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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES AND THE DECOMPOSITION KINETICS OF PROPELLANT INGREDIENTS

QUARTERLY PROGRESS REPORT AFRPL-TR-66-176
(1 April 1966 to 30 June 1966)

July 1966

AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
EDWARDS AIR FORCE BASE, CALIFORNIA

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(Prepared under Contract Nr. AF 04(611)-11202 by
The Dow Chemical Company,
Midland, Michigan)

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Report Nr. T-202-2Q-66

QUARTERLY PROGRESS REPORT (U)
(1 April 1966 to 30 June 1966)

July 1966

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SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. AF 04(611)-11202. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties and the Decomposition Kinetics of Propellant Ingredients." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the second quarterly report, covering the work performed during 1 April 1966 through 30 June 1966. The Dow report number is T-202-2Q-66.

The work was performed by R. V. Petrella, G. C. Sinke, J. S. Skelcey, A. C. Swanson, and L. C. Walker under the technical supervision of Dr. D. R. Stull, and Dr. F. M. Brower, and management supervision of Dr. R. P. Ruh.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

George F. Babits, Lt. Colonel, USAF
Chief, Propellant Division

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SECTION I

SUMMARY

(C) The heat of dissociation of nitrogen trifluoride and the heat of reaction of sulfur with nitrogen trifluoride have been determined and are reported. The heat of formation of aqueous hydrogen fluoride has been determined from the nitrogen trifluoride work and are compared with the previously reported data. Research in progress on TVOPA, lithium-doped Beane, and the reaction of nitrogen trifluoride and cyanogen is described. The work on sample purification and the synthesis of trifluoromethoxydifluoroamine is also recorded. The results of the study of the combustion kinetics of Beane, nitrocellulose, TMETN and DEGDN are discussed.

SECTION II

THERMOCHEMISTRY

A. HEAT OF DISSOCIATION OF NITROGEN TRIFLUORIDE

1. Introduction

In our first quarterly report (1), a preliminary value for the heat of dissociation of NF_3 to the elements was given. This work has now been completed and a value for the heat of formation of NF_3 obtained.

2. Equipment

A platinum-lined bomb was revamped by Parr Instrument Company according to the bomb design shown in Figure 1, and is the same as the experimental bomb head built by Parr as described in our first quarterly report (1). The revamped bomb performed very well except for the two-piece ignition post, which was replaced by an all-platinum one-piece post during the course of the work. A rotating bomb calorimeter was used for the heat measurements. A vacuum system equipped with a precision Wallace-Tiernan pressure gauge was used for bomb charging operations.

3. Materials

Nitrogen trifluoride was purified by low temperature distillation. Infrared and mass spectrometry and gas chromatography led to an estimate of better than 99.9% purity. The hydrogen was a commercial "ultra-pure" grade. No impurities were detected by mass and infrared spectrometry.

4. Procedure

The bomb cylinder and head were dried at 110°C. for one hour, assembled, connected to a vacuum line, and evacuated while still hot. After cooling to room temperature, the bomb was surrounded by a constant-temperature water bath and pumped until a pressure of at least 1 μ was achieved. The bomb was then charged with 799.0 mm. of hydrogen as measured by a Wallace & Tiernan precision dial manometer which could be read to 0.1 mm. Nitrogen trifluoride was contained in a small stainless steel cylinder which could be weighed on a 200 g. capacity analytical balance. The cylinder was connected to the vacuum line and the bomb charged with about 0.75 g. of nitrogen trifluoride (10% excess) or 1.38 g. of nitrogen trifluoride (100% excess) in alternate runs. Sample remaining in the connecting lines was recondensed in the cylinder with liquid nitrogen and the exact amount charged determined by reweighing. In the 10% excess runs, an additional 0.5 g. of research grade nitrogen was charged to the bomb in order to make the final state of the bomb products as similar as possible in the two cases.

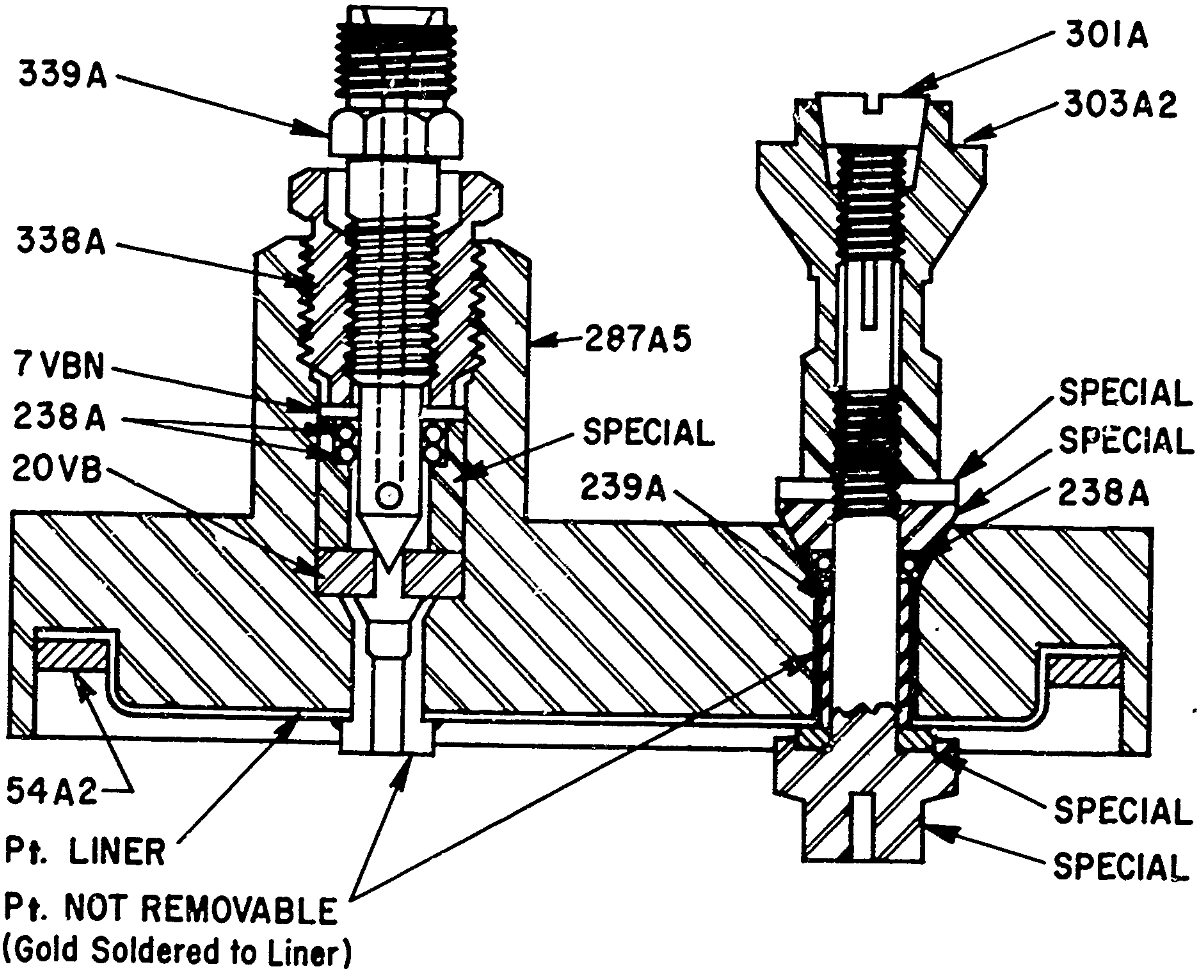


Fig. 1 - New Bomb Head Design

The bomb was placed in a conventional combustion calorimeter and the charge was fired by discharging a condenser through a fine platinum fuse wire. The condenser voltage before and after firing was a measure of the ignition energy. The calorimeter was calibrated with National Bureau of Standards benzoic acid 39 i. An average of 0.55 g. of acid was used and the bomb was charged with 1 ml. of water and 30.3 atm. of oxygen. The calorimeter equivalent was 3436.18 cal./deg. with a standard deviation of 0.52 cal./deg. for five experiments. The calorimeter equivalent adjusted to conditions for the dissociation experiments was 3436.84 cal./deg.

After the calorimetry was completed, the gaseous reaction products were passed over a sodium fluoride trap to remove hydrogen fluoride and into a bulb containing mercury to react out the fluorine. The remaining gas was examined by infrared and mass spectroscopy. Only nitrogen and a small amount of carbon tetrafluoride (from reaction of fluorine with a fluorocarbon gasket) was found. In some of the 100% nitrogen trifluoride runs, a trace of nitrogen trifluoride (less than 0.05%) was also observed. After flushing with nitrogen, the bomb was opened and the surface washed with 6 N hydrogen chloride to dissolve small amounts of platinic fluoride and auric fluoride formed by fluorine attack on the fuse wire and electrodes. The solutions were analyzed for platinum and gold by atomic absorption techniques.

5. Results

The results for six 10% excess nitrogen trifluoride experiments are given in Table I. The correction for fluorine attack on the fluorocarbon was taken as 123.7 kcal./mole of carbon tetrafluoride formed (2). The enthalpy of formation of platinic fluoride was estimated at -180 kcal./mole and of auric fluoride as -130 kcal./mole. The runs were adjusted to an exact quantity of 0.7500 g. of nitrogen trifluoride using an interative procedure for the enthalpy of dissociation of nitrogen trifluoride. Results for the 100% excess nitrogen trifluoride experiments are given in Table II. These runs are adjusted to an exact quantity of 1.3800 g. of nitrogen trifluoride. The difference between the two sets of experiments, 273.7 cal., is the enthalpy of dissociation of 0.6300 g. of nitrogen trifluoride at constant volume. Employing atomic weights of 14.0067 and 18.9984 for nitrogen and fluorine, respectively, there is derived for the reaction:

$$NF_3(g) \rightarrow 1/2\ N_2(g) + 3/2\ F_2(g)$$

$$\Delta E_{r_{298}} = 30.85 \text{ kcal.}$$

Calculating to constant pressure conditions:

$$\Delta H_{f_{298}} = 31.44 \text{ kcal.}$$

Table I

Experimental Results for the Determination of Heat of Dissociation of Nitrogen Trifluoride Using 10% Excess

Mass NF_3, g.	EΔt, cal.	Corrections, cal. CF_4	PtF_4	AuF_3	Ign.	Adj.	Net Calories
0.7559	-1744.0	0.8	1.6	0.1	0.2	-2.6	-1743.9
0.7581	-1740.0	1.0	1.1	0.3	0.7	-3.5	-1740.4
0.7485	-1745.6	0.7	1.0	0.4	0.2	0.7	-1742.6
0.7584	-1737.2	0.5	1.0	0.1	0.7	-3.6	-1738.5
0.7401	-1749.2	0.6	1.3	0.3	0.2	4.3	-1742.5
0.7486	-1745.4	0.6	1.5	0.1	0.2	0.6	-1742.4
						Average	-1741.7

Table II

Experimental Results for the Determination of Heat of Dissociation of Nitrogen Trifluoride Using 100% Excess

Mass NF_3, g.	EΔt, cal.	Corrections, cal. CF_4	PtF_4	AuF_3	Ign.	Adj.	Net Calories
1.3754	-1477.0	5.4	2.5	0.2	0.4	2.0	-1466.5
1.3880	-1471.5	6.5	2.9	0.2	0.2	-3.5	-1465.2
1.3961	-1473.9	5.7	2.6	0.2	0.2	-7.0	-1472.2
1.3783	-1478.2	4.6	2.6	0.3	0.2	0.8	-1469.7
1.3765	-1475.7	5.0	1.8	0.2	0.2	1.5	-1467.0
1.3655	-1483.2	5.6	1.8	0.1	0.2	6.4	-1469.1
1.3775	-1474.0	4.6	1.5	0.1	0.2	1.1	-1466.5
						Average	-1468.0

The reverse process is the enthalpy of formation of nitrogen trifluoride:

$$\Delta H_{f298}(NF_3,\ g) \quad = \quad -31.44 \text{ kcal./mole}$$

The overall uncertainty taken as twice the estimated standard deviation is 0.3 kcal./mole. This does not include any systematic errors which may be inherent in the method. The derived heat of formation is independent of any other thermal data.

B. HEAT OF REACTION OF SULFUR AND NITROGEN TRIFLUORIDE

1. Introduction

Difficulties encountered in measuring the heat of reaction of sulfur and nitrogen trifluoride were discussed in the first quarterly report (1). These difficulties have been overcome and an accurate value has been obtained.

2. Equipment

The calorimeter used for this study was an isothermal static type operating from 23° to 25°C. The following modifications were made prior to this study.

i. A new constant speed stirring motor and stirring gland similar to that used on the Argonne type rotating bomb was installed.

ii. The calorimeter canister was replated with gold due to surface corrosion.

iii. A new nickel bomb head was machined with O-ring seal valves for precision vacuum work and fitted to a nickel bomb body.

Temperature measurements were made with a standard thermistor - Wheatstone bridge circuit. Calibration of the bomb was by combustion of benzoic acid (NBS Sample 39i) in oxygen under the prescribed conditions. Eight determinations gave a value of $E_c = -3203.7 \pm 1.5$ cal./deg. A vacuum system equipped with a pressure gauge was used for bomb loading operations.

3. Materials

Two samples of sulfur were burned in nitrogen trifluoride. The first, laboratory designation DOW 1-S, was supplied by the Inorganic Research Group of the Analytical Laboratories of The Dow Chemical Company. X-Ray analysis showed the sample to be of the orthorhombic crystal structure, and neutron activation analysis indicated 40 ppm oxygen and 0.1% chlorine. Infrared analysis showed no chlorine containing organics. The purity was taken as 99.99%. A second sample, USBM-47, was supplied by Mr. W. D. Good, U. S. Bureau of

Mines, Bartlesville, Oklahoma. This material was of the same batch that was used at Argonne National Laboratory for the determination of the heat of reaction of sulfur and fluorine. An accompanying analysis showed the sulfur sample to be of the orthorhombic variety and to contain total impurities amounting to 109 ppm. The sample purity was taken as 99.99%.

Research Grade nitrogen trifluoride was purchased from Air Products Corporation. Mass and infrared spectroscopy showed 0.15% carbon tetrafluoride. By difference the nitrogen trifluoride was taken to be 99.85% pure.

4. Nature of the Reaction

Pelletized samples of sulfur were found to burn smoothly and completely in five atmospheres of nitrogen trifluoride when ignited by a 8-10 cm. length of molybdenum fuse wire. The reaction is shown below.

$$S(r,c) + 2\,NF_3(g) \rightarrow SF_6(g) + N_2(g)$$

Mass spectral and infrared analysis showed sulfur hexafluoride gas as the only fluoride of sulfur. A small amount of nitrogen trifluoride was thermally dissociated to the elements and necessitated a correction. The molybdenum fuse wire burned quantitatively to molybdic hexafluoride (MoF_6)(g) with the exception of a small easily weighed piece. Data for this correction were available (3). Reaction with the crucible apparently did not occur, as weight checks showed a constant mass. Ignition energy was measured by discharging a standardized capacitor. The sum of the above corrections amounted to approximately 1-2% of the total measured heat.

5. Experimental Procedure

After the benzoic acid calibration experiments were carried out, the nickel bomb was passivated by carrying out several of the initial exploratory determinations. Between runs the bomb was kept under vacuum to preserve the nickel fluoride coating, and all loading operations were carried out in a nitrogen atmosphere glove box.

Sulfur was pelletized in one-half and one-gram quantities, weighed in air on a microgram balance, and transferred to the dry box with the evacuated bomb and fuse. After placing the pellet in the nickel crucible, the molybdenum fuse was placed around the pellet and attached securely to two electrode posts. The bomb was then evacuated to less than 5 μ and charged with five atmospheres of nitrogen trifluoride. The bomb was weighed before and after charging on a 10 kg. capacity balance to determine the mass of nitrogen trifluoride. The loaded bomb was then placed in the calorimeter and the heat of combustion measured.

Immediately after the heat measurement theproduct gases were analyzed for free fluorine by reaction with mercury (4). The analysis vessel consisted of a 250 ml. round flask with a tube extension on the bottom to contain 3-5 ml. of mercury. The flask was evacuated, then filled to one atmosphere with product gases from the bomb. The gases were allowed to condition the bulb and vacuum system for a minimum of four hours before a gas sample was taken for quantitative analysis. This technique was checked out both with mixtures of fluorine and nitrogen and with fluorine of 99.5% purity. Recoveries on these gases averaged ±0.2% of theory. From the gas sampling, one could calculate the grams of fluorine per gram of gas and from this the moles of nitrogen trifluoride decomposed. The residual gases sulfur hexafluoride, nitrogen trifluoride, and nitrogen were then checked by mass and infrared spectroscopy.

6. Results

Results of eight determinations are listed in Table III. The first four experiments utilized the Dow sulfur sample and the last four utilized the Bureau of Mines sulfur sample. Corrections to the total heat, $E\Delta t$, are for dissociation of nitrogen trifluoride, the molybdenum fuse, the ignition energy, and adjustment to standard states (ΔE_{gas}). The adjustment to standard states was made by means of the Berthelot equation of state and critical constants for nitrogen trifluoride, sulfur hexafluoride, and fluorine. Employing an atomic weight of 32.064 for sulfur, the average $-\Delta E_c^\circ/M$ from Table III yields for the reaction:

$$S(rh) + 2\ NF_3(g) \rightarrow SF_6(g) + N_2(g)$$

$$\Delta E_c^\circ = -228.27 \pm 0.19 \text{ kcal.}$$

Since there is no change in the number of moles of gas during the reaction, ΔE_c° is equal to ΔH_c°. Employing a heat of formation of sulfur hexafluoride of -291.77 kcal./mole (5) there is derived:

$$\Delta H_{f298}^\circ (NF_3,\ g) = -31.75 \pm 0.20 \text{ kcal./mole}$$

This result is in agreement within experimental error with the dissociation work discussed earlier in this report. The only other datum for nitrogen trifluoride which does not involve hydrogen fluoride as a product is the heat of combustion of boron in nitrogen trifluoride by Ludwig and Cooper (6) of -239.7 ± 1.2 kcal./mole. Using the most recent heat of formation for boron trifluoride of -271.65 kcal./mole (7) there is derived for nitrogen trifluoride a $\Delta H_{f298}^\circ = -32.0 \pm 1.5$ kcal./mole, in agreement within experimental error with our values.

Table III

Experimental Combustion Data for the Sulfur-Nitrogen Trifluoride Reaction

E = -3203.7 ± 1.5 cal./deg.

Run No.	Sample mass g.	EΔt cal.	Corrections, cal. NF_3	Mo	Ign.	ΔE gas	$-\Delta E_c^\circ/M$ cal./g.
7[a]	0.95642	-6,715.0	-115.0	31.4	1.6	0.2	7,106.5
8[a]	0.48179	-3,249.5	-213.3	31.4	1.6	-0.3	7,119.5
9[a]	0.47001	-3,160.2	-231.2	43.2	1.5	-0.3	7,121.1
11[a]	0.96877	-6,814.0	-116.4	37.7	1.4	0.2	7,113.2
12[b]	0.92868	-6,536.5	-128.6	41.1	1.4	0.2	7,131.0
14[b]	0.91896	-6,452.6	-126.6	42.6	1.0	0.2	7,111.7
17[b]	0.93002	-6,536.5	-115.8	28.9	1.0	0.2	7,120.5
18[b]	0.93922	-6,640.0	-97.1	38.6	1.1	0.2	7,130.6
						Average	7,119.3

σ = ± 6 cal./g.

[a] Denotes Dow sulfur sample.

[b] Denotes Bureau of Mines sulfur sample.

C. HEAT OF FORMATION OF AQUEOUS HYDROGEN FLUORIDE

One of the purposes of the work on nitrogen trifluoride was to supply a heat of formation of aqueous hydrogen fluoride. The two values for nitrogen fluoride given in this report, -31.44 ± 0.30 and -31.75 ± 0.20 kcal./mole, are independent of the heat of formation of hydrogen fluoride. An average of -31.6 kcal./mole can be combined with previous work from this laboratory (8) on the heat of reaction of nitrogen trifluoride and hydrogen to form hydrogen fluoride (1 in 123 H_2O) to derive for hydrogen fluoride (1 in 123 H_2O) a heat of formation of -77.03 kcal./mole. This can be taken as the same as hydrogen fluoride (1 in 100 H_2O) according to heat of dilution data from Cox and Harrop (9). Several other recent investigations can be compared with this result. Teflon fluorocarbon has been burned in oxygen (10) and in fluorine (11). Combination of these data yields ΔH = -170.0 kcal. for the reaction:

$$2\ F_2(g) + 2\ H_2O(l) \rightarrow 4\ HF\ (1\ \text{in}\ 10\ H_2O)(l) + O_2(g)$$

From this is derived a ΔH°_{f298} for hydrogen fluoride (1 in 10 H_2O) of -76.06 kcal./mole, and appropriate dilution data yield for hydrogen fluoride (1 in 100 H_2O) a ΔH°_{f298} of -76.74 kcal./mole. Measurements of the heat of hydrolysis of silicon tetrafluoride (12) combined with work on the heat of formation of silicon dioxide (13) and silicon tetrafluoride (13) yield for hydrogen fluoride (1 in 650 H_2O) a value of -77.04 kcal./mole, which when adjusted to hydrogen fluoride (1 in 100 H_2O) yields a ΔH°_{f298} of -76.93 kcal./mole.

(U) Domalski and Armstrong (14) reported the heat of combustion of graphite in fluorine, which can be combined with the heat of hydrolysis of carbon tetrafluoride reported by Cox, Gundry, and Head (15) to yield for hydrogen fluoride (1 in 20 H_2O) a ΔH°_{f298} of -76.71 kcal./mole. This is adjusted to -76.76 kcal./mole for hydrogen fluoride (1 in 100 H_2O). A final value is derived from measurements of the heat of combustion of boron in fluorine (4), the heat of combustion of boron in oxygen (16) to give aqueous fluoboric acid, and the heat of solution of boron trifluoride in aqueous hydrogen fluoride (17) to yield the heat of formation of hydrogen fluoride (1 in 3 H_2O) as -76.34 kcal./mole. These results are presented graphically in Figure 2, along with the present "selected best value" of the National Bureau of Standards which is also used for the JANF Thermochemical Tables. The need for revision is obvious. A final selection of a new "best value" will be deferred pending completion of pertinent work at the National Bureau of Standards on direct combination of hydrogen and fluorine in a flame calorimeter and at Argonne National Laboratory on the heats of formation of alkali metal fluorides.

D. WORK IN PROGRESS (U)

(C) After some exploratory experiments, it was concluded that the optimum method for the heat of formation of 1,2,3-tris[1,2-bis(difluoroamino)ethoxy]propane (TVOPA) is combustion in oxygen of a solution in 2-octanone sealed in a Mylar bag. Several combustions have been run, but calculations and analysis are incomplete. A similar approach will be used for poly-bis(difluoroamino)epoxypropane (P-BEP), a sample of which is on hand.

(C) A dry box facility for beryllium compounds is nearly complete. Work on lithium-doped beryllium hydride will begin when this facility is operative.

(U) Exploratory work has shown that nitrogen trifluoride and cyanogen (C_2N_2) can be mixed without reacting. When ignited by a hot wire, the mixture explodes to carbon tetrafluoride and nitrogen. This reaction is appealing as a means to the heat of formation of carbon tetrafluoride, since the heat of formation of cyanogen is well established.

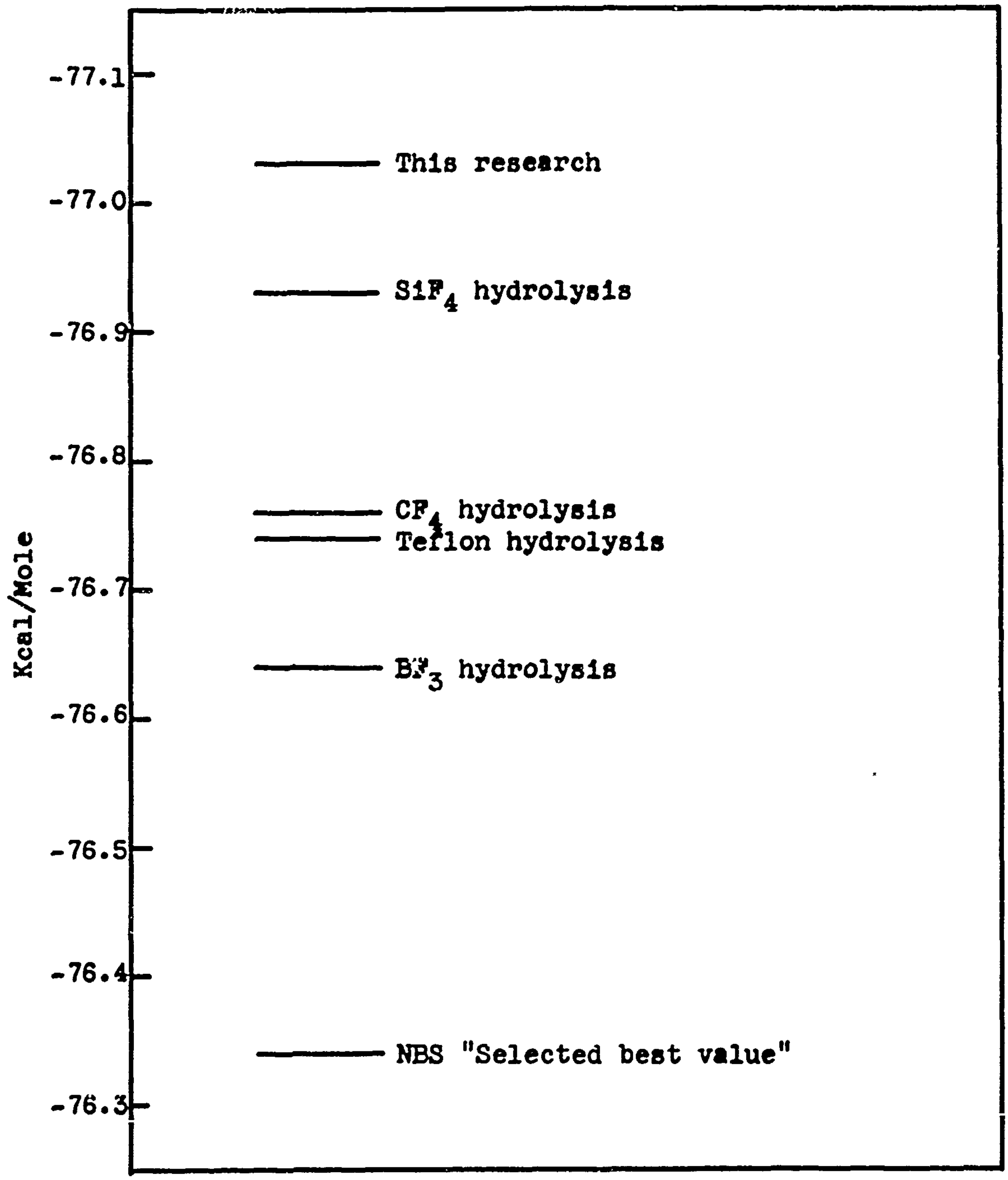


Fig. 2 - Heat of Formation of Hydrogen Fluoride (1 in 100 H_2O) by Various Approaches

E. SAMPLE PURIFICATION AND SYNTHESIS (U)

1. Purification (U)

(C) In support of the thermal measurements, four compounds were received and purified for heat of formation studies. Thirty grams of nitrogen trifluoride, NF_3, were purified by a codistillation procedure using a column packed with fluorinated magnesium metal beads. A 10 g. sample of beryllium hydride was received from Ethyl Corporation. From Rohm and Haas Company was received 15 g. of TVOPA, which is 1,2,3-tris[1,2-bis(difluroramino)ethoxy]-propane. Also obtained was a 10 g. sample of P-BEP, poly-bis-(difluoroamino)epoxypropane, from Shell Development Company. TVOPA and P-BEP were received as methylene chloride solutions, and, upon demand, 0.5-1.5 g. samples of these materials have been prepared for the Thermal Reseach Laboratory by evaporation of the solvent *in vacuo*. Vacuum pumping on the samples was continued for two days with constant agitation to assure complete removal of the solvent.

2. Synthesis (U)

a. General (U)

(U) Because of difficulty in finding a source, trifluoromethoxydifluoroamine, CF_3ONF_2, is being prepared by the photochemical reaction of fluoroxytrifluoromethane and tetrafluorohydrazine:

$$CF_3OF + N_2F_4 \rightarrow CF_3ONF_2 + COF_2 + NF_3 + CF_4$$

Different chromatography columns were used to purify the CF_3ONF_2. The temperature was varied from -30°C. to -80°C. with three column packings; 25% KEL-F on chromosorb W, 25% FS 1265 on chromosorb W and TBA. With all three columns the incomplete removal of all the tetrafluorohydrazine from the product prevented the use of these particular columns. The use of an acid wash to remove the excess N_2F_4, and then a base wash to eliminate NO, NO_2, and SiF_4 was effective. However, the duration of the acid wash was critical; if it was too long, some hydrolysis occurred.

(U) The method which gave the best separation and purest product was codistillation. The product identification and purity were followed with infrared, mass, and nuclear magnetic resonance spectroscopy.

b. Experimental (U)

(U) The tetrafluorohydrazine for the reaction was obtained from an outside source, and the fluoroxytrifluoromethane was prepared by the reaction of fluorine and carbon monoxide in a nitrogen stream at 400°C.

Fluoroxytrifluoromethane and 25% excess tetrafluorohydrazine were mixed in a five-liter reaction vessel and irradiated with ultraviolet light from a 450 watt mercury lamp for 24 hrs. A corex glass filter was used to screen out light which activates the NF_2-group.

The gaseous products were stored in a 30 cc. stainless steel cylinder and purified in half-gram lots by codistillation. The purity of the sample was estimated to be greater than 90% from the infrared spectrum. A small amount of tetrafluorohydrazine was still present in the sample. Complete removal of the tetrafluorohydrazine may be accomplished by washing with 50% sulfuric acid followed by a second codistillation.

SECTION III

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) The study of the combustion characteristics of a beryllium-containing propellant has been continued. The major interest during this period has been centered on the decomposition and combustion of nitrocellulose and the plasticizers, TMETN and DEGDN. Additional work was carried out on the system BeH_2-NH_4ClO_4, with prime emphasis on the state of the beryllium-containing species.

(U) The work on the binder and plasticizer completes the initial phase of the investigation.

B. EXPERIMENTAL PROCEDURE (U)

(U) Separate studies were carried out in the following manner. A solution of plastisol-grade nitrocellulose (PGNC) in diethyl ether was allowed to drip over the graphite strips, as described in earlier reports (1). The strips were placed in the reactor cell and the cell evacuated. The samples were then exposed to 800-1500 joules from the flash lamp. Spectra were taken from 45-500 µsec. after the initiating flash. The spectral range analyzed was 2300-4200 Å.

(U) The plasticizers, TMETN and DEGDN, were each diluted with diethyl ether to solution of 50% by volume. The solutions were applied to the strips in the conventional manner. The flash conditions and analyses were the same as those for PGNC. The spectra for all of the work were recorded on KODAK I-O, I-F, 103-O and 103-F spectrographic plates, with the latter plates being used for densitometer determinations.

(U) Additional combustion studies of PGNC in oxygen were carried out to study the role of the NO_2 group as a combustion promoter. Spectral analyses were carried out prior to, and immediately after, each flash to insure sample integrity. The position of the absorption lines was measured with a linear comparator against a mercury arc standard. Positional errors of no more than ±0.3 Å were detected.

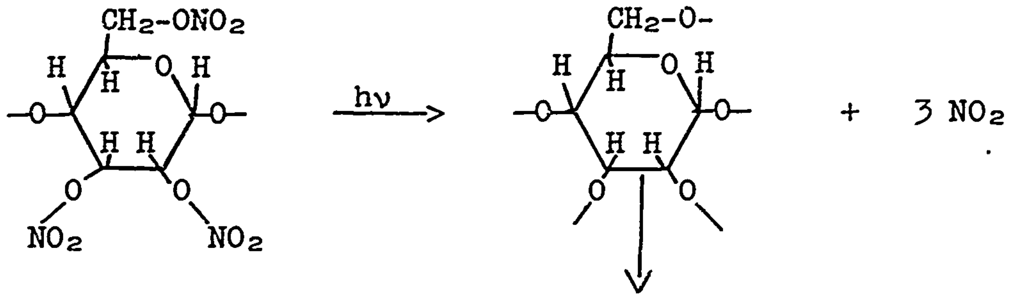
(U) Combustion spectra of selected hydrocarbon-NO_2 mixtures were recorded for the purpose of determining which combustion species were the result of the hydrocarbon part of the binder and plasticizer.

(C) Additional mixtures of BeH_2-NH_4ClO_4 were also flashed. The weight ratio of the mixture was 75% NH_4ClO_4 to 25% BeH_2. The prime interest was centered on the spectral range 2500-3500 Å. This is the region in which the species BeH^+ is found.

C. DISCUSSION AND RESULTS (U)

(U) The thermal decomposition of PGNC yielded NO_2 immediately upon flashing. The NO_2 decomposed to NO + O within the first 100 μsec. The O atoms from the NO_2 apparently attacked the hydrocarbon portion of the molecule, as the main reaction products were H_2CO and CH_3CHO, with a small amount of CO and CO_2. The data show that the pyrolysis of PGNC yields partial oxidation products of the backbone rather than CO, H_2O, and C. The nitrogen species seen during and after the pyrolysis is NO.

(U) Using an idealized structure for PGNC, the pyrolysis can be written as follows:



$$H_2CO + [C_5H_5O_5]$$

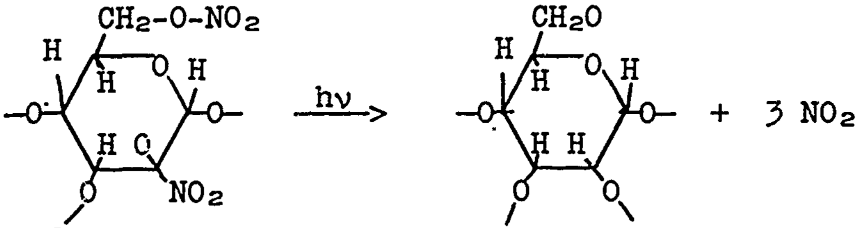
$$[C_5H_5O_5] \xrightarrow{\text{slow}} CH_3CHO + CO_2 + HCO + CO$$

$$NO_2 \rightarrow NO + O$$

$$2\,HCO + O \rightarrow H_2O + CO$$

(U) When oxygen is added in stoichiometric amounts or greater, the postulated reaction products H_2CO and CH_3CHO decrease, and CO and CO_2 increase. It was observed that NO_2 reappeared at the completion of the combustion when O_2 was in excess, apparently from the reaction of NO and O atoms in the cool outer part of the flame. The combustion of PGNC is similar to that of methane and ethane when O_2 is in excess.

(U) The following steps are proposed for the combustion of PGNC in oxygen:



(I)

$$NO_2 \rightarrow NO + O$$

$$I \xrightarrow{\Delta} H_2CO + [C_5H_5O_5] \xrightarrow{slow} CH_3CHO + CO_2 + HCO + CO$$

$$HCO + O \xrightarrow{slow} CO + OH$$

$$HCO + O_2 \longrightarrow CO_2 + OH$$

$$CH_3CHO \longrightarrow CH_3 + HCO$$

$$CH_3CHO \longrightarrow CH_4 + CO$$

$$CH_4 + O \longrightarrow CH_3 + OH$$

$$CH_3 + O_2 \longrightarrow H_2CO + OH$$

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$

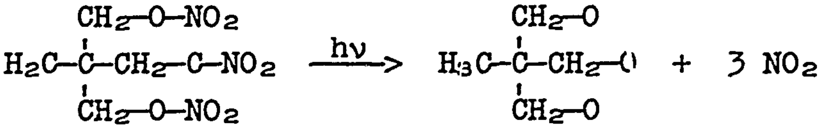
$$H_2CO + O \longrightarrow H_2O + CO$$

$$NO + O \longrightarrow NO_2 \text{ (excited)}$$

The intense OH spectrum attests to its role as chain-carrier in the combustion of PGNC.

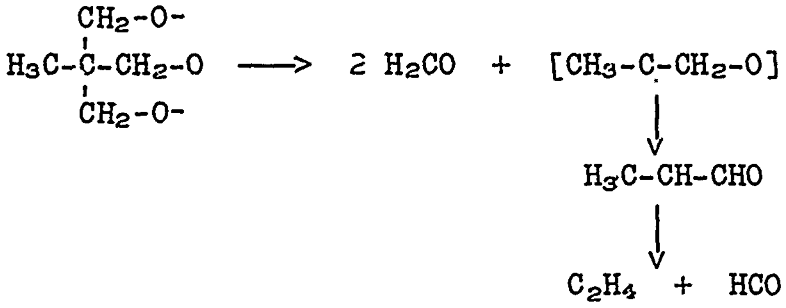
The plasticizer TMETN, when flashed with more than 1000 joules, yields C_2H_4, H_2CO and CO as products, the species of H_3CO and CO being predominant.

The pyrolysis products can be accounted for by the following scheme:



$$H_2C\!-\!\underset{CH_2-O-NO_2}{\overset{CH_2-O-NO_2}{C}}\!-\!CH_2\!-\!C\!-\!NO_2 \xrightarrow{h\nu} H_3C\!-\!\underset{CH_2-O}{\overset{CH_2-O}{C}}\!-\!CH_2\!-\!O + 3\,NO_2$$

$$NO_2 \longrightarrow NO + O$$

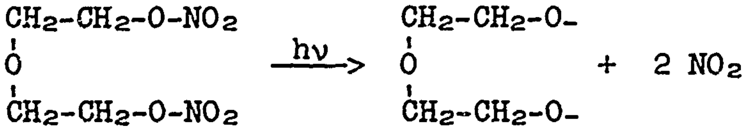


$$H_3C-\overset{\overset{\textstyle CH_2-O-}{|}}{\underset{\underset{\textstyle CH_2-O-}{|}}{C}}-CH_2-O \longrightarrow 2\ H_2CO + [CH_3-\dot{C}-CH_2-O] \rightarrow H_3C-CH-CHO \rightarrow C_2H_4 + HCO$$

$$HCO + O \longrightarrow CO + OH$$

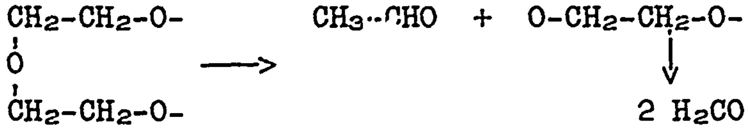
$$2\ HCO \longrightarrow H_2CO + CO$$

(U) It can be assumed that DEGDN pyrolyzes in a manner similar to TMETN, giving mainly H_2CO as product. The proposed scheme for the pyrolysis is:



$$\begin{matrix} CH_2-CH_2-O-NO_2 \\ | \\ O \\ | \\ CH_2-CH_2-O-NO_2 \end{matrix} \xrightarrow{h\nu} \begin{matrix} CH_2-CH_2-O- \\ | \\ O \\ | \\ CH_2-CH_2-O- \end{matrix} + 2\ NO_2$$

$$NO_2 \longrightarrow NO + O$$



$$\begin{matrix} CH_2-CH_2-O- \\ | \\ O \\ | \\ CH_2-CH_2-O- \end{matrix} \longrightarrow CH_3-CHO + O-CH_2-CH_2-O- \rightarrow 2\ H_2CO$$

(U) The combustions of TMETN and DEGDN in oxygen yield more of CO, CO_2 and H_2O than PGNC. Again, NO_2 is seen very late in the reaction. The combustion steps are similar to those of PGNC and will not be detailed.

(C) The pyrolytic decomposition of BeH_2 was carried out in a manner similar to that previously described (1). The data obtained in these latter experiments correlate with those obtained earlier, i.e., the species BeH^+ seems to be more stable than BeH. Additional lines with low J_K values were observed in the 0-0 band of BeH at 4991 Å.

(U) The photomultiplier tape-recorder circuit for continuous recording of species has been installed. Calculations are under way to determine the extent to which the instrument can resolve weak absorption lines. The very narrowness of the BeH and BeH^+ lines (0.1-0.2 Å) makes them hard to observe. The narrowness of the slit required to resolve these lines also makes them difficult to find. In addition to these mechanical difficulties, the problem of a constant intensity light source is yet to be resolved. The electronic balancing of the various components is being done by L. T. Finlayson, who also helped construct the original apparatus.

(C) Calibration of the photometer circuit is being carried out by observation of the 0-0 band of the OH radical resulting from the combustion of methylacetylene. The OH lines from this system are wide (0.3-0.7 Å) and relatively intense. The work to resolve the relationship between BeH and BeH^+ will begin shortly.

D. FUTURE WORK (U)

(C) The problems associated with the photomultiplier - tape recorder will receive the major share of our interest during the next quarter. Additional work will be done on the reaction between beryllium hydride and cyanogen in attempts to prepare HCN from the hydrogen of the beryllium hydride and the CN from cyanogen. The amount of HCN found should equal the amount of BeH_2 decomposed to BeH, BeH^+, and H. Our data show that the reaction between BeH and/ or BeH^+ is slow compared to their rate of formation from BeH_2. Thus, the amount of HCN prepared should equal the amount of H atoms formed from the decomposition of BeH_2 as follows:

$$BeH_2 \xrightarrow{h\nu} [BeH + BeH^+] + H$$

$$C_2N_2 \xrightarrow[Fast]{h\nu} CN$$

$$H + CN \xrightarrow{Fast} HCN$$

$$2\begin{bmatrix} BeH \\ BeH^+ \end{bmatrix} \xrightarrow[Slow]{} 2\,Be + H_2$$

(C) Preliminary work has shown that HCN is indeed formed from H_2 and C_2N_2 and from NH_2 and C_2N_2. The preliminary work shows that the proposed reaction is feasible. The extent to which it can be applied to BeH_2 is yet to be determined.

SECTION IV

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13 ABSTRACT

The heat of dissociation of nitrogen trifluoride and the heat of reaction of sulfur with nitrogen trifluoride have been determined and are reported. The heat of formation of aqueous hydrogen fluoride has been determined from the nitrogen trifluoride work and are compared with the previously reported data. Research in progress on TVOPA, lithium-doped Beane, and the reaction of nitrogen trifluoride and cyanogen is described. The work on sample purification and the synthesis of trifluoromethoxydifluoroamine is also recorded. The results of the study of the combustion kinetics of Beane, nitrocellulose, TMETN, and DEGDN are discussed.

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Thermochemistry						
Heat of Foratmion						
Heat of Dissociation						
Nitrogen Trifluoride						
Nitrogen Trifluoride with Sulfur						
Aqueous Hydrogen Fluoride						
NF Compounds						
Combustion Kinetics						
Beane						
Nitrocellulose						
TMETN						
DEGDN						

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