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AFRPL-TR-68-26

(Unclassified Title)

INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PROPELLANT INGREDIENTS AND THE BURNING MECHANISMS OF PROPELLANTS
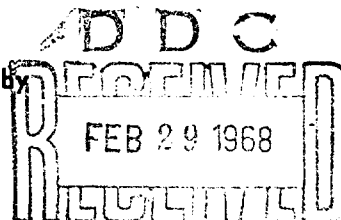
ANNUAL PROGRESS REPORT AFRPL-TR-68-26

(2 January 1967 to 31 December 1967)

January 1968

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

DDC

FEB 29 1968

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Report Nr. T-0025-4Q-67

ANNUAL PROGRESS REPORT (U)
(2 January 1967 to 31 December 1967)

January 1968

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
EDWARDS, CALIFORNIA 93523
CONTRACT NR. F04611-67-C-0025

CHEMICALS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, under USAF Contract Nr. F04611-67-C-0025. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties of Propellant Ingredients and the Burning Mechanisms of Propellants." 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 first annual report, covering the work performed during 2 January 1967 through 31 December 1967. The Dow Report Number is T-0025-4Q-67.

This work was performed by R. W. Anderson, R. V. Petrella, G. C. Sinke, A. C. Swanson, and L. C. Walker under the technical supervision of Dr. D. R. Stull and management supervision of Dr. D. A. Rausch.

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.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

(C) The heat of formation of crystalline lithium-doped beryllium hydride was derived from heat of hydrolysis in aqueous Cl as -5.0 kcal/mol. This is slightly more negative than previously found values for amorphous beryllium hydride.

(C) A sample of alane-terminated liquid beryllium hydride was successfully hydrolyzed in a dioxane-HCl-water mixture. Analysis of the reaction products demonstrated that the sample was not a simple compound but probably a complex mixture of a composition about $Al_9Be_{11}(CH_3)_{29}H_{20}$. The heat of formation of this mixture from the elements was calculated from the heat of hydrolysis and appropriate auxiliary heats of mixing to be -35.7 ± 2.1 kcal/100 grams.

(C) The heat of combustion of TVOPA in oxygen was determined. First results showed large variations due to residual chlorinated and/or fluorinated solvent. When high purity material became available, reasonably precise values were obtained. The average heat of combustion led to $\Delta Hf_{298} = -208.1 \pm 2.9$ kcal/mol, in good agreement with work at Rohm and Haas Co.

(C) DAHTP from Thiokol Chemical Corporation was found to be a 2:1 mixture of NH_4ClO_4 and $N_2H_6(ClO_4)_2$. Heat of solution measurements yielded a heat of formation of -210.4 kcal/mol. Further work on perchlorate combustion calorimetry is in progress.

(U) The heat of formation of CF_4, a "key" datum in fluorine compound calorimetry, was determined from the explosive reaction of C_2N_2 and NF_3. The heat of explosion was determined in a nickel bomb. When combined with the heat of formation of NF_3 previously measured in this laboratory, the heat of formation of $CF_4(g)$ was calculated to be -223.23 ± 0.60 kcal/mol, in excellent agreement with recent work at other laboratories.

(U) Gaseous CF_3ONF_2 when mixed with hydrogen was found to explode when ignited, yielding HF, N_2, and CO. This reaction was

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employed for a calorimetric study in a platinum-lined combustion bomb fitted with a reservoir of water. The water could be forced into the bomb after the explosion, producing aqueous HF which is a better defined state than gaseous HF. The heat of formation of $CF_3ONF_2(g)$ was derived as -189.1 ± 0.8 kcal/mol. This value is slightly more negative than would be estimated from bond energy terms.

(C) The heat of hydrolysis of ClF_3O (Florox), obtained from Rocketdyne Corp., was measured in the same apparatus employed for CF_3ONF_2. Appropriate heats of mixing showed no significant thermal effects from the complex final solution. The heat of formation of Florox was found to be -33.2 ± 0.5 kcal/mol (gas) or -40.2 ± 0.5 kcal/mol (liquid), in good agreement with work at Rocketdyne.

(U) Tetrafluorohydrazine (N_2F_4) could be mixed with cyanogen without reacting until ignition. This was the basis for a calorimetric study leading to $\Delta Hf(N_2F_4, g) = -4.7\pm0.6$ kcal/mol. This value, as well as that given above for CF_4, is independent of the heat of formation of HF. All other data in this report for fluorine compounds are based on NBS Technical Note 270-1 values for HF (aq).

(U) Removal of solvent from TVOPA and preparation and purification of CF_3ONF_2 have both been completed. A photochemical process and a low temperature fluorination procedure have been used to prepare CF_3NF_2. The latter was the better method.

(U) The combustion of boron for air-augmented combustion has been studied by the technique of flash pyrolysis. The combustion behavior of boron-oxygen, boron-oxygen-water and boron-oxygen-fluorine-containing systems have been analyzed from the time of initiation to 3000 μsec. The combustion intermediates have been characterized and the flame temperatures calculated.

(U) The presence of water in the combustion system increases the formation of the intermediate HOBO and results in a lowered flame temperature. The addition of fluorine to the system

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precludes the formation of water and likely that of HOBO. The result is a more efficient utilization of the boron and oxygen resulting in a higher flame temperature.

(U) The combustion of boron in the presence of ammonium perchlorate has also been studied. The combustion of the boron takes place in an atmosphere of gaseous products resulting from the deflagration of the AP. Only small amounts of water are present in this system.

(U) Previous studies have shown water to be a major product in the combustion of hydrocarbon binders. This, along with the present work, suggests that in order to minimize the formation of HOBO, via:

$$H_2O + BO_2 \rightarrow HOBO + OH$$
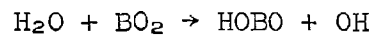
the hydrocarbon binder should be modified in such a way as to minimize the formation of water. The results of the fluorine work reported herein show that a fluorocarbon binder would minimize the formation of water and HOBO.

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SECTION I

(U) THERMOCHEMISTRY

A. HEAT OF FORMATION OF LITHIUM-DOPED BERYLLIUM HYDRIDE (C)

1. Introduction (U)

(C) A sample of lithium-doped beryllium hydride was furnished by Dr. Fred W. Frey of Ethyl Corporation. The sample was characterized by Ethyl Corporation as follows:

<u>Ethylane Sample No. E-166</u>

Constituent:

Purity[a]	91.4%
Beryllium Metal	1.4%
Beryllium Alkyls[b]	
C_4	0.7%
C_3	0.0%
C_2	0.7%
Lithium[c]	1.4%
Chloride	0.31%
Beryllium Alkoxides	0.11%
Carbon	1.17%
Hydrogen	16.91%
Absolute Density	0.76 g/cc

X-Ray Phase 378-295 - 60%
       Phase 338-208 - 40%

[a] Purity is average of deuterolysis and carbon-hydrogen, assuming all hydridic hydrogen bound to beryllium, none to lithium.

[b] All alkyls assigned to beryllium.

[c] Probably present as lithium hydride or lithium beryllium tetrahydride.

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(C) The heat of formation of this crystalline beryllium hydride was derived from measurements of the heat of solution in hydrochloric acid. Analytical data agree in general with those of Ethyl Corporation, but differ in some quantitative aspects.

2. Equipment (U)

(U) A rotating bomb calorimeter and a platinum-lined rotating bomb were used for the calorimetry. An automatic bridge developed under a previous contract was employed for the time-temperature curves. The calorimeter was calibrated by combustion of NBS standard samples of benzoic acid. The value obtained for E_{calor} was 3428.05 cal/°C with a standard deviation of 0.01%.

3. Procedure (U)

(C) A thin walled glass bulb was filled with 7.26 N HCl, sealed off, and placed in the platinum-lined bomb. The bomb was closed and thoroughly flushed with dry prepurified nitrogen. The bomb was locked into a dry box and opened. An analytical balance in the dry box was used to weigh out an appropriate amount of beryllium hydride which was then added to the bomb. The bomb was closed, removed from the dry box and placed in the calorimeter. After initial drift rate readings were taken, rotation of the bomb was started. The tumbling glass bulb broke open and reaction took place. After completion of the calorimetric readings, the bomb gases were analyzed by combustion to CO_2 and H_2O and adsorption in Ascarite and magnesium perchlorate. The bomb solution was recovered and analyzed for beryllium and lithium.

(C) To eliminate any systematic errors, the same procedure was used for the heat of solution of a sample of beryllium metal. The difference between heats of solution of the hydride and the metal is a measure of the heat of formation of beryllium hydride.

4. Analytical Results (U)

(C) A summary of the analytical data for the beryllium hydride is given in Table I. The interpretation of these results

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Table I

(C) Analytical Data for Beryllium Hydride (Sample E-166)

Element	% of Sample	Analysis Technique
Chlorine	0.29 ± 0.03	Neutron activation
Oxygen	4.44 ± 0.01	Neutron activation
Copper	0.10 ± 0.01	Neutron activation
Manganese	Negligible	Neutron activation
Iron	Negligible	Neutron activation
Beryllium	75.6 ± 0.2	Precipitation of BeO from bomb solutions, firing at 1000°C and weighing
Lithium	1.34 ± 0.04	Atomic absorption analysis of bomb solutions after removal of beryllium
Total Carbon Total Hydrogen	1.76 ± 0.1 16.60, 16.73	Direct combustion of sample in oxygen and absorption of CO_2 and H_2O
Carbon Hydrogen	1.16 ± 0.02 33.20 ± 0.06	Combustion of bomb gases formed by hydrolysis and absorption of CO_2 and H_2O
Carbon	0.32	Carbon in bomb solutions formed by hydrolysis and analyzed by a combustion-infrared method

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is arbitrary. The results of both Ethyl Corporation and Dow were used to arrive at the proposed composition given in Table II. The calculated elemental composition compares well with the experimental results of Table I. There is also good agreement with Ethyl Corporation data except that our total hydrogen, as well as our hydridic hydrogen, is slightly lower.

<u>Table II</u>

(C) Proposed Composition of Beryllium Hydride (Sample E-166)

Molecular Composition	Calculated Elemental Analysis For This Composition, %
0.125 CuO	0.10 Cu
0.327 BeCl$_2$	0.29 Cl
1.535 LiH	4.32 O
0.775 Be(C$_2$H$_5$)$_2$	1.34 Li
0.775 Be(C$_4$H$_9$)$_2$	75.62 Be
0.110 Be(OC$_2$H$_5$)$_2$	16.74 H
6.463 BeO	1.59 C
88.740 BeH$_2$	
0.560 Be	1.16 C (gas phase)[a]
0.590 Residual ether or solvent	33.23 H (gas phase)[b]

[a]Assuming only the beryllium alkyls contribute to gas phase carbon gives 1.16% C.

[b]Assuming LiH, BeH$_2$, Be, and beryllium alkyls contribute to gas phase hydrogen gives 33.23% H.

(U) Two samples of beryllium metal were used. A sample obtained from Electronic Space Industries, Inc., was found to contain 1.5% oxygen and gave erratic heat of solution results. A second sample obtained from United Minerals and Chemicals Corporation contained 0.012% oxygen by neutron activation analysis. X-Ray fluorescence analysis of this second sample indicated no other metals present in amounts greater than 0.001% each. The total metallic impurity was indicated as less than 0.01%.

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5. Calorimetric Results (U)

(U) The results of five successful experiments on beryllium metal are given in Table III. These values differ slightly from those originally reported in Dow Quarterly Progress Report AFRPL-TR-67-113 covering the period 1 January 1967 to 31 March 1967. After that report was issued, it was discovered that the computer program for calculating the calorimeter temperature rise contained incorrect mathematical expressions. The corrected results given here are considerably improved in precision. Two runs previously rejected because they were far outside the usual limits of error are now found to agree well with the other five, and a total of seven experiments are now given in Table III.

(U) The sample weight was corrected to mass in vacuum. The density of beryllium was taken as 1.85 g/cc. The product of the calorimeter equivalent and the corrected temperature rise is equal to the total calories absorbed by the system. Additional heat was absorbed by the glass bulb, the acid, beryllium metal, platinum added to the system, and one atmosphere of nitrogen in the bomb. Heat capacity values for these substances are given in Table IV. The vaporization correction is due to the vaporization of water and HCl into the dry atmosphere of the bomb. The average $-\Delta E_R/M$ for the five runs is corrected for 0.02% BeO to yield for the process (Be at. wt. = 9.0122):

$$Be(c) + 2 HCl (1 in 6.52 HCl) \rightarrow BeCl_2 (in aq HCl) + H_2(g)$$
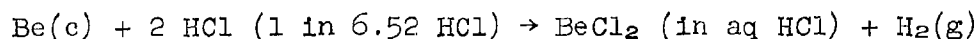
$$\Delta E_R = -90.15 \text{ kcal/mol}$$

$$\Delta n(g) = +1, \Delta nRT = +0.59 \text{ kcal/mol}$$

$$\Delta H_R = -89.55 \text{ kcal/mol}$$

(C) The results of five runs on beryllium hydride are given in Table V. The density was taken as 0.76 g/cc to correct weights to mass in vacuum. Additional heat terms for bomb contents were calculated as for the beryllium metal runs. Heat capacity data

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Table III

(U) Heat of Solution of Beryllium in 7.26 N HCl

	Experiment Number						
	1-A	2-A	3-A	4-A	5-A	6-A	7-A
Be mass, g	0.37607	0.38219	0.37059	0.40458	0.40693	0.40692	0.40296
Δt_c, °C	1.09217	1.10912	1.07546	1.17239	1.17980	1.18012	1.16851
$\Sigma \Delta t_c$, cal	3744.01	3802.12	3686.73	4019.01	4044.41	4045.51	4005.71
ΔE glass, cal	0.64	0.72	1.14	0.59	0.55	0.62	0.61
ΔE_{HCl}, cal	17.61	18.22	17.04	20.37	20.63	20.49	20.27
ΔE_{Be}, cal	0.18	0.18	0.17	0.21	0.21	0.21	0.20
ΔE_N, cal	0.07	0.07	0.07	0.08	0.08	0.08	0.07
ΔE_{pt}, cal	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Vaporization corr., cal	2.15	2.15	2.15	2.15	2.15	2.15	2.15
$-\Delta E_R/M$ cal/g	10010.7	10004.2	10003.9	9991.7	9997.0	9999.8	9998.7

Average $-\Delta E_R/M$ = 10000.9 cal/g

Corrected for 0.02% BeO = 10002.8 cal/g

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are listed in Table IV. The vaporization correction is the same
as for the beryllium runs, since the ratio of acid to sample was
adjusted to make the final solution for the two sets of experiments
identical. The average $-\Delta E_R/M$ for four runs is adjusted for
impurities by means of data given in Table VI. The final value
for pure crystalline beryllium hydride applies to the process
(BeH_2 mol. wt. = 11.02814):

$$BeH_2(c) + 2\ HCl\ (1\ in\ 6.52\ HCl) \rightarrow BeCl_2\ (in\ aq\ HCl) + 2\ H_2(g)$$
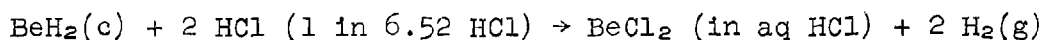
$$\Delta E_R = -85.76\ kcal/mol$$

$$\Delta n(g) = +2\ \Delta nRT = +1.18\ kcal/mol$$

$$\Delta H_R = -84.57\ kcal/mol$$

Table IV

(C) Heat Capacity of Bomb Contents

Substance	Cp, cal/g°K
Pyrex glass	0.17
7.26 N HCl	0.658
Platinum	0.0317
Nitrogen	0.178
Beryllium	0.436
Beryllium hydride	0.60

(C) Combining this result with the previous value for
beryllium metal yields for the hydride:

$$\Delta Hf_{298}(BeH_2, c) = -5.0\ kcal/mol$$

(U) The uncertainty is difficult to assess because of the
large impurity corrections, but does not appear likely to exceed
±1 kcal/mol. The result obtained for this crystalline sample
is only slightly more negative than -4.5 kcal/mol obtained earlier
in this laboratory for an amorphous sample.

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Table V

(C) Heat of Solution of Beryllium Hydride in 7.26 N HCl

	Experiment Number				
	1-A	2-A	3-A	4-A	5-A
BeH_2 mass, g	0.5497	0.5200	0.5243	0.5162	0.5446
Δt_c, °C	1.13213	1.07153	1.08053	1.06750	1.12238
$\varepsilon \Delta t_c$, cal	3881.00	3673.26	3704.11	3659.44	3847.57
ΔE glass, cal	0.60	0.55	0.54	0.60	0.56
ΔE_{HCl}, cal	19.92	18.02	18.37	18.27	19.44
ΔE_{BeH_2}, cal	0.37	0.33	0.34	0.33	0.36
ΔE_N, cal	0.07	0.07	0.07	0.07	0.07
ΔE_{Pt}, cal	0.05	0.05	0.05	0.05	0.05
Vaporization corr., cal	2.15	2.15	2.15	2.15	2.15
$-\Delta E_R/M$, cal/g	7102.4	7104.7	7105.9	7130.8*	7106.5

*Not included in average; failed statistical test.

$-\Delta E_R/M = 7104.9$ cal/g

Corrections in Calories

CuO	- - - -	0.17	$Be(C_4H_9)_2$ - - - -	7.43
$BeCl_2$	- - -	1.88	$Be(OC_2H_5)_2$ - - -	0.14
LiH	- - - -	89.03	Be - - - - - -	55.68
BeO	- - - -	36.71	corrected sample mass = 0.8874 g
$Be(C_2H_5)_2$	- -	13.25	corrected $-\Delta E_R/M$ = 7776.2 cal/g

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Table VI

(U) Heat of Reaction of Impurities with 7.26 N HCl

Impurity	$-\Delta E_r/M$, cal/g
CuO	137
$BeCl_2$	576
LiH	5800
BeO	568
$Be(C_2H_5)_2$	1710
$Be(C_4H_9)_2$	958
$Be(OC_2H_5)_2$	124
Be	9943

B. HEAT OF FORMATION OF ALANE-TERMINATED LIQUID BERYLLIUM HYDRIDE, ATBH (C)

1. Introduction (U)

(C) A sample of ATBH was furnished by Dr. Frank Gunderloy of Rocketdyne Division of North American Aviation, Inc. According to a Rocketdyne Data Sheet accompanying the sample, BeH_2 and insoluble impurities were filtered off and excess $Al(CH_3)_3$ removed in vacuum to leave a clear mobile liquid. The density was ca. 0.7 g/ml at 25°C. Analytical data furnished by Rocketdyne implied a composition close to $[(CH_3)_2AlH]_2 \cdot (CH_3BeH)_3$. The material is pyrophoric and moisture-sensitive.

(U) Thermochemical characterization of this sample is described in the present work. A modified acid hydrolysis technique proved to be successful. Analytical data obtained in the course of this work do not agree well with the Rocketdyne values and the sample composition is reinterpreted.

2. Equipment (U)

(U) A rotating bomb calorimeter and platinum-lined rotating bomb were used for the calorimetry. An automatic bridge was employed for recording time-temperature curves. The calorimeter was calibrated by combustion of National Bureau of Standards benzoic acid. The value obtained for E (calor.) was 3428.05 cal/°C with a standard deviation of 0.01%.

3. Procedure (U)

(C) Hydrolysis of the sample with aqueous HCl gave large amounts of carbon and other unidentified insoluble residues.

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Drawing on past experience with other reactive compounds, hydrolysis was tried with a mixture of 60 wt. % dioxane and 40 wt. % 7.26 N HCl. This mixture was found to react rapidly enough for good calorimetry, but not so violently as to produce decomposition. Additional thermochemical measurements were necessary to define the complex final state of $BeCl_2$ and $AlCl_3$ dissolved in the dioxane-HCl mixture.

(C) For the sample hydrolysis experiments, a thin walled, 40 ml glass bulb was filled with the dioxane-HCl mixture and sealed off. The filled bulb was placed in the bomb; the bomb was closed and flushed with dry nitrogen. The bomb was locked into a dry box and opened. A dried glass syringe was filled with about 1 ml of the liquid polymer and weighed on an analytical balance in the dry box. The syringe was emptied into the bomb and reweighed to obtain the weight of polymer charged to the bomb. The bomb was closed, removed from the dry box, and placed in the calorimeter. After initial drift rate readings, rotation was initiated, the glass bulb broke open, and the reaction took place. After completion of the calorimetric readings, the bomb gases were analyzed for carbon and hydrogen. The bomb solution was recovered and analyzed for aluminum and beryllium.

(C) To define the final state, comparison experiments were made as follows. The average composition of the final solutions in the sample hydrolysis experiments were duplicated by mixing appropriate amounts of (i) dioxane sealed in a glass bulb, (ii) 5.70 N HCl sealed in a glass bulb, (iii) $BeCl_2$ dissolved in HCl sealed in a glass bulb, and (iv) solid $AlCl_3 \cdot 6\ H_2O$. The heats of formation of these components are known. The sealed glass bulbs and solid $AlCl_3 \cdot 6\ H_2O$ were placed in the bomb and calorimetric readings taken in as nearly as possible the same way as for the sample hydrolysis runs.

(U) To complete the calculations, the heat capacity of the dioxane-HCl mixture and the heat of mixing of HCl and dioxane were needed. These quantities were measured in a simple glass Dewar calorimeter.

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4. Analytical Results (U)

   (U) A summary of the analytical data is given in Table VII. The bomb gases were analyzed in two instances. The gases were slowly released through a train consisting of a dry ice trap (to remove dioxane), a sulfuric acid bubbler, a furnace to convert CH_4 and H_2 to CO_2 and H_2O, and absorption tubes for weighing CO_2 and H_2O. Blank runs established a correction for a small amount of dioxane which passed through the dry ice trap. The carbon and hydrogen analyses are in reasonable agreement with those supplied by Rocketdyne.

   (U) The bomb solutions were analyzed in three sample hydrolysis runs. Known mixtures of aluminum and beryllium in aqueous hydrochloric acid were made up and two methods were tested on these mixtures. A 20.00 ml portion of 0.1000 M aluminum solution with excess ethylene dinitrilotetraacetic acid (EDTA) gave a titration of 19.96 ml of 0.100 M zinc solution, but the same mixture in combination with 25 ml of 0.1 M beryllium gave a titration of only 19.4 ml. This shows that beryllium interferes in the EDTA method.

Table VII

(U)   Analytical Data on ATBH

Experiment No.	% Al	% Be	% CH_3	% H (hydride)	Total
Dow - 2	30.54	12.36			
Dow - 3	30.51	12.46	54.85	2.44	100.26
Dow - 4	30.57	12.40	54.38	2.43	99.78
Rocketdyne - 1	30.6	15.5	54.6	2.7	103.4
Rocketdyne - 2	29.3	15.5	54.6	2.7	102.1
Rocketdyne - 3	30.8	15.4	52.5	2.7	101.4
Calculated for $Al_9Be_{11}(CH_3)_{29}H_{20}$	30.42	12.42	54.63	2.53	100.00

   (C) Next cyclohexene dinitrilotetraacetic acid (CDTA) was tried. This method gave quite good results and was the one used for the subsequent work. A known solution of 20.00 ml of 0.100 M aluminum mixed with 25.00 ml of 0.1 M beryllium with excess CDTA

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gave a net titration of 19.94 ml of 0.1 M standard zinc solution.
A correction factor of 1.003 was used for the aluminum titration.

(U)   Bomb solutions were made up to volume and a portion was
used for titration for aluminum by the CDTA method.   Another portion
was used for the co-precipitation of aluminum and beryllium
hydroxides with a slight excess of ammonium hydroxide.   The filtrate
was neutralized back just to the alkaline side of methyl red
indicator with hydrochloric acid and refiltered on another filter.
This was done to collect any aluminum that may have remained in
solution with the excess ammonium hydroxide during the first
filtration.   Both papers with precipitates were slowly ignited at
the start and finally taken to 1000°C for one hour.   The combined
oxides of beryllium and aluminum were cooled in a desiccator for
one hour and weighed.   The weight obtained from known amounts of
aluminum and beryllium was found to be slightly higher than the
amount calculated.   A calculated weight of 0.16461 g of combined
oxides gave the actual weight of 0.16535 g.   All of the weights
of oxides of the unknown samples were multiplied by the factor of
0.9955 to correct for the high weights obtained with knowns.

(C)   As a check on the technique, the solution from one of
the comparison runs was also analyzed.   The results agreed very
well with the known amounts of beryllium and aluminum used in the
comparison runs.

(C)   The Dow and Rocketdyne analytical data are compared in
Table VII.   The results are in good agreement except for the
beryllium content.   Since the Dow results total close to 100% and
extra precautions were taken to insure correct beryllium values, the
Dow results are adopted.   The empirical formula $Al_9Be_{11}(CH_3)_{28}H_{20}$
has a composition close to the average of the analytical results
and this formula is used for further calculations on the heat of
formation.   The calculated composition for this formula is compared
with experimental values in Table VII.

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5. Calorimetric Results (U)

(U) Calorimetric results for the sample hydrolysis experiments are given in Table VIII. The values differ slightly from those originally reported in Dow Quarterly Progress Report AFRPL-TR-67-210, covering the period 1 April 1967 to 30 June 1967. After that report was issued, it was discovered that the computer program for calculating the temperature rise contained incorrect mathematical expressions. The corrected results given here are considerably improved in precision. The heat absorbed by the basic calorimeter system is the product of Δtc, the temperature rise corrected for heat leak, and E (calor), the heat capacity of the system as determined by calibration with benzoic acid. The remaining terms are for heat absorbed by the various bomb contents. Heat capacity values for the various solutions, glass, etc. used in the calculations are given in Table IX.

(U) Five comparison runs were made, each with the various reagent weights adjusted to reproduce within 0.1% the average composition of the final solutions of the sample hydrolysis runs. Duplicate determinations of the heat of mixing of dioxane and 7.26 N HCl were in good agreement at 16.11 cal/g of dioxane.

(C) The reaction scheme used to calculate the heat of formation is given in Table X. In these reactions, quantities enclosed in brackets are solutions. The value for ΔE_1 is simply the average $\Delta E_R/M$ from Table VIII multiplied by the molecular weight of $Al_9Be_{11}(CH_3)_{29}H_{20}$, 798.14. This gives ΔE_1 = -2271.0. The value for ΔE_2 is the average of five comparison experiments, yielding +421.1 kcal. The heat of mixing of dioxane and 7.26 N HCl measurements gives ΔE_3 = -433.8 kcal. The heat of solution of Be metal in 7.26 N HCl was reported in our Quarterly Report for Jan. - Mar., 1967, in connection with work on beryllium hydride, and gives ΔE_4 = +991.6 kcal. The heats of solution of HCl (gas) in water can be calculated from data given in National Bureau of Standards Technical Note 270-1 as ΔE_5 = +879.3 kcal and ΔE_6 = -1332.2 kcal.

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Table VIII

(U) Heat of Hydrolysis of ATBH

	Experiment Number					
	1	2	3	4	5	6
Sample mass, g	0.7614	0.7479	0.7806	0.7729	0.7850	0.7367
Δt_c, °C	0.62993	0.61510	0.64606	0.62875	0.65461	0.60306
$E\Delta t_c$, cal	2159.4	2108.6	2214.7	2155.4	2255.0	2057.3
ΔE glass, cal	0.8	0.8	0.9	0.8	0.8	0.7
ΔE sample, cal	0.2	0.2	0.3	0.2	0.3	0.2
ΔE mixture, cal	15.1	14.7	15.2	14.9	15.8	14.3
ΔE platinum, cal	0.2	0.2	0.2	0.2	0.2	0.2
$-\Delta E_R/M$, cal/g	2857.	2841.	2858.	2810.	2880.	2827.

$-\Delta E_R/M$ (average) = 2845.5 cal/g

Table IX

(U) Heat Capacity of Bomb Contents at 25°C

Substance	C_p, cal/g/°C	Source
Pyrex glass	0.1855	T. De Vries, Ind. Eng. Chem. **22**, 617 (1930).
ATBH	0.5	Estimated
Dioxane-HCl Mixture	0.540	Measured, this work.
Dioxane	0.415	C. J. Jacobs and G. S. Parks, J. Am. Chem. Soc. **56**, 1513 (1934).
5.70 N HCl	0.720	Measured, this work.
$BeCl_2$-HCl Solution	0.65	Estimated
$AlCl_3 \cdot 6\ H_2O$	0.293	Unpublished data, Dow Thermal Research Laboratory.
Platinum	0.032	K. K. Kelley and E. G. King, U. S. Bur. Mines Bull. 592 (1961).

(C) The algebraic sum of these six reactions gives reaction seven, for which $\Delta E_7 = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 + \Delta E_5 + \Delta E_6 = -1745.0$ kcal. Noting that Reaction 7 involves an increase of 11 moles of gaseous substances, ΔH_7 can be calculated from:

$$\Delta H_7 = \Delta E_7 + 11RT$$

$$= -1745.0 + 6.5$$

$$\Delta H_7 = -1738.5 \text{ kcal}$$

The enthalpies of formation given in National Bureau of Standards Technical Note 270-1 are adopted: HCl(g), -22.062 kcal/mol; H_2O(liq) = 68.315 kcal/mol; CH_4(g) = -17.88 kcal/mol; and $AlCl_3 \cdot 6\ H_2O$ = -643.3 kcal/mol. Combined with our measured ΔH_7, these data yield for $Al_9Be_{11}(CH_3)_{29}H_{20}$:

$$\Delta Hf_{298}°(\text{liq}) = -285.0 \text{ kcal/mol}$$

$$= -35.7 \text{ kcal/100 g}$$

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Table X

(U) Reaction Scheme for Heat of Formation of ATBH

$Al_9Be_{11}(CH_3)_{29}H_{20}$ + Solution A → Solution B + $29CH_4(g)$ + $20H_2(g)$ ΔE_1

Solution B → $9AlCl_3 \cdot 6H_2O$ + $305.6\ C_4H_8O_2$ + [$11BeCl_2$ + $18.37HCl$ + $263.06\ H_2O$] + [$57.94HCl$ + $499.23H_2O$] ΔE_2

$305.6\ C_4H_8O_2$ + [$125.31HCl$ + $816.25H_2O$] → Solution A ΔE_3

[$11BeCl_2$ + $18.37HCl$ + $263.06H_2O$] + $11H_2(g)$ → $11Be$ + [$40.37HCl$ + $263.06H_2O$] ΔE_4

[$57.94HCl$ + $499.23H_2O$] → $57.94HCl(gas)$ + $499.23H_2O$ ΔE_5

$84.94HCl(gas)$ + $553.19H_2O$ → [$84.94HCl$ + $553.19H_2O$] ΔE_6

$Al_9Be_{11}(CH_3)_{29}H_{20}$ + $27HCl(gas)$ + $54H_2O(liq)$ → $11Be$ + $9AlCl_3 \cdot 6H_2O$ + $29CH_4(g)$ + $9H_2(g)$ ΔE_7

(C) The over-all uncertainty is calculated as twice the over-all standard deviation to be ±16.4 kcal/mol or ±2.1 kcal/100 grams. The uncertainty amounts to about 0.15% of the heat of combustion in oxygen; it seems unlikely that the heat of combustion could be directly measured to a higher degree of certainty.

C. HEAT OF FORMATION OF TVOPA, 1,2,3-tris[1,2-bis(DIFLUOROAMINO-ETHOXY)]PROPANE (C)

1. Introduction (U)

(U) Rohm and Haas Company (1) reported a heat of formation for TVOPA. The purpose of the present work was to obtain a second value for the $\Delta Hf^\circ_{298.15}$ and to compare the two values. Both the Rohm and Haas and the Dow Thermal Research Laboratory values were obtained by measuring the heat of combustion of TVOPA in oxygen.

2. Materials (U)

(U) Three samples, designated as Batches A, B, and C, were supplied us by Dr. B. F. Aycock of Rohm and Haas Company. The first sample, Batch A, was shipped as a 10 per cent solution in methylene chloride. It was designated TVOPA ATG-6 by Rohm and Haas and had been partially purified by acid washing and rough stripping of production solvents. A second sample, Batch B, was shipped as production grade TVOPA (R and H batch No. 364-7) in a 70 per cent Freon 113-30 per cent chloroform mixture. A third sample of TVOPA, Batch C, was shipped in a 65 per cent chloroform-35 per cent Freon 113 mixture. This batch was from the same Rohm and Haas Batch No. 364-7 as Batch B, but C was acid washed while B was not. Table XI shows the infrared analytical data supplied by Rohm and Haas with these three batches of TVOPA. Dr. Aycock of Rohm and Haas stated, "It is a mixture of stereoisomers," (and), "statements about its purity are approximate at best" (2).

(U) Batch A was burned in combustion Exp-1 through Exp-12 (Table XII), as reported earlier (3). At the time, a strong dependence of the heat of combustion ($\Delta Ec/M$) on the chloride content was noted. Then a large portion of Batch B was expended in the

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evaluation of various purification techniques in cooperation with the Dow synthesis group. Purified samples were burned in a platinum-lined combustion bomb to determine the heat of combustion, and the bomb solution was recovered for chloride analysis. The remainder of Batch B and part of C were then used in a final series of heat of combustion determinations on the TVOPA obtained by the best purification technique. (See Synthesis Section of this report for details on this technique.) Combustion experiment Exp-21 (Table XIII) used a sample of this purified TVOPA. To differentiate between that part of the experimental scatter which was due to the calorimetry and that part of the scatter due to variations in sample purification, combustion experiments Exp-22 through Exp-28 were done on a 5.9 g sample made by thoroughly mixing six, small, specially purified samples. Ordinarily, the amount of TVOPA purified at one time was less than one gram due to the explosive hazard. TVOPA is reported to have the shock sensitivity of nitroglycerin (2).

Table XI

Standard Infrared

(U)   Analytical Data Supplied by Rohm and Haas

Infrared	R and H Batch ATG-6 (Dow Batch A)	R and H Batch 364-7 (Dow Batch B)	R and H Batch JEE1022-4* (Dow Batch C)
EtOH, %	<0.02	0.40	Trace
O-C=C, %	<0.02	-	-
C=C, %	-	Nil	Nil
NONF	0.36	0.80	Trace
NF $\overset{\parallel}{C}$-CN, %	0.15	-	-
5.78 μ	0.010(absorb.)	0.237	0.19
5.92 μ	0.031(absorb.)	0.047	0.047
6.23 μ	-	0.60(0.23)	0.059(0.23)
6.40 μ	Nil	Nil	Nil

*R and H Batch JEE1022-4 = R and H Batch 364-7 acid washed.

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Table XII

(U) Analytical Results and Energy of Combustion of TVOPA

Exp. No.	Analysis Nitrate mg as N_2	Analysis Fluoride mg/spl	Fluoride Recovered %	Chloride mg Chloride per g TVOPA	$-\Delta E_c/M$ cal per g TVOPA
			First Series		
1	13.4	268	92.9	26.5	3,241.0
2	10.9	259	96.8	20.5	3,265.2
3	12.0	294	98.0	12.7	3,291.0
4	10.0	328	98.4	10.1	3,286.0
5	12.1	336	99.7	5.8	3,330.8
6	11.8	339.5	99.8	13.1	3,289.3
7	12.1	293	97.8	16.4	3,261.0
8	9.3	294	97.7	2.3	3,345.5
9	11.4	270	96.3	2.0	3,354.3
10	11.2	268	99.4	3.0	3,314.1
11	11.0	225	100.2	8.6	3,320.6
12	11.4	285	100.0	16.8	3,271.1
			Second Series		
13	9.3	223	100.2	19.8	3,214.0
14	10.0	236	99.4	19.5	3,311.1
15	10.0	240	99.3	13.1	3,296.0
16	10.4	218	98.0	4.5	3,331.0
17	9.5	198	90.7	4.6	3,344.4
18	10.5	226	97.2	3.5	3,327.2
19	10.0	239	98.5	3.5	3,324.0
20	10.0	217	98.3	3.3	3,413.5
21	10.0	223	95.1	' 1.4	3,366.9
			Third Series		
22	9.5	219	99.3	1.9	3,372.1
23	9.7	217	98.6	1.9	3,369.6
24.	9.8	221	99.3	1.5	3,374.8
25	9.4	220	99.3	1.5	3,363.6
26	9.5	223	100.2	2.1	3,360.0
27	12.5	221	98.5	1.7	3,352.7
28	9.7	216	95.4	2.1	3,352.7
				*1.8±0.3	

*Average of No. 22 through No. 28

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Table XIII

(U) Results of Elemental Analyses on TVOPA

Sample	Carbon %	Hydrogen %	Nitrogen %	Fluoride %
Dow (Exp. No. 22-28)	22.85	3.13	17.7	46.6
Dow (Exp. No. 18 & 19)	22.70	3.20	17.6	46.3
Dow (Exp. No. 21)	22.70	3.12	17.6	46.0
R & H ATG-6	22.48	3.26	17.25	45.9
Stoichiometric	22.41	2.93	17.43	47.28

3. Equipment (U)

(U) A typical rotating bomb calorimeter with a platinum-lined combustion bomb was used for the calorimetry.

4. Procedure (U)

(U) It was necessary to burn the TVOPA as a solution or mixture with a diluent, since the undiluted TVOPA detonated under bomb conditions. The TVOPA and the diluent, 2-octanone, were sealed in a Mylar bag for the combustion. A limited amount of a diluent sample purified by preparative chromatography was first used. When this was expended, an older sample was substituted. This sample had a lower heat of combustion, and analysis showed it contained 0.3 per cent water (3). It was also found that to get clean combustion less than a third of the total heat (about 6,500 cal/g) could be contributed by the TVOPA. All of the experimental inaccuracies were thus included in a third or less of the measured heat.

(U) The procedure used to determine the sample weights was previously reported in detail (3) and can be summarized as follows. A weighed Mylar polyester film tube is divided into two compartments by a small screw clamp across its center. The two components (TVOPA and 2-octanone) are sealed in the two compartments in turn.

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By weighing after sealing each component, the weights of TVOPA
and diluent are obtained by difference. This procedure avoided
loss of the purified TVOPA, since the seals could be checked for
leaks before removal of the clamp and mixing.

(U) The sealed bag containing the diluted TVOPA was folded
and placed in a platinum crucible. A cotton fuse was tied to
the bag. The sample was burned in 40 atm of oxygen, with 10 cc
of water in the bomb. After each combustion the solution in the
bomb was quantitatively recovered by washing the bomb interior.
Analyses were made on the bomb washings for chloride, nitrate,
and fluoride.

(U) The heats of combustion of the polyester film and the
two samples of 2-octanone were run using 30 atm of oxygen and 1
ml of water in the bomb.

(U) The individual $\Delta Ec/M$ values for the polyester film, and
the 2-octanone samples were given in an earlier report (3). The
average values are listed below:

Sample	Average $\Delta E_c^\circ/M$ cal/g	Std. Deviations cal/g
Polyester film	5,466.2	±0.6
*(1) 2-Octanone (pure)	9,397.0	±2.0
(2) 2-Octanone (0.3% H_2O)	9,367.7	±1.9

*Sample No. 1 is in good agreement with Geiseler and Ratzsch (4).

TVOPA combustion experiments No. 1 through 8 used 2-octanone Sample
No. 1, while 2-octanone Sample No. 2 with 0.3% water was used for
experiments No. 9 through 28.

(U) The calorimeter was calibrated twice, since slight modi-
fications were made after burning some of the earlier samples. The
calorimeter was calibrated in both cases with NBS benzoic acid
391. The first E (calor) value, 3423.35 cal/g with a standard

deviation of 0.13 cal/g, was used for TVOPA combustion Experiments No. 1 through 16. The second E (calor) value, 3427.37 cal/g with a standard deviation of 0.15 cal/g, was used for Experiments No. 17 through 28.

5. Analytical Result   (U)

(U)   The progress of the various purification techniques for TVOPA was followed by a chloride analysis on the bomb solutions recovered after the heat of combustion measurements. The chloride content was found to vary from 2 to 26 mg of chloride/gram of sample for TVOPA Batch A as reported earlier (3) and in Table XII of this report.

(U)   In the TVOPA purification experiments, parts of Batches B and C were used for Experiments No. 13 through 21. The chloride content varied from 19.8 to 1.4 mg of chloride/gram of sample. This series of experiments was run to check on the chloride while developing a good purification technique.

(U)   The last series of combustion experiments was performed on TVOPA aliquots from a relatively large (≃6 g) sample. This sample was well mixed prior to burning in seven experiments (22 through 28). However, the chloride content found in the bomb solutions varied from 1.5 to 2.1 mg of chloride/gram of sample (average: 1.8±0.3 mg chloride/gram of sample). This average and the corresponding spread of values give a good idea of the precision of the other chloride figures.

(U)   In addition to showing the chloride content, Table XII shows the results obtained for the nitrate and fluoride as well. The nitrate value was used for the Washburn corrections program. The fluoride in solution is reported as both mg found per sample and as percentage recovered, assuming the amount calculated from the sample weights was 100%. The average of ` ` moles of fluoride found in solution and moles calculated from sample weights was used in the Washburn corrections program.

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(U)   Table XIII gives the results of micro-analysis for carbon, hydrogen and nitrogen on small portions of three combustion samples. Theoretical values are compared with experimental values for these elements.   Also listed is the per cent fluoride calculated from the fluoride found in the bomb solutions.   In addition, Table XIII includes the elemental analysis provided by Rohm and Haas (1) for Batch A (i.e. Rohm and Haas Batch ATG-6).   They supplied no elemental analysis for Batches B and C.

(U)   Tracer experiments with radio-active benzene were used by the Synthesis Group to show that no benzene (<2 cal/g) was inadvertently introduced as a contaminant during the purification process.   (For details see the Synthesis Section of this report.)

(U)   No definite statement of percentage purity is possible for these samples.   The elemental analyses agree with stoichiometry within experimental error.

6.   Calorimetric Results   (U)

(U)   The results of the calorimetric work were processed by means of the computer program for C-H-O-N-F compounds described earlier (3,5).   Constant factors needed as input for this program are given in Table XIV and other variables in Table XV.   Table XV is limited to Exp. No. 21 and No. 22 through 28 because these experiments used samples prepared by standardized purification technique developed by the Synthesis Group.

(C)   From the individual $\Delta Ec/M$ values in Table XV (with the exception of Exp. No. 21) an average $\Delta Ec/M = -3,364.4$ cal/g with a standard deviation of ± 3.05 cal/g can be calculated.   The heat of solution of TVOPA in 2-octanone has been reported earlier (3). (See page 43, Section G.)   The two ΔH_{soln} values given there average as $\Delta H_{soln} = -4.61$ cal/g.   If one combines this with the above average $\Delta Ec/M$, one obtains a value of $-3,369.0$ cal/g for neat TVOPA, which relates to the reaction:

$$C_9H_{14}O_3N_6F_{12}(liq) + 8O_2(g) + 359H_2O(liq) \longrightarrow$$
$$9CO_2(g) + 3N_2(g) + 12(HF \cdot 30H_2O)(liq)$$
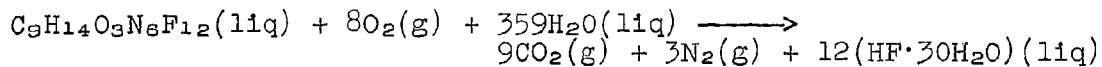
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Table XIV

(U) Constant Factors in TVOPA Combustion Calculations

Empirical formula of TVOPA (2)	$C_9H_{14}O_3N_6F_{12}$
Empirical formula of 2-octanone	$C_8H_{16}O$
Empirical formula of film	$C_{10}H_8O_4$
Empirical formula of fuse	$C_1H_{1.774}O_{0.887}$
Density of TVOPA (2)	1.535
Density of 2-octanone	0.818
Density of film	1.380
Density of fuse	
Bomb volume	0.347 liter
Initial oxygen pressure	40 atm
Initial water in bomb	10.0 g
Reference temperature	25°C
Final ratio, H_2O/HF	30
$(E/P)_T$ of TVOPA (2)	-0.00380 cal/g/atm
$(E/P)_T$ of 2-octanone	-0.00899 cal/g/atm
$(E/P)_T$ of film	-0.00800 cal/g/atm
$(E/P)_T$ of fuse	Negligible
ΔE_c° of 2-octanone (Sample 1)	-1204.84 kcal/mol
ΔE_c° of 2-octanone (Sample 2)	-1201.08 kcal/mol
ΔE_c° of film	-1050.31 kcal/mol
ΔE_c° of fuse	-103.35 kcal/mol
Cp of TVOPA (2)	0.4 cal/g/°C
Cp of 2-octanone	0.5049 cal/g/°C
Cp of film	0.315 cal/g/°C
Cp of fuse	0.4 cal/g/°C
E (calor) (Exp. No. 1 through Exp. No. 16)	3423.35 cal/°C
E (calor) (Exp. No. 17 through Exp. No. 28)	3427.37 cal/°C

Table XV

(U) Heat of Combustion Experiments for TVOPA Exp. No. 21 through No. 28

Parameter	Experiment Number							
	21	22	23	24	25	26	27	28
Wt. TVOPA, g	0.495948	0.466376	0.465458	0.470693	0.468560	0.470883	0.474662	0.479095
Wt. 2-octanone, g	0.392591	0.352759	0.364317	0.375019	0.379124	0.373297	0.364379	0.377673
Wt. Film, g	0.128261	0.124494	0.141253	0.121338	0.140505	0.134380	0.122320	0.004820
Wt. Fuse, g	0.005935	0.004870	0.004900	0.004565	0.004633	0.004754	0.004065	0.004820
Moles HNO_3 (x10^4)	7.14	6.78	6.93	7.00	6.71	6.78	8.92	6.93
Moles HF(x10^2)	1.2039	1.1566	1.1502	1.1673	1.1620	1.1728	1.1722	1.1646
Mass, added Pt., g	26.5401	26.5401	26.5401	26.5401	26.5401	26.5401	26.5401	26.5401
t_i, °C	23.19955	23.34817	23.28881	23.28681	23.24727	23.27106	23.31139	23.23976
t_f, °C	25.02931	25.03590	25.04188	25.04183	23.03671	25.03592	25.04115	25.04114
Δt corr., °C	0.05936	0.06152	0.06981	0.06876	0.06490	0.06426	0.06912	0.07182
-ΔEc/M, cal/g	3,366.89	3,372.12	3,369.61	3,374.79	3,363.63	3,359.99	3,358.17	3,352.68

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The data are reduced to $\Delta Hf^{\circ}_{298.15}$ in the following manner:

$$\text{Mol. Wt.} = 482.23068 \text{ g/mol}$$

$$\Delta Ec = -1624.64 \pm 1.47 \text{ kcal/mol}$$

$$\Delta n = +4 \qquad RT = 0.5925 \text{ kcal/mol}$$

$$\Delta Hc = \Delta nRT + \Delta Ec = -1622.27 \text{ kcal/mol}$$

Then using auxiliary data from NBS Technical Note 270-1:

$$\Delta Hf^{\circ}_{298.15} = -208.1 \pm 2.9 \text{ kcal/mol}$$

where the uncertainty is twice the standard deviation.

7. Conclusion (U)

(C) The $\Delta Hf = -208.1 \pm 2.9$ kcal/mol compares with the Rohm and Haas (1) $\Delta Hf = 207.3 \pm 3$ kcal/mol when the latter is recalculated with the same auxiliary data used in these calculations. The Rohm and Haas ΔHf° value is obtained assuming no heat of solution for TVOPA dissolved in the diamyl ketone diluent. A more reasonable estimate (from our measured $\Delta H_{soln} = -2.2$ kcal/mol) for the TVOPA-diamyl ketone ΔH_{soln} would be -2 kcal/mol. The Rohm and Haas value of ΔHf° becomes -205.3 ± 3 kcal/mol with this estimate.

(U) Figure 1 shows the dependence of the ΔHc ($\Delta Ec/M$) on removal of impurities apparently closely associated with the chloride containing manufacturing solvents. The low chloride experiments plotted on Figure 1 indicate that the $\Delta Ec/M$ dependence on chloride content is not linear for near zero chloride values. A 2 per cent (by weight) chloride-containing batch of TVOPA could have a ΔHc lower than our best value by over 100 cal/g.

(U) This is probably significant in I_{sp} calculations on a propellant containing TVOPA. Some test (chloride analysis or ΔHc determination) might be desirable on each batch of TVOPA unless it was known to be significantly below 2 per cent in chloride content.

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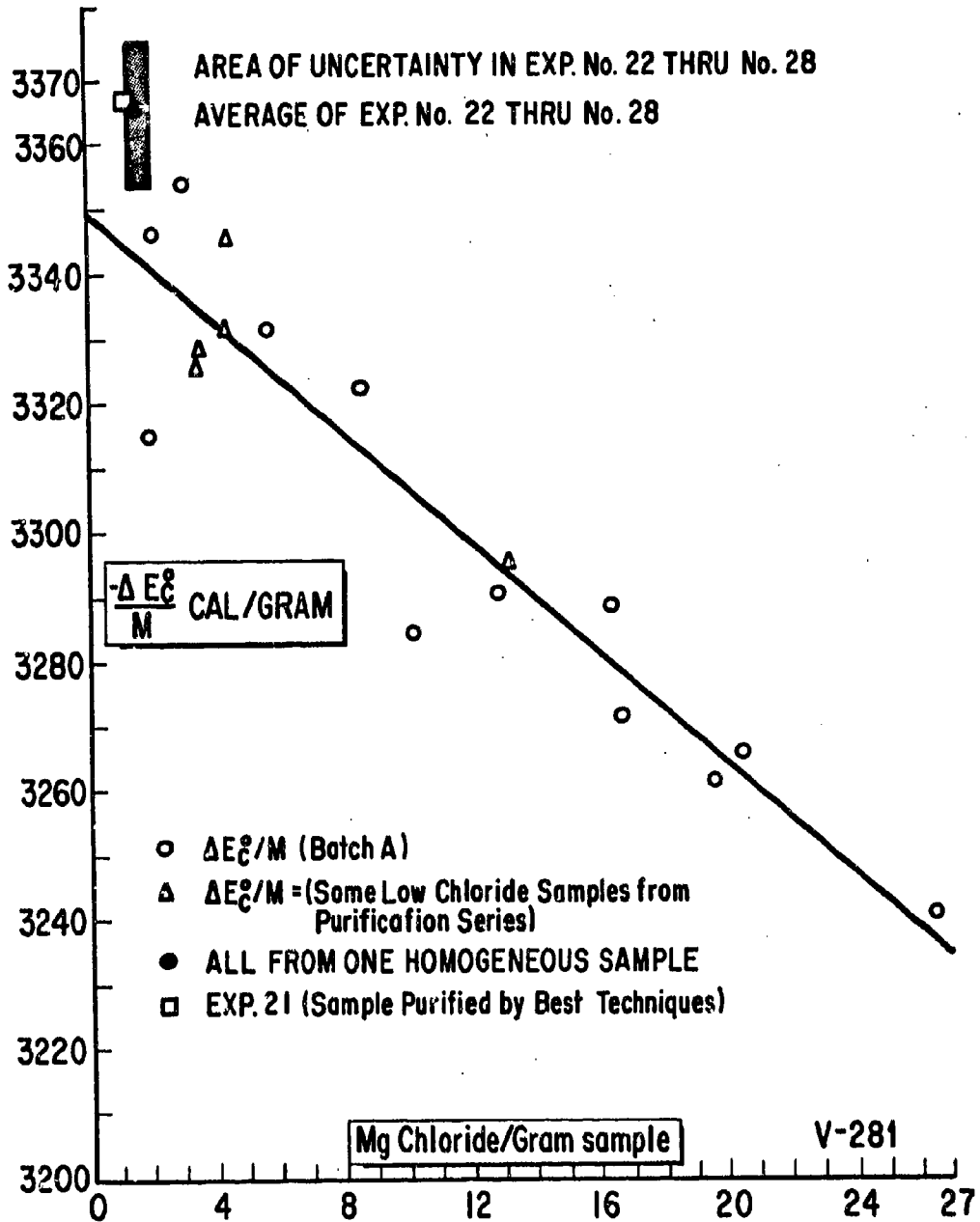
(U) Fig. 1 - Effect of Chloride on the Heat
of Combustion of TVOPA

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D. HEAT OF FORMATION OF DIAMMONIUM HYDRAZINIUM TETRAPERCHLORATE
    (DAHTP)   (C)

1. Introduction   (U)

(C)   A sample of DAHTP was received from Thiokol Chemical
Corporation.   Information sent by Delmar B. Davis of Thiokol in-
cluded the empirical formula $N_4H_{14}Cl_4O_{16}$ and a molecular weight
of 468.   The material is a white crystalline solid, nonhygroscopic
and chemically stable.

2. Analytical Results   (U)

(C)   Although not specifically stated by Thiokol, it seemed
obvious from information given that the compound was a mixture or
double salt of ammonium perchlorate and hydrazinium diperchlorate.
The material was therefore assayed for ammonia and hydrazine con-
tent, giving 99.6% in each case for a formula of $2NH_4ClO_4 \cdot N_2H_6(ClO_4)_2$.

(C)   For a check on calorimetric measurements to be described,
a sample of Fisher Reagent Grade NH_4ClO_4 was dried at 110°C for
several hours.   Analysis for ammonia content gave 99.9% of theory.

3. Equipment   (U)

(U)   A conventional Dickinson type isothermal shield calorim-
eter usually used for bomb work was employed for this heat of
solution study.   The calorimeter vessel had an internal volume of
3500 cc and had been plated inside and out with gold to resist
corrosive fluids.   Removal of the bomb then converts the calorim-
eter to a solution unit.   Temperatures were measured as a func-
tion of time with a calibrated thermistor (2300 ohms at 25°C) and
a drum chronograph.   The corrected temperature changes were calcu-
lated by computer from the resistance-time data using standard
procedures.   Calibration of the calorimeter was carried out elec-
trically using current-time integration techniques and an inte-
grating digital voltmeter.   (4.1840 joules = 1 thermochemical
calorie).   Power was taken from a Lambda constant voltage power

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supply. In this manner, the solution calorimeter could be cali-
brated after each experiment with a precision of a few hundredths
of a percent.

4. Procedure (U)

(C) Since the heats of formation and solution of NH_4ClO_4
and $N_2H_4 \cdot 2HClO_4$ have been published (6,7,8), it seemed that a
heat of solution measurement of DAHTP would be advantageous in
that its heat of solution could be compared to the sum of the
heats of solution of the constituents. The procedure used was to
weigh 5-10 g portions of the solid into glass ampoules. The
ampoules were then supported in the calorimeter vessel by means
of a Kel-F fitting and glass rod. The calorimeter was then filled
with 3,300 g of H_2O and the temperature adjusted to 25.2°C. After
equilibration, the glass rod was forced downward, crushing the
thin walled ampoule on the bottom of the calorimeter. A rapid
endotherm resulted with the solution products equilibrating at
25°C. After the final rating period had been recorded, a measured
amount of electrical energy corresponding closely to the heat of
solution was put back in the system. The calorimeter was calibrated
in this manner after each heat of solution measurement.

(U) The ΔH_{sol} of NH_4ClO_4 was also determined as a check
against literature values.

5. Results and Discussion (U)

(U) Table XVI lists the measured and calculated values for
five heat of solution measurements on DAHTP. All weights are
corrected to mass under vacuum; however, a purity factor has not
been applied. The energy equivalent E (calor) has been discussed
before and all other entries are of standard terminology. The
last column lists the dilution states for one mole of DAHTP.
Deviations are calculated as the arithmetic mean. Table XVII lists
three experiments on the solution of AP in water. The results
are compared with literature data in Figure 1 and are seen to be
in excellent agreement.

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Table XVI

(U) Heat of Solution of DAHTP in Water

Run	Sample Mass, g	E (calor) cal/°C	E Δtc cal	ΔHsol cal/g	ΔHsol kcal/mol	$\frac{n_{H_2O}}{n_{DAHTP}}$
1	5.5382	-3,425.2	+254.1	+45.88	+21.47	15,508
2	10.1570	*(-3,422)	+486.3	+47.88	+22.40	8,455
3	9.8728	-3,422.0	+466.3	+47.23	+22.10	8,688
4	10.7793	-3,421.0	+511.2	+47.43	+22.19	7,957
5	11.0005	-3,417.0	+531.1	+48.28	+22.59	7,797
			Average	+47.35	+22.15	
			Std. dev.	0.6	0.3	

*Taken from Run No. 3

Table XVII

(U) Heat of Solution of NH_4ClO_4

Run	Sample Mass, g	E (calor) cal/°C	E Δt_c cal	ΔHsol cal/g	ΔHsol kcal/mole	$\frac{n_{H_2O}}{n_{DAHTP}}$
1	17.9221	-3,424.0	+1,231.5	+68.71	+8,073	1,200
2	15.6211	-3,427.8	+1,075.4	+68.84	+8,088	1,380
3	24.2052	-3,422.0	+1,655.1	+68.38	+8,034	890

(C) If one calculates the heat of solution of DAHTP on the basis of +6.29 ± 0.5 kcal/mol for $N_2H_4 \cdot 2HClO_4$ (8) and +8.06 ± 0.02 kcal/mol for NH_4ClO_4 (this work), we find ΔHsol DAHTP = +22.4 ± 0.6 kcal/mol as compared to the measured value in Table XVI of +22.2 ± 0.3 kcal/mol. This suggests "zero bond energy" between the AP and HDP molecules in DAHTP or that the DAHTP is a 2:1 mixture of AP and HDP. X-Ray diffraction patterns on DAHTP showed only lines of AP and HDP, confirming this observation. No new lines were observed.

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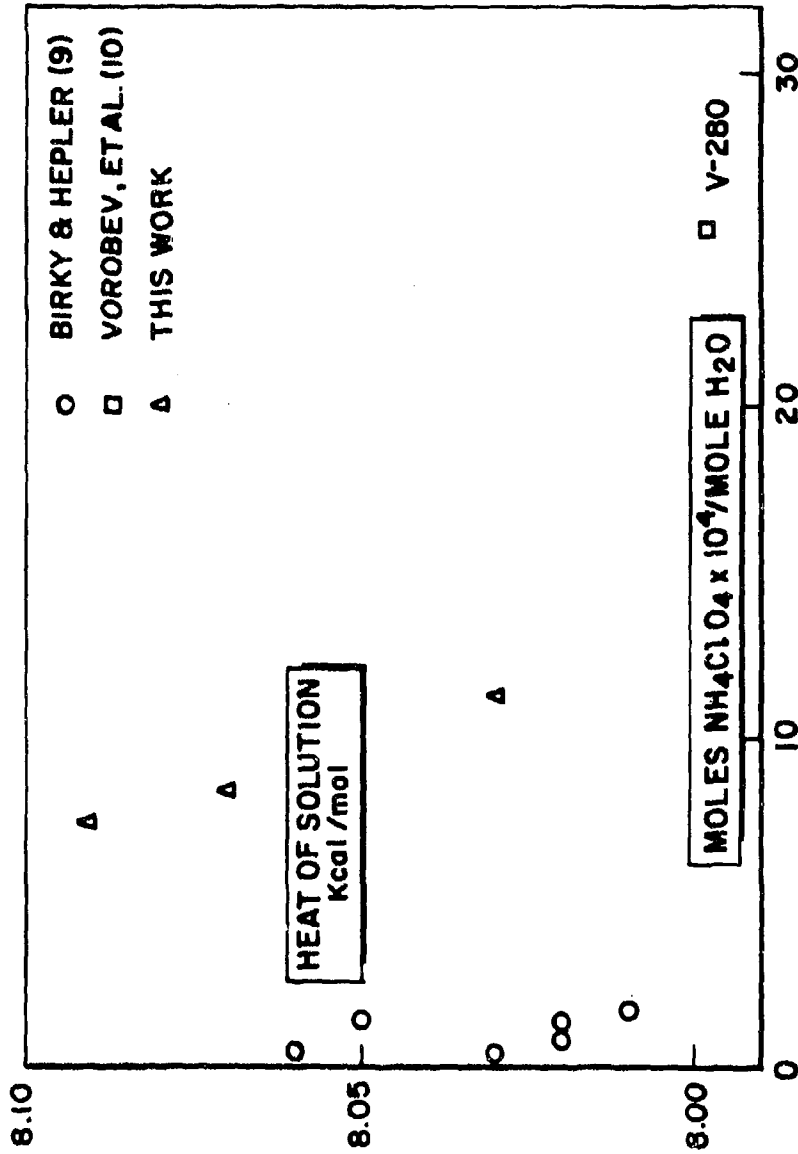
(U) Fig. 2 - Heat of Solution of Ammonium Perchlorate

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(C)   The heat of formation of DAHTP is therefore merely the
sum of $2\Delta Hf$ (NH_4ClO_4) and $\Delta Hf[N_2H_6(ClO_4)_2]$.   The value for
$\Delta Hf(NH_4ClO_4)$ is taken from Reference 8 as -70.58 kcal/mol.   For
HDP, two values are available, -69.2 kcal/mol from Reference 6
and -70.1 kcal/mol from Reference 7.   The desired sum is calcu-
lated as -210.4 and -211.3 kcal/mol, respectively.   The value -210.4
kcal/mol is recommended.

(U)   Further work on this compound by combustion calorimetry
is planned.

E.   HEAT OF FORMATION OF CARBON TETRAFLUORIDE   (U)

1.   Introduction   (U)

(U)   The heat of formation of carbon tetrafluoride is a "key"
datum in calorimetry.   Carbon tetrachloride appears as a product
in fluorine or NF_3 combustion calorimetry of compounds containing
carbon.   It also appears as a product in oxygen combustion calor-
imetry of compounds containing carbon and a large percentage of
fluorine.   In order to reduce calorimetric results to accurate
heats of formation, the heat of formation of CF_4 must be well
defined.

(U)   The first attempt at measuring the heat of formation of
CF_4 was that of von Wartenberg and Schuette (11) in 1933 by direct
combination of the elements.   Their result is now recognized as
much too low.   Twenty years later, von Wartenberg (12) published
a much higher value based on the reaction of CF_4 and alkali metal
to form carbon and alkali fluoride.   Kirkbride and Davidson (13)
used a similar technique, and some years later Vorobev and
Skuratov (14) repeated the work.   The results were in agreement to
within a few kilocalories but depended on the heat of formation
of fluoride ion.   Several other investigations were made which
used indirect means, including the heat of hydrogenation and de-
composition of C_2F_4 (15,16), the heat of combustion of methane in
fluorine (17), and the heat of combustion of perfluorocarbons in
oxygen (18,19,20,21).   None of these was completely independent of

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the heats of formation of gaseous and/or aqueous hydrogen fluoride, quantities not yet well defined.

(U) Three recent investigations give well defined results. Domalski and Armstrong (22) measi ed the heat of combustion in fluorine of graphite mixed with Teflon. After correcting for the Teflon, they derived $\Delta Hf^{o}_{298}(CF_4,g)$ = -222.87 kcal/mol. Greenberg and Hubbard (23) measured the heat of combustion in fluorine of pure graphite. After correcting for a small amount of C_2F_6 formed, they derived $\Delta Hf^{o}_{298}(CF_4,g)$ = -223.05 kcal/mol. Concurrently with these direct measurements, we determined the heat of reaction of cyanogen and nitrogen trifluoride with the results described below. In the course of several years of work on the calorimetry of rocket fuels and oxidizers, we have found NF_3 to be a useful fluorinating agent. Recent work in this laboratory has defined the heat of formation of NF_3 as -31.6 ± 0.2 kcal/mole (24,25). The heat of formation of cyanogen was carefully measured by Knowlton and Prosen (26) at the National Bureau of Standards. When preliminary work showed that a mixture of NF_3 and cyanogen exploded when sparked, a full scale measurement was undertaken.

2. Materials (U)

(U) Both cyanogen and nitrogen trifluoride were purchased from Air Products and Chemicals, Inc. The cyanogen was found to contain about 1% CO_2 as an impurity. This was removed by low temperature distillation through a 3/8" I.D. copper column packed with magnesium beads. The distillation was carried out using a thermocouple detector and recorder usually used for chromatography. Approximately 0.5 g center cuts were trapped out from the helium carrier gas stream. Mass and infrared analysis of the purified material indicated no detectable impurities.

(U) Research grade NF_3 was analyzed by mass and infrared spectroscopy, both of which indicated 0.15% CF_4 as the only impurity. Since the CF_4 could not be further oxidized, it was not necessary to remove it from the NF_3.

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3. Nature of the Reaction (U)

(U) Cyanogen and nitrogen trifluoride were found to react in the gas phase when the mixture was sparked according to the equation shown:

$$1/2 \; C_2N_2(g) \; + \; 4/3 \; NF_3(g) \; \longrightarrow \; CF_4(g) \; + \; 7/6 \; N_2(g)$$
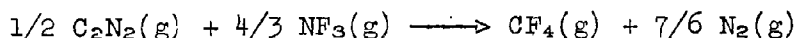
Ignition was accomplished by discharging a standardized capacitor across a 0.5 cm length of nickel fuse wire. There was an audible "click" when the reaction took place. The reaction was run with a 3 mole percent excess of nitrogen trifluoride, all of which was dissociated to fluorine and nitrogen during the explosion. Gas samples taken at the conclusion of each experiment were placed in contact with mercury to remove fluorine, and analyzed by mass and infrared spectroscopy. Tetrafluoromethane and nitrogen were the only gaseous products found.

4. Equipment (U)

(U) A Dickinson-type 25°C isothermal shield calorimeter was used for this project. The combustion bomb was constructed of "A" nickel and had a volume of 0.352 l. For vacuum work, O-ring seal needle valves were employed. The energy equivalent of the system was measured by combustion of benzoic acid (National Bureau of Standards sample 391) in oxygen under the prescribed conditions. Eight determinations gave a value of $E(calor)$ = -3200.7 cal/deg with a standard deviation of the mean equal to ± 1.7 cal/deg (1 cal = 4.1840 absolute joules). The following expression was employed to calculate reaction heats from temperature measurements (27):

$$Q_v = E(calor) \; (t_i - t_f + \Delta t_{cor}) + E^i \; (contents) \; (t_i - t_h) \\ + E^f \; (contents) \; (t_h - t_f + \Delta t_{cor})$$

Temperature measurements were made in terms of the resistance change of a calibrated thermistor - Wheatstone bridge. The corrected temperature changes were calculated by computer using standard procedures.

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5. Procedure (U)

(U) After the benzoic acid calibration experiments the nickel bomb was passivated by carrying out several preliminary C_2N_2-NF_3 reactions. Between reactions, the bomb was kept under vacuum and opened only in a nitrogen dry box. After four explosion reactions, the internal surfaces of the bomb were noticeably glazed with NiF_2.

(U) A determination involved first fitting a weighed nickel fuse between the electrodes of the bomb while in the drybox. The bomb was then evacuated for several hours to less than one micron pressure. Cyanogen, contained in a 10-ml stainless steel cylinder, was metered into the bomb to a pressure of about 350 mm. The bomb was closed and the cyanogen in the manifold contained in the bomb was determined by weighing the cylinder before and after the loading. Nitrogen trifluoride was admitted to the bomb to a total pressure of 1335 mm using the same procedure.

(U) After the heat measurement, the bomb was again attached to the vacuum line for gas sampling and evacuation. The bomb was then opened in the dry box and unburned pieces of nickel fuse wire recovered. These were cleaned and weighed to determine the net amount burned to NiF_2. Data for this correction were available (28).

6. Results (U)

(U) Table XVIII lists the results of ten determinations. Qv is the calorimetrically determined heat derived from the temperature change. Column four is the NF_3 dissociation correction based upon the amount of excess NF_3 over stoichiometry. Columns five and six are corrections for nickel fuse wire consumed as NiF_2 and the electrical energy necessary for fusion, respectively. These have been discussed earlier. Column seven lists the standard state internal energy change per gram of cyanogen.

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(U)   The average $\Delta E_r^o/M$ from Table XVIII and a molecular weight of 52.0357 for cyanogen yields for the reaction at 298.15°K:

$$1/2\ C_2N_2(g) + 4/3\ NF_3(g) \longrightarrow CF_4(g) + 7/6\ N_2(g)$$
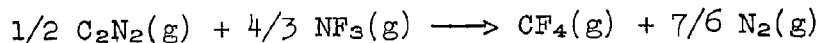
$$\Delta E_r^o = -218.33 \pm 0.20 \text{ kcal}$$
$$\Delta n(gas) = +1/3 \text{ mole}$$
$$\Delta nRT = +0.20 \text{ kcal}$$
$$\Delta H_r^o = -218.13 \pm 0.20 \text{ kcal}$$

Taking $\qquad \Delta Hf^o_{298.15}(C_2N_2,g) = +73.85 \pm 0.4 \text{ kcal/mol}$

and $\qquad \Delta Hf^o_{298.15}(NF_3,g) = -31.6 \pm 0.15 \text{ kcal/mol}$

we calculate $\Delta Hf^o_{298.15}(CF_4,g) = -223.23 \pm 0.6 \text{ kcal/mol}$.

This result is in excellent agreement with the previously quoted values from fluorine combustion of graphite. A weighted average of -223.0 kcal/mole is recommended for future use.

F.   HEAT OF FORMATION OF TRIFLUOROMETHOXYDIFLUOROAMINE   (U)

1.   Introduction   (U)

(U)   Trifluoromethoxydifluoroamine (CF_3ONF_2) was first prepared and characterized by G. H. Cady and L. C. Duncan several years ago. It was first described in the open literature by Hale and Williamson (29). In order to define the contribution of the $-ONF_2$ group to the heat of formation of a molecule, the heat of formation of this compound was measured.

2. Materials   (U)

(U)   The sample was prepared at the Dow Scientific Projects Laboratory. The methods of synthesis and purification have been previously described in the first quarterly report of this year. A batch of five grams was provided.

(C)   Molecular weight measurements were carried out by measuring the gas density at 22°C. These measurements, when corrected for gaseous non-ideality using estimated critical constants and the Berthelot equation of state, yielded 137.0 ± 0.1 g/mol

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Table XVIII

(U)   Heat of Reaction of Cyanogen and Nitrogen Trifluoride

Run No.	C_2N_2, g	Qv, cal	Corr. in cal. NF$_3$	Fuse	Ign.	$\Delta Er°/M$ cal/g
3	0.3496	-2,919.0	-17.0	3.7	0.4	-8,386.4
6	0.3496	-2,925.8	-10.8	4.0	0.4	-8,387.3
8	0.3515	-2,947.1	- 8.0	4.3	0.6	-8,393.2
9	0.3495	-2,992.6	-16.6	2.9	0.6	-8,399.7
11	0.3488	-2,929.8	-12.7	3.5	0.4	-8,399.6
12	0.3518	-2,954.9	-11.7	3.4	0.6	-8,399.4
13	0.3519	-2,946.7	-10.0	4.4	0.6	-8,373.7
14	0.3510	-2,947.6	-10.9	4.2	0.4	-8,397.7
15	0.3518	-2,942.8	-15.8	3.8	0.7	-8,372.1
16	0.3515	-2,955.2	-11.3	4.1	0.7	-8,407.4

Avg. = -8,391.6 cal/g

Standard deviation = 3.7 cal/g

for the molecular weight. Theory is 137.01 g/mol. The analytical results described later also indicate the sample was of high purity.

(U) Ultra-high purity hydrogen from Air Products and Chemicals, Inc., was used without further treatment. Mass and infrared spectral analysis detected no impurities.

3. Equipment (U)

(U) An Argonne National Laboratory type of rotating bomb calorimeter was used for this project. The platinum-lined combustion bomb had been fitted with an external tank so that water could be forced into the bomb after the explosion reaction. This apparatus has been described in an earlier report (30). O-Ring sealed valves were employed for vacuum work.

(U) The energy equivalent of the system was measured by combustion of benzoic acid (NBS sample 391) in oxygen under the prescribed conditions. Eleven determinations gave a value of E (calor) = 3352.1 cal/deg with a standard deviation of the mean equal to 2.4 cal/deg (1 cal = 4.1840 absolute joules). This value was adjusted to 3402.0 cal/deg for the conditions of the CF_3ONF_2 experiments. Temperature measurements were made in terms of the resistance change of a calibrated thermistor - Wheatstone bridge. The corrected temperature changes were calculated by standard procedures.

4. Nature of the Reaction (U)

(U) Exploratory experiments carried out in a platinum-lined reaction bomb indicated that CF_3ONF_2 underwent reduction to CO, HF and N_2 when sparked with a 10-20% excess of H_2. Fifty ml of H_2O was then forced into the bomb and the bomb rotated to produce a homogeneous solution of aqueous HF. The reaction is shown below:

$$CF_3ONF_2(g) + 5/2\ H_2(g) \longrightarrow CO(g) + 1/2\ N_2(g) + 5\ HF\ (1:150\ H_2O)$$
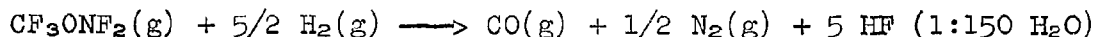
(U)   Mass and infrared spectral analysis of the gaseous products showed only CO and N_2.   The calorimetric experiments were followed by an analysis for CO by sweeping the bomb gases through a furnace and collecting and weighing the CO_2 formed.   A side reaction was indicated by the fact that CO analyses were low by 1 to 2%.   Slight carbon deposits were observed around the electrodes, indicating the side reaction to be:

$$CO(g) + H_2(g) \longrightarrow C(s) + H_2O(l)$$
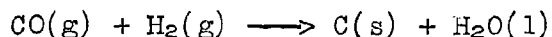
Corrections for this reaction could be applied, based upon the CO_2 recovery in each experiment.

(U)   Reactions at 1-2% excess H_2 were carried out for analytical purposes to establish the purity of the CF_3ONF_2.   These reactions yielded CO, N_2 and HF as in the former case; however, a few tenths of a percent of HNF_2 was observed by mass spectral analysis.   No spots of carbon were observed in these determinations and carbon recoveries were complete within the limits of error. The HF solution was titrated with base to determine the total equivalents of acid; however, this determination was consistently short both in the purity experiments and in the calorimetric runs. Table XIX gives the analytical data.

Table XIX

(U)   Analytical Data for Trifluoromethoxydifluoroamine

	Experiment No. 1	Experiment No. 2
Sample mass, g	0.5246	0.2031
CO_2 recovered, mg	169.24	65.22
Theory, %	100.4	100.0
HF recovered, meq	18.6	
Theory, %	97.2	

5.   Procedure   (U)

(U)   The bomb was first dried and evacuated to one micron pressure on a vacuum manifold.   A one-half gram portion of CF_3ONF_2

was then metered into the bomb to 200 mm pressure from a weighed steel U-tube fitted with miniature Hoke valves. The bomb was closed off after the charging and the amount of sample in the system condensed to a total pressure of 800 mm with hydrogen. To complete the loading operation, the external annular tank on the bomb was loaded with 50 ml of water and charged to 60 psig with argon.

(U) The loaded bomb was placed in the calorimeter and, after the initial drift rate was established, the gaseous mixture was ignitt͜l. A few seconds later, the tank valve was tripped and water was forced into the bomb. After a few more seconds, bomb rotation was started to ensure a homogeneous final aqueous solution. Final drift rate measurements completed the energy determination.

(U) The bomb was removed from the calorimeter and the gases discharged through an analytical train to determine carbon as CO_2. The bomb was then opened and carefully washed out with distilled water. The solution was analyzed for HF by titration with standard base.

6. Results (U)

(U) Table XX lists the results of eight experiments. Qv is the calorimetrically determined heat change in calories. The carbon correction arises from a small amount of $CO(g)$ being reduced to carbon during the explosion. This reaction is exothermic and amounts to 40.718 kcal/g atom of carbon. Column five is a correction based upon the energy released when a standardized capacitor is discharged during ignition. $\Delta E_T^o/M$ is the internal energy change in calories per gram of CF_3ONF_2.

(U) The average $\Delta E_T^o/M$ from Table XX and the molecular weight of 137.009 for CF_3ONF_2 yield for the reaction at 298.15°K:

$$CF_3ONF_2(g) + 5/2\ H_2(g) \longrightarrow CO(g) + 1/2\ N_2(g) + 5\ HF\ (1{:}150\ H_2O)$$

$$\Delta E_T^o = -217.85 \pm 0.80\ \text{kcal/mol}$$

-40-
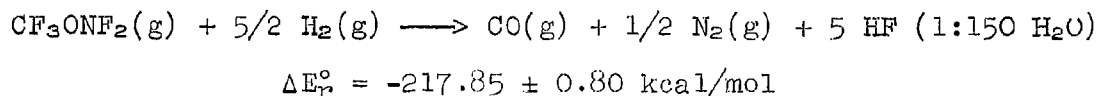
Table XX

(U) Heat of Reaction of Gaseous Hydrogen and Trifluoromethoxydifluoroamine

Run No.	Sample Mass, grams	Qv, calories	Corrections, calories		$-\Delta E_r^o/M$ cal/g
			Carbon	Ign.	
1	0.5886	942.4	(2.3)*	0.3	1,596.2
2	0.5244	838.2	(2.3)*	0.3	1,593.4
5	1.0492	1,683.2	3.7	0.4	1,600.4
6	0.5254	835.9	1.2	0.2	1,588.3
7	0.5216	833.7	3.1	0.2	1,592.0
8	0.5250	829.0	2.8	0.3	1,573.1
9	0.5263	837.9	2.2	0.3	1,586.4
10	0.5247	836.6	1.6	0.7	1,590.0

Avg. = 1,590.0

Std. dev. = 2.8

* Note: Carbon corrections for Runs 1 and 2 were estimated from Runs 5 to 10.

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$$\Delta n(gas) = -2 \text{ moles}$$
$$\Delta nRT = -1.18 \text{ kcal/mol}$$
$$\Delta H_r^o = -219.03 \pm 0.80 \text{ kcal/mol}$$

From Reference 31:

$$\Delta Hf_{298}^o \text{ (HF·150 H}_2\text{O)} = -76.35 \text{ kcal/mol}$$
$$\Delta Hf_{298}^o \text{ (CO,g)} = -26.42 \text{ kcal/mol}$$

From these values we calculate:

$$\Delta Hf_{298}^o(CF_3ONF_2, \text{ g}) = -189.1 \pm 0.8 \text{ kcal/r }.$$

The uncertainty is equal to twice the over-all standard deviation of the experiments.

7. Bond Energy Comparisons (U)

(U) It is of interest to compare our experimental result with predictions from bond energy terms. We shall use the bond energy terms and heats of atomization adopted in a recent publication from this laboratory (32) and listed in Table XXI.

Table XXI

(U) Terms for Calculation of Heats of Formation

$$E \text{ (C-F)} = 117.5 \text{ kcal/mol}$$
$$E \text{ (N-F)} = 67.1 \text{ kcal/mol}$$
$$E \text{ (C-N)} = 65.2 \text{ kcal/mol}$$

$$\Delta Hf \text{ (C,g)} = 171.5 \text{ kcal/mol}$$
$$\Delta Hf \text{ (N,g)} = 113.0 \text{ kcal/mol}$$
$$\Delta Hf \text{ (F,g)} = 18.9 \text{ kcal/mol}$$

Resonance energy of CF_3 group
is 1.4 kcal per bond less than
that of CF_4.

Resonance energy of CF_2 group
is 6.4 kcal per bond less than
that of CF_4.

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In addition, the heat of atomization of oxygen is taken from Reference 31 as 69.55 kcal/mol and bond energies E (C-O) = 85.5 and E (N-O) = 53.0 kcal/mol are from Reference 33. There is then calculated:

$-\Delta Hf = \Sigma$ (bond energies) $- \Sigma$ (heats of atomization) + K

where K is any correction term for resonance, steric effects, or other terms.

$$-\Delta Hf = 625.2 - 438.4 - 4.2$$
$$\Delta Hf^0_{298}(g) = -182.6 \text{ kcal/mol}$$

(U)   This is slightly less negative than experimentally measured, which implies that CF_3ONF_2 is a relatively stable molecule. This is in agreement with the observation of Hale and Williamson (29) that CF_3ONF_2 is stable at 140°C. At higher temperatures, cleavage to CF_4 and FNO occurred. Our result is not in accord with a bond energy E (N-O) = 35 kcal, which might be inferred from work of Paulett and Lustig (34) on mass spectrometer appearance potentials from FSO_2ONF_2.

G.   HEAT OF FORMATION OF FLOROX (ClF_3O)   (C)

1. Introduction (U)

(C)   A sample of oxychlorine trifluoride (ClF_3O, code name Florox) was obtained from Rocketdyne Division of North American Aviation, Inc. through the courtesy of Dr. D. Pilipovich. The heat of formation of liquid Florox was determined at Rocketdyne as -39.3±3 kcal/mol [aqueous HF based on Cox and Harrop (35)] or -36.5±3 kcal/mol [aqueous HF based on Reference (31)] by reaction with hydrogen and water. The present work involves reaction of Florox with aqueous arsenious oxide with the aim of confirming the heat of formation by a different method.

2. Material (U)

(C)   The Rocketdyne sample was accompanied by the following assay:

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ClF_3O	98.7 % min.
ClF_3	0.92% max.
$FClO_2/ClO_2$	0.01%
HF	0.25%

The first three chemical components were ascertained by GLC while the HF concentration was established by near-infrared spectrophotometric analysis.

(C) A Dow assay was carried out as follows. A weighed amount of Florox was charged to a platinum-lined combustion bomb in the same fashion as the calorimetric experiments described in following sections of this report. The bomb was connected to a cylinder of ammonia (Matheson Co. 99.99%). Ammonia was charged into the bomb to a pressure of 5 atm. Reaction occurred spontaneously. Excess ammonia was vented, the bomb was opened, and the white NH_4Cl and NH_4F washed out with hot distilled water. The solution was analyzed for chloride and fluoride. The method is not sensitive for distinguishing ClF_3O and ClF_3, but the chloride content found, 32.61%, indicated a maximum of 99.7% $[ClF_3O + ClF_3]$. The fluoride content found, 53.0%, is consistent within experimental error with 0.3% HF impurity (calculated 52.8% F). The sample composition was therefore taken as 98.8% ClF_3O, 0.9% ClF_3, and 0.3% HF.

(C) From the known bomb volume, the pressure, the ambient temperature and sample mass, the molecular weight of the sample was calculated as 111.82. With a very reasonable estimate of 0.97 for the compressibility factor of the unassociated gas, the molecular weight at zero pressure is 108.5, in excellent agreement with theory for ClF_3O.

3. Equipment (U)

(U) The platinum-lined combustion bomb fitted with an annular tank has been previously described (30). A metal vacuum system was employed for loading the bomb with gaseous Florox. A rotating-bomb calorimeter and automatic resistance bridge were used to determine the heats of reaction.

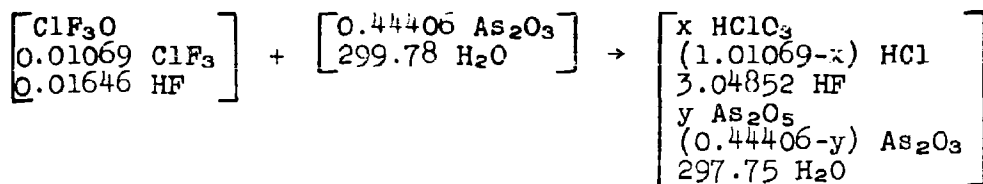# CONFIDENTIAL

4. Procedure (U)

(U) The bomb was connected to the vacuum system and evacuated. Florox was admitted to the system and bomb to about 100 mm pressure and allowed to condition the system for about 30 minutes. This Florox was pumped off and discarded. An appropriate amount of Florox was then transferred from the supply cylinder to a small Monel double valved trap which was disconnected from the system and weighed. After reconnecting, sample was transferred from this trap to the bomb to a pressure of 475 mm. The bomb was closed off and Florox remaining in the system recondensed in the trap which was then removed and reweighed. Blank experiments showed a small loss of 1.3 mg in this operation and this blank was subtracted from all sample weights.

(U) The bomb was disconnected and 50 ml of 0.0839 M As_2O_3 charged to the tank. The tank was then pressured to 60 psig with argon and closed off. The loaded bomb and tank assembly was placed in the calorimeter and, after the foredrift was established, a valve was opened allowing the aqueous As_2O_3 to be forced into the bomb. Rotation of the bomb was begun when 0.6 of the temperature rise had occurred. The final drift rate readings completed the calorimetric part of the experiment.

(U) The bomb was vented, opened, and the contents washed out with distilled water. The solutions were analyzed for As_2O_3, F^-, Cl^-, and ClO_3^-. Fluoride recoveries were about 99±1% of theory, while the sum of Cl^- and ClO_3^- averaged about 100±1% of theory. These recoveries were taken as satisfactory in view of the complexity of the solutions. For calculation purposes, the ClO_3^- was taken as the difference between theoretical Cl^- and the found Cl^-, since the chloride analysis was considerably more reliable than ClO_3^- in blank experiments.

5. Results (U)

(C) The process described in the preceding section refers to the reaction:

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$$\begin{bmatrix} ClF_3O \\ 0.01069 \ ClF_3 \\ 0.01646 \ HF \end{bmatrix} + \begin{bmatrix} 0.44406 \ As_2O_3 \\ 299.78 \ H_2O \end{bmatrix} \rightarrow \begin{bmatrix} x \ HClO_3 \\ (1.01069-x) \ HCl \\ 3.04852 \ HF \\ y \ As_2O_5 \\ (0.44406-y) \ As_2O_3 \\ 297.75 \ H_2O \end{bmatrix}$$

Several heats of mixing were run which established that no
significant net thermal effect was associated with mixing the
components of the final solution. The heats of formation of HCl
and HF in this solution were therefore taken to be the same as
those in pure water at a ratio of 1 mole to 75 moles of water.
Two corrections were applied to the experiments: A correction
for oxidation of aqueous As_2O_3 to aqueous As_2O_5 was calculated
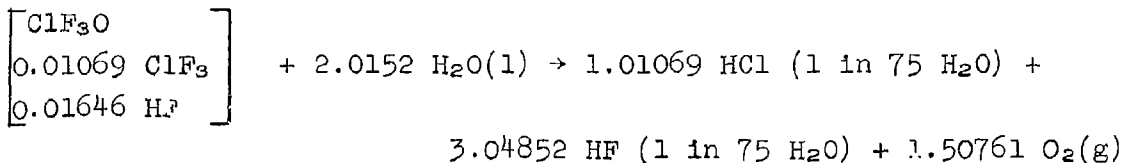from data of Sunner and Thoren (36) as:

$$As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq)$$
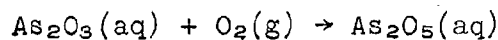
$$\Delta E_R = -76,577 \ cal/mol$$

A correction for conversion of $HClO_3(aq)$ to $HCl(aq)$ from Reference
(31) as

$$HClO_3(aq) \rightarrow HCl \ (1 \ in \ 75 \ H_2O) + 3/2 \ O_2(g)$$
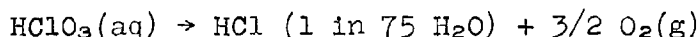
$$\Delta E_R = -16,798 \ cal/mol$$

(C) Benzoic acid calibration experiments established
E(Calor) as 3346.55 cal/°C. To this was added the heat capacity
of the bomb contents: 49.64 cal/°C for 50 ml of 0.0839 M As_2O_3
and 0.14 cal/°C for 1.0 gram of ClF_3O gas. Results of the
calorimetric experiments are given in Table XXII. The "Total
Calories" column is the product of the corrected temperature rise
and [E(Calor) + Cp(contents)]. The average $-\Delta E_R/M$ refers to the
reaction:

$$\begin{bmatrix} ClF_3O \\ 0.01069 \ ClF_3 \\ 0.01646 \ HF \end{bmatrix} + 2.0152 \ H_2O(l) \rightarrow 1.01069 \ HCl \ (1 \ in \ 75 \ H_2O) +$$

$$3.04852 \ HF \ (1 \ in \ 75 \ H_2O) + 1.50761 \ O_2(g)$$

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$$\Delta E_R = -100.70 \text{ kcal}$$

$$\Delta H_R = -100.42 \text{ kcal}$$

Auxiliary heat of formation data are taken from Reference (31):

	ΔHf kcal/mol
HCl (1 in 75 H_2O)	-39.609
HF (1 in 75 H_2O)	-76.333
H_2O (liq)	-68.315
ClF_3 (g)	-38.0
HF (g)	-64.8

There is then derived:

$$\Delta Hf \begin{bmatrix} ClF_3O \\ 0.01069 \ ClF_3 \\ 0.01646 \ HF \end{bmatrix} = -34.65 \text{ kcal/mol}$$

and after correction for ClF_3 and HF:

$$\Delta Hf_{298} \ (ClF_3O, \ g) = -33.17 \text{ kcal/mol}$$

The heat of vaporization at 25°C is calculated from the vapor pressure equation given by Rocketdyne and an estimated compressibility factor of 0.97 as 6.98 kcal/mol. This value yields:

$$\Delta Hf_{298} \ (ClF_3O, \ liq) = -40.15 \pm 0.50 \text{ kcal/mol}$$

The uncertainty estimate includes 0.25 kcal/mol for statistical variation and 0.25 kcal/mol for uncertainty in sample composition. The result is in reasonable agreement with the Rocketdyne value, -36.5±3 kcal/mol (aqueous HF based on Reference 31).

(C) It may be noted that the heat of formation of ClF_3O is less negative than that of ClF_3; a mixture of ClF_3 and O_2 is, therefore, less energetic than the compound ClF_3O.

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(This Page is Unclassified)

## Table XXII

(U) Heat of Reaction of Florox and Aqueous As_2O_3

Expt. No.	Sample Mass, grams	Total Calories	As_2O_3 Corr'n, Calories	$HClO_3$ Corr'n, Calories	$-\Delta E_R/M$ cal gram
4	1.0100	-1158.3	246.6	-16.6	919.2
5	1.0091	-1171.0	256.2	-12.7	919.1
6	1.0076	-1163.7	252.8	-16.3	920.3
7	1.0071	-1159.5	248.9	-15.2	919.3
8	1.0072	-1158.8	252.8	-14.1	913.5
				Average	918.3
				Std. dev.	1.2

H. THE HEAT OF FORMATION OF TETRAFLUOROHYDRAZINE (U)

1. Introduction (U)

-(U) Tetrafluorohydrazine is a comparatively new compound first described in 1958 by Kennedy and Colburn (37). Later papers have appeared describing the mass and NMR spectra (38,39).

(U) Early calorimetry on N_2F_4 is limited to a series of measurements by Armstrong, Marantz, and Coyle (40) on the heat of reaction of ammonia and 95% pure N_2F_4. Their result is dependent on the heat of formation of NH_4F which is in turn dependent on the heat of formation of aqueous HF. Published values for the heat of formation of aqueous HF vary by several tenths of a kcal/mol.

(U) It seemed desirable to carry out a calorimetric study that would not involve aqueous HF. Recent work in this laboratory on the reaction between $NF_3(g)$ and $C_2N_2(g)$ suggested that the same techniques could be applied to a reaction between $N_2F_4(g)$ and $C_2N_2(g)$. The reaction is explosive and is initiated by a spark:

$$N_2F_4(g) + 1/2\ C_2N_2(g) \rightarrow CF_4(g) + 3/2\ N_2(g)$$
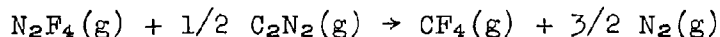
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The heats of formation of cyanogen (41) and CF_4 (23,35,42) are now well established as +73.84±0.40 and -223.0±0.2 kcal/mol, respectively. An accurate value derived from the above reaction would also better define the heat of formation of NF_2 radical, produced by thermal dissociation of N_2F_4.

2. Equipment (U)

(U) A Dickinson-type 25°C isothermal shield calorimeter was used for this project. The combustion bomb (laboratory designation NIB-2) was constructed of "A" nickel and had a volume of 0.352 l. O-Ring seal valves were employed for vacuum work. The energy equivalent of the system was measured by electrical heat inputs over the same temperature range in which the N_2F_4-C_2N_2 reactions took place. Three calibrations of the system gave a value of $E(Calor) = -3202.1 \frac{cal}{deg}$ (±0.01%). Comparisons of benzoic acid combustion calibrations vs. electrical calibrations using a similar nickel bomb (NIB-1) indicated the values to be the same within experimental error of ±0.01%. (1 cal ≡ 4.1840 abs. joules).

(U) Temperature measurements were made in terms of the resistance change of a calibrated thermistor-Wheatstone bridge. The corrected temperature changes were calculated by computer program using standard procedures.

3. Materials (U)

(U) The cyanogen and tetrafluorohydrazine were purchased from Air Products and Chemicals, Inc. Purification and analysis of the C_2N_2 as previously described (43) confirmed it to be at least 99.9% pure. "Research grade" N_2F_4 specified at 99.8% was purified further by low temperature distillation. A small amount of a lower boiling substance was cut out in this fashion. A reddish-blue color in the "as received" liquid N_2F_4 suggested the presence of a nitrogen oxide complex (44). The collected material after distillation was white in the solid and colorless in the liquid.

(U) Infrared measurements indicated the complex band between 900 and 1060 cm^{-1} and also the strong broad band at 735 cm^{-1} as described by Colburn and Kennedy (37) and by Durig (45). A mass spectral analysis was carried out on a consolidated Electrodynamics Mass Spectrograph with the following fragmentation pattern.

Table XXIII

(U) Mass Frequentation Pattern of Tetrafluorohydrazine(g)

m/e	Ion	Intensity, %
14	N^+	16.95
19	F^+	9.36
28	N_2^+	7.98
33	NF^+	103.46
47	N_2F^{3+}	7.48
52	NF_2^{2+}	100.00
66	$N_2F_2^{2+}$	6.03
85	$N_2F_3^+$	6.80
104	N_2F_4	1.48

The instrument reference was the n-butane 58 peak.

(U) In addition, molecular weight measurements were carried out by measuring the gas density. Two measurements, when corrected for gaseous non-ideality using estimated critical constants (Pc = 41.87 atm, Tc = 304.6°K) and the Berthelot equation of state, yielded 103.76±0.1 g/mol. Theory is 104.0 g/mol.

4. Nature of the Reaction (U)

(U) $N_2F_4(g)$ and $C_2N_2(g)$ were found to react in the gas phase when the mixture was sparked to form nitrogen and CF_4. Ignition was accomplished by discharging a standardized capacitator across a 0.5 cm length of nickel fuse wire. An audible "click"

could be heard when the reaction took place. The reaction was
run with an approximately 2 mole % excess of N_2F_4, all of which
was dissociated to N_2 and F_2 during the explosion. Gas samples
were taken at the conclusion of each run, placed in contact with
mercury to remove F_2, and analyzed by mass and infrared spectroscopy.
CF_4 and N_2 were the only gaseous products found.

5. Procedure (U)

(U) The nickel bomb was passivated by carrying out several
preliminary C_2N_2-N_2F_4 reactions. Between reactions the bomb was
kept under vacuum and opened only in a nitrogen dry box. After
four explosion reactions the internal surfaces of the bomb were
noticeably glazed with NiF_2.

(U) A determination involved first fitting a weighed nickel
fuse between the electrodes of the bomb while in the dry box. The
bomb was then evacuated for several hours to less than one micron
pressure. Cyanogen, contained in a 10 ml stainless steel cylinder,
was metered into the bomb to a pressure of about 250 mm. The
bomb was closed and the C_2N_2 in the manifold condensed back into
the small cylinder. The mass of C_2N_2 contained in the bomb was
determined by weighing the cylinder before and after the loading.
N_2F_4 was admitted to the bomb to a total pressure of 760 mm using
the same procedure.

(U) After the heat measurement, the bomb was again attached
to the vacuum line for gas sampling and evacuation. The bomb was
then opened in the dry box and unburned pieces of nickel fuse
wire recovered. These were cleaned and weighed to determine the
net amount burned to NiF_2. Data for this correction were available
(28).

6. Results (U)

(U) Table XXIV lists the results of five determinations.
$\Delta\theta$ is the calorimetrically determined temperature change and Q_v
is the product of $E(Calor)$ and $\Delta\theta$. Column four is the correction

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Table XXIV

(U) Heat of Reaction Data

$$N_2F_4(g) + 1/2 \ C_2N_2(g) \longrightarrow CF_4(g) + 3/2 \ N_2(g)$$

Expt. No.	Corrected Temp. Rise. $\Delta\Theta$, °C	Total Calories, Q_v	Corrections in Calories			Sample Mass, g,C_2N_2	$\Delta E/M$ cal/g C_2N_2
			N_2F_4	NiF_2	Ig'n		
5	0.7719	-2471.7	-1.0	2.5	0.4	0.2509	-9,843.8
6	0.7660	-2452.8	-0.45	0.9	0.2	0.2495	-9,828.3
7	0.7731	-2475.5	-0.8	1.2	0.3	0.2517	-9,832.3
9	0.7709	-2468.5	-1.0	0.9	0.3	0.2514	-9,818.2
10	0.7710	-2468.8	-0.7	1.4	0.2	0.252	-9,832.3

Avg. = -9,831.0

σ = 4.1

for decomposition of N_2F_4 to the elements based upon the amount
of excess N_2F_4 over stoichiometry and its energy of dissociation
of 5.915 kcal/mol as determined in this work. Columns five and
six are corrections for nickel fuse wire consumed as NiF_2, and
the electrical energy necessary for fusion, respectively. Column
seven lists the weighed mass of C_2N_2 and the final column is the
change in internal energy in calories per gram of C_2N_2. The
uncertainty interval of ±8.2 cal/g represents twice the standard
deviation arising from statistical variation in calibration and
the N_2F_4-C_2N_2 heat measurements.

(U) The standard state enthalpy of reaction per mole of
N_2F_4 is calculated as follows:

$$\Delta Er_{298°K} = -255.78 \pm 0.21 \text{ kcal/mol}$$

$$\Delta nRT = 0.59 \text{ kcal/mol}$$

$$\Delta Hr_{298°K} = -255.19 \pm 0.21 \text{ kcal/mol}$$

(U) Taking $\Delta Hf_{298°K}(CF_4,g) = -223.0 \pm 0.2$ kcal/mol and
$\Delta Hf_{298°K}(C_2N_2,g) = +73.85 \pm 0.4$ kcal/mol we calculate $\Delta Hf_{298°K}$
$(N_2F_4,g) = -4.73 \pm 0.6$ kcal/mol. It should be noted that this is
the $\Delta Hf(N_2F_4,$ Real Gas$)$ since at room temperature there is present
approximately 0.057% of N_2F_4 in the NF_2 form. The ΔHr of
$(N_2F_4,$ Real Gas$)$ with C_2N_2 would be expected to be more negative
than the ideal gas. This correction amounts to 0.16 kcal/mol
making ΔHf_{298} $(N_2F_4,$ Ideal Gas$) = -4.89 \pm 0.6$ kcal/mol.

(U) Because of the uncertainty in the heat of formation of
aqueous HF, this result is not directly comparable with the previous
work of Armstrong, Marantz, and Coyle (40). The fact that the
present result is more negative than the previous work is in
accord with the recent thermochemical data indicating the heat of
formation of aqueous HF is more negative than the values adopted
in recent NBS compilations.

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(U) Combination of the present result with the enthalpy of dissociation to NF_2 radicals adopted in the JANAF Thermochemical Tables, 22.26 ± 2.0 kcal/mol, leads to a revised enthalpy of formation of NF_2 radical:

$$\Delta Hf_{298}(NF_2,g) = +8.7 \pm 2.0 \text{ kcal/mol}$$

I. SYNTHESIS (U)

(U) During the past year CF_3ONF_2, TVOPA, and CF_3NF_2 have been supplied to the Thermal Research Laboratory. CF_3ONF_2 was prepared by the photochemical reaction of CF_3OF and N_2F_4 (46), i.e.,

$$CF_3OF + N_2F_4 \xrightarrow[\substack{\text{Corex} \\ \text{filter}}]{h\nu} CF_3ONF_2$$
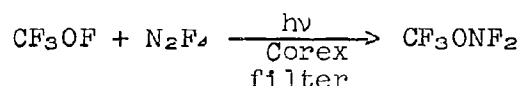
(U) This project was concluded with the preparation and purification of 6 g of material, which was supplied to the Thermal Research Laboratory for completion of their study.

(U) The removal of solvent from TVOPA was achieved by several methods. A lot was obtained in which the solvent was a mixture of 65% chloroform and 35% Freon 113. Simple high vacuum techniques, which were adequate for removal of methylene chloride from the previous lot, were not effective. Therefore, a new procedure had to be developed. After small amounts of impurities were removed by elution of pure TVOPA with a 50% benzene - 50% methylene chloride mixture from an acid washed silica gel column, the solvent was removed by high vacuum ($<5\,\mu$) on a Rotovac apparatus. This procedure gave TVOPA with low residual chloride.

(U) Since our supply of acid-washed material was exhausted, a solution of 30 g of production grade material was passed through a bed of sulfonic acid resin (Dowex 50, acid form). This was the same procedure used by Rohm and Haas in their preparation of acid-washed material.

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(U) Using this acid-washed supply, five batches of TVOPA totaling 5.9 g were purified, and the homogeneous mixture was supplied to the Thermal Research Laboratory for calorimetric studies. Chloride analysis of six samples of this material indicated an average of 1.8 mg of chloride per gram of sample.

(U) Since benzene was used in one step of the purification process, it was desirable to determine the quantity of benzene remaining in the final material. To accomplish this, a sample of TVOPA was treated with C^{14} tagged benzene, which was subsequently removed by the procedure described above. Any non-volatile impurity which might have been present in the benzene was retained in the TVOPA. Another sample of TVOPA was then treated similarly with the benzene removed from the previous sample. Both samples contained only negligible benzene from the standpoint of making corrections in the thermal data.

(U) Upon completion of this project, the preparation of pure CF_3NF_2 was undertaken. Although production of CF_3NF_2 by a photochemical process, i.e.,

$$CF_3I + N_2F_4 \xrightarrow[\text{Corex filter}]{h\nu} CF_3NF_2 + \text{side products}$$
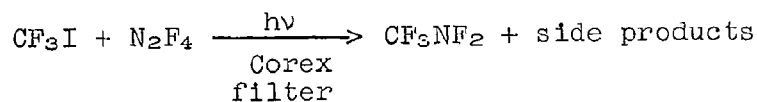
was originally believed to be an adequate means of producing this material, a better method was found (47). The photochemical method gave many side products, including SiF_4 and nitrogen oxides, which required codistillation and vapor phase chromatography to remove. The better method involved low temperature direct fluorination of KSCN, i.e. (47),

$$KSCN + 6 F_2 \xrightarrow[\text{KF}]{-70°C} CF_3NF_2 + SF_6 + KF$$
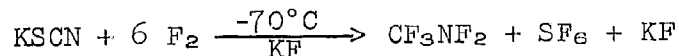
(U) The initial attempt of this reaction gave a quantitative yield of gaseous products consisting of CF_3NF_2 and SF_6, which could be separated completely by two codistillations. However, subsequent attempts failed to yield CF_3NF_2. Since the solid materials used in the reaction were found to be fused after each reaction failure,

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the problem was assumed to be lack of dissipation of heat produced by a very rapid reaction. Therefore, several methods for slowing the reaction and removing heat were employed. The only operation which could be credited with solving the problem was placing granular KSCN in a cylinder and adding KF on top of it, taking precautions not to mix the two since mixing gave poor results.

(U) The preparation and purification of CF_3NF_2 is now progressing smoothly. Although the amount of pure material originally needed has been prepared, there is now a need for an additional 3 g. The preparation of this is in progress.

J. EXPERIMENTAL (U)

1. Purification of TVOPA (U)

(U) To purify TVOPA, a 1.5 g sample was placed on a Rotovac apparatus under a high vacuum ($<5 \mu$) at room temperature for two hours. This was followed by chromatography on an acid-washed silica gel column with an eluent of 50% methylene chloride-50% benzene. The TVOPA was again put on a Rotovac apparatus under high vacuum ($<5 \mu$) and room temperature for a 48 hour period. Material treated in this manner contained 1.8 mg of chloride per gram of sample.

2. Photochemical Preparation of CF_3NF_2 (U)

(U) Into a 5-liter flask was vacuum transferred 5.8 g (0.03 mole) of CF_3I and 3.15 g (0.03 mole) of N_2F_4. This mixture was irradiated for 24 hours with an immersion ultraviolet lamp surrounded by a 9700 Corex glass filter (eliminates wavelength below 260 millimicrons). The crude product was codistilled to remove the bulk of impurities, then it was passed through a bed of KOH pellets where most of the remaining SiF_4 was removed. Subsequent gas chromatography through a 21 ft. Kel-F tetramer column (25% oil on Chromosorb W) at -65°C gave 1.82 g (50% of theory) of pure material.

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3. Fluorination of KSCN   (U)

(U)   About 5.0 g (0.0515 mole) of anhydrous KSCN was placed into a 1000 ml stainless steel Hoke cylinder, and 15 g (0.259 mole) of anhydrous KF was carefully placed on top of the KSCN. Special care was taken not to mix the two. Fluorine (0.091 mole) was admitted to the cylinder at -196°C. The cylinder was then allowed to warm to -78°C and stand at this temperature overnight. A quantitative yield of volatile material was obtained which consisted of approximately equal quantities of CF_3NF_2 and SF_6. This mixture was separated by two careful codistillations through a column packed with magnesium beads.

(U)   This procedure could be repeated until all of the KSCN was consumed as long as there was always a KF blanket on the KSCN.

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SECTION II

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) The use of elemental boron as a fuel for augmented rocket propulsion has revived the problem of the inefficiency of the combustion of boron. The combustion of boron in the presence of water or water-producing materials results in the formation of HOBO as an intermediate product. This compound can arise from the reaction between the desired combustion product B_2O_3 and water (48,49), as well as from the highly reactive intermediate BO_2 and water (50).

(U) The primary physical parameters of boron combustion are due to the fact that the melting point and, especially, the boiling point of the metal exceed the boiling point of the boric oxide (B_2O_3), which is the ultimate product of the combustion. The high vapor pressure of the oxide at the ignition temperature of boron in oxygen (2200°K) (48) places boron in the realm of a surface burning metal, in contrast to aluminum, which burns primarily in the gas phase (51). Table XXV shows the melting and boiling points of boron and some of its oxidation products.

Table XXV

(U) Physical Properties of Boron, Its Oxides and Acids[a]

|	M.P., °K	B.P., °K
Boron	2450 ± 20	3931 (estimate)
HBO_2	509 ± 1	Sublimes
H_3BO_3	441.1 ± 0.2	Dissociates at 330
B_2O_3	723 ± 2	2316

[a]JANAF Tables

(U) It can be seen from Table XXV that the melting point of elemental boron is higher than the boiling point of any of its

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reaction products. In fact, the products H_3BO_3 and HOBO dissociate below 600°K.

(U) The inefficiency in the combustion of elemental boron, as well as in the borane fuels, has been attributed to the formation of HOBO. The first definite evidence for the existence of gaseous HOBO at high temperature was the infrared emission studies of White, Mann, Walsh and Sommer (48). From the intensity vs. temperature variation of the 2030 cm^{-1} band, the heat of reaction for:

$$1/2\ B_2O_2(1) + 1/2\ H_2O(g) = HBO_2(g) \qquad (1a)$$
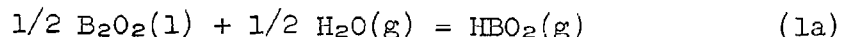
was found to be 39.0 ± 2.5 kcal/mol at 1350°K, corresponding to a $\Delta Hf°$ of -135.0 ± 3.0 kcal/mol for $HBO_2(g)$. This work has led to the assertion that the formation of HBO_2 is an endothermic process. Using the latest JANAF data, a heat of reaction of +36.6 kcal/mol is calculated if the B_2O_3 is liquid at 2500°K. The temperature is approximately that calculated for the flame temperature of elemental boron in oxygen. In fact, Fassell et al. (52) calculated an adiabatic flame temperature at 3786°K for the combustion of boron to B_2O_3 in oxygen.

(U) There is some doubt that the actual process in a rocket combustion is simulated by this static equilibrium experiment. Accepting Talley's work at Experiment Inc., that the flame temperature of elemental boron combustion is equal to the oxide boiling point, then we could conclude that the primary reaction between B_2O_3 and water is a homogeneous gas phase reaction since the gaseous H_2O would first come in contact with gaseous B_2O_3. JANAF Table data show that this reaction:

$$1/2\ B_2O_3(g) + 1/2\ H_2O(g) = HOBO(g) \qquad (1b)$$
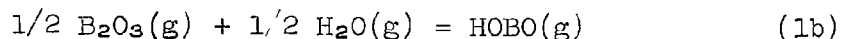
is exothermic by 6.7 kcal/mol.

(U) There is some reason to doubt that the formation and existence of HOBO is detrimental from a purely thermodynamic point of view. Another possibility for the low combustion efficiency of boron-containing fuels could be the dissociation of B_2O_3 via:

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$$B_2O_3(g) = BO(g) + BO_2(g) \tag{2}$$
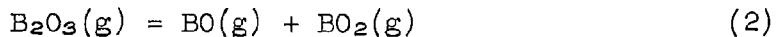
Calculation shows the above reaction to be endothermic by 131 kcal/mol at 2500°K.

(U) The gas phase reaction is discussed for two reasons. First, it is recognized that problems are encountered with the oxide layer surrounding a burning boron particle, and this effect will not be discussed again. The problems associated with the low efficiency combustion characteristics of elemental boron may be due largely to this. However, this oxide layer effect does not exist in the combustion of volatile boron fuels (boranes, borazines, etc.), while the low combustion efficiency does still exist, indicating, perhaps, a gas phase combustion problem. Second and more important from an experimental point of view, the flash heating apparatus "sees" only gas phase products which have electronic spectra. In reporting data on the combustion of elemental boron, species which cannot be detected by the apparatus are not ruled out, but the investigation will be concentrated mainly on these species which can be identified.

(C) In order to more completely understand the chemistry involved in the combustion of a boron-containing solid propellant for air augmented combustion, it is necessary to study the combustion of boron and some of its primary oxidation products in atmospheres corresponding to those resulting from the deflagration of the ammonia perchlorate (AP) oxidizer and the polybutadiene-acrylonitrile (PBAN) binder.

(U) Primary emphasis is placed on those combustion systems which would be expected to yield HOBO as a combustion product.

B. EXPERIMENTAL RESULTS FOR PROPOSED STUDIES (U)

(U) The flash heating apparatus employed in the present work has already been described (53). It was employed to study the combustion of LMH-2 on Contracts AF 04(611)-7554 and AF 04(611)-11202.

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(U)   The boron used in the present work is "Avco 400." The elemental analysis of the metal is:

$$B = 89.75\% \text{ (avg. of } 90.0\% \text{ and } 89.5\%)$$

$$C = 0.95\%$$

$$H = 0.76\%$$

The remainder is B_2O_3.

(U)   The oxygen, chlorine and HCl used in the combustion studies were Dow gases of 99 mole percent purity. The H_3BO_3 used in supplementary studies was obtained from Jarrell-Ash Company and showed only 1 ppm of magnesium as an impurity. The studies carried out on B_2O_3 employed an oxide obtained for Matheson-Coleman and Bell. This material was of at least 99 mole percent purity.

1.   Volatilization of Boron   (U)

(U)   The first study undertaken was on the volatilization of the elemental boron to determine which absorption lines of the element were present.

(U)   The pyrolysis of elemental boron was studied at 1815 joules for the time delay of only 0 to 210 µsec. No attempt was made to study the volatilization at longer delay, since it was desired only to identify boron lines. If the combustion of boron proceeds as expected, the lines should be present in greater intensity at longer delays. The purpose of this study was to determine the time delay for the first absorption boron lines. The shortest line delay at which boron lines were seen was 105 µsec. The lines identified were the 2486.8 Å and the 2497.7 Å lines of BI. Also seen were the 0-0 lines of the $^3\Sigma \leftarrow \Sigma g$ transition of the diatomic molecule B_2 at 3272.8 Å and the 3-3 bands of the same transition at 3300.4 Å (54).

(U)   In subsequent studies described below, additional lines of B_2 were identified. The present study proved that elemental
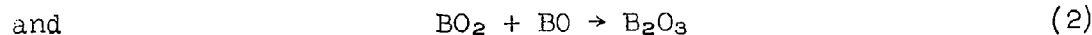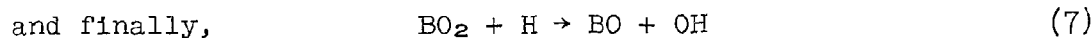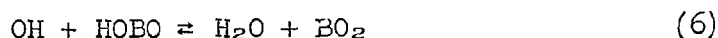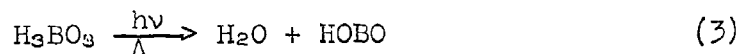
boron could be volatilized in the flash heating apparatus and its gas phase products identified. Once the gaseous species B and B_2 are detected, it could be concluded that some part of the boron combustion, small though it may be, is a homogeneous gas phase reaction.

2. Reactions of HOBO and H_3BO_3 (U)

(U) The role of HOBO has been thought to be that of a heat-sink such as Reaction (1a). In order to ascertain the absorption lines due to the reaction of HOBO, H_3BO_3 (HOBO·H_2O) was pyrolyzed and its spectrum analyzed.

(U) The spectra of OH and BO_2 were seen in greatest intensity. Since BO_2 was seen prior to BO, the following scheme for the dissociation of HOBO is suggested:

$$H_3BO_3 \xrightarrow[\Delta]{h\nu} H_2O + HOBO \qquad (3)$$

$$H_2O \rightarrow H + OH \qquad (4)$$

$$HOBO \rightarrow H + BO_2 \qquad (5)$$

$$OH + HOBO \rightleftharpoons H_2O + BO_2 \qquad (6)$$

and finally, $\qquad BO_2 + H \rightarrow BO + OH \qquad (7)$

and $\qquad BO_2 + BO \rightarrow B_2O_3 \qquad (2)$

It is important to note that the results suggest, at least under our experimental conditions of vacuum pyrolysis, that the O-H bond of HOBO is ruptured, not the O-B bond.

(U) The combustion of H_3BO_3 in 30 mm of oxygen showed the same lines to be present but of a greater intensity. This tends to indicate that the combustion of HOBO proceeds via the OH radical arising from:

$$H_2O + O_2 \rightarrow 2 OH + O \qquad (8)$$

and $\qquad$ $HOBO + O \rightarrow OH + BO_2$ $\qquad$ (9)

Additional studies were carried out on HOBO and H_3BO_3 as the need became apparent.

3. Reactions of B_2O_3 (U)

(U) The high temperature vacuum pyrolysis of B_2O_3 has been analyzed in detail. The species BI, B_2, and BH were seen when B_2O_3 was flashed. No BO_2 has been detected. Until a careful analysis is carried out, Step (2):

$$B_2O_2 \xrightarrow[\Delta]{h\nu} BO + BO_2 \qquad (2)$$

cannot be eliminated as possible reaction step in favor of:

$$B_2O_3 \xrightarrow[\Delta]{h\nu} B_2O_2 + O \qquad (10)$$

$$B_2O_2 \rightarrow B_2O + O \qquad (11)$$

$$B_2O \rightarrow BO + O \qquad (12)$$
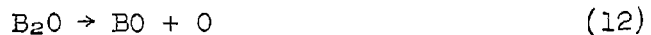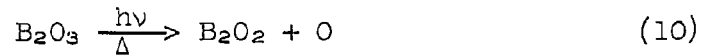
(U) G. S. Bahn, at the 1966 Spring Meeting of the Western States Section of the Combustion Institute, suggested the possibility of the species B_2O playing a prominent role in the combustion of boron (56). A series of lines in the range 3500-3770 Å cannot be identified. These lines decrease in intensity as the pressure of oxygen is increased. The same type of behavior would be expected from B_2O, as oxygen would cause it to react to B_2O_2 and B_2O_3 via:

$$B_2O + O_2 = B_2O_2 + O \qquad (13)$$
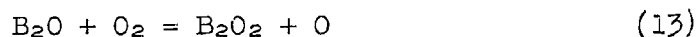
and $\qquad$ $B_2O_2 + O = B_2O_3$ $\qquad$ (14)

For a more detailed treatment of the formation of B_2O from boron, the original paper (56) should be consulted. Time did not permit a vibrational analysis of the bands to be carried out to determine if the bands do correspond to B_2O.

(U)   In general, it can be said that the gas phase oxidation of elemental boron is limited by the rate of volatilization of the metal.   The reaction products include a large number of partially oxidized boron compounds, having very fast interconversion rates. The balance between oxygen and boron greatly influences the formation and stability of the desired product, B_2O_3.

## 4.   Combustion of Boron in Oxygen and Water   (U)

(U)   This study deals with the gas phase products from the reaction between liquid and gaseous boron and oxygen and in a mixture of oxygen and water.   These studies were carried out at an oxygen pressure of 30 mm, although a few reactions were carried out at 20 mm oxygen.   The delay time ranged from 14 to 3000 µsec at 1500-2000 joules.   The time-intensity curve for the boron species observed during the combustion of boron is shown in Figure 3.

(U)   The first thing that is noticed in the combustion of boron in oxygen is the multitude of lines seen in absorption.   These include OH (from the "glue" used to adhere the boron to the graphite strips plus that from the 0.76% H_2 in the boron itself), α-BO, β-BO, BO_2, B_2O_2, BH, and the species NH and CN, from the volatilization of the graphite strips and their subsequent reaction with the adsorbed nitrogen from the dry box.   One spectrum for example, contained 265 absorption lines between 3000 and 4500 Å.

(U)   The α-BO absorption lines were identified from the work of Mulliken (55) and Jenkins and McKellar (69).   The β-BO spectrum was compared to that reported by Mulliken (55) and by Lagerqvist, Nilsson and Wigartz (70).

(U)   The BO bands, both α- and β-systems, were intense.   The α-bands were the 1-1 band at 4363 Å; the 2-0 band between 3838 and 3846 Å.   The β-BO bands identified were the 0-4 band with the heat at 2810 Å, the 1-5 band at 2851 Å, and the 3390 Å band of the 2-9 absorption.   The high ν'' values of the BO bands indicate the extreme thermal effects of the combustion.
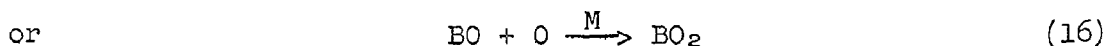
-64-
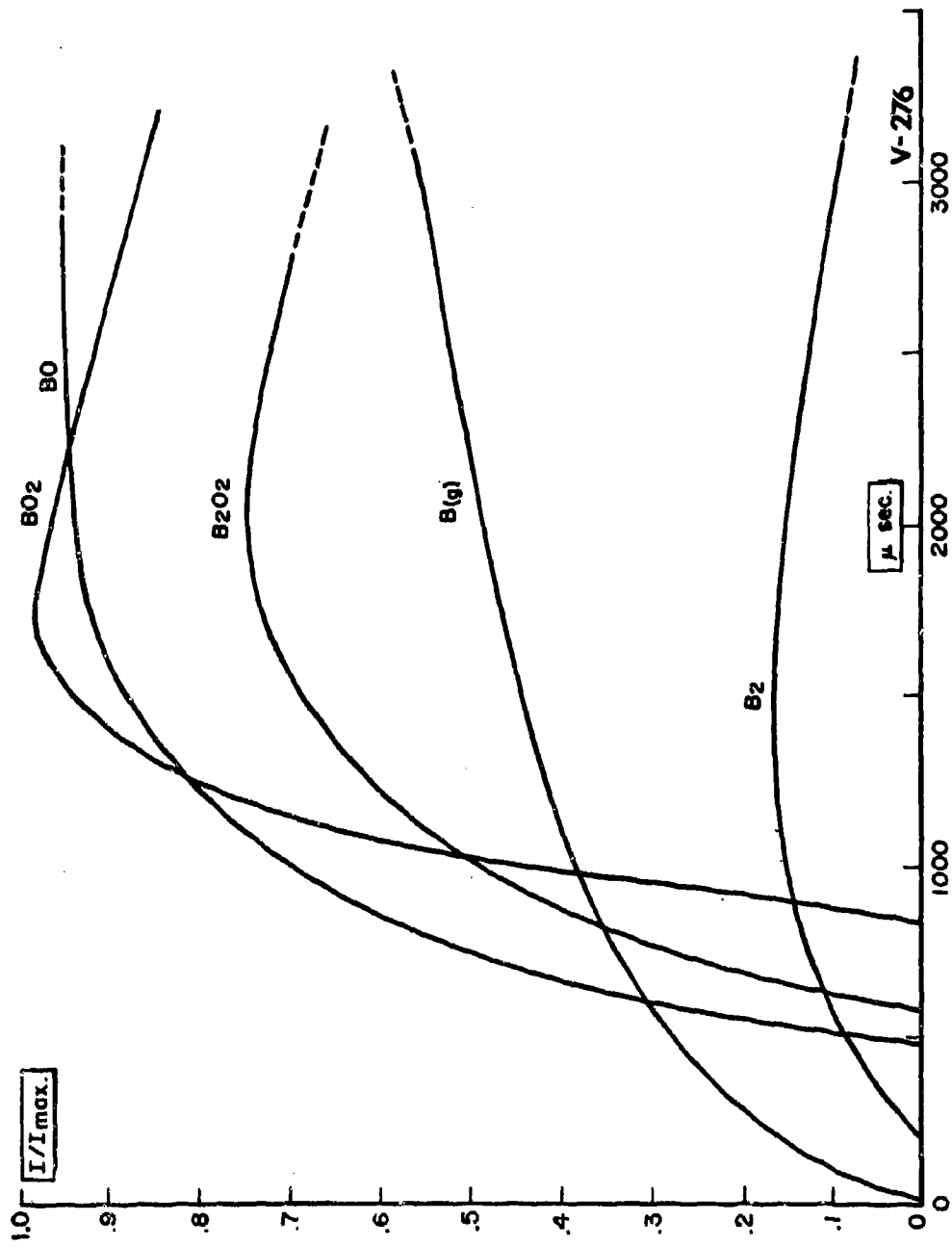
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(U) Fig. 3 - Boron Species Observed During The Flash Pyrolysis of Boron
in 30 mm Oxygen at 2000 Joules

(U)   The BO_2 could be accounted for by the reactions:

$$BO + O_2 = BO_2 + O_2 \tag{15}$$

or $$BO + O \xrightarrow{M} BO_2 \tag{16}$$

The spectrum was identified with the aid of the bands reported by Johns (57). The intensity of the BO_2 lines increases as the oxygen pressure is raised from 20 to 30 mm.

(U)   The species B_2O_2 was identified by the absorption at 4292, 4346, and 4355 Å, respectively. These bands correspond well to those reported by Porter and Dows (58). The intensity of the B_2O_2 lines is greatest early in the reaction, indicating it might be due to

$$B_2 + O_2 \xrightarrow{M} B_2O_2 \tag{17}$$

or $$BO + BO \xrightarrow{M} B_2O_2 \tag{18}$$
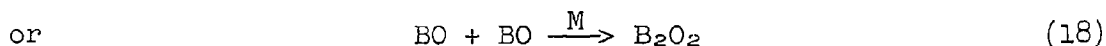
(U)   The species BH was identified through the absorption at 3396 Å, 3682-3745 Å, and especially from the lines 4319, 4331, and 4333 Å of the $'\pi \longleftarrow {}'\Sigma$ transition (59,60). The source of the hydrogen for the BH is most likely to be found in the hydrocarbon "glue" used to adhere the boron to the graphite strips.

(U)   As reported above, this boron-oxygen reaction has been studied only for delay times as long as 3000 μsec. The very complex spectrum of the boron-oxygen system suggested that many of the early combustion products (H_3BO_3, HOBO, BO_2, etc.) were dissociating in the first 1000 μsec, while at the same time the bulk of the elemental boron was just beginning to burn. The proliferation of B-H-O species early in the reaction (0-1000 μsec), as well as the predominance of BO at longer times, suggests that indeed the first products of the combustion dissociate early in the reaction.

(U)   The combustion of elemental boron in oxygen is characterized by numerous absorption lines in the range 2400-4500 Å.

Most of the lines fall in the range 3000-4500 Å. The boron-containing species detected in absorption are α-BO, β-BO, BO_2, B_2O_2, B, B_2 and BH. Weak OH lines are also seen. The absorption spectrum of BO_2 contains the strongest lines of the boron-containing species. The β-BO system is the most extensive.

(U) Since no recorded spectrum for B_2O_3 is known in the UV or visible spectrum, this species was not detected in the gas phase during flash pyrolysis. However, B_2O_3 was detected when the solid residue from the combustion cell was analyzed.

(U) The time-intensity curve for the boron species observed during the flash pyrolytic combustion of boron is shown in Figure 3. The first species seen is B(g); after about 500 μsec, BO is seen to increase rapidly in intensity until 1500 μsec when the increase in intensity seems almost to stop. At about 570 μsec after initiation, the absorption of B_2O_2 is first detected. The intensity of B_2O_2 increases, to about 2000 μsec, where a maximum is reached, after which the intensity decreases. The BO_2 is first detected at 820 μsec after initiation. It reaches peak intensity at about 1400 μsec, after which its intensity decreases.

(U) The intensity of the OH radical was also recorded for the boron-oxygen system. Its total intensity was much less than that observed for the boron species, amounting to only about 30% of that for BO_2 at maximum intensity. The curve for OH as a function of time is shown in Figure 4. It is interesting to note that the curve shows two maxima at about 100 μsec and another between 2000-3000 μsec.

(U) Since it has been assumed the HOBO arises from the reaction between water and B_2O_3 (Equation 1), it was decided to study the combustion of boron in the presence of water in the hope of elucidating the mechanisms which account for HOBO.

(U) The studies on the combustion of boron in the presence of both water and oxygen duplicated as near as possible the above
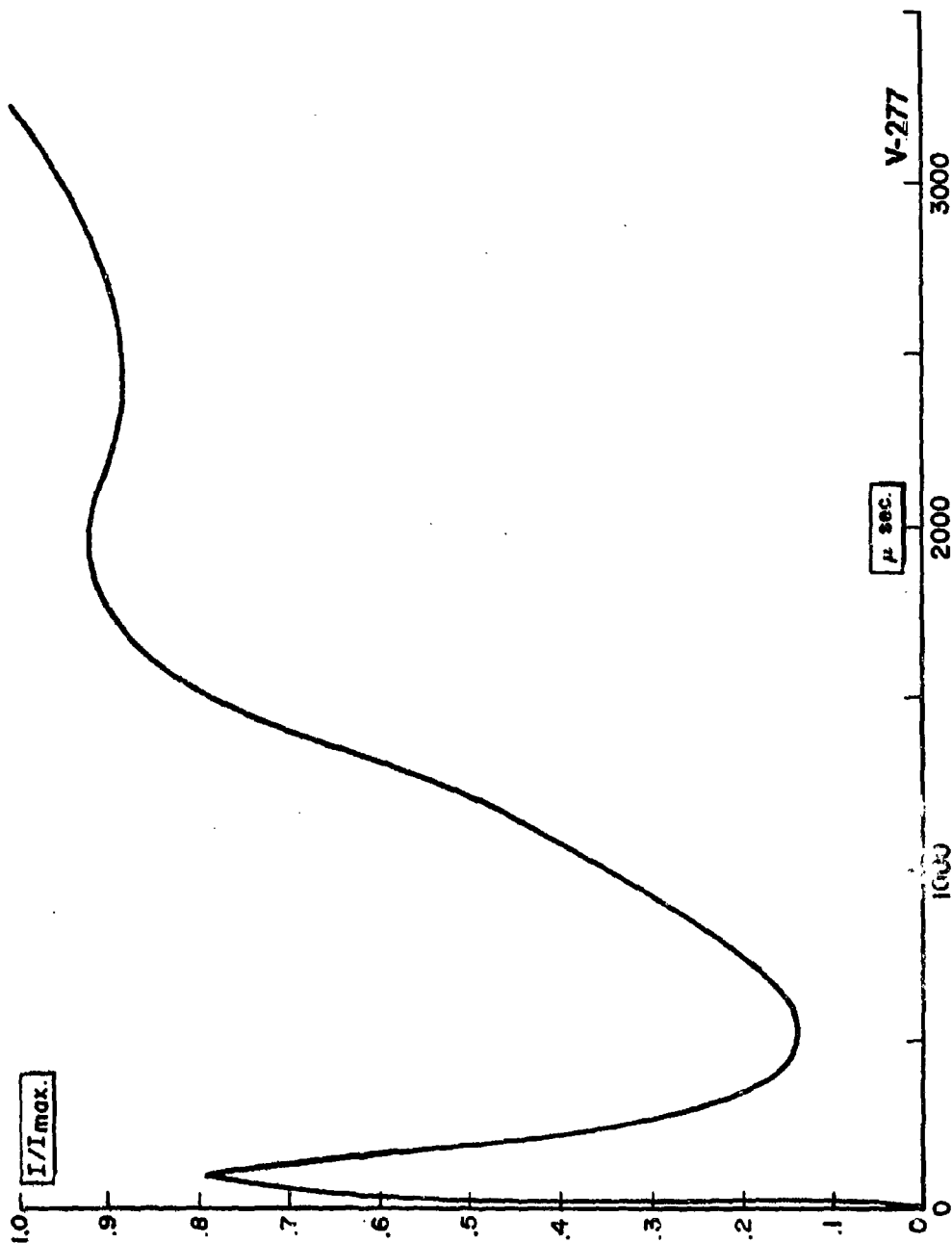
(U) Fig. 4 - Hydroxyl Radicals Observed During the Flash Pyrolysis of Boron in 30 mm Oxygen at 2000 Joules
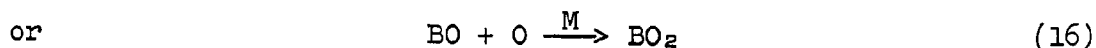
conditions, with the exception that the gas phase contained 20 mm O_2 and 18 mm H_2O.

(U) The species seen in the study were the same species seen for the boron-oxygen system. The main difference in the two studies was the change in intensity of the observed species.

(U) The presence of B and BO can be accounted for by the Steps (19) and (20). (Unless otherwise stated, all species are gaseous).

$$B(s) \xrightarrow[\Delta]{h\nu} B(l,g) + B_2 \tag{19}$$

$$B(s,l,g) + O_2 \rightarrow BO + O \tag{20}$$
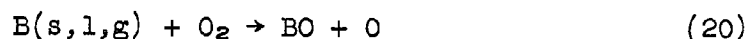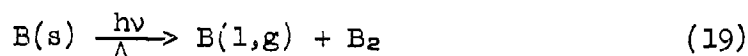
The species BO_2 could be formed by:

$$BO + O_2 \rightarrow BO_2 + O \tag{15}$$

or

$$BO + O \xrightarrow{M} BO_2 \tag{16}$$

with the three-body Reaction (16) much less likely to occur than Reaction (15). Both BO and BO_2 can form if the oxide B_2O_3 dissociates at temperatures above its boiling point, via:

$$B_2O_3(g) \xrightarrow{\Delta} BO_2 + BO \tag{2}$$
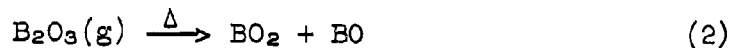
(U) Data previously presented (57) indicate that Reaction (6) indeed does occur. However, the extent of this dissociation has not been ascertained. The intermediate B_2O_2 can occur by:

$$BO_2 + B \rightarrow B_2O_2 \tag{21}$$

or by the three-body collisions:

$$B_2 + O_2 \xrightarrow{M} B_2O_2 \tag{17}$$

and

$$BO + BO \xrightarrow{M} B_2O_2 \tag{18}$$
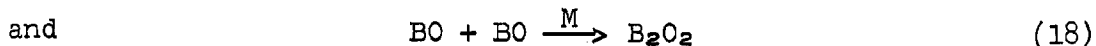
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or even by:

$$B_2O_3 \xrightarrow{h\nu} B_2O_2 + O \tag{10}$$

The situation is made more complex when the possibility of the formation of HOBO via Reaction (1), is considered, or by:

$$1/2 \ B_2O_3(1,g) + 1/2 \ H_2O \rightarrow HOBO(g) \tag{1}$$
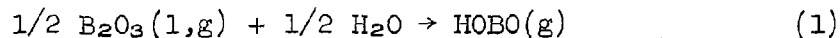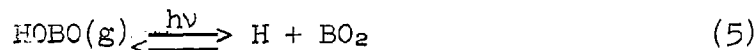
The water arises either from the hydrogen in the boron or from the "glue" used to adhere the boron to the graphite strips (Apiezon N dissolved in benzene).

(U) As reported previously (57), the HOBO (formed by heating H_3BO_3) seems to dissociate at high temperatures to H and BO_2 by:

$$HOBO(g) \underset{\xrightarrow{\hspace{1cm}}}{\overset{h\nu}{\longleftarrow}} H + BO_2 \tag{5}$$

(U) Only BO_2 was observed, since HOBO has no UV or visible spectrum. Reaction (5) is probable in light of Equation (6), where the OH radical would scavenge the hydrogen atom, formed along with the BO_2, to form water. It is believed that by Reaction (5) the elementary process for the dissociation of HOBO is observed.

(U) In the presence of a third body (such as other exhaust products), the left hand side of Reaction (5) would predominate.

(U) The OH time-intensity curve of Figure 4 indicates that OH is formed rapidly up to around 100 μsec, after which it reacts with some other species in the gas phase to such an extent that its intensity is reduced to a minimum at about 500 μsec. The second increase in OH intensity could arise either from dissociation of an OH containing species, or from the lack of species to react with OH. No definite conclusions could be drawn from the graph alone.

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(U)   In order to study the effect of water on the boron-oxygen system, a study was carried out at 20 mm O_2 pressure and 18 mm H_2O (just enough water to saturate our cell at 25°C and still not have condensation).   Figure 5 shows the time-intensity curve for the OH radical derived from these experiments.   The correction for OH due to the flash photolysis and pyrolysis of water alone has been applied to this curve.   The resulting curve in Figure 5 shows only the OH due to the reaction between the boron and the oxygen/water mixture, uncorrected for hydrogen in the boron or in the "glue."   This total intensity of OH in Figure 5 is about one order of magnitude brighter than that in Figure 4. The OH intensity in Figure 5 is greater than that for any boron species detected in this study.   The intensity of BO and BO_2 are each about 35% as great as that of OH.

(U)   The greatest dissimilarity between Figure 4 and 5 is that the second OH peak in Figure 5 occurs at ~1400 μsec, while that in Figure 4 occurs at times greater than 2000 μsec.   At 2500 μsec the OH of Figure 5 is quite weak, indicating a low concentration of OH in the gas phase.

(U)   The total effect of the water on the OH concentration seems to be shown by the time compression of the second maximum of OH.   It could be that the water reacts very fast with the BO_2 to produce HBO_2 and OH, resulting in the second maximum of OH occurring at ~1500 μsec, whereas in the low water case of Figure 4 the increase in OH is much slower.   The decrease in OH at times in excess of 1500 μsec could result from the reaction of OH with BO to form HOBO via:

$$OH + BO \rightarrow HOBO \tag{9}$$

or from the combination of OH radicals to form water:

$$OH + OH \rightarrow H_2O + O \tag{8}$$
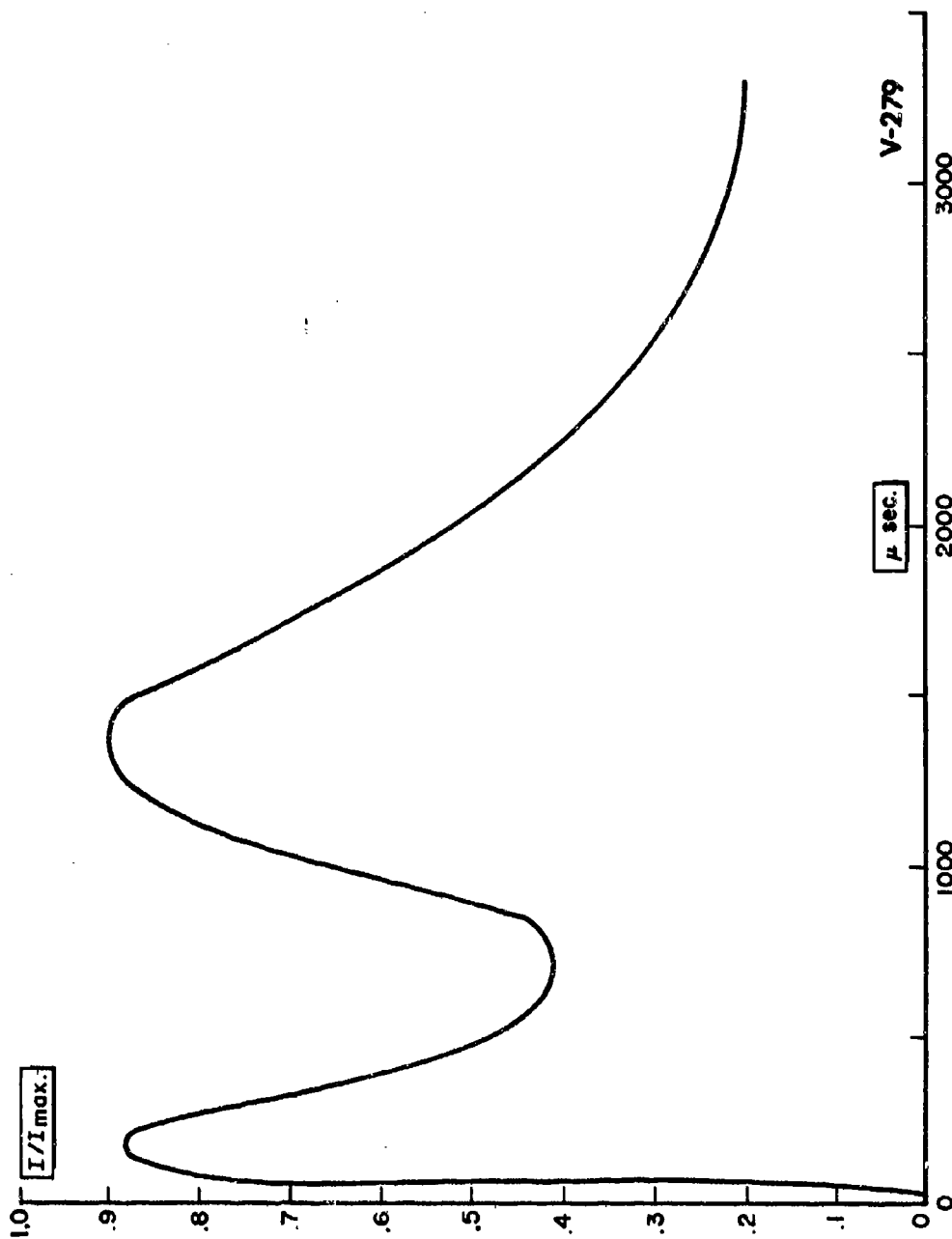
(U) Fig. 5 - OH Radicals Observed During the Flash Pyrolysis of Boron
in 20 mm Oxygen and 18 mm Water at 2000 Joules
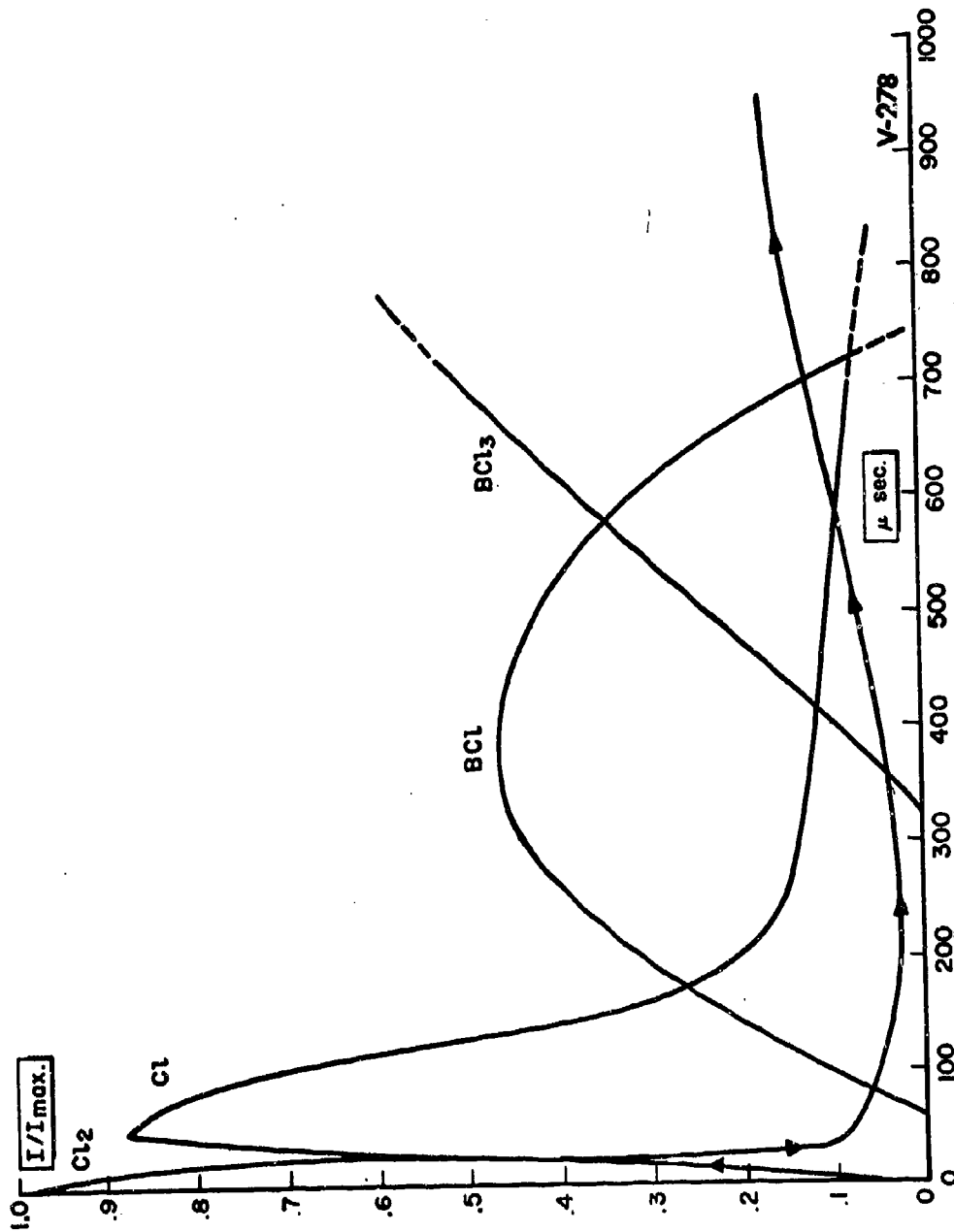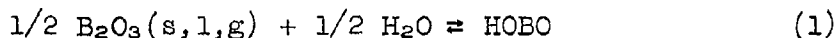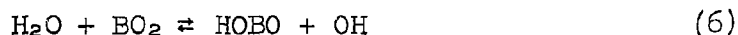
(U) Fig. 6 - Species Observed During the Flash Pyrolysis of Boron in 35 mm Chlorine at 2000 Joules

(U) A further possibility is the reaction between B(g) and ˙OH to form the yet undetected HBO by:

$$B + OH \xrightarrow{M} HBO \tag{22}$$

(U) In conclusion, it is shown that HOBO can be formed in four ways from the oxidation products of boron combustion in the presence of a source of hydrogen:

$$H_2O + BO_2 \rightleftharpoons HOBO + OH \tag{6}$$

$$1/2\ B_2O_3(s,l,g) + 1/2\ H_2O \rightleftharpoons HOBO \tag{1}$$

$$H + BO_2 \rightleftharpoons HOBO \tag{7}$$

$$OH + BO \underset{M}{\rightleftarrows} HOBO \tag{23}$$

(U) It must also be recognized that, as long as water or any source of water is present in a boron-oxygen system, the formation of HOBO cannot be prevented. The high temperatures encountered in boron-combustion also favor HOBO as the combustion product in the above four equations. The reverse of Equation (1) probably takes place outside of the rocket engine to give the desired product of combustion. Equations (6), (7), and (23) are the most probable causes of the formation of HOBO, particularly (6) and (7).

5. Combustion of Boron in Chlorine and HCl (U)

(U) Combustion studies of boron in chlorine and HCl were being carried out concurrently with the studies involving oxygen and water. The data from these chlorine studies produced no unexpected results.

(U) The combustion studies employing chlorine as the oxidizer were carried out at a pressure or 35 mm. Flash energy was held constant at 2000 joules. Delay time ranged from 30 to 10,000 μsec.

(U) The products observed in the reaction between boron and chlorine are Cl, Cl_2, BCl and BCl_3. The Cl_2 and Cl spectra were recognizable from our earlier work on NH_4ClO_4 and are described

there (53). The BCl spectrum was correlated to the $^1\pi \leftarrow {}^1\Sigma$
transition in the range 2650-2880 Å described by Mlescher (62)
and Herzberg and Hushley (63). The BCl_3 was correlated with a
diffuse reaction with that observed when pure BCl_3 was analyzed.
Figure 6 shows the time-intensity curve for the species Cl_2, Cl,
BCl and BCl_3 observed during the reaction. The observed absorp-
tions due to B and B_2 were not sufficiently strong to warrant
being plotted.

(U) The rapid disappearance of Cl_2 and appearance of Cl in
the combustion of boron could be explained by:

$$Cl_2 \xrightarrow{h\nu} 2 \ Cl \tag{24}$$

Since Cl_2 is almost gone when BCl is first formed, the following
steps are quite probable for the initial formation of BCl:

$$B(s) \xrightarrow[\Delta]{h\nu} B_{(1)} + B_{(g)} \tag{25}$$

and

$$B_{(s,1,g)} + Cl \xrightarrow{M} BCl \tag{26}$$
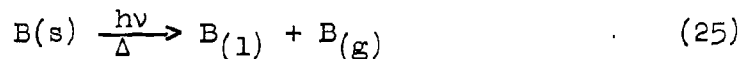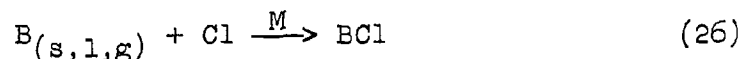
(U) The very fast recombination of Cl to Cl_2 should cause
Cl_2 to reappear at a rate proportional to the disappearance of Cl.
Since this is not seen, it is believed that BCl reacts with the
reformed Cl_2 to generate Cl and BCl_2 and BCl_3 by:

$$BCl + Cl_2 \rightarrow BCl_2 + Cl \tag{27}$$

$$BCl_2 + Cl_2 \rightarrow BCl_3 + Cl \tag{28}$$
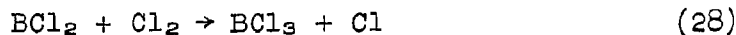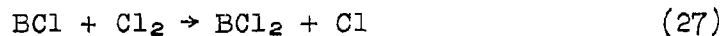
with the final step:

$$Cl + Cl \xrightarrow{M} Cl_2 \tag{29}$$

accounting for the increase in Cl_2 as time increases.

(U) Although BCl_2 was not observed spectroscopically, its
formation would account for the induction time for the formation
of BCl_3 as well as for the low intensity of Cl_2 and long persistence

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of Cl. If the reaction:

$$BCl + Cl_2 \rightarrow BCl_3 \tag{30}$$

were to proceed instead by the stepwise route, the disappearance
of Cl would be immediate and would terminate when BCl reached a
maximum.

(U) The reaction between boron and chlorine is clean and not
unexpected, yielding gaseous BCl_3 as the final product.

(U) When B was flashed in the presence of HCl, the species
B, B_2, BCl, BCl_3 and BH were detected. The reaction was not
systematically studied, as it seemed similar to that of boron and
chlorine with the exception of small amounts of BH present.

C. EXPERIMENTAL RESULTS FOR MODIFIED STUDIES (U)

1. Introduction (U)

(C) The work carried out on the combination of boron in the
presence of water and oxygen led to the conclusion that one way to
minimize the formation of HOBO was to decrease the amount of water
found in the combustion system. There are two sources of water
in the combustion system, namely, the hydrogen from the oxidizer
AP and the hydrogen from the binder PBAN.

(C) Work carried out at Thiokol Chemical Corporation has shown
that, at least to a first approximation, the flame temperature of
a boron-AP formulation is strongly dependent upon the boron/AP
ratio (64) and less strongly on the binder composition. Keeping
in mind that a flame temperature of at least 2200°K is necessary
to insure combustion of the boron, it seemed prudent to try to
modify the binder composition in such a way as to decrease the
amount of water formed during binder combustion.

(C) It was decided, on thermodynamic grounds, to study the
combustion of boron in oxygen and a fluorine-containing compound.
The fluorine should react with the hydrogen (in this case from the

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boron and the "glue") to form HF, which, being thermodynamically
more stable than water, would preclude its formation as well as
that of OH.

(U) A reduction in the concentration of these two species
would reduce the formation of HOBO, and thereby increase the
combustion efficiency of the boron/AP reaction. However, any
combustion system supplying elemental boron to the air supported
combustion process must have a flame temperature in excess of
$\sim 2300°K$. Therefore, it is imperative that the flame temperature
for any modified system supporting air augmented combustion be
determined. This last statement included the flame temperature
for the boron/oxygen and boron/oxygen/water system previously
studied.

(C) The study of the effect of fluorine atoms on the combus-
tion of boron in oxygen was studied in several systems by flash
pyrolysis and kinetic spectroscopy.

2. Systems Studied (U)

(U) The compositions of the systems studied were:

    (i) ~ 45 mg boron/30 mm O_2

   (ii) ~ 45 mg boron/20 mm O_2/18 mm H_2O

  (iii) ~ 45 mg boron/10 mm O_2/10 mm F_2

   (iv) ~ 45 mg boron/15 mm O_2/30 mm F_2

   (v) ~ 45 mg boron/25 mm O_2/10 mm CH_2F_2

 (vi) ~ 45 mg boron/25 mm O_2/10 mm CHF_3

(U) All combustion studies were initiated by a 2000 joule
flash. Initial analyses were made at a delay time of 100 μsec
and analyzed for as long as 2.5 milliseconds after initiation.
The data were recorded by photographing the absorption spectrum
of each reaction in the spectral range 2000-6000 Å, using Kodak
103-0 and 103-F spectroscopic plates.

(U)   The first two systems, (i) (61) and (ii) (65), were studied to give base line values for the effect of water on the combustion of boron in oxygen.

(C)   Systems (iii) and (iv) were studied to show the effect of fluorine atoms on the combustion of boron in oxygen, and, in particular, to determine the extent of reduction of the OH radical concentrat ι.   Hydrogen was always present in our system as a result of the 0.8% hydrogen in the boron itself plus that due to the Apiezon stopcock grease needed to bond the boron to the graphite plates used in our pyrolytic technique.   Systems (v) and (vi) were studied to determine the effect of introducing fluorine atoms at two different H/F ratios in the prototype monomers into the solid propellant system.   Primary consideration was given to the distribution of combustion products and to the flame temperature for each of the above systems, since the flame temperature of the solid propellant combustion process greatly influences the amount of boron supplied to the incoming air, as well as the physical state of the boron [M.P. = 2450°C (JANAF)].

(C)   The proposed stoichiometry of the reaction between oxygen and CH_2F_2 is:

$$CH_2F_2 + O_2 \rightarrow CO_2 + 2 \, HF \tag{31}$$
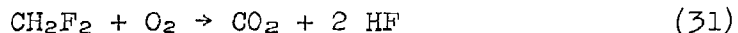
The reaction between O_2 and CHF_3 is proposed to be:

$$CHF_3 + O_2 \rightarrow CO_2 + HF + F_2 \tag{32}$$
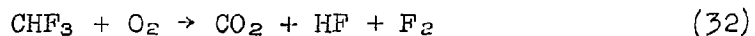
(C)   System (v) was studied to determine the effect of a prototype binder, CH_2F_2, which was stoichiometrically balanced to form HF by itself, on the reaction between boron and oxygen. System (vi) is an example of a fluorine-rich system (one which has an F/H ratio >1).   The excess fluorine is available to react with the hydrogen from the oxidizer as well as from the plasticizer.

(U)   Thermochemical calculations show that if BF_3 and H_2O were found, instead of B_2O_3 and HF at 2500°K, the reaction:

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$$2 BF_3(g) + 3 H_2O(g) \rightarrow B_2O_3(g) + 6 HF(g) \qquad (33)$$
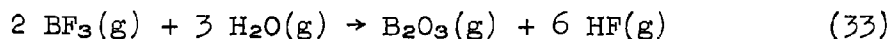
would have a free energy of -33.3 kcal. This negative value for the free energy means the right side of (33) would be favored. The overall effect of the fluorine would be to minimize the formation of H_2O and, hopefully, that of HOBO.

(U)   Plate intensities were read with a Jarrell-Ash ratio recording microphotometer. A mercury arc was used to calibrate the spectrograph and the spectroscopic plates.

(U)   The flame temperature was inferred from the rotational distribution of the (0,0) band of the $A^2\Sigma^+ - X^2\pi$ transition of the OH radical (54). The technique is that of Dieke and Crosswhite (66) and involves the distribution of intensity among lines of the rotational fine structures of a band spectrum. A discussion of the merits of the technique can be found in NBS Circular 523 (67).

(U)   The experimental observations are discussed below. Analysis and interpretation of these observations are presented later in the Discussion Section.

3.   Results   (U)

a.   Combustion of Boron in Oxygen and Water   (U)

(U)   The experimental results and the discussion for the combustion of boron in oxygen and in a mixture of oxygen and water has been previously described (B-2). However, the calculation of the flame temperatures for these systems had not been carried out at that time.

(U)   Figure 3 shows the correlative intensity of boron species observed during the combustion of boron in 30 mm of O_2. The relative concentration of the OH radical observed during the same reaction is seen in Figure 4. The second and more prominent OH maximum seems to correspond in time to the rate of formation of BO_2. The OH intensity is about 30% of that for BO_2 at maximum intensity. The hydrogen for this weak OH spectrum probably came

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From the stopcock grease "glue" used to bond the boron to the graphite strip, as well as from the 0.8% hydrogen in the boron metal itself.

(U)   The flame temperature of the boron-oxygen system discussed above is shown in Figure 7.   The lines through the experimental points are the uncertainty in the temperature measurement. The maximum in the flame temperature correlates quite well with the first significant appearance of BO_2 at about 1000 μsec after initiation.   The steady state flame temperature of about 2350-2400°K is reached at about 2000 μsec after initiation.   This corresponds in time to the steady state concentration of BO being attained (compare Figures 3 and 7).

(U)   There seems to be no direct correlation between the flame temperature and the OH concentration for the boron-oxygen system other than both approach some equilibrium value at about 2000 μsec (Figures 4 and 7).

(U)   The time-intensity curve for the OH radical observed during the combustion of boron in the presence of oxygen and water is shown in Figure 6.   The total intensity of the OH in Figure 6 is about 10 times that in Figure 4.   The total intensity of BO and BO_2 are reduced to a value below that seen in Figure 3.

(U)   The flame temperature for the boron-oxygen-water system is seen in Figure 8.   The lack of coincidence of the flame temperature with the OH radical concentration indicates that the process or processes which give rise to the initial large amount of OH are not necessarily those which govern the combustion temperature of boron in an oxygen/water mixture.   The profile of the flame temperature which occurs at times greater than 1000 μsec seems to parallel the concentration change of the OH radical during the same time period.   This could indicate that the process which governs the rate of formation and disappearance of the OH radical could also control the temperature of the whole combustion process.

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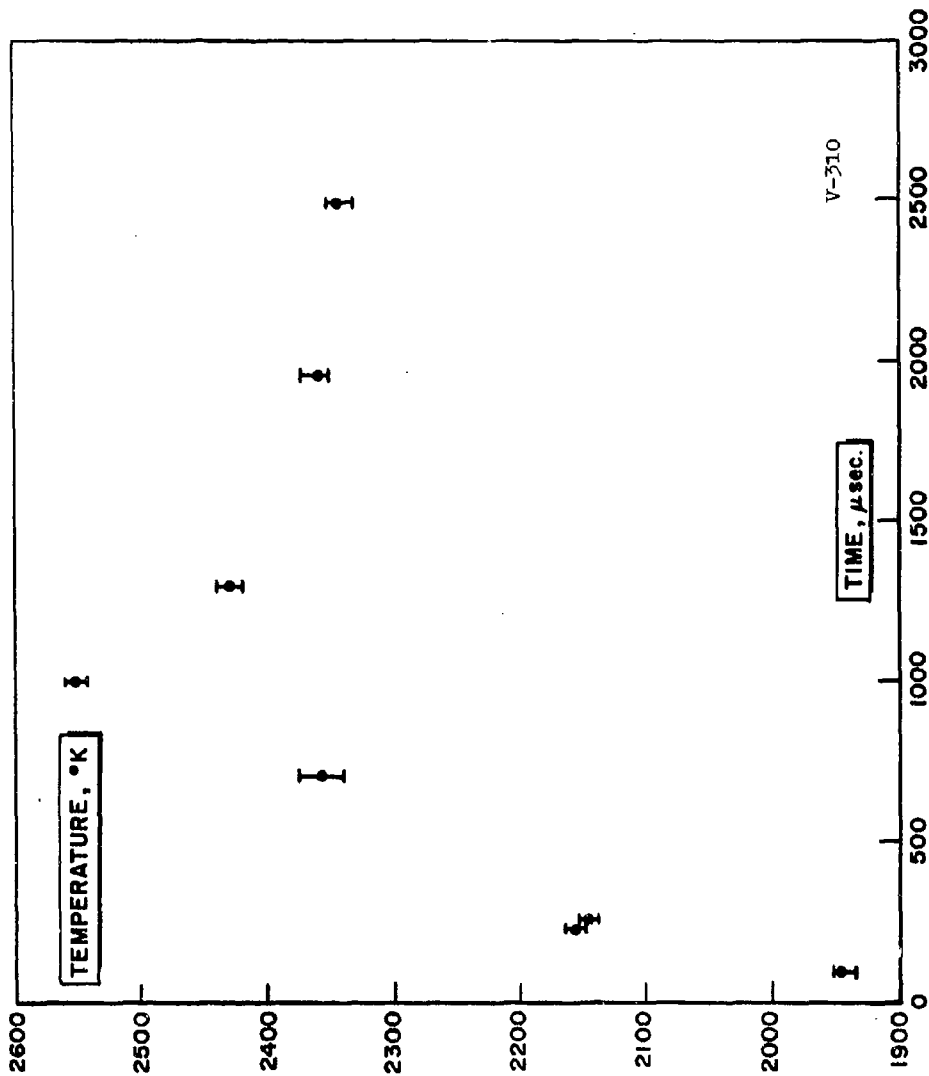
(U)   Fig. 7 - Flame Temperature Observed During the Combustion
of Elemental Boron in Oxygen in System (1)

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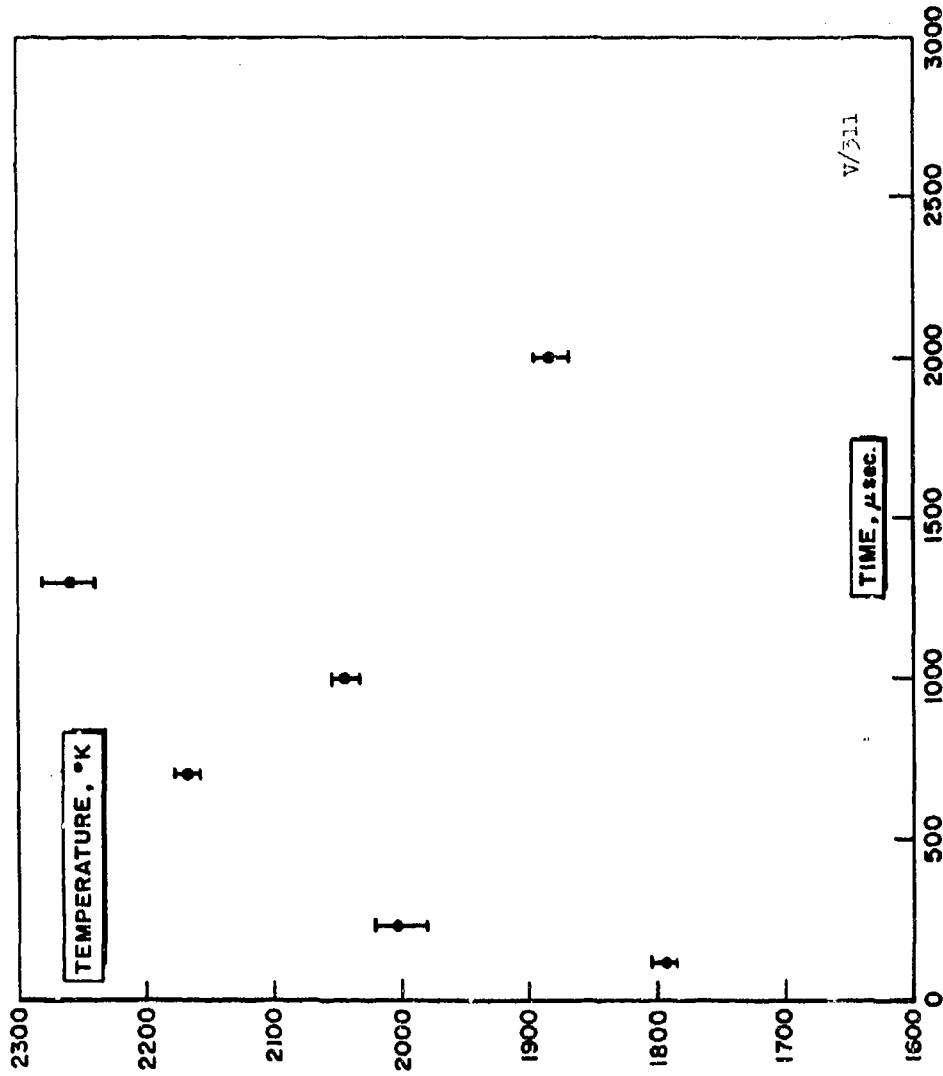
(U) Fig. 8 - Flame Temperature Observed During the Combustion of Elemental Boron in Oxygen and Water in System (11)

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(U)   It is important to note that the addition of water to a boron-oxygen system reduces the maximum flame temperature by about 300°K.   This effect is in the direction indicated by the reaction:

$$H_2O(g) + BO_2(g) \rightarrow OH + HOBO \quad \Delta H_{R\ 2500} = +7.5 \text{ kcal} \qquad (6)$$
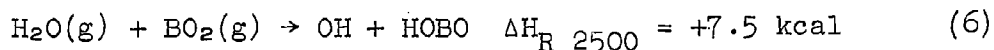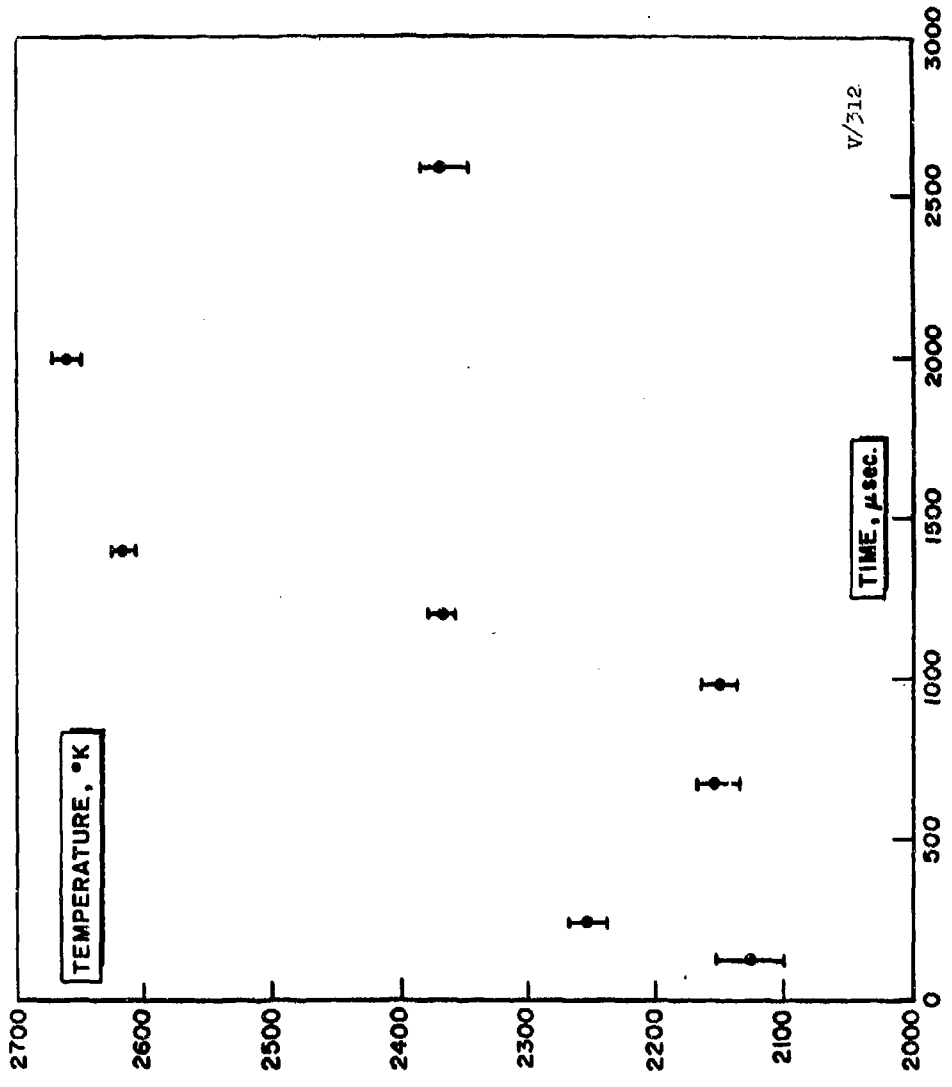
b.   Combustion of Boron in Fluorine and Oxygen   (U)

(U)   Detailed analysis of these combustion systems has not been completed; however, certain gross features were observed.   The products at 100 μsec in both Systems (iii) and (iv) were primarily BF and HF.   The BF/HF ratio was greater in the fluorine-rich System (iv) than it was in System (iii).

(U)   The OH intensity was reduced considerably by the addition of fluorine, showing the preferential formation of HF over OH. The OH intensity is about 15-20% of that of a boron-oxygen system.

(U)   The maximum flame temperature for System (iii), which contained equal amounts of fluorine and oxygen, was 2663 ± 37°K, as shown in Figure 9.   The flame temperature for a boron/oxygen/flame which has twice as much fluorine as oxygen is seen in Figure 10. In this case, maximum flame temperature is observed at 100 μsec (~2047°K).   A minimum is reached at 500 μsec (~1730°K) and a second maximum at 2000 μsec (~2030°K).   This is considerably below the 2663°K attained in System (iii).   The flame temperature seems to decrease as the F/O ratio is increased.   The OH intensity is about 10% of that observed in a boron/oxygen system.

(U)   The overall effect of the addition of fluorine to a boron-oxygen combustion system is to decrease the OH concentration with the subsequent decrease in the amount of water formed.   The flame temperature also decreases as the fluorine concentration is increased.

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(U) Fig. 9 - Flame Temperature Observed During the Combustion of Elemental Boron in an Equimolar Mixture of Oxygen and Fluorine in System (111)

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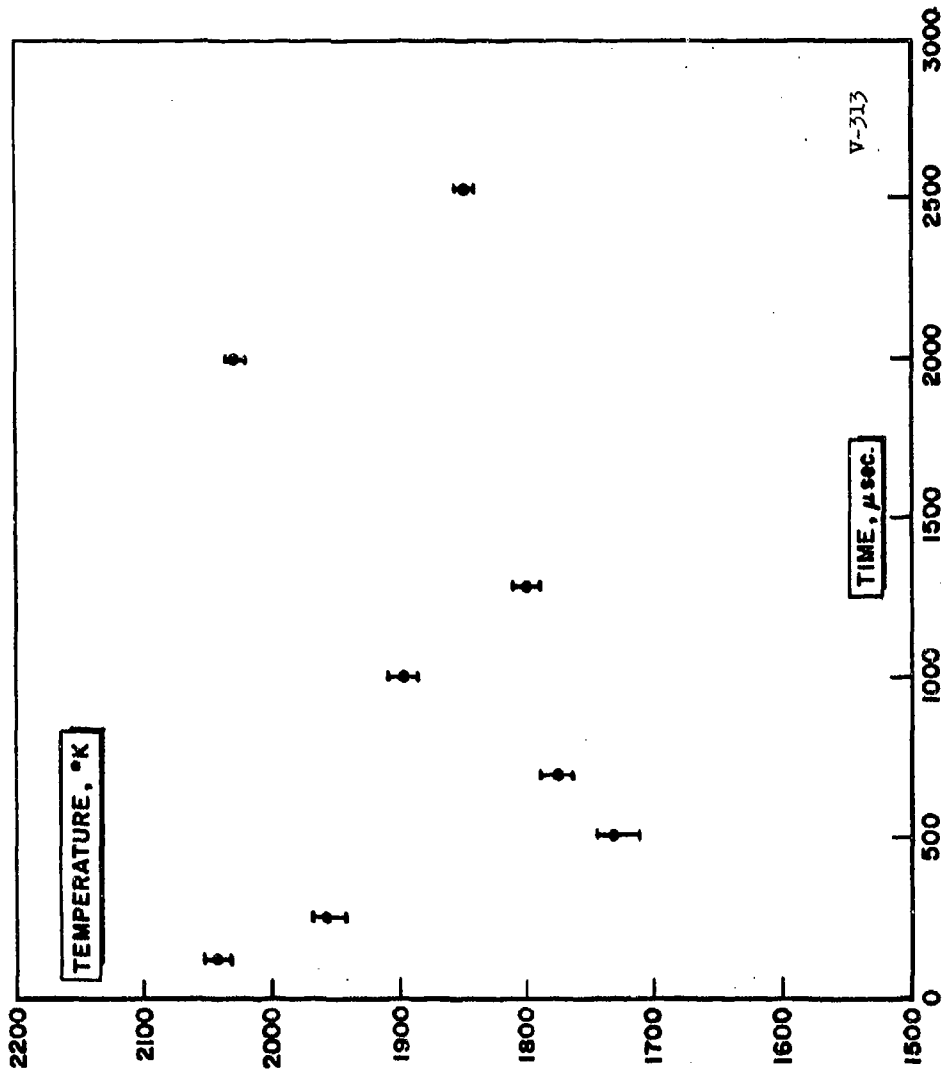
(U) Fig. 10 - Flame Temperature Observed During the Combustion of Elemental Boron in the Presence of 15 mm Oxygen and 30 mm Fluorine in System (iv)

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c. Combustion of Boron in Oxygen/Fluorinated Binder Prototype
Systems (C)

(C) The combustion of boron in 25 mm O_2 and 10 mm CH_2F_2 decreases the OH intensity to almost 45% of that observed when no additive was present. The flame temperatures for this system are seen in Figure 11. Two temperature maxima are seen; the first at 500 μsec is about 2640°K, with the second at 2000 μsec about 2515°K. These are about equal to the temperatures for a straight boron/oxygen system. The two maxima could be indication of a two-process flame reaction. No attempt has been made to evaluate this phenomenon.

(C) The addition of CH_2F_2, which has the same H/F ratio as a polyvinyl fluoride binder $\text{---}(CH_2\text{-}CF_2\text{---})_x$, has very little effect on the flame temperature of the overall combustion. It seems to minimize the OH concentration, yet does not seem to prolong the combustion process.

(C) The combustion of boron in an atmosphere of 25 mm O_2 and 10 mm CHF_3 was studied to determine whether the excess fluorine of the prototype binder had a detrimental effect on the flame temperature.

(U) As seen from Figure 12, the maximum flame temperature was only ~2410°K. As in all other cases, two maxima are seen, with the first maximum occurring at ~200 μsec. The temperature minimum at ~500 μsec is not very pronounced and leads smoothly to the second maximum at about 1000 μsec. The second maximum occurs earlier than for any system studied, excepting the fluorine-rich System (iv), where the second maximum also occurs at 1000 μsec.

(U) The total OH intensity is about 20% of that for the boron-oxygen system. This result and the increased BO and BO_2 intensities suggest a scavenger effect of the fluorine atom toward the hydrogen.

(U) All studies involving the addition of fluorine-containing molecules indicated a decrease in the amount of OH formed. The

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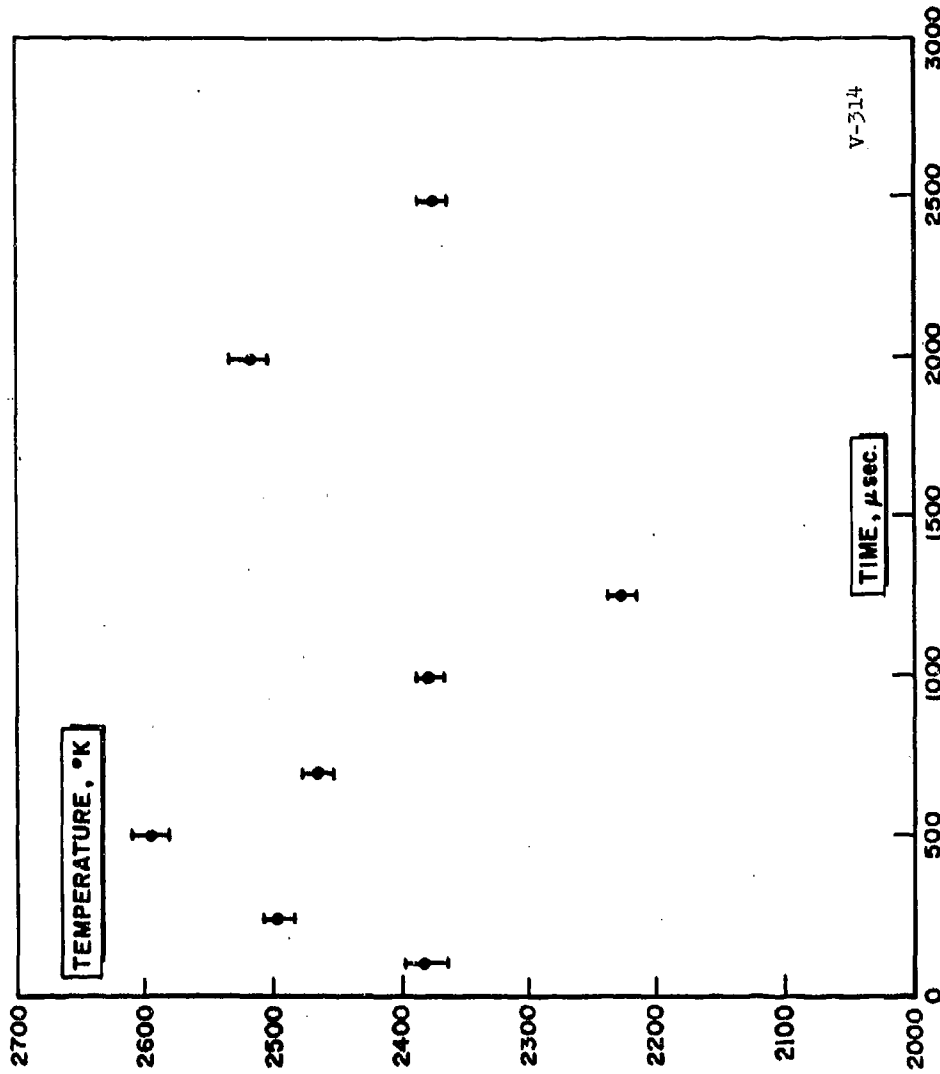
(U) Fig. 11 – Flame Temperature Observed During the Combustion of Elemental Boron
in 25 mm of Oxygen and 10 mm of Methylene Fluoride in System (v)
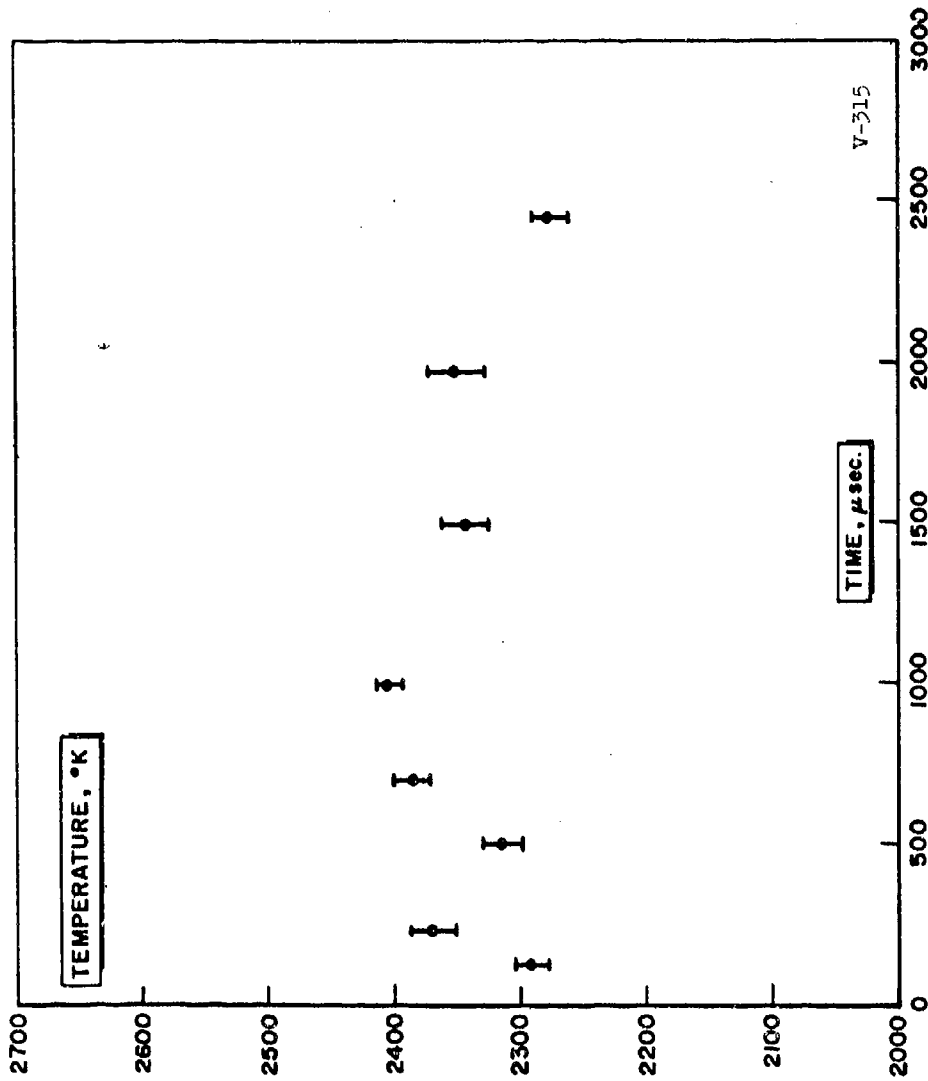
(U) Fig. 12 - Flame Temperature Observed During the Combustion of Elemental Boron in 25 mm of Oxygen and 10 mm of Fluoroform in System (vi)

initial boron products were BF and BF_3, whereas those in the last 1000 μsec were BO, BO_2, and B_2O_2, almost to the total exclusion of BF as BF_3. The final fluorine product was HF. White B_2O_3 was the ultimate condensed phase low temperature product. The major carbon species was CO, not CO_2 as postulated in Reactions (31) and (32).

d. Discussion of Results (U)

(1) Combustion of Boron in Oxygen and Water (U)

(U) The combustion of boron in oxygen has already been discussed in detail (31). The addition of water causes a decrease in the intensity of BO_2 and increases the intensity of OH, as expected if Equation (6):

$$H_2O(g) + BO_2(g) \rightarrow OH + HOBO \quad \Delta H_{R\ 2500} = +7.5 \text{ kcal} \qquad (6)$$
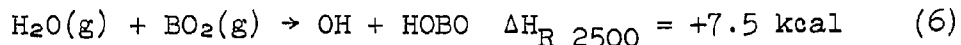
is obeyed. The endothermic reaction could cause a lower flame temperature.

(U) The overall effect of the addition of water primarily lowers the ignition temperature with the subsequent lowering of the flame temperature. These two effects, along with the recognized formation of HOBO, can account for the lowered combustion efficiency of the boron-AP-PBAN system. We believe the cause of this reduced efficiency is due to the large amount of H_2O found in the system. The water reacting with the BO_2 promotes the formation of HOBO at the expense of B_2O_3, the desired product.

(U) The above conclusion, if valid, immediately suggests its own remedy: reduce the formation of water in a B-AP system and the formation of HOBO will be reduced by minimizing the following reactions:

$$H_2O(g) + BO_2(g) \rightarrow OH + HOBO \qquad (6)$$

$$1/2 \ H_2O(g) + 1/2 \ B_2O_3(l,g) \rightarrow HOBO \qquad (1)$$

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and $$BO + OH \xrightarrow{M} HOBO \qquad (9)$$
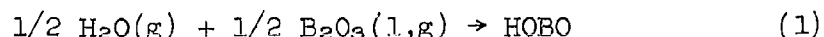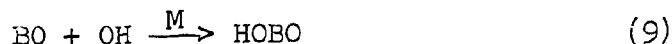
The studies on the combustion of boron in oxygen and in fluorine-containing ingredients were initiated to prove the validity of this conclusion.

(2) Combustion of Boron in Oxygen and Fluorine (U)

(U) The decrease in OH intensity to about 10-20% of that for the pure boron-oxygen system, coupled to the increased intensity of BO and BO_2, and the appearance of HF, indicates that the addition of fluorine does decrease the amount of water and OH in the system. The decreased H_2O and OH seem to be due to the preferential formation of HF over these two species.

(U) The anomalous flame temperature of 2663°K for System (iii) is still a mystery (Figure 9). This flame temperature is about 100°K higher than that for a boron-oxygen flame and is almost 1000°K higher than that reported by Texaco for a pure boron-fluorine flame having $\Delta E_a = 0$ (68). The two temperature maxima seen in Figure 8 could be due to two different and separate processes. The second maximum is in the range of that for a boron-oxygen flame. It also has almost the same induction time as a boron-oxygen flame, as can be seen by comparing the rise of reaction products in Figures 3, 4, 7 and 9. The increase in BO and BO_2 concentration of Figure 3 correlates fairly well with the rise of the OH concentration of Figure 4. The shorter induction time of the maximum flame temperature of Figure 5 can also be correlated to Figures 3 and 4. The slightly longer induction time of Figure 8 can be explained as being due to the diluent effect of the HF.

(U) According to the work reported by Texaco (68), a lower flame temperature can be expected from a fluorine-rich system. This lowered flame temperature is exactly that seen for System (iv) in Figure 10. The product BF was obs. 'd to be present at times later than that observed in System (iii). This increased amount of BF could account for the lowered flame temperature, as some of the boron is not available to react with the oxygen at times less than 2000 μsec.

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(U)   In summary, the gross overall effects of the addition of fluorine to a boron-oxygen combustion system are:

(a)   A decrease in the amount of OH and H_2O found.

(b)   The final hydrogen-containing product is HF.

(c)   The BO and BO_2 are seen in increased intensities.

(d)   The flame temperature is decreased as the con-
centration of fluorine in the system is increased.

(U)   From a spectroscopic point of observation, the addition of fluorine itself seems to alter the intensity of OH, BO, and BO_2 in a manner consistent with a reduction of the OH and an increase of the BO and BO_2. The flame temperature of an equivalent mixture of oxygen and fluorine is about the same as that for a boron-oxygen flame. A fluorine-rich system reduces the flame temperature.

e.   Combustion of Boron in Oxygen/Fluorinated Binder System   (C)

(C)   The combustion of boron in 25 mm O_2 and 10 mm CH_2F_2 resulted in a substantial decrease in the OH intensity. The flame temperature out to 1100 μsec is higher than that for an equivalent mixture of O_2 and F_2 (compare Figures 9 and 11). This could be due to two causes: first, the prototype monomer CH_2F_2 has within itself the equivalent to form 2 HF in an exothermic way; and secondly, the heat of combustion of the carbon to CO generates a higher temperature. These two reactions probably take place immediately (~100 μsec) after the flash. The temperature minimum at 1250 μsec could be due to the above two reactions being finalized while the reaction of boron and oxygen is just beginning. If some CO_2 were formed along with the CO, the flame temperature would be increased above that normally expected. The formation of CO_2 would also result in a depletion of the oxygen available for combustion, with boron giving a lower flame temperature for this reaction (compare second temperature maximum in Figure 11 with the flame temperature maximum in Figure 7).

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(C)   The flame temperature range for the combustion of boron
in a mixture of O_2 and CH_2F_2 compares favorably with that for a
pure boron-oxygen flame.   The addition of CH_2F_2 does seem to de-
crease the OH and H_2O formed while still maintaining a high flame
temperature.   The cause for this effect should be studied further,
as it is unexpected due to the stoichiometry of CH_2F_2.

(C)   The temperature of boron in 25 mm O_2 and 10 mm CHF_3, while
giving a lower flame temperature than does CH_2F_2, seems to yield
a smoother reaction as evidenced by the lesser variation in flame
temperature.   The greater intensity of BF at times approaching
1000 μsec tends to indicate that some of the fluorine originally
present in the CHF_3 would be available to scavenge the hydrogen
from the NH_4ClO_4 and form additional HF directly or by a reaction
similar to Reaction (33).

$$2 \; BF_3(g) + 3 \; H_2O(g) \rightarrow B_2O_3(g) + 6 \; HF(g) \qquad (33)$$
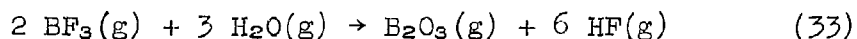
(C)   The flame temperature of the $B/CHF_3/O_2$ system is inter-
mediate between that for $B/CH_2F_2/O_2$ and $2 \; F_2/O_2/B$.   Again, the
indication is that the more fluoride that is added to the system,
the lower is the flame temperature.

(C)   We believe that we have demonstrated, from a combustion
point of view at least, that certain prototype fluorinated monomers
are helpful in reducing the amount of OH and H_2O present during
the combustion of boron in a system containing oxygen and hydrogen.
Furthermore, we believe that a binder which contains just enough
fluorine to give HF stoichiometrically when all the hydrogen in
the system is reacted will yield a flame temperature comparable
to that of pure boron-oxygen flame.

4.   Recommendations   (U)

(C)   We recommend that additional work be performed to pursue
more intensively the use of fluorinated binders for air augmented
boron-containing solid rocket propellants.   The work reported above
shows that it may be possible to minimize the formation of HOBO by

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reducing the OH and H_2O in the combustion system by the addition
of certain fluorinated binders.

D.   EXPERIMENTAL STUDIES ON BORON/AP SYSTEMS   (U)

1.   Introduction   (U)

(U)   In order to more fully exploit the recommendation made in
the last section, it is imperative to know if the major source of
water and OH is indeed the PBAN binder, as postulated, or whether
the AP itself is a major source of OH and water.

(U)   Previous studies carried out at Dow (53) show that OH is
indeed a product of the high temperature decomposition of AP.   The
question, however, remains: In a boron-rich system, is the OH
from the AP sufficiently reactive to interact with the boron and
be destroyed, or is it stable enough that it can react with
oxygenated species from the boron combustion to produce HOBO?

(U)   A reaction system containing boron and AP was subjected
to flash pyrolysis in order to determine the mode of interaction
of the two ingredients at combustion temperatures.

2.   Experimental Results   (U)

(U)   The boron used in this study was "Avco 400."   The AP was
from the same batch as that used in our study on AP decomposition (6).
Flash energies varied from 1600 to 2000 joules.   Spectroscope
delay times varied from 12 to 3800 μsec.   The sample composition
was 75% boron and 25% AP by weight.   Apiezon N stopcock grease
was needed to b o n d the boron particles to the graphite surface.
Thus, the system contained a source of hydrogen other than that
found in the boron and AP.

(U)   The spectra are particularly rich in lines in the region
3400-3800 Å.   The OH intensity, at all delays, is weak.   A strong
and persistent absorption spectra of BH is observed.   A weak
absorption spectra of BCl is seen early in the reaction.   Lines due
to the α system of BO are noted early and increase in intensity as

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the reaction proceeds. A few lines of CH and CO are also seen. They are probably due to the combustion of the stopcock grease. A few lines of BO_2 and B_2O_2 are also seen. The waxing and waning of the observed lines indicate that the AP is dissociated at a temperature much lower than that needed to produce B and B_2 vapor from the elemental boron.

(U) The weak intensity of the OH spectra and the absence of lines due to water suggest that hydrogen sources other than AP are responsible for the formation of water and ultimately that of HOBO found in the combustion system. The obvious conclusion that can be reached is that the alternate source of water is the PBAN binder. If this proves to be the case, then the remedy suggested in the previous section should be valid and worthy of continued effort.

(U) The surprising intensity of the diatomic molecule BH suggest that it also could react with oxygen to form HOBO via

$$BH + O_2 \rightarrow HBO + O \tag{34}$$

$$HBO + O_2 \rightarrow HOBO + O \tag{35}$$
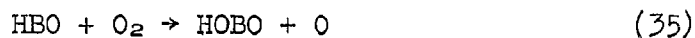
(U) This mechanism would also account for the formation of HBO, suggested as an intermediate by some people.

E. EXPERIMENTAL STUDIES ON THE COMBUSTION OF ALUMINUM (U)

1. Introduction (U)

(U) The fuel given second priority to boron for use in air augmented combustion is aluminum. For this reason, work was initiated on the combustion of aluminum in oxygen. The combustion of aluminum in general is well known and will not be discussed in detail.

2. Experimental Results (U)

(U) About 30 mg of 99% pure aluminum powder was flash pyrolyzed in the presence of 50 mm O_2. No "glue" was needed to adhere the aluminum to the graphite substrates. The flash energy was held at

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a constant 1815 joules (11 KV at 30 μfd). Delay times were varied
from 22 to 2500 μsec. Intense line spectra at 3082, 3092 and 3961 Å
were observed. These correspond to the persistent lines of atomic
aluminum vapor AlI. Band spectra corresponding to AlO were seen
to increase in intensity after 100 μsec and reach an apparent
maximum at ~1500 μsec. Black body radiation was seen to appear at
times greater than ~500 μsec and was seen to increase in intensity
as time proceeded. This was attributed to radiation from the solid
Al_2O_3 found in the reaction.

(U)   The persistence of the AlI lines indicates that a good
portion of the aluminum was in vapor state during the course of
the combustion.

(U)   No OH lines were seen, attesting to the purity of the alu-
minum.

F. SUMMARY   (U)

(C)   The work reported herein shows that HOBO probably is
formed from the reaction of OH and H_2O with BO and BO_2 rather than
from liquid B_2O_3 and water. Further, it is shown that the
substitution of a fluorinated binder for PBAN decreases the amount
of OH and H_2O formed during combustion. This reduction of OH and
H_2O results directly in a decrease in the amount of HOBO formed.
The effects of this reduction of HOBO are manifested in an
increased flame temperature and increased combustion efficiency.

(U)   The primary source of OH and H_2O in a boron propellant
for air augmented combustion is the hydrocarbon binder, not the AP.

(U)   The combustion of aluminum seems to be smooth, resulting in
condensed Al_2O_3 as final product.

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SECTION III

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13. ABSTRACT

The heat of formation of crystalline lithium-doped BeH_2, TVOPA, DAHTP, CF_4, $CF_3ONF_2(g)$, Florox(g), and $N_2F_4(g)$ were determined as -5.0, -208.1±2.9, -210.4, -223.23±0.60, -189.1±0.8, -33.2±0.5, -4.7±0.6 kcal/mol, respectively, and alane-terminated BeH_2 analyzed as $Al_9Be_{11}(CH_3)_{29}H_{20}$, as -35.7±2.1 kcal/100 g. Removal of solvent from TVOPA and preparation and purification of CF_3ONF_2 have both been completed. A photochemical process and a low temperature fluorination procedure have been used to prepare CF_3NF_2. The latter was the better method. Using the technique of flash pyrolysis, the combustion behavior of B-O, B-O_2-H_2O and B-O-fluorinated monomer system have been analyzed from the time of initiation to 3000 μsec. The presence of H_2O in the combustion system increases the formation of the intermediate HOBO and results in a lowered flame temperature. The addition of fluorine to the system precludes the formation of H_2O and likely that of HOBO, resulting in a higher flame temperature. The combustion of B in the presence of AP takes place in an atmosphere of gaseous products resulting from the deflagration of the AP. Only small amounts of water are present in this system. The present work suggests that in order to minimize the formation of HOBO, via: $H_2O + BO_2 \rightarrow HOBO + OH$, the hydrocarbon binder should be changed to a fluorocarbon binder.

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