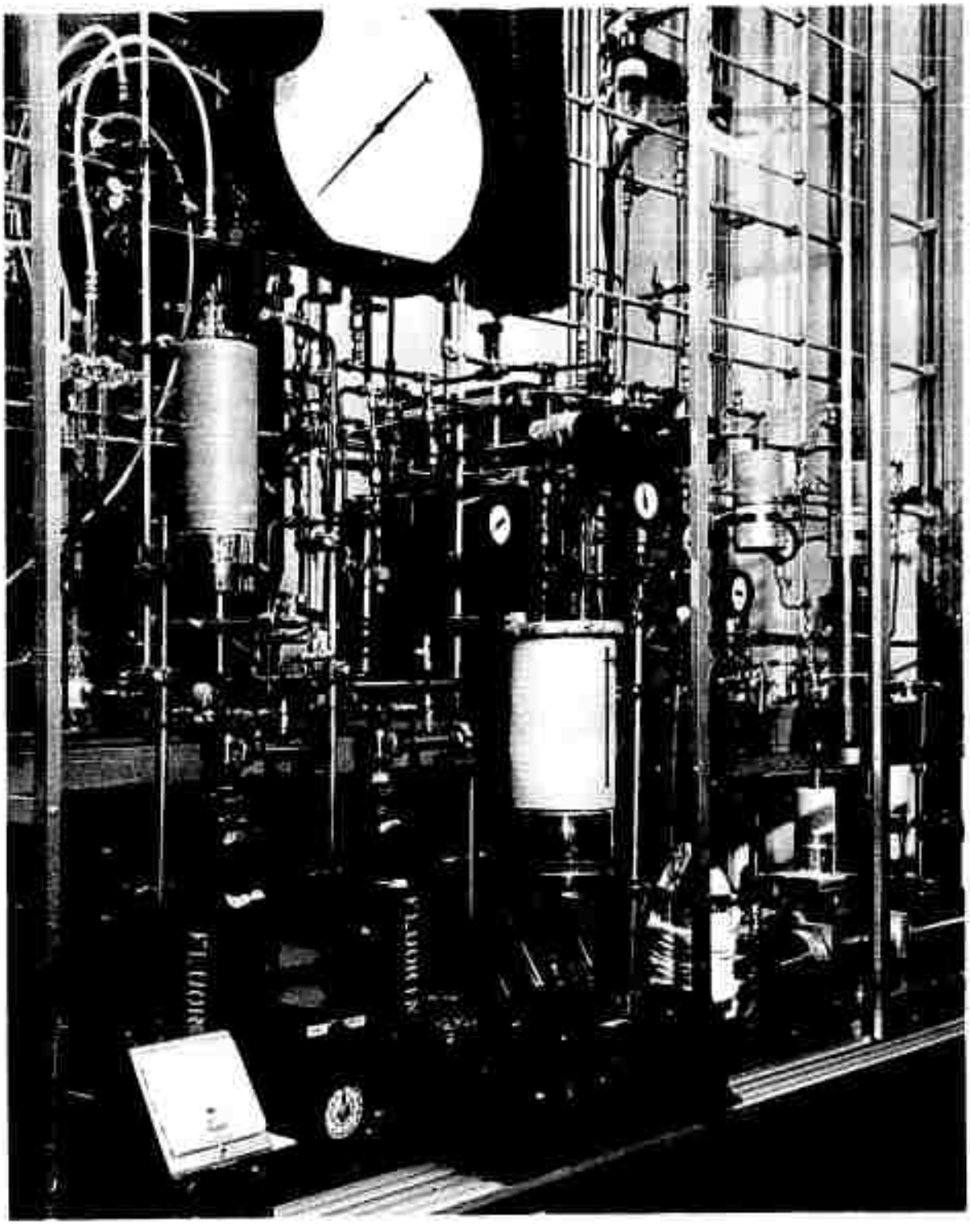

FIGURE 2. ASSEMBLED CALORIMETRIC SYSTEM AND SUPPORT EQUIPMENT

Several checkout experiments have been completed on the heat of formation of $NO_2F$, using the flow calorimeter shown in Figure 2. A typical time-temperature curve for a $NO_2F$ heat of formation determination is shown in Figure 3. The important data for this run are listed in Table I. The heat of formation is derived from the measurements utilizing Hess's law.

The heat of formation per mole of $NO_2F$ utilizing the reaction

$$1/2\ F_2 + NO_2 \longrightarrow NO_2F \qquad (1)$$

and Hess's law is:

$$\Delta H_f(NO_2F) = \Delta H_f(1/2\ F_2) + \Delta H_f(NO_2) + \Delta H_r \qquad (2)$$

The standard heat of formation of $NO_2$ is accurately known and has a reported value of 8.091 kcal/gmol* while the heat of formation of $F_2$ is zero by definition. With the insertion of the appropriate values of the terms in Equation 2, the heat of formation per mole of $NO_2F$ becomes

$$\Delta H_f(NO_2F) = 8.091 + \Delta H_r$$

* Rossini, et. al., Circular of the National Bureau of Standards, 500, U.S. Government Printing Office, Wash., D.C., 1952

## TABLE I. EXPERIMENTAL DATA OF CHECKOUT RUN FOR HEAT OF FORMATION OF $NO_2F$

| | |
|---|---|
| Moles $NO_2$ used | = 0.060 |
| Moles $NO_2F$ formed | = 0.052 |
| Percent yield | = 87% |
| Heat Capacity of Calorimeter | = 1.585 kcal/°C |
| Temperature rise of Calorimeter | = 0.910°C |

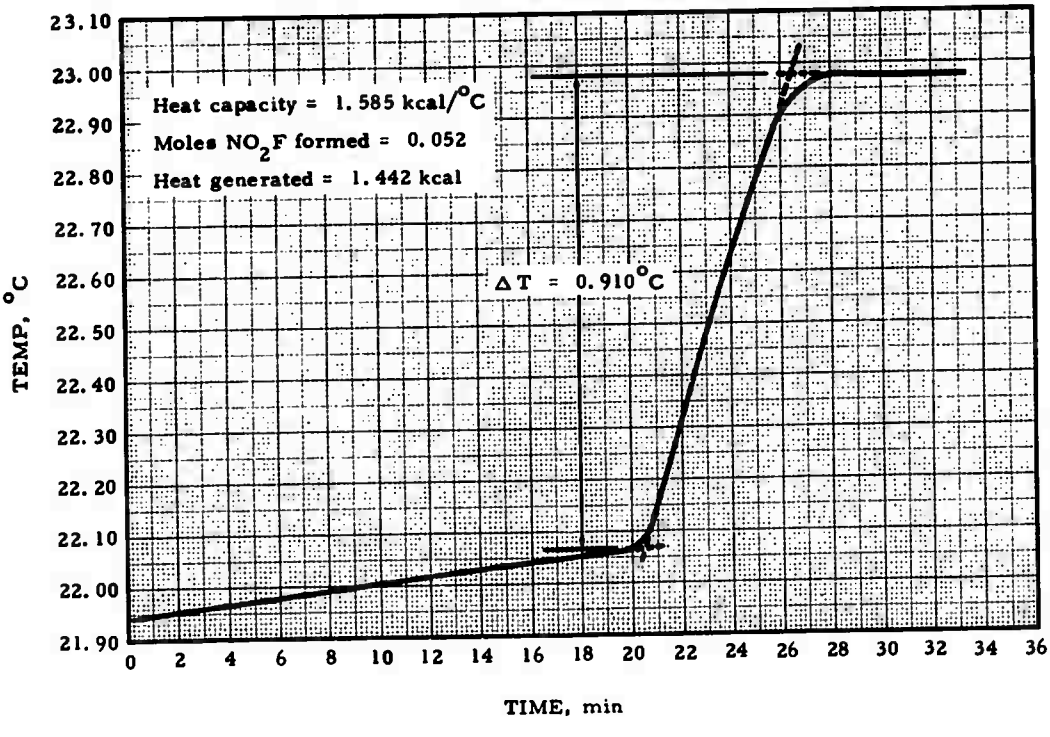


FIGURE 3. TEMPERATURE VERSUS TIME CURVE IN CALORIMETER FOR $NO_2F$ FORMATION REACTION

A preliminary heat of formation of $NO_2F$ as determined from this experiment is -20 ± 5 kcal/gmol. The heat of formation of $NO_2F$ derived from these checkout studies is not sufficiently accurate for final reporting because the analysis of $NO_2F$ is insufficiently prccise and accurate at this time to establish the concentrations of the primary and secondary reaction products. The purity of the $NO_2F$ for the experiment listed in Table I was determined by a simple fractionation only.

## 2.3 STUDY OF $NO_3F$

### 2.3.1 Synthesis

$NO_3F$ has been synthesized in low yields directly from concentrated $HNO_3$ and $F_2$. The yield in the present synthesis equipment is in the order of 10 percent based on the amount of fluorine used ($HNO_3$ is in excess). Modifications of the reactor for a longer contact time are necessary for larger conversions.

### 2.3.2 Analysis

A. The $NO_3F$ is being analyzed initially by hydrolysis. A typical synthesis product of $NO_3F$ after purification by distillation gives the following results upon hydrolysis. These results are listed in Table II.

$NO_3F$ hydrolyzes according to the reaction

$$NO_3F + H_2O \longrightarrow HNO_3 + HF + \tfrac{1}{2}O_2$$

The reaction should give equal moles of $NO_3^-$ and F- and twice the moles of $H^+$ upon hydrolysis. The results in Table II are essentially correct for $NO_3F$. The size of the sample of $NO_3F$ hydrolyzed as reported in Table II was 7.6 millimoles indicating a purity of approximately 70 percent $NO_3F$.

TABLE II. HYDROLYSIS RESULTS OF PURIFIED $NO_3F$

| | |
|---|---|
| $NO_3^-$ | 5.27 millimoles |
| F- | 5.10 millimoles |
| $H^+$ | 10.69 millimoles |

B. The infrared spectra of the $NO_3F$ synthesized is shown in Figure 4. This agrees well with the spectra reported.* The prominent absorption bands at 920, 1030, 1430, 1950, and 3060 $cm^{-1}$ are characteristic of $NO_3F$.

## 2.4 STUDY OF $ClO_4F$

The synthesis, purification, and analysis of $ClO_4F$ will begin as soon as satisfactory results on $NO_2F$ and $NO_3F$ are obtained.

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* W. E. Skiens and G. H. Cady, "Thermal Decomposition of Fluorine Nitrate," J. Am. Chem. Soc. 80, 5640 (1958).


FIGURE 4. INFRARED SPECTRA OF FLUORINE NITRATE ($NO_3F$)

## 3.0 FUTURE WORK

Synthesis, analysis, and purification of $NO_2F$ will be continued to provide more quantitative information on the $NO_2 + F_2$ reaction. The calorimetric studies will be completed upon satisfactory resolution of the reaction products.

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Synthesis, analysis, and purification of $NO_3F$ will be continued to provide more quantitative information on the $F_2$ + (conc) $HNO_3$ reaction. Conversions greater than the present 10 percent are required to permit accurate measurement of the heat of formation of $NO_3F$. Continued effort will be expended to obtain greater conversions. The calorimetric studies will be initiated upon satisfactory resolution of the reaction products.

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The O-F bonded compound $ClO_4F$ will be synthesized and the composition of the reaction products will be established.

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Vapor pressures and densities will be measured for $NO_2F$, $NO_3F$, and $ClO_4F$.

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There will be a theoretical correlation of these data to obtain reliable information on the stability and properties of O-F bonded compounds.

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