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INVESTIGATION OF THE THERMODYNAMIC PROPERTIES OF PROPELLANT INGREDIENTS AND THE BURNING MECHANISMS OF PROPELLANTS

QUARTERLY PROGRESS REPORT AFRPL-TR-67-210

(1 April 1967 to 30 June 1967)

July 1967

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

(Prepared under Contract Nr. F04611-67-C-0025 by
The Dow Chemical Company,
Midland, Michigan 48640)

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Report Nr. T-0025-2Q-67

QUARTERLY PROGRESS REPORT (U)

(1 April 1967 to 30 June 1967)

July 1967

AIR FORCE SYSTEMS COMMAND
RESEACH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
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CONTRACT NR. F04611-67-C-0025

SCIENTIFIC PROJECTS LABORATORY
THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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 second quarterly report, covering the work performed during 1 April 1967 through 30 June 1967. The Dow Report Number is T-0025-2Q-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 Dr. D. A. Rausch, and management supervision of Dr. R. P. Ruh.

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

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

ABSTRACT (U)

(C) Work on the heat of formation of alane-terminated liquid beryllium hydride (code ATBH) was completed. The composition of the sample was found to correspond closely to the empirical formula $Al_9Be_{11}(CH_3)_{29}H_{20}$, indicating the material is probably a mixture and not a unique compound. From heat of hydrolysis in an HCl-dioxane-water mixture, the heat of formation was derived as -268.6 kcal/mole or -33.65 kcal/100 grams.

(C) Heat of solution measurements and X-ray diffraction results indicate diammonium hydrazinium tetraperchlorate (code DAHTP) from Thiokol Chemical Corporation is a physical mixture of ammonium perchlorate and hydrazinium diperchlorate and not a new compound. The heat of formation of DAHTP is therefore taken as the sum of the heats of formation of two moles of AP and one mole of HDP. Our recommended value is -210.4 kcal/mole.

(C) The heat of combustion of purified 1,2,3-tris[1,2-bis (difluoroaminoethoxy)]propane (code TVOPA) in oxygen was measured by rotating bomb calorimetry. The derived heat of formation of TVOPA is -208.1 kcal/mole (heat of formation of aqueous HF from NBS Tech. Note 270-1). This agrees well with Rohm and Haas Company results when calculated to the same basis. Our extensive work on this compound points out the importance of complete solvent removal if the full potential is to be realized.

(C) Work in progress includes the heat of formation CF_3ONF_2 by explosion of a mixture with hydrogen and the heat of explosion of mixtures of cyanogen and NF_3 with the aim of defining the heat of formation of CF_4. A sample of ClF_3O (Florox) is expected from Rocketdyne Corporation in the near future.

(U) In the area of synthesis, solvent has been removed from chromtographed, acid-washed TVOPA to produce a high purity material with a low chloride content and with no appreciable quantities of benzene. This effort has now been concluded. Work toward preparation of high purity CF_3NF_2 has continued using previously reported techniques.

(C) The flash pyrolytic combustions of boron in oxygen, oxygen and water, and in chlorine are described in terms of the time history of selected species as measured by kinetic spectroscopy. Evidence for the mechanistic role of H_2O and OH in the formation of HOBO is presented. The step-wise chlorination of boron is discussed. Recommendations to inhibit the formation of HOBO by reducing the amount of H_2O and OH in the system are presented. Studies aimed at replacing the PBAN binder by a fluorocarbon binder (to give HF rather than H_2O) are suggested.

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SECTION I

(U) THERMOCHEMISTRY

A. 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 was reacted with excess $Al(CH_3)_3$ at 110-120°C. Unreacted BeH_2 and insoluble impurities were filtered off and excess $Al(CH_3)_3$ removed in vacuo 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 a 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 3426.85 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. Drawing on past experience with other reactive compounds, hydrolysis with a mixture of 60 wt. % dioxane and 40 wt. % 7.26 N HCl was tried. 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 was 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 $AlCl_3 \cdot 6H_2O$. The heats of formation of these components are known. The sealed glass bulbs and solid $AlCl_3 \cdot 6H_2O$ 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.

4. Analytical Results (U)

(U) A summary of the analytical data is given in Table I. 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.

(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 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.

Table I

Analytical Data on ATBH (U)

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 $Al_9Be_{11}(CH_3)_{28}H_{20}$	30.42	12.42	54.63	2.53	100.00

(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 I. 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 I.

5. Calorimetric Results (U)

(U) Calorimetric results for the sample hydrolysis experiments are given in Table II. 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 III.

(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 IV. In these reactions, quantities enclosed in brackets are solutions. The value for ΔE_1 is simply the average $\Delta E_R/M$ from Table II multiplied by the molecular weight of $Al_9Be_{11}(CH_3)_{29}H_2O$, 798.14. This gives $\Delta E_1 = -2254.7$ kcal. The value for ΔE_2 is the average of five comparison experiments, yielding +394.3 kcal. The heat of mixing of dioxane and 7.26 N HCl measurements give $\Delta E_3 = -433.8$ 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 $\Delta E_4 = +985.7$ 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 $\Delta E_5 = +879.3$ kcal and $\Delta E_6 = -1332.2$ kcal.

(C) The algebraic sum of these six reactions gives ΔE_7, for which $\Delta E_7 = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 + \Delta E_5 + \Delta E_6 = -1761.4$ kcal. Noting that reaction 7 involves an increase of 11 moles of gaseous substances, ΔH_7 can be calculated from:

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

$$= -1761.4 + 6.5$$

$$\Delta H_7 = -1754.9 \text{ kcal}$$

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 $AlCl_3 \cdot 6H_2O$ = -643.3 kcal/mol. Combined with our measured ΔH_7, these data yield for $Al_9Be_{11}(CH_3)_{29}H_2O$:

$$\Delta Hf_{298}^\circ(\text{liq}) = -268.6 \text{ kcal/mol}$$

$$= -33.65 \text{ kcal/100 g}$$

Table II

Heat of Hydrolysis of ATBH (U)

	Experiment Number					
	1	2	3	4	5	6
Sample mass, g	0.7614	0.7497	0.7806	0.7729	0.7850	0.7367
Δt_c, °C	0.62909	0.60689	0.63874	0.62603	0.65921	0.59196
$E\Delta t_c$, cal	2155.8	2079.7	2188.9	2145.3	2259.0	2028.6
ΔE glass, cal	0.8	0.7	0.9	0.8	0.8	0.7
ΔE sample, cal	0.2	0.2	0.2	0.2	0.3	0.2
ΔE mixture, cal	15.1	14.5	15.0	14.8	15.9	14.0
ΔE platinum, cal		0.2	0.2	0.2		0.2
$-\Delta E_R/M$, cal/g	2853	2802	2825	2796	2899	2774

$-\Delta E_R/M$ (average) = 2825 cal/g

Table III

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

Substance	Cp, 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
$AlCl_3 \cdot 6H_2O$	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).

Table IV

Reaction Scheme for Heat of Formation of ATBH (U)

$Al_9Be_{11}(CH_3)_{29}H_2O$ + Solution A ⟶ Solution B + $29CH_4(g)$ + $20H_2(g)$ ΔE_1

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

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

(C) The overall uncertainty is calculated as twice the overall standard deviation to be ± 31.9 kcal./mol. or ± 4.0 kcal/100 grams. The uncertainty amounts to about 0.3% 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.

B. 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 included 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 content, 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 calorimeter 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 calorimeter to a solution unit. Temperatures were measured as a function of time with a calibrated thermistor (2300 ohms at 25°C) and a drum chronograph. The corrected temperature changes were calculated by computer from the resistance-time data using standard procedures. Calibration of the calorimeter was carried out electrically using current-time integration techniques and an integrating digital voltmeter. (4.1840 joules = 1 Thermochemical calorie). Power was taken from a Lambda constant voltage power supply. In this manner, the solution calorimeter could be calibrated after each experiment with a precision of a few hundredths of a percent.

4. Procedure (U)

(C) Since both the heats of formation solution of NH_4ClO_4 and $N_2H_4 \cdot 2HClO_4$ have been published (1,2,3), 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)

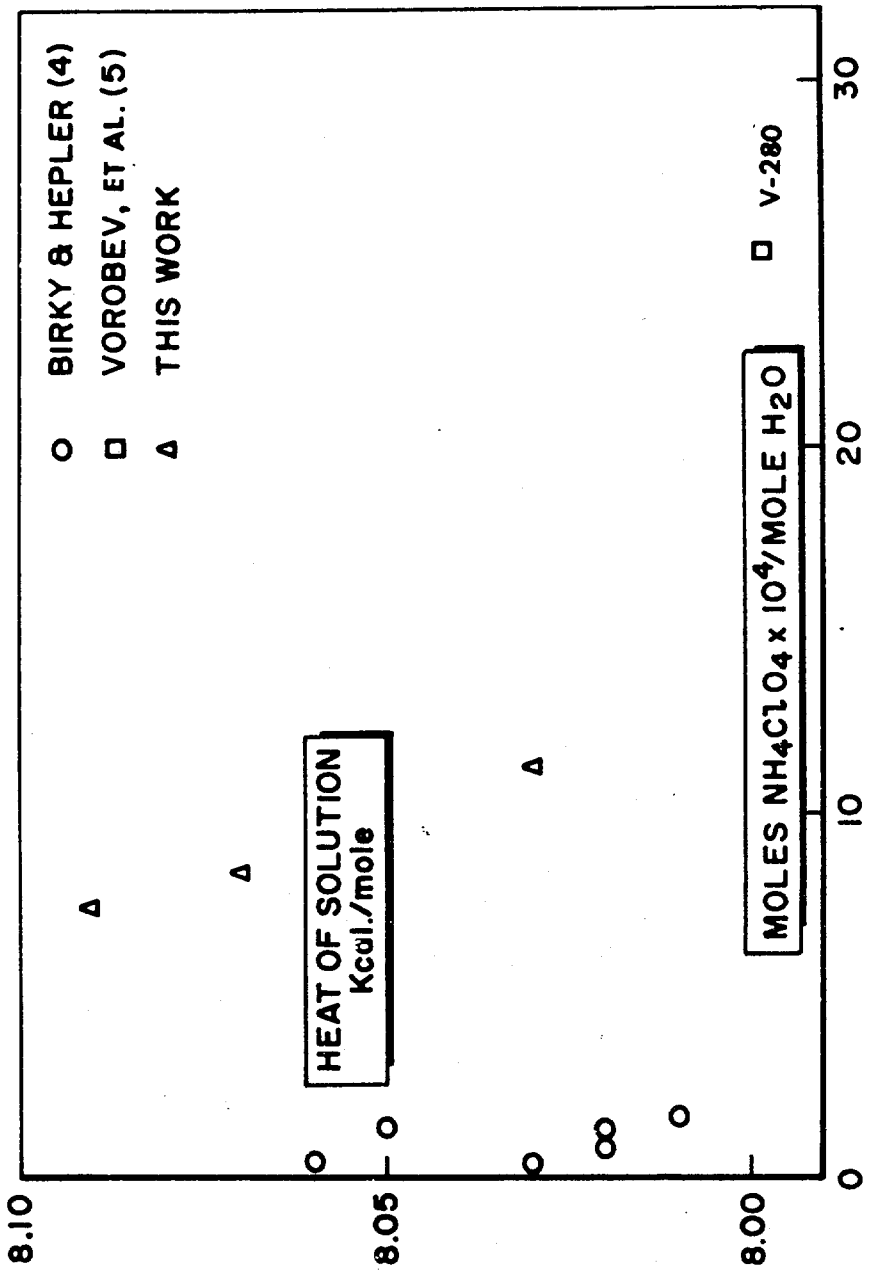
(U) Table V lists the measured and calculated values for five heat of solution measurements on DAHTP. All weights are corrected to mass in vacuum; however, a purity factor has not been applied. The energy equivalent E (calor) has been discussed before and all other entries are of standard terminology. The last column lists the dilution states for one mole of DAHTP. Deviations are calculated as the arithmetic mean. Table VI 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.

Table V

Heat of Solution of DAHTP in Water (U)

Run	Sample Mass, g	E (calor) cal/°C	E Δtc cal	ΔHsol cal/g	ΔHsol kcal/mole	$\frac{n_{H_2O}}{n_{DAHTP}}$
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



(U) Fig. 1 - Change in ΔEc/M for TVOPA with a change in Chloride Content

Table VI

Heat of Solution of NH_4ClO_4 (U)

Run	Sample Mass, g	E (calor) cal/°C	E Δt_c cal	ΔHsol cal/g	ΔHsol kcal/mole	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 $N_2H_4 \cdot 2HClO_4$ (3) 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 V 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.

(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 3 as -70.58 kcal/mol. For HDP, two values are available, -69.2 kcal/mol from reference 1 and -70.1 kcal/mol from reference 2. The desired sum is calculated 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.

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 (6) has reported a heat of formation for TVOPA. The purpose of the present work was to obtain a second value for the $\Delta Hf°_{298.15}$ 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)

( ) Three samples, designated as Batches A, B, and C, which is a liquid at room temperature, 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 VII 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 (7)."

Table VII

Standard Infra-red

Analytical Data Supplied by Rohm and Haas (U)

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 " C-CN, %	0.15	-	-
5.78 μ	0.010(absorb.)	0.237	0.19
5.92 μ	0.031 "	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.

(U) Batch A was burned in combustion Exp-1 through Exp-12 (Table VIII), as reported earlier (8). 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 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 IX) 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 throughly 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 (7).

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 (8). 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 (8) and can be summarized. 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. 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.

Table VIII

Analytical Results and Energy of Combustion of TVOPA (U)

Exp. No.	Analysis: Nitrate mg. as N_2	Analysis: Fluoride /spl	Fluoride Recovered %	Chloride mg. Chloride per g. TVOPA	-ΔEc/M calories 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

Table IX

Results of Elemental Analyses on TVOPA (U)

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

(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 (8). The average values are listed below:

	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 (9).

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

(U) The calorimeter was calibrated twice, since slight modifications were made after burning some of the earlier samples. The calorimeter was calibrated in both cases with N.B.S. benzoic acid 39i. The first E (calor) value, 3423.35 cal/g with a standard deviation of 0. 13 cal/g, was used for TVOPA combustion Exp-1 through Exp-16. The second E (calor) value, 3427.37 cal/g with a standard deviation of 0.15 cal/g, was used for Exp-17 through Exp-28.

5. Analytical Results (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 (8) and in Table VIII 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 VIII 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 were 100%. The average of the moles of fluoride found in solution and moles calculated from sample weights was used in the Washburn corrections program.

(U) Table IX 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 IX includes the elemental analysis provided by Rohm and Haas (6) 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 (8, 10). Constant factors needed as input for this program are given in Table X and other variables in Table XI. Table XI 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 XI (with the exception of Exp-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 (8). (See page 30, 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:

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

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

Mol. Wt. = 482.23068 g/mol

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

$\Delta n = +4$ $\quad RT = 0.5925$

$\Delta Hc = \Delta nRT + \Delta Ec = -1622.27$ 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 (6) $\Delta Hf = 207.3 \pm 3$ 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.

Table X

Constant Factors in TVOPA Combustion Calculations (U)

Empirical formula of TVOPA [7]	$C_9H_{14}O_3N_8F_{12}$
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 [7]	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 ration, H_2O/HF	30
$(\partial E/\partial P)T$ of TVOPA [7]	-0.00380 cal./g./atm.
$(\partial E/\partial P)T$ of 2-octanone	-0.00899 cal./g./atm.
$(\partial E/\partial P)T$ of film	-0.00800 cal./g./atm.
$(\partial E/\partial P)T$ of fuse	Negligible
ΔE_c° of 2-octanone (Sample 1)	-1204.84 kcal /mole
ΔE_c° of 2-octanone (Sample 2)	-1201.08 kcal /mole
ΔE_c of film	-1050.31 kcal /mole
ΔE_c of fuse	-103.35 kcal /mole
Cp of TVOPA [7]	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 XI

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

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	0.1406505	0.134380	0.122320	0.140459
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
$-\Delta Ec/M$, 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

(U) Figure 2 shows the dependence of the ΔHc (ΔEc/M) on removal of impurities apparently closely asscciated with the chloride containing manufacturing solvents. The low chloride experiments plotted on Figure 2 indicate that the ΔEc/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.

D. WORK IN PROGRESS (U)

(U) Work on the heat of explosion of mixtures of CF_3ONF_2 and hydrogen is nearly completed. New analytical results indicate the sample of CF_3ONF_2 is of high purity. Low results for carbon found after the calorimetric experiments may have been due to use of too large an excess of hydrogen with some reduction of CO to free carbon. A correction for this can be applied and calculations are in progress.

(U) Preliminary results were obtained for the heat of explosion of mixtures of C_2N_2 and NF_3. A preliminary value of -223.2±0.5 kcal/mole was obtained for the heat of formation of CF_4, in good agreement with other recent work. Confirmatory experiments are in progress.

(C) A sample of ClF_3O is scheduled to arrive from Rocketdyne Corp. in the near future.

E. TRIP (U)

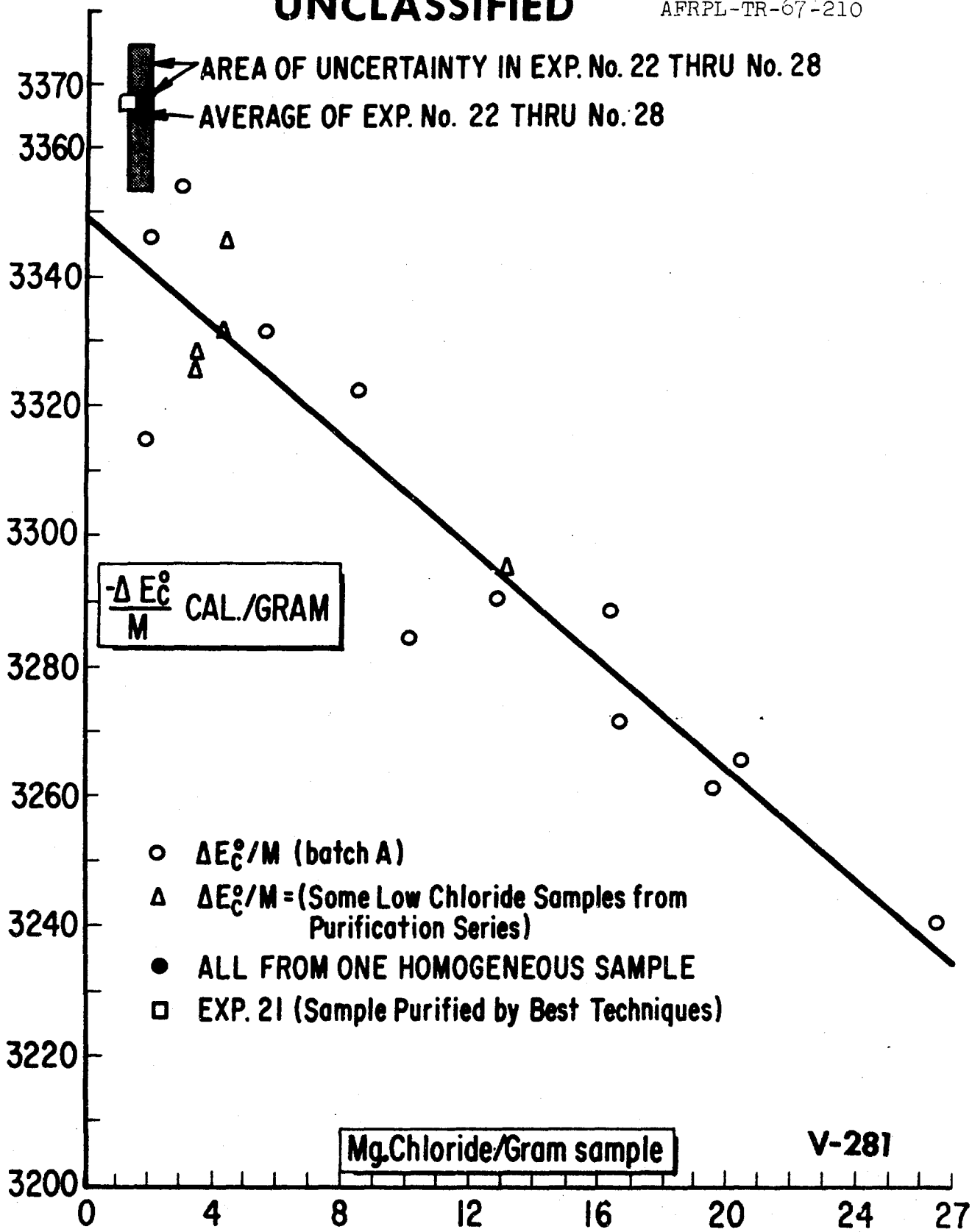
(U) G. C. Sinke and L. C. Walker attended the Calorimetry Conference held at Thousand Oaks, California, June 19-22.

F. SYNTHESIS (U)

1. Discussion (U)

(U) Work has been continued toward the removal of solvent from TVOPA. 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 is the same procedure used by Rohm and Haas in their preparation of acid-washed material.

(U) Starting with this acid-washed material, five batches of TVOPA totaling 5.9 g have been purified, and the homogenous mixture has been 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, which is almost as low as has ever been obtained on small purification runs.



(U) Fig. 2 - Effect of Chloride on the Heat of Combustion of TVOPA

(U) Since benzene was used in one step of the purification process, it seemed desirable to determine how much, if any, benzene remained in the final material. To accomplish this, previously purified TVOPA was redissolved in methylene chloride and radioactive benzene. The solvent was then removed as in the original purification procedure. Two samples run in this manner with tagged benzene indicated a radioactive material remained in the TVOPA. This radioactivity could not be decreased by dilution with normal benzene and subsequent solvent removal, indicating that the residual radioactivity was due to either a non-volatile residue or reactive impurity present in the radioactive benzene. To confirm the above conclusion, additional experiments are being designed.

(U) The determination of the amount of benzene remaining in TVOPA will conclude this project.

(U) The preparation of pure CF_3NF_2 has been continued with the synthesis of additional crude material in a manner described in a previous report. Purification will be effected with the completion of the work on TVOPA.

2. Experimental (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 forty-eight hour period. Material treated in this manner contained 1.8 mg of chloride per gram of sample.

SECTION II

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) The use of elemental boron as a fuel for augumented 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 (11, 12), as well as from the highly reactive intermediate BO_2 and water (13).

(C) In either case, the formation of HOBO was proven to be detrimental, since a large percentage of the combusted boron propellant is expelled from the rocket as this species and not as B_2O_3. By preventing the formation of B_2O_3, the HOBO causes a loss in combustion efficiency equal to the heat of condensation of B_2O_3. Therefore, the combustion of boron in an oxygen atmosphere has been studied with and without the presence of water to determine the effect of water on the formation of HOBO.

(U) The decomposition of the oxidizer NH_4ClO_4 yields Cl_2 as a product. For this reason, the combustion of boron in chlorine, in addition to the system B-H-O, was also studied.

B. EXPERIMENTAL (U)

(U) The flash heating apparatus employed in the present study has already been described (14). It was employed to study the combustion of LMH-1 and LMH-2 on contracts AF 04(611)-7554 and AF 04 (611)-11202.

(U) The boron used in this study is "Avco 400." Its analysis has already been reported (15). The oxygen and chlorine were prepared by Dow and were at least 99 mole percent pure. The first part of the work deals with the combustion of boron in oxygen at 30 mm pressure of oxygen at 1300-2000 joules of flash energy. The delay range was varied from 14 to 3000 μsec.

(U) The studies on the combustion of boron in the presence of both water and oxygen duplicated as near as possible the above conditions, with the exception that the gas phase contained 20 mm O_2 and 18 mm H_2O.

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

(U) In addition, a few preliminary studies were carried out on the combustion of boron in HCl, one of the products of the decomposition of NH_4ClO_4.

C. EXPERIMENTAL RESULTS (U)

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

(U) Most of this period was spent studying the combustion of boron in oxygen alone and in the presence of water vapor. Flash photolytic and flash pyrolytic decomposition studies of water are underway to determine the amounts of O, O_2 and OH formed from the decomposition of water. The amount of OH formed from the decomposition of water is pertinent to the problem, since OH is also a product of the reaction of water with BO_2.

$$H_2O + BO_2 \rightleftarrows OH + HOBO \qquad (1)$$

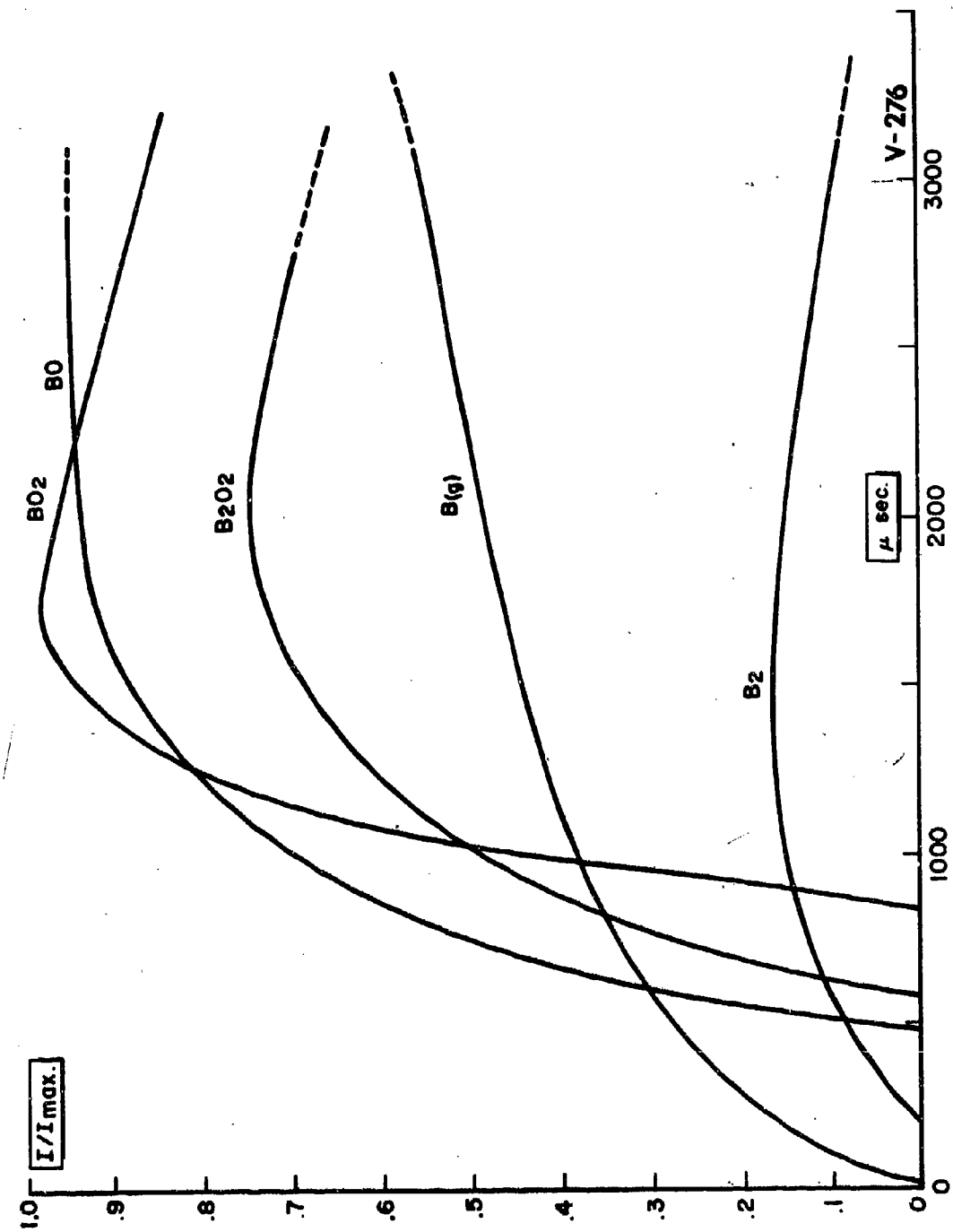
(U) Thus, when the total intensity of OH is corrected for that due to the dissociation of water, the remaining OH should be a result of Reaction (1), indicating the extent to which HOBO and OH are found by this reaction.

(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.

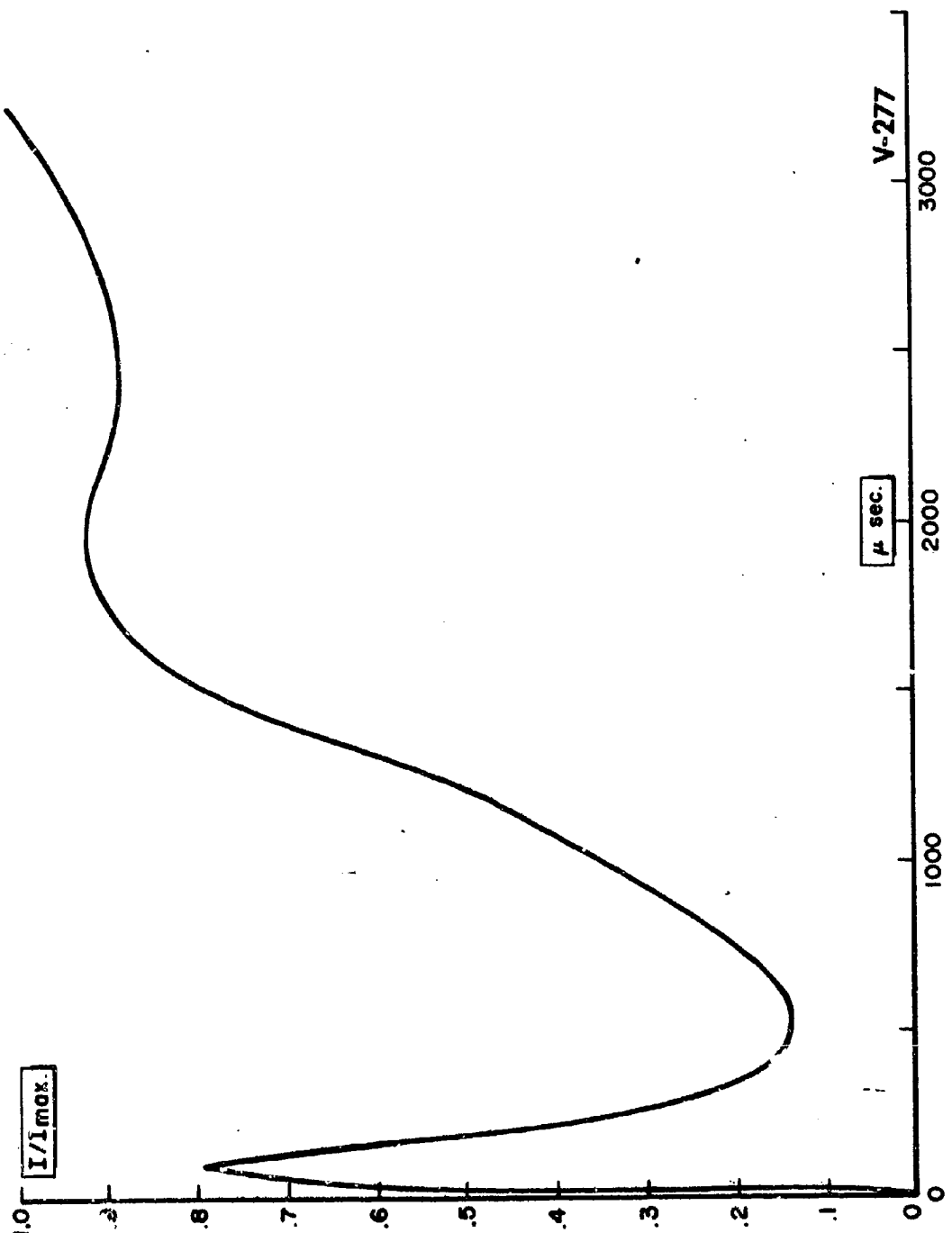
(U) Since no recorded spectrum for B_2O_3 is known in the UV or visible spectrum, this species was not detected in the gas phase during flash pyrolysis. However, B_2O_3 was detected when the solid residue from the combustion cell was analyzed.

(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 in B(g); after about 500 μsec, BO is seen to increase rapidly in intensity until 1500 μsec when the increase in intensity seem to almost 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) Fig. 3 - Boron Species Observed During The Flash Pyrolysis of Boron in 30 mm Oxygen at 2000 Joules



(U) Fig. 4 - Hydroxyl Radicals Observed During the Flash Pyrolysis of Boron in 30 mm Oxygen at 2000 Joules

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

(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 (14). The BCl spectrum was correlated to the $^1\pi \leftarrow {}^1\Sigma$ transition in the range 2650-2880 Å described by Miescher (16) and Herzberg and Hushley (17). The BCl_3 was correlated with a diffuse reaction with that observed when pure BCl_3 was analyzed. Figure 5 shows the time-intensity curve for the species Cl_2, Cl, BCl and BCl_3 observed during the reaction. The observed absorptions due to B and B_2 were not sufficiently strong to warrant being plotted.

D. DISCUSSION (U)

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

(U) The presence of B and BO can be accounted for by the Steps (2) and (3). (Unless otherwise stated, all species are gaseous).

$$B(s) \xrightarrow[\Delta]{h\nu} B(1,g) + B_2 \qquad (2)$$

$$B(s,1,g,) + O_2 \longrightarrow BO + O \qquad (3)$$

The species BO_2 could be formed by:

$$BO + O_2 \longrightarrow BO_2 + O \qquad (4)$$

or

$$BO + O \xrightarrow{M} BO_2 \qquad (5)$$

with the three-body Reaction (5) much less likely to occur than Reaction (4). Both BO and BO_2 can form if the oxide B_2O_3 dissociates at temperatures above its boiling pint, via:

$$B_2O_3(g) \xrightarrow{\Delta} BO_2 + BO \qquad (6)$$

(U) Data previously presented (15) 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:

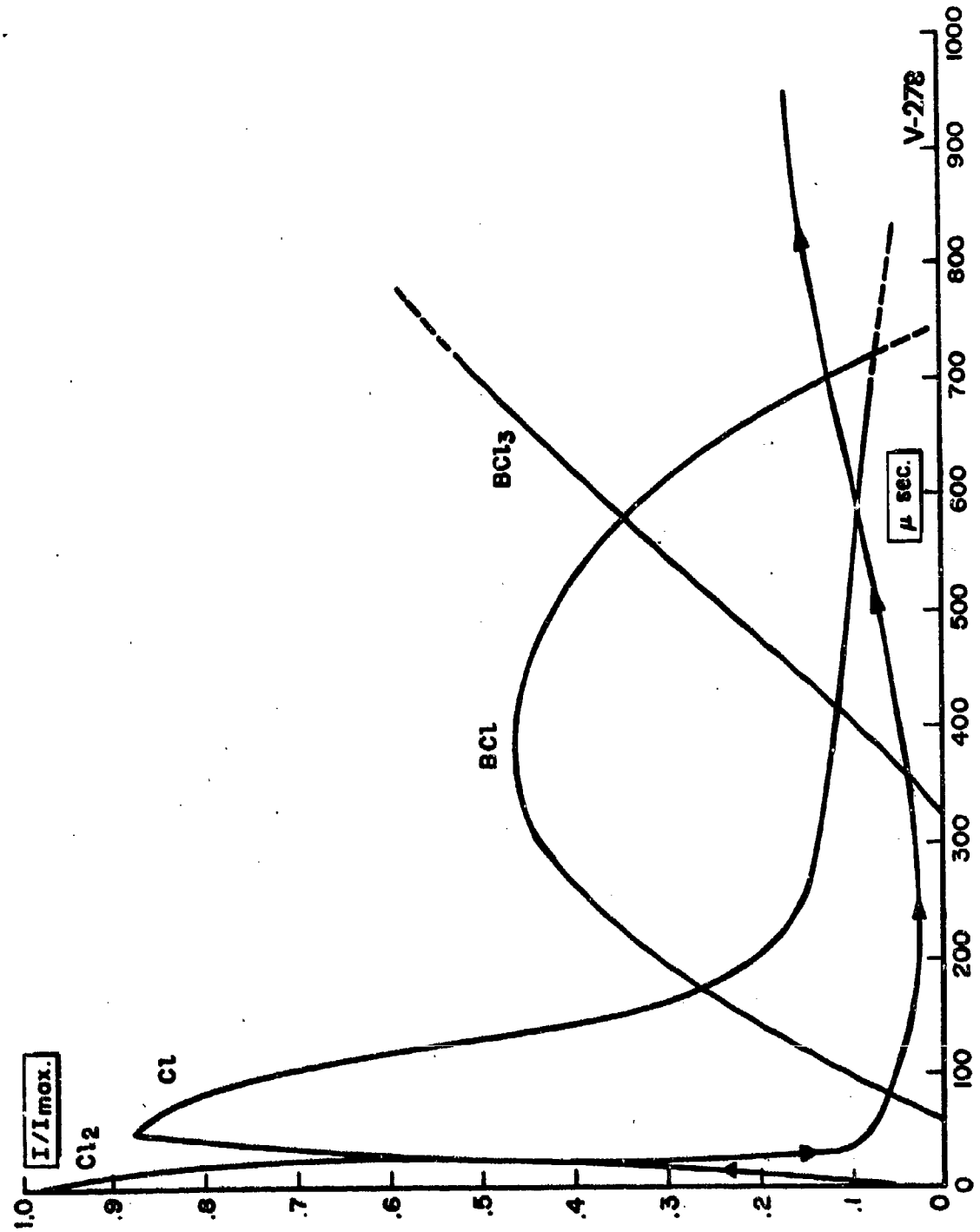
$$BO_2\ B \longrightarrow B_2O_2 \qquad (7)$$

or by the three-body collisions:

$$B_2 + O_2 \xrightarrow{M} B_2O_2 \qquad (8)$$

and

$$BO + BO \xrightarrow{M} B_2O_2 \qquad (9)$$



(U) Fig. 5 - Species Observed During the Flash Pyrolysis of Boron in 35 mm. Chlorine at 2000 Joules

or even by:

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

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

$$^1/_2\ B_2O_3(l,g) + {}^1/_2\ H_2O \longrightarrow HOBO(g) \qquad (11)$$

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 on previously (15), the HOBO (formed by heating H_3BO_3) seems to dissociate at high temperatures to H and BO_2 by:

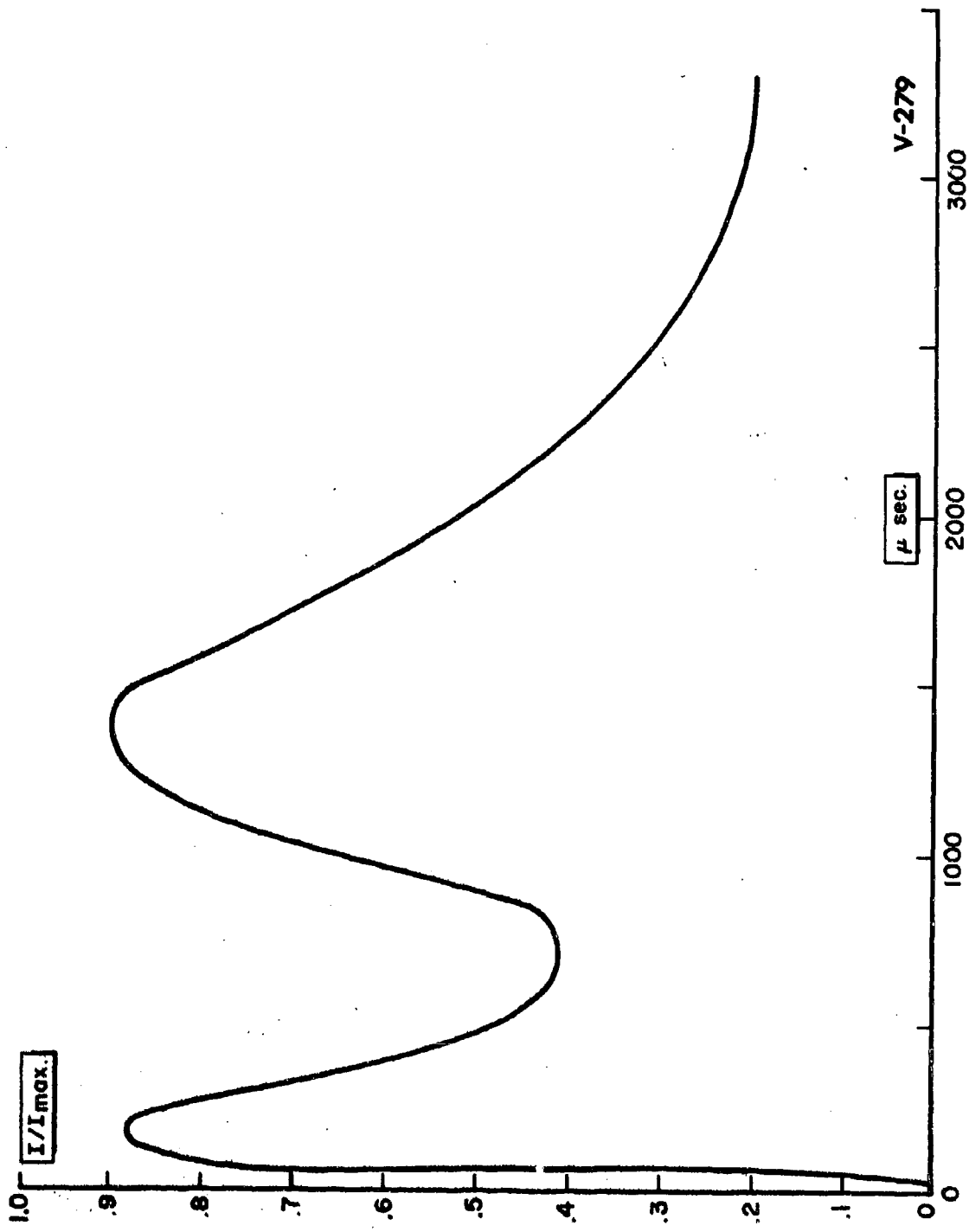
$$HOBO(g) \underset{\Delta}{\xrightarrow{h\nu}} H + BO_2 \qquad (12)$$

(U) Only BO_2 was observed, since HOBO has no UV or visible spectrum. Reaction (12) is probable in light of Equation (1), where the OH radical would scavenge the hydrogen atom, formed along with the BO_2, to form water. It is believed that by Reaction (12) 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 (12) would predominate.

(U) The OH time-intensity curve of Figure 3 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.

(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 6 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 6 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 6 is about one order of magnitude brighter than that in Figure 4. The OH intensity in Figure 6 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) Fig. 5 - OH Radicals Observed during the Flash Pyrolysis of Boron in 20 mm. Oxygen and 18 mm. Water at 2000 Joules

(U) The greatest dissimilarity between Figure 4 and 6 is that the second OH peak in Figure 6 occurs at ~1400 μsec while that in Figure 4 occurs at times greater than 2000 μsec. At 2500 μsec the OH of Figure 6 are 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 occuring 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:

$$OH + BO \longrightarrow HOBO \qquad (13)$$

or from the combination of OH radicals to form water:

$$OH + OH \longrightarrow H_2O + O \qquad (14)$$

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

$$B + OH \xrightarrow{M} HBO \qquad (15)$$

Further analysis of the $B\text{-}O_2\text{-}H_2O$ system is underway. It is hoped that a time-intensity curve for the boron species similar to that of Figure 3 will be constructed. In this way, the role of water will be assessed from a mechanistic viewpoint.

(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:

$$H_2O + BO_2 \rightleftharpoons HOBO + OH \qquad (1)$$

$$^1/_2\, B_2O_3(s,l,g) + {}^1/_2\, H_2O \rightleftharpoons HOBO \qquad (11)$$

$$H + BO_2 \rightleftharpoons HOBO \qquad (12)$$

$$OH + BO \overset{M}{\rightleftharpoons} HOBO \qquad (13)$$

(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. Equation (11) probably takes place outside of the rocket engine to give the desired product of combustion. Equation (1), (12), and (13), are the most probable causes of the formation of HOBO, particularly (1), and (12).

Denver Research Institute in its first quarter report to AFRPL (16) reports mainly BO_2 and OH being detected in emission when the combustion of boron in an acetylene-oxygen flame was analyzed spectroscopically. This strengthens the conclusions that BO_2 is the primary boron species responsible for the formation of HOBO and that B_2O_3 is formed after HOBO has cooled considerably.

(U) It is recommended that any future boron-containing propellant be composed and formulated to eliminate or minimize the formation of water (and its components H and OH).

(C) To reach this goal the effect of fluorine on a B-O-H system will be studied. It is believed the formation of HF will minimize the amount of water in the system, thus reducing the amount of HOBO formed. Furthermore, a fluorine binder would improve the combustion efficiency of boron for the following reasons:

(i) The higher flame temperatures of a B-O-F system would volatilize more boron, thus placing more boron in the exit stream of the solid motor where it would be burned by the incoming air.

(ii) The formation of water would be prevented by formation of HF as the primary product of the binder combustion, thus minimizing the amount of HOBO present.

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

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

$$Cl_2 \xrightarrow{h\nu} 2\ Cl \qquad (14)$$

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

$$B(s) \xrightarrow[\Delta]{h\nu} B_{(l)} + B_{(g)} \qquad (15)$$

and

$$B_{(s,l,g)} + Cl \xrightarrow{M} BCl \qquad (16)$$

(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:

$$BCl + Cl_2 \longrightarrow BCl_2 + Cl \qquad (17)$$

$$BCl_2 + Cl_2 \longrightarrow BCl_3 + Cl \qquad (18)$$

with the final step:

$$Cl + Cl \xrightarrow{M} Cl_2 \qquad (19)$$

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 of Cl. If the reaction:

$$BCl + Cl_2 \longrightarrow BCl_3 \qquad (20)$$

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.

E. RECOMMENDATIONS (U)

(U) It is recommended that the scope of the work be expanded to include the study of the effect of OH scavengers on the rate of formation of HOBO. If the concentration of the OH radical can be reduced, its reaction with BO_2 to form HOBO can be minimized. Some typical OH scavengers are tetraethyl lead, PbF_2 and manganese carbonyls.

(C) It is also recommended that vinyl $\{CH_2\text{-}CF_2\}_2$ type binders be studied in conjunction with boron combustion to correlate the effect of fluorine on the rate of formation of H_2O and HOBO.

F. FUTURE WORK (U)

(C) The study of the combustion of PBAN binder will be started. Studies on the combustion of boron in the presence of NH_4ClO_4 as per our milestone chart will also begin.

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13 ABSTRACT Work on the heat of formation of ATBH was completed. The composition of the sample was found to correspond closely to an empirical formula, indicating the material is probably a mixture and not a unique compound. From heat of hydrolysis in an HCl-dioxane-water mixture, the heat of formation was derived as -268.6 kcal/mole or -33.65 kcal/100 grams. Heat of solution measurements and X-ray diffraction results indicate DAHTP, from Thiokol Chem. Corp., is a physical mixture and not a new compound. The heat of formation of DAHTP is therefore taken as the sum of the heats of formation. Our recommended value is -210.4 kcal/mole. The heat of combustion of purified TVOPA in oxygen was measured by rotating bomb calorimetry. The derived heat of formation of TVOPA is -208.1 kcal/mole, agreeing well with Rohm and Haas Company results when calculated to the same basis. Our extensive work on this compound points out the importance of complete solvent removal if the full potential is to be realized. Work in progress includes the heat of formation of CF_3ONF_2 by explosion of a mixture with hydrogen and the heat of expolsion of mixtures of cyanogen and NF_3 with the aim of defining the heat of formation of CF_4. A sample of Florox is expected from Rocketdyne Corporation in the near future. In the area of synthesis, solvent has been removed from chromtographed, acid-washed TVOPA to produce a high purity material with a low chloride content and with no appreciable quantities of benzene. This effort has now been concluded. Work toward preparation of high purity CF_3NF_2 has been continued using previously reported techniques. The flash pyrolytic combustions of boron in oxygen, oxygen and water, and in chlorine are described in terms of the time history of selected species as measured by kinetic spectroscopy. Evidence for the mechanistic role of H_2O and OH in the formation of HOBO is presented. The step-wise chlorination of boron is discussed. Recommendations to inhibit the formation of HOBO by reducing the amount of H_2O and OH in the system are presented.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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