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APRPL-TR-67-39

AD 381406

(Unclassified Title)

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

QUARTERLY PROGRESS REPORT AFRPL-TR-66-176

(1 January 1966 to 31 December 1966)

January 1967

AIR FORCE ROCKET PROPULSION LABORATORY

RESEARCH AND TECHNOLOGY DIVISION

EDWARDS AIR FORCE BASE, CALIFORNIA

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(Prepared under Contract Nr. AF 04(611)-11202 by
The Dow Chemical Company,
Midland, Michigan 48640)

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Dow Report Nr. T-202-4Q-66

FINAL REPORT (U)

Investigation of the Thermodynamic Properties and the Decomposition Kinetics of Propellant Ingredients

(1 January 1966 through 31 December 1966)

January 1967

AIR FORCE SYSTEMS COMMAND
RESEARCH AND TECHNOLOGY DIVISION
ROCKET PROPULSION LABORATORY
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SCIENTIFIC PROJECTS 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. AF 04(611)-11202. The contract was initiated under Air Force Program Nr. 750 G, AFSC Project Nr. 3148, "Investigation of the Thermodynamic Properties and the Decomposition Kinetics of Propellant Ingredients." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. Curtis C. Selph acting as Air Force Project Officer.

This is the final report, covering the work performed during 1 January 1966 through 31 December 1966. The Dow report number is T-202-4Q-66.

This work is continuing with Rocket Propulsion Laboratory sponsorship under Contract Nr. F04611-67-C-0025.

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

This report has been reviewed and is approved.

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

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SECTION I

(U) SUMMARY

(U) The heat of formation of compound Delta was determined by heat of explosion measurements to be +2.6 ± 2.8 kcal./mole. This result correlates well with previous work on R and H. An estimate of -164 kcal./mole was derived for $CF_3(NF_2)$.

(U) The heat of combustion of TVOPA in oxygen was found to show a strong trend to low values with increasing residual solvent. By extrapolation to zero solvent, a heat of formation of -217.4 ± 3.5 kcal./mole was derived. More work is planned.

(U) The heat of formation of NF_3 was measured by two different methods. The heat of dissociation was directly determined and yielded $\Delta Hf=-31.44 \pm 0.3$ kcal./mole. The heat of reaction of NF_3 and sulfur was measured and gave $\Delta Hf=-31.75 \pm 0.2$ kcal./mole. An average of -31.6 kcal./mole was employed to calculate values for HF (aq) which compared well with other recent work.

(C) The heat of combustion of P-BEP in oxygen was determined by rotating bomb calorimetry. Prolonged stripping of the sample under vacuum resulted in satisfactorily low residual solvent. Appropriate techniques for handling the polymer were worked out and six successful determinations made. The heat of combustion in oxygen was 3629.0 cal./g. If one assumes a molecular weight of exactly 100 and the empirical composition $C_{2.238}H_{3.240}O_{0.898}$-$N_{1.094}F_{2.114}$, the derived heat of formation is -47.8 ± 0.7 kcal./mole.

(U) Heats of solution of TVOPA and P-BEP in 2-octanone were determined in a Beckman 190B microcalorimeter as -4.6 and -3.0 cal./g., respectively.

(U) In support of the thermal measurements, N_2F_4, NF_3, TVOPA, and P-BEP, all obtained from outside sources, were purified. CF_3ONF_2 and CF_3OOCF_3 were synthesized and then purified. These pure compounds were supplied to the Thermal Research Laboratory upon demand.

(C) The study of the kinetics of decomposition and deflagration of a solid propellant containing LMH-2 to determine the cause of the low combustion efficiency was accomplished by flash pyrolysis combined with kinetic spectroscopy. The mechanism of deflagration and combustion of beryllium hydride above 2000°K. shows the existence of BeH and BeH^+. In the temperature range 2200° - 2800°K., the species BeH appear to be about three times as plentiful as the ion BeH^+. The ion BeH^+ appears to be more stable at high temperatures than is BeH, although it accounts for only a small fraction of the gaseous beryllium-containing decomposition product. Its reaction with oxygen is much slower than that of BeH.

(U) The study of the decomposition of ammonium perchlorate shows the first step to be the dissociation to gaseous ammonia and anhydrous perchloric acid. The subsequent reactions are the combustion of the various nitrogen species with the perchlorate species. The hydrogen atoms, oxygen atoms, and chlorine atoms also recombine to H_2, O_2, and Cl_2 by three body collisions.

(C) The reaction between beryllium hydride and ammonium perchlorate produces BeO, but does not produce the BeCl or $BeCl_2$.

(U) The decomposition and combustion of nitrocellulose and the plasticizers TMETN and TEGDN are also discussed. Their combustion chemistry is that which would be expected from hydrocarbon combustion studies.

(C) The large amount of BeH^+ found in the deflagration of beryllium hydride may be responsible for the low combustion efficiency. Because of its low reactivity, this charged ion can pass through the combustion chamber and rocket nozzle without undergoing appreciable reaction with the NH_4ClO_4 or its decomposition products.

SECTION II

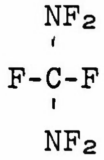
(U) THERMOCHEMISTRY

A. HEAT OF FORMATION OF TETRAKIS(DIFLUOROAMINO)METHANE (COMPOUND DELTA) (C)

1. Introduction (U)

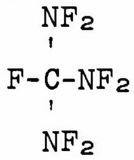
(C) Single carbon compounds such as:

Compound H



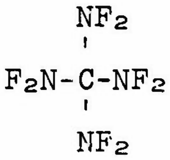
$$F\text{-}\overset{NF_2}{\underset{NF_2}{C}}\text{-}F$$

Compound R



$$F\text{-}\overset{NF_2}{\underset{NF_2}{C}}\text{-}NF_2$$

Compound Delta



$$F_2N\text{-}\overset{NF_2}{\underset{NF_2}{C}}\text{-}NF_2$$

containing (NF_2) groups form a homologous series with carbon tetrafluoride as the parent fluorocarbon and Delta as the final fully substituted compound. The heats of formation of H, R, and CF_4 are relatively well established. Previously reported $\Delta Hf_{298.15}$ values for Delta were based on a single explosion and a single combustion. This report contains the results of five successful explosions of Delta.

2. Sample Purity (U)

(U) About 6 g. of crude Compound Delta were purified by vapor phase chromatography on a perfluorinated tributylamine column at 40°C. and 20 psi of helium carrier gas. Final purification with approximately 0.5 g. quantities was made with a siloxane column at 25°C. and 20 psi just prior to loading the sample in the bomb. An IR spectrum of one random sample after the siloxane column showed no difference from the best reference spectrum.

(U) The molecular weight was obtained on each sample from the mass of the sample based on direct weighing plus P.V.T. data. The sample was weighed in the gas and liquid phase in a pyrex bulb. The bulb was then connected to a vacuum line to which was attached the bomb and a Wallace-Tiernan pressure gauge. The bomb temperature was measured with a mercury-in-glass thermometer in contact with the bomb. No attempt was made to insulate the bomb or to maintain a constant temperature during the P.V.T. readings; however, the temperature seldom varied more than a tenth of a degree.

(U) The bomb volume was determined to be 348.1 ml. This value was determined by weighing the evacuated bomb and the water-filled bomb. The molar volumes of the samples were calculated using Berthelot's equation:

$$V = \frac{RT}{P} + \frac{9RT_c}{128P_c}\left[1-6\frac{T_c^2}{T^2}\right]$$

For this calculation the critical temperature and pressure were estimated as T_c = 400°C.; P_c = 20 atms. from data for $C_5F_{11}H$ and C_4F_{10}.

(U) From the bomb volume, molar volume and sample weights, molecular weights were calculated. The results shown in Table I agree with theory within experimental error.

Table I

(U) Molecular Weight of Delta Samples[a]

Exp. No.	Sample Mass g.	Temp. °K.	Press. mm.	Molar Volume ml.	Mol. Wt. g./mole
1	0.728	295.9	173.5	105,220	220.1
2	0.870	295.0	205.5	88,366	220.9
3	0.498	295.6	119.0	153,760	220.0
4	0.978	295.3	231.5	78,395	220.3
5	1.102	295.8	263.7	69,140	219.0
				Average	220.1
				Theory	220.0
				T Deviation	0.05

[a] Bomb Volume = 348.1 ml.

(U) The IR spectrum of the Delta plus these calculated molecular weights are evidence for fairly pure starting material. Further evidence of the purity of the Delta is provided by the analysis of the explosion products.

3. Explosion Products (U)

(C) Mass spectroscopic analysis of the reaction gases after removal of fluorine with mercury (see Table II) showed the products N_2 and CF_4 in the expected ratio of 2:1 within experimental error. Standard mixtures of N_2 and CF_4 (2:1) were submitted along with each experimental mixture for comparison.

(U) The samples were ignited in the gold-spattered, platinum-lined bomb previously used for the BTU experiments. Visual inspection of the bomb in a dry box atmosphere after an explosion showed platinum or gold attack by fluorine, observed as a light yellow deposit on the walls and electrodes. Exposure of the bomb walls to moist air gave dark insoluble hydrolysis products. Washing the bomb with ~6 N HCl solution before exposure to the moist air cleanly dissolved the platinum and gold fluorides. Analysis of these solutions by activation analysis for gold, and atomic absorption analysis for gold and platinum, showed erratic amounts of platinum and gold fluoride formed. Table III shows that the formation of these fluorides was not directly related to the size of the Delta sample. A correction for the heat of formation of these fluorides was made using estimated heats (1) of 0.9 cal./mg. of Pt as PtF_4 and 0.65 cal./mg. of Au as AuF_3.

Table II

(U) Mass Spectrographic Analysis of Bomb Gases from Delta Explosions

Run No.	% N_2	% CF_4	N_2/CF_4
1	63.5	36.0	1.76
Std.	66.6	33.4	1.99
2	64.7	35.1	1.84
Std.	65.4	34.6	1.89
3	65.4	34.2	1.89
Std.	64.6	35.4	1.82
4	65.9	34.1	1.93
Std.	66.1	33.9	1.95
5	62.3	36.4	1.71
Std.	65.6	34.4	1.91

Ave.(N_2/CF_4) Ratios, Delta Explosions = 1.83
Std. Dev. of Mean = ±0.09
Standards = 1.91
Std. Dev. of Mean = ±0.06

4. Heats of Explosion (U)

(U) The heats of explosion were measured in a standard rotating bomb calorimeter. The calorimeter was calibrated from five combustions of NBS benzoic acid 39i. The masses varied from about 1 to 0.1 g. There was no apparent trend with amount of benzoic acid burned. The average calorimeter equivalent was 3,417.5 ± 2.5 cal./°C.

(U) The results of the Delta explosions are listed in Table IV.

Table III

(U) Analysis of 6 N HCl Bomb Washing Solutions

		Gold		Platinum
Sample No.	Sample Mass g.	Activation Analysis mg./Sample	Atomic Absorption mg./Sample	Atomic Absorption mg./Sample
1	0.728	8.6 ± 0.13[a]	8.4	9.1
2	0.870	8.4 ± 0.13	9.2	42.3
3	0.498	3.4 ± 0.05	3.7	3.4
4	0.978	13.9 ± 0.21	15.6	24.0
5	1.102	2.9 ± 0.04	3.4	16.5

[a] Plus/minus numbers are indication of precision of triplicate analysis.

Table IV

(U) Results of Delta Explosion Experiments

Expt. No.	Mass g.	Δt °C.	$-\varepsilon\Delta t$[a] cal.	$\Delta E_{cont.}$ cal.	ΔE_{Au} cal.	ΔE_{Pt} cal.	$-\Delta E/M$ cal./g.
1	0.729	0.22329	- 763.1	-0.2	5.5	8.2	1028.3
2	0.870	0.27244	- 931.1	-0.2	6.0	38.0	1019.9
3	0.498	0.15040	- 514.0	-0.1	2.4	3.0	1021.5
4	0.978	0.30398	-1038.9	-0.2	10.1	21.6	1030.1
5	1.102	0.33876	-1157.7	-0.2	2.2	14.9	1035.2

Mean $\Delta E°/M = 1027.0$ cal./g.

Std. dev. of mean = ±6.3 cal./g.

[a] Calorimeter Equivalent, cal./deg.

5. Results (U)

(C) Employing a molecular weight of 220.03 there is derived:

$$C(NF_2)_4(g) \longrightarrow CF_4(g) + 2\ F_2(g) + 2\ N_2(g)$$

$$\Delta E° \text{ explosion} = 225.97 \text{ kcal./mole}$$

$$\Delta nRT = +4(0.5925)$$

$$\Delta H^\circ \text{ explosion} = -223.6 \text{ kcal./mole}$$

Using for $CF_4(g)$ a $\Delta H\overset{o}{f}_{298.15} = -221.0$ kcal./mole from N.B.S. Technical Note 270-1, there is derived for Delta:

$$\Delta H\overset{o}{f}_{298.15}\,(g) = +2.6 \pm 2.8 \text{ kcal./mole}$$

(C) The uncertainty is twice the standard deviation of the mean. This heat of formation may be compared to previous work as follows: American Cyanamid Company (2) reports a single heat of combustion which we have re-calculated:

$$C(NF_2)_4(l) + 4\ H_2O(l) \longrightarrow CO_2(g) + 8\ HF(1 \text{ in } 150\ H_2O) + O_2(g) + 2\ N_2(g)$$

$$\Delta E^\circ_c = -433.85 \text{ kcal./mole}$$

$$\Delta n = +4$$

$$\Delta H\overset{o}{v}_{298.15} = +6.61 \text{ kcal./mole}$$

$$\Delta H\overset{o}{f}_{298.15} = +6.5 \text{ kcal./mole}$$

(C) Minnesota Mining and Manufacturing Company (3) reported a single heat of explosion:

$$\Delta E^\circ \text{ explosion} = -233.2 \text{ kcal./mole}$$

$$\Delta n = +4$$

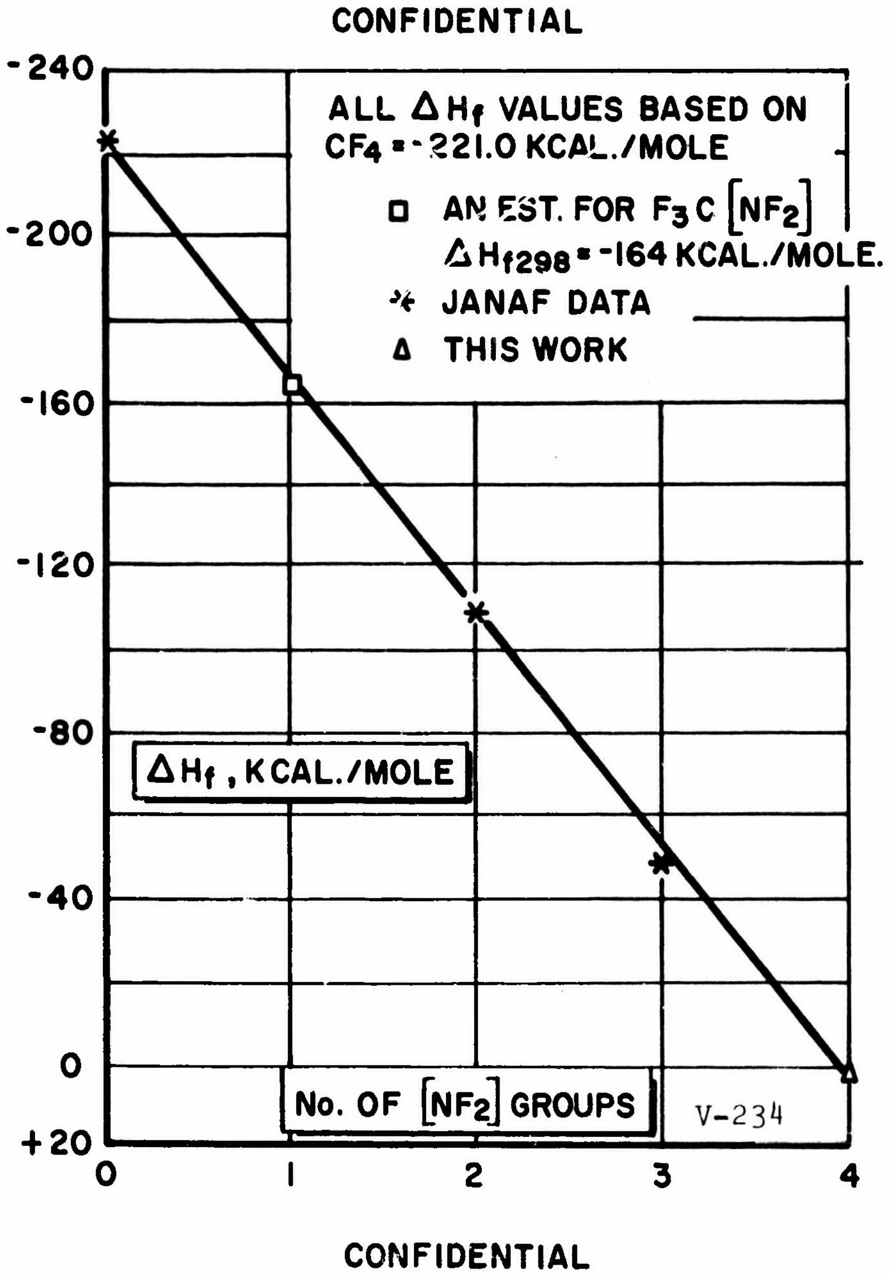
$$\Delta H\overset{o}{f}_{298.15}\,(g) = +9.8 \text{ kcal./mole}$$

(C) The heats of formation of the Delta-CF_4 family of NF_2-substituted fluorocarbons may be plotted against the number of (NF_2) groups/molecule (see Figure 1). They seem to form practically a straight line. Also from this plot the missing member of the family, the mono(difluoroamino) substituted carbon tetrafluoride, $CF_3(NF_2)$, is estimated to have a $\Delta Hf_{298.15}$ of about -164 kcal./mole.

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

1. Introduction (U)

(U) TVOPA is a high energy compound supplied by Rohm and Haas Company. Its shock sensitivity is such that the sample had



(U) Fig. 1 - Change in Heat of Formation with a Number of Difluoroamino Groups in Carbon Tetrafluoride Family of Compounds to be shipped as a 10% solution in methylene chloride. Unfortunately, the processes of solution and recovery from solution gave samples of varying quality as evidenced by large variations in the heat of combustion.

2. Equipment (U)

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

3. Materials (U)

(U) The sample, a 10% solution of purified TVOPA in methylene chloride, was prepared for combustion by stirring and pumping at low pressures (about 1 mm. Hg) to remove most of the methylene chloride. Analysis of the sample indicated the amount of solvent remaining was from 2 to 26 mg./g. of TVOPA, varying roughly with the time of pumping (see Table V).

Table V

(U) Variation of Chloride Content with Sample Treatment

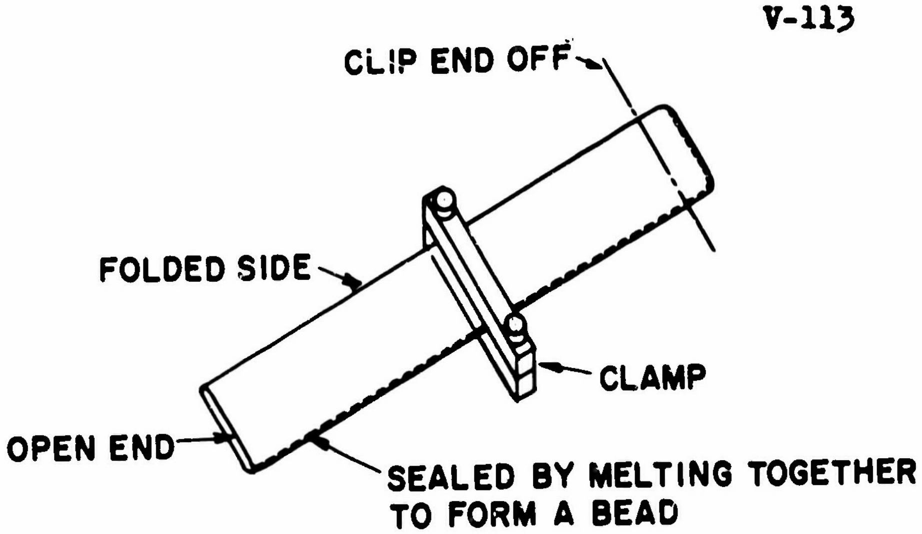
Treatment of Sample[a]	mg. Chloride/ g. Sample
Pumped on for ~3 hrs. at 25°C.	21 to 27
Warmed to 50°C. while pumping ~2 hrs.	6 to 13
Pumped at 25°C. over weekend, 3 days	2 to 3

[a] All samples were stirred and pumped simultaneously.

(U) 2-Octanone was used as a solvent for combustion studies, since neat TVOPA detonates under bomb conditions. Two samples of 2-octanone were used. A limited amount of a sample made 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% water.

4. Procedure (U)

(U) The following procedure was used to determine sample weights. Referring to Figure 2, a small clamp was placed on a weighed Mylar polyester bag and the weight of the clamp and bag determined. TVOPA was added to the open end and the bag was sealed and reweighed. The empty half of the bag was opened, filled with the appropriate amount of 2-octanone, resealed, and weighed. The clamp was then removed and the two substances mixed by manipulation of the bag. This procedure avoided loss of the mixture by liquid leakage or evaporation, since the quality of the seals could be checked before mixing.



(U) Fig. 2 - Clamp for Determining Sample Weights

(U) The calorimeter was calibrated with NBS benzoic acid. The calorimeter equivalent was 3423.35 cal./°C. with a standard deviation of 0.73 cal./°C. for ten experiments.

(U) The sample was burned in 40 atm. of oxygen, with 10 cc. of water in the bomb. Clean combustions required keeping the total calories around 6,500 and keeping the ratio of the weight of TVOPA to the weight of 2-octanone below 1.7. After each combustion the solution in the bomb was quantitatively recoverd by washing the bomb interior. Analyses were made on the bomb washings for chloride, nitrogen, and fluoride.

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

5. Results and Discussion (U)

(U) Results of the 2-octanone experiments are given in Table VI and of the polyester film in Table VII.

Table VI

(U) Heat of Combustion of 2-Octanone

	Sample 1 $-\Delta E_c^{\circ}/M$ (cal./g.)		Sample 2[a] $-\Delta E_c^{\circ}/M$ (cal./g.)
	9,401.1		9,372.9
	9,414.8		9,365.1
	9,387.4		9,364.9
	9,399.7		9,357.7
	9,398.5		9,370.6
	9,399.1		9,372.5
	9,395.0		9,370.0
Ave.	9,397.0 = ±2.0 cal./g.	Ave.	9,367.7 = ±1.9 cal./g.

[a] This sample contained about 0.3% water.

Table VII

(U) Heat of Combustion of Polyester Film

$-\Delta E_c^{\circ}/M$ (cal./g.)
5,464.5
5,466.7
5,467.0
5,466.3
5,465.4
5,464.4
5,468.9
5,466.2 = ±0.6 cal./g.

(U) The average value for 2-octanone Sample No. 1, which was made by preparative chromatography, is in good agreement with 9397.5 cal./g. reported by Geiseler and Ratzsch (4).

(U) Results of analyses of bomb washings in the TVOPA experiments are given in Table VIII.

Table VIII

(U) Results of Analyses of Bomb Washings

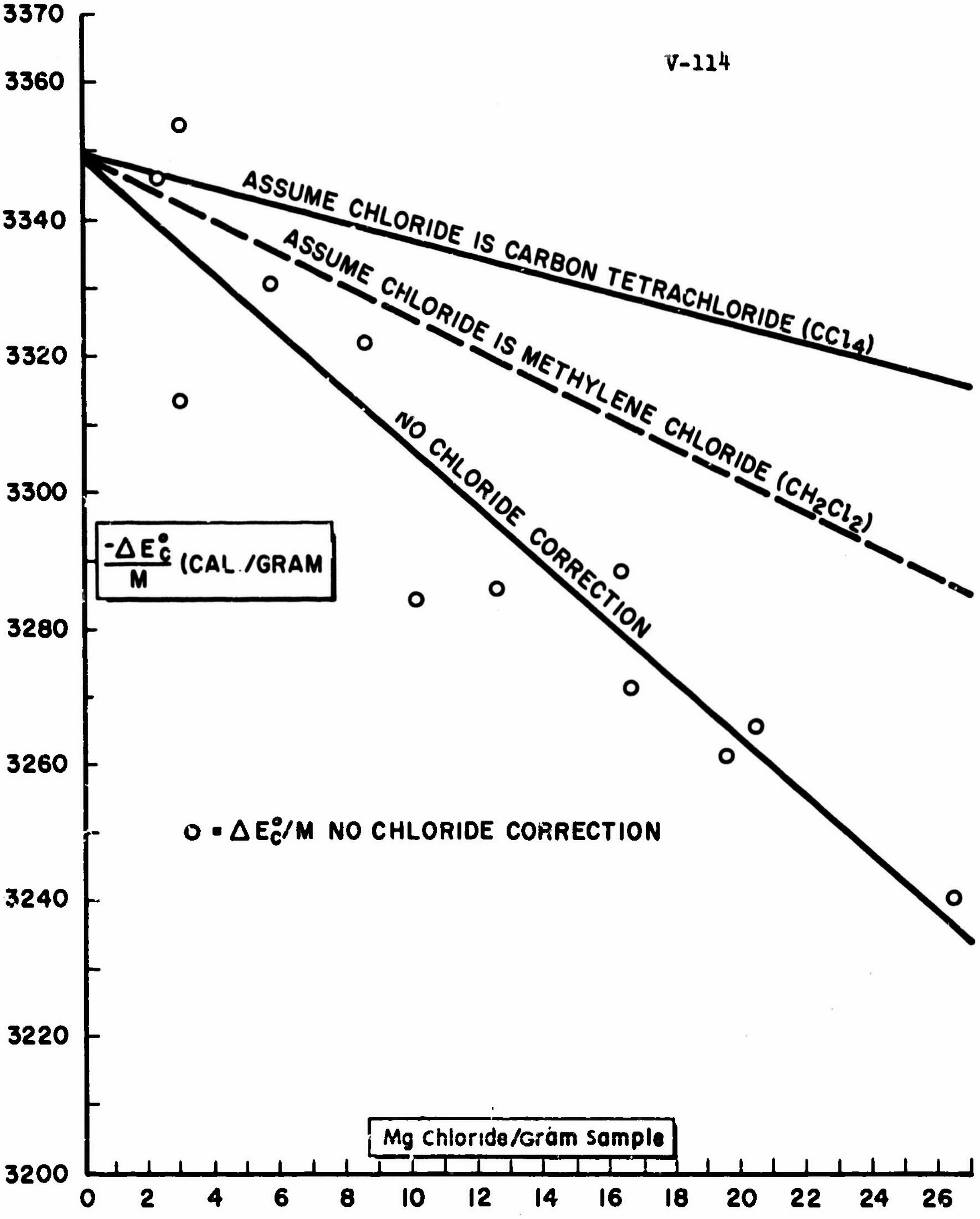
Experiment No.	Fluoride %	Chloride %	Nitrogen %
1	92.9	16.2	13.2
2	96.8	11.6	10.9
3	98.0	8.1	12.0
4	98.4	7.1	10.0
5	99.7	4.1	12.0
6	99.8	11.8	12.2
7	97.8	12.4	12.1
8	97.7	1.5	9.3
9	96.3	1.8	11.4
10	99.4	1.1	11.2
11	100.2	4.1	11.0
12	100.0	10.1	11.4

(U) The fluoride analyses are considered to check the empirical formula within experimental error. The nitrogen analyses were used to correct for nitric acid formation. The chloride analyses indicated that prolonged pumping was required to remove most of the methylene chloride solvent (see Table VIII).

(U) Results of the TVOPA combustion experiments are given in Table IX.

(C) For calculation of the "Washburn corrections," the following data were taken from the Rohm & Haas report (5): density 1.535 g./cc.; specific heat, 0.4 cal./g.°C.; and $(\partial E/\partial P)_T$, -0.0038 cal./g. atm.

(C) For the reaction $CH_2Cl_2 + O_2(g) \rightarrow CO_2(g) + 2\ HCl(aq.)$, a heat of reaction of 1707.2 cal./g. was calculated from data in National Bureau of Standards Technical Note 270-1. From this heat and the grams of CH_2Cl_2 per gram of sample, a $-\Delta E_c^\circ/M$ values from calculated (Table IX). A plot (Figure 3) of these $-\Delta E_c^\circ/M$ values from Table V against the mg. of chloride found per gram of sample shows an apparent dependence on the amount of chloride found. If the $-\Delta E_c^\circ/M$ values are corrected for chloride assuming it is all CH_2Cl_2, a trend in $-\Delta E_c/M$ with chloride is still apparent.



(U) Fig. 3 - Extrapolation to Zero Chloride Concentration in the Heat of Combustion of TVOPA

Even a correction assuming the chloride was all present as CCl_4 would not completely eliminate the trend in $-\Delta E_c^\circ/M$ with chloride content. The chloride content also had an apparent dependence on the purification treatment, i.e., stirring, warming at 50°C., and time of pumping (see Table IX). In order to obtain a zero chloride value for $-\Delta E_c^\circ/M$, a straight line fit was made by a least squares treatment to the data plotted in Figure 3 and listed in Table IX. The intercepts of these lines at zero chloride content were for $\Delta E_c^\circ/M = 3{,}348.9 \pm 3.7$, $-3{,}348.9 \pm 3.8$, $-3{,}348.6 \pm 3.9$ cal./g. The standard deviations of the respective $-\Delta E_c^\circ/M$ values in Table IX from the least squares lines were calculated from the equation $\sigma = \Sigma X_i/n(n-2)$. These σ values, along with the heats of combustion calorimetry, was satisfactory. However, the uncertainty in the intercept of the least square line, due to scatter in the $\Delta E_c^\circ/M$ values and due to uncertainty in the chloride values, was calculated to be ±7.2 cal./g. This uncertainty does not include any uncertainty due to an error in the assumption that the $\Delta E_c^\circ/M$ values vary linearly with the chloride content from none to 25 mg. chloride per gram of sample.

Table IX

(U) Results of TVOPA Combustion Experiments

Experiment No.	Mg. Chloride/ g. Sample	Calories		
		A[a]	B[b]	C[c]
1	26.5	3,241.0	3,290.7	3,319.5
2	20.5	3,265.2	3,304.7	3,327.3
3	12.7	3,290.9	3,315.5	3,329.2
4	10.1	3,286.0	3,305.3	3,316.2
5	5.8	3,330.8	3,342.1	3,348.2
6	16.4	3,289.3	3,321.0	3,338.8
7	19.6	3,261.0	3,297.0	3,317.6
8	2.3	3,345.5	3,349.9	3,352.4
9	3.0	3,354.3	3,360.2	3,363.4
10	3.0	3,314.1	3,317.9	3,320.0
11	8.6	3,322.6	3,339.7	3,349.1
12	16.8	3,271.2	3,303.2	3,321.4

[a] No correction for chloride in sample.

[b] Corrections made assuming the chloride was from CH_2Cl_2.

[c] Corrections made assuming the chloride was from CCl_4.

(C) The average intercept of the least squares lines, -3,348.9 cal./g., gives a ΔH_c° of -1613.0 ± 3.5 kcal./mole for the reaction:

$$C_9H_{14}O_3N_6F_{12}(l) + 8\ O_2(g) \rightarrow 9\ CO_2(g) + 3\ N_2(g) + H_2O(l) + 12(HF\cdot 30\ H_2O).$$

(C) The $\Delta Hf^\circ_{298.15}$ calculated from this ΔH_c° and from data in National Bureau of Standards Technical Note 270-1 was found to be -217.4 ± 3.5 kcal./mole for TVOPA (2).

(C) This result may be compared with the ΔH_c° = 1623 kcal./mole reported by Rohm & Haas (5) which yields a $\Delta Hf^\circ_{298.15}$ of -207.3 ± 3.0 kcal./mole. It should be noted that this value, -207.3 kcal./mole, does not involve any $-\Delta E_c^\circ/M$ extrapolation to zero chloride content.

C. HEAT OF DISSOCIATION OF NITROGEN TRIFLUORIDE (U)

1. Introduction (U)

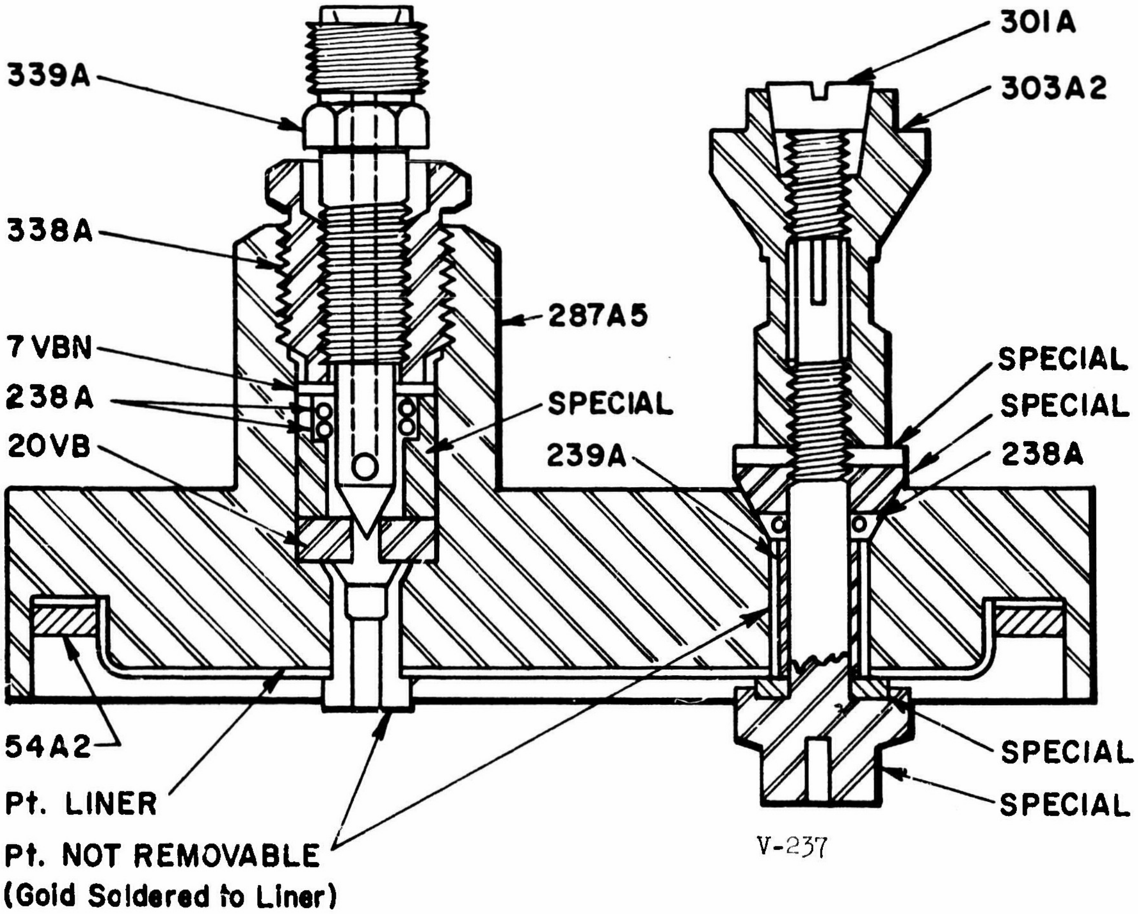
(U) Nitrogen trifluoride has proved to be a useful oxidizer in calorimetry. Its present heat of formation, however, is dependent on the value adopted for aqueous hydrogen fluoride and is uncertain by perhaps as much as 2 kcal./mole. In working with nitrogen trifluoride as a calorimetric oxidizer, it has been noted that, when mixtures of nitrogen trifluoride and a gaseous fuel are detonated, any excess nitrogen trifluoride is dissociated to the elements. This suggested the possibility of determining the heat of dissociation of nitrogen trifluoride by measuring the heats of explosion of mixtures of hydrogen and nitrogen trifluoride, with the latter present in varying degrees of excess. Experiments have been carried out and a value for the heat of formation of nitrogen trifluoride obtained which differs significantly from the presently accepted "best" value.

2. Equipment (U)

(U) A platinum-lined bomb was revamped by Parr Instrument Company according to the bomb design shown in Figure 4, and is the same as the experimental bomb head built by Parr as described in our first quarterly report. The revamped bomb performed very well except for the two-piece ignition post, which was replaced by an all-platinum one-piece post during the course of the work. A rotating bomb calorimeter was used for the heat measurements. A vacuum system equipped with a precision Wallace-Tiernan pressure gauge was used for bomb charging operations.

3. Materials (U)

(U) Nitrogen trifluoride was purified by low temperature distillation. Infrared and mass spectrometry and gas chromatography



(U) Fig. 4 - New Bomb Head Design

led to an estimate of better than 99.9% purity. The hydrogen was a commercial "ultra-pure" grade. No impurities were detected by mass and infrared spectrometry.

4. Procedure

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

The bomb was placed in a conventional combustion calorimeter and the charge was fired by discharging a condenser through a fine platinum fuse wire. The condenser voltage before and after firing was a measure of the ignition energy. The calorimeter was calibrated with National Bureau of Standards benzoic acid 39 i. An average of 0.55 g. of acid was used and the bomb was charged with 1 ml. of water and 30.3 atm. of oxygen. The calorimeter equivalent was 3436.17 cal./deg. with a standard deviation of 0.52 cal./deg. for five experiments. The calorimeter equivalent adjusted to conditions for the dissociation experiments was 3436.84 cal./deg.

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

5. Results

The results for six excess nitrogen trifluoride experiments are given in Table X. The correction for fluorine attack on the fluorocarbon was taken as 123.7 kcal./mole of carbon tetrafluoride formed (23). The enthalpy of formation of platinic fluoride was estimated at -180 kcal./mole and of auric fluoride as -130 kcal./mole. The runs were adjusted to an exact quantity of 0.7500 g. of nitrogen trifluoride using an interative procedure for the enthalpy of dissociation of nitrogen trifluoride. Results for the 100% excess nitrogen trifluoride experiments are given in Table XI. These runs are adjusted to an exact quantity of 1.3800 g. of nitrogen trifluoride. The difference between the two sets of experiments, 273.7 cal., is the enthalpy of dissociation of 0.6300 g. of nitrogen trifluoride at constant volume. Employing atomic weights of 14.0067 and 18.9984 for nitrogen and fluorine, respectively, there is derived for the reaction:

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

$$\Delta Er_{298} = 30.85 \text{ kcal.}$$

Calculating to constant pressure conditions:

$$\Delta Hf_{298} = 31.44 \text{ kcal.}$$

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

$$\Delta Hf_{298}(NF_3,\ g) = 31.44 \text{ kcal./mole}$$

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

D. HEAT OF REACTION OF SULFUR AND NITROGEN TRIFLUORIDE

1. Introduction

In order to relate nitrogen trifluoride oxidation calorimetry to the fluorine combustion work at Argonne National Laboratory, work is in progress on the heat of reaction of sulfur and nitrogen trifluoride. The heat of formation of sulfur hexafluoride has been established at Argonne, and an accurate heat of reaction would give an independent path to the heat of formation of nitrogen trifluoride.

2. Equipment

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

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

Table X

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

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

Table XI

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

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

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

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

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

3. Materials

Two samples of sulfur were burned in nitrogen trifluoride. The first, laboratory designation DOW 1-S, was supplied by the Inorganic Research Group of the Analytical Laboratories of The Dow Chemical Company. X-Ray analysis showed the sample to be of the orthorhombic crystal structure, and neutron activation analysis indicated 40 ppm oxygen and 0.1% chlorine. Infrared analysis showed no chlorine containing organics. The purity was taken as 99.99%. A second sample, USBM-47, was supplied by Mr. W. D. Good, U. S. Bureau of Mines, Bartlesville, Oklahoma. This material was of the same batch that was used at Argonne National Laboratory for the determination of the heat of reaction of sulfur and fluorine. An accompanying analysis showed the sulfur sample to be of the orthorhombic variety and to contain total impurities amounting to 109 ppm. The sample purity was taken as 99.99%.

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

4. Nature of the Reaction

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

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

Mass spectral and infrared analysis showed sulfur hexafluoride gas as the only fluoride of sulfur. A small amount of nitrogen trifluoride was thermally dissociated to the elements and necessitated a correction. The molybdenum fuse wire burned quantitatively to molybdic hexafluoride (MoF_6)(g) with the exception of a small easily weighed piece. Data for this correction were available (6). Reaction with the crucible apparently did not occur, as weight checks showed a constant mass. Ignition energy was measured by discharging a standardized capacitor. The sum of the above corrections amounted to approximately 1-2% of the total measured heat.

5. Experimental Procedure

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

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

Immediately after the heat measurement the product gases were analyzed for free fluorine by reaction with mercury (7). The analysis vessel consisted of a 250 ml. round flask with a tube extension on the bottom to contain 3-5 ml. of mercury. The flask was evacuated, then filled to one atmosphere with product gases from the bomb. The gases were allowed to condition the bulb and vacuum system for a minimum of four hours before a gas sample was taken for quantitative analysis. This technique was checked out both with mixtures of fluorine and nitrogen and with fluorine of 99.5% purity. Recoveries on these gases averaged ±0.2% of theory. From the gas sampling, one could calculate the grams of fluorine per gram of gas and from this the moles of nitrogen trifluoride decomposed. The residual gases, sulfur hexafluoride, nitrogen trifluoride, and nitrogen, were then checked by mass and infrared spectroscopy.

6. Results

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

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

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

Since there is no change in the number of moles of gas during the reaction, ΔE_c° is equal to ΔH_c°. Employing a heat of formation of sulfur hexafluoride of -291.77 kcal./mole (8) there is derived:

$$\Delta H f^\circ_{298}\ (NF_3,\ g) = -31.75 \pm 0.20\ \text{kcal./mole}$$

Table XII

Experimental Combustion Data for the Sulfur-Nitrogen Trifluoride Reaction

$E = -3203.7 \pm 1.5$ cal./deg.

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

$\sigma = \pm 6$ cal./g.

[a] Denotes Dow sulfur sample.

[b] Denotes Bureau of Mines sulfur sample.

This result is in agreement within experimental error with the dissociation work discussed earlier in this report. The only other datum for nitrogen trifluoride which does not involve hydrogen fluoride as a product is the heat of combustion of boron in nitrogen trifluoride by Ludwig and Cooper (9) of -239.7 ± 1.2 kcal./mole. Using the most recent heat of formation for boron trifluoride of -271.65 kcal./mole (10), there is derived for nitrogen trifluoride a $\Delta H f^\circ_{298} = -32.0 \pm 1.5$ kcal./mole, in agreement within experimental error with our values.

E. HEAT OF FORMATION OF AQUEOUS HYDROGEN FLUORIDE

One of the purposes of the work on nitrogen trifluoride was to supply a heat of formation of aqueous hydrogen fluoride. The two values for nitrogen fluoride given in this report, -31.44 ± 0.30 and -31.75 ± 0.20 kcal./mole, are independent of the heat of formation of hydrogen fluoride. An average of -31.6 kcal./mole can be combined with previous work from this laboratory (11) on the heat of reaction of nitrogen trifluoride and hydrogen to form hydrogen fluoride (1 in 123 H_2O) to derive for hydrogen fluoride (1 in 123 H_2O) a heat of formation of -77.03 kcal./mole. This can be taken as the same as hydrogen fluoride (1 in 100 H_2O) according to heat of dilution data from Cox and Harrop (12). Several other recent investigations can be compared with this result. Teflon fluorocarbon has been burned in oxygen (13) and in fluorine (14). Combination of these data yields ΔH = -170.0 kcal. for the reaction:

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

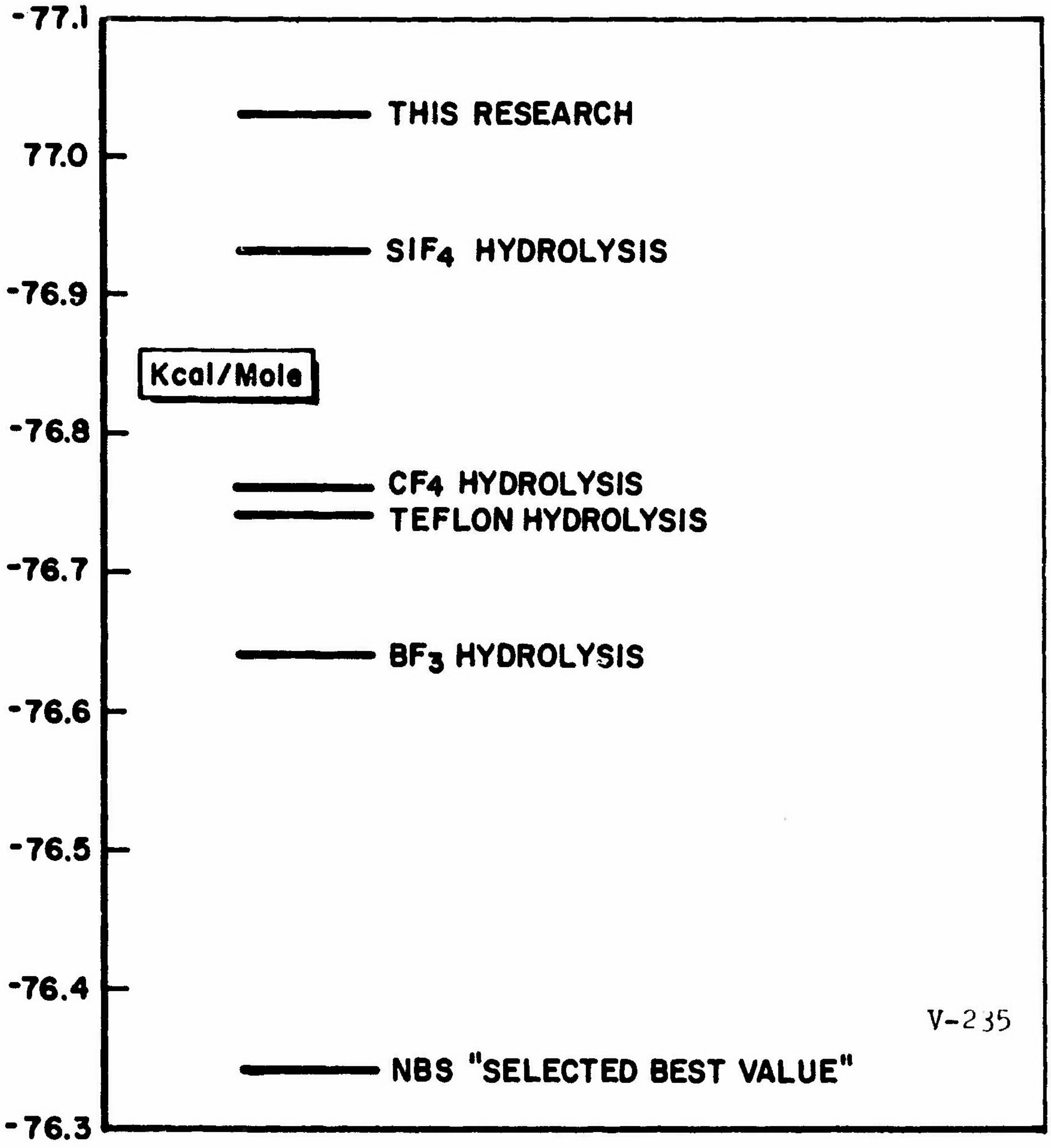
From this is derived a $\Delta H^\circ_{f\,298}$ for hydrogen fluoride (1 in 10 H_2O) of -76.66 kcal./mole, and appropriate dilution data yield for hydrogen fluoride (1 in 100 H_2O) a $\Delta H^\circ_{f\,298}$ of -76.74 kcal./mole. Measurements of the heat of hydrolysis of silicon tetrafluoride (15) combined with work on the heat of formation of silicon dioxide (16) and silicon tetrafluoride (16) yield for hydrogen fluoride (1 in 650 H_2O) a value of -77.04 kcal./mole, which when adjusted to hydrogen fluoride (1 in 100 H_2O) yields a $\Delta H^\circ_{f\,298}$ of -76.93 kcal./mole.

(U) Domalski and Armstrong (17) reported the heat of combustion of graphite in fluorine, which can be combined with the heat of hydrolysis of carbon tetrafluoride reported by Cox, Gundry, and Head (18) to yield for hydrogen fluoride (1 in 20 H_2O) a $\Delta H^\circ_{f\,298}$ of -76.71 kcal./mole. This is adjusted to -76.76 kcal./mole for hydrogen fluoride (1 in 100 H_2O). A final value is derived from measurements of the heat of combustion of boron in fluorine (10), the heat of combustion of boron in oxygen (19) to give aqueous fluoboric acid, and the heat of solution of boron trifluoride in aqueous hydrogen fluoride (20) to yield the heat of formation of hydrogen fluoride (1 in 3 H_2O) as -76.34 kcal./mole. These results are presented graphically in Figure 5, along with the present "selected best value" of the National Bureau of Standards which is also used for the JANAF Thermochemical Tables. The need for revision is obvious. A final selection of a new "best value" will be deferred pending completion of pertinent work at the National Bureau of Standards on direct combination of hydrogen and fluorine in a flame calorimeter and at Argonne National Laboratory on the heats of formation of alkali metal fluorides.

F. HEAT OF FORMATION OF P-BEP (U)

1. Introduction (U)

(C) P-BEP is the code name for poly[1,2-bis(difluoroamino)-2,3-epoxypropane], an energetic solid propellant binder supplied to us by Dr. K. D. Oetting of Shell Development Company. Estimated heats of formation for various grades of P-BEP are given in Table XIII which is taken from reference (21).



(U) Fig. 5 - Heat of Formation of Hydrogen Fluoride (1 in 100 H_2O) by Various Approaches

Table XIII

(C) Heat of Formation and Composition of P-BEP

	P-BEP (ideal)	P-BEP (with initiator)	P-BEP-XL-Binder (crosslinked)
ΔH_f, kcal./100 g.	-26.988	-36.024	-43.675
Analysis, wt. %			
C	22.5	23.2	29.4
H	2.5	2.7	3.3
O	10.0	10.8	14.1
N	17.5	17.1	15.4
F	47.5	46.3	37.8

(U) The PBEP samples actually used by UTC for evaluation work (21) did not correspond exactly to any of the above grades. Average analytical data supplied to UTC by Shell for the batches used for evaluation work are given in Table XIV and are taken from pages 19 and 20 of reference (21). The Shell analytical data for our P-BEP sample (92313-88c) and the Dow analytical data for this same sample are also listed in Table XIV. The material used for the heat of combustion studies is seen to correspond closely to that used by UTC for evaluation work.

Table XIV

(C) Elemental Analysis of P-BEP

Element	(92313-88c) Shell	Dow	UTC[a]
% C	25.4	26.83	26.86
% H	3.1	3.26	3.39
% N	15.7	15.28	15.32
% F	40.6	40.09	41.20
% Cl	1.6	0.19	
% O (by diff.)	13.6	14.35	

[a] Average Shell development Company analytical data for several batches supplied to UTC. See reference (21) pp. 16-20.

2. Equipment (U)

(U) A typical rotating-bomb calorimeter, a platinum-lined combustion bomb, and standard oxygen combustion techniques were employed.

3. Material (U)

(U) Carbon, hydrogen, and nitrogen were determined by microanalysis of a part of each combustion sample, while fluoride and chloride were measured in the solutions recovered after the calimetry. An earlier study of TVOPA showed the necessity of complete stripping of the solvent for good results. The low residual solvent as indicated by the low chloride analysis was achieved by prolonged stripping under vacuum. Stripping time versus chloride content data are given in Table XV.

Table XV

(U) Residual Solvent as a Function of Stripping Time

Experiment Number	Chloride mg.	Chloride Wt. % of Sample	Stripping Time[a] days
1	1.35	0.21	3
2	0.90	0.20	10
3	0.55	0.11	18
4	0.20	0.05	18
5	0.60	0.11	15
6	1.00	0.17	11

[a] Time held under vacuum (<0.01 mm.) at room temperature.

(U) 2-Octanone was used as a solvent for heat of combustion experiments since neat P-BEP detonated under bomb conditions. The 2-octanone contained about 0.3% water and its heat of combustion was determined. Polyester film used to contain the solution was also evaluated by heat of combustion studies. Thermochemical data are given in Table XVI. Heat of solution data are given in Section G of this report.

4. Procedure (U)

(U) The P-BEP sample was placed into a weighed (Mylar) polyester film bag. The P-BEP and bag were weighed while the bag was open. The 2-octanone solvent was added and the bag + P-BEP + solvent was sealed and weighed. Sufficient solvent and sample were used to give a final combustion solution of about 50% P-BEP by weight. The sealed bag was manipulated until all of the P-BEP had dissolved. The filled bag was then placed in a crucible and burned in 40 atmospheres of oxygen in a platinum-lined rotating bomb calorimeter. The bomb contained 10 cc. of water.

(U) At room temperature the P-BEP was difficult to transfer cleanly into the bag without leaving small pieces of P-BEP on the open end of the bag. The sample was in between being a soft-tacky plastic and a brittle easily fractured solid. Alternately warming the P-BEP just above room temperature and cooling with liquid nitrogen greatly facilitated handling the sample. The warm soft P-BEP was scraped onto a spatula and then cooled. The cold sample fractured into particles which were then easily put into the bag through a rolled paper tube used as a funnel. This procedure eliminated tacky P-BEP particles sticking to the open end of the bag with the possibility of sample loss during the sealing operation. The entire loading procedure was done in a glove bag filled with dry nitrogen to prevent condensation and entrapment of water in the sample. The P-BEP was handled at all times with protective clothing because of the possible explosive hazard involved.

5. Results (U)

(C) The results of the calorimetric work were processed by means of the computer program for C-H-O-N-F compounds discussed elsewhere in this report. Constant factors needed as input for this program are given in Table XVI and other variables in Table XVII. The $-\Delta E_c^\circ/M$ values calculated by the computer are then slightly corrected for residual methylene chloride to give the final $-\Delta E_c^\circ/M$ values. The heat of solution of P-BEP in 2-octanone reported in the next section combined with the average $-\Delta E_c^\circ/M$ yields $-\Delta E_c^\circ/M$ for neat P-BEP as 3629.0 cal./g. Assuming a molecular weight of 100.00, the empirical formula given in Table XVI,

$$\Delta E_c^\circ = -362.9 \text{ kcal./mole}$$

which refers to the process:

$$C_{2\cdot238}H_{3\cdot240}O_{0\cdot898}N_{1\cdot094}F_{2.114} + 2.0705\ O_2(g) \rightarrow 2.238\ CO_2(g) + 2.114\ HF\ (\text{in } 30\ H_2O) + 0.563\ H_2O(1) + 0.547\ N_2(g)$$

(C) Calculating to constant pressure conditions:

$$\Delta n(g) = +0.7145 \text{ mole}$$

$$\Delta nRT = +0.4 \text{ kcal./mole}$$

$$\Delta H_c^\circ = \Delta E_c^\circ + \Delta nrt = -362.9 + 0.4 = -362.5 \text{ kcal./mole}$$

Table XVI

(U) Constant Factors in P-BEP Combustion Calculations

Empirical formula of P-BEP	$C_{2.238}H_{3.240}O_{0.898}N_{1.094}F_{2.114}$
Empirical formula of 2-octanone	$C_8H_{16}O$
Empirical formula of film	$C_{10}H_8O_4$
Empirical formula of fuse	$C_{1.000}H_{1.774}O_{0.887}$

Density of P-BEP (estimated)	1.5 g./cc.
Density of 2-octanone	0.818 g./cc.
Density of film	1.380 g./cc.
Density of fuse	1.5 g./cc.

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

$(\delta E/\delta P)T$ of P-BEP (estimated)	-0.00380 cal./g./atm.
$(\delta E/\delta P)T$ of 2-octanone	-0.00899 cal./g./atm.
$(\delta E/\delta P)T$ of film	-0.00800 cal./g./atm.
$(\delta E/\delta P)T$ of fuse	Negligible

ΔE_c° of 2-octanone	-1201.08 kcal./mole
ΔE_c° of film	-1050.31 kcal./mole
ΔE_c° of fuse	-103.35 kcal./mole

C_p of P-BEP (estimated)	0.4 cal./g./°C.
C_p of 2-octanone	0.5094 cal./g./°C.
C_p of film	0.315 cal./g./°C.
C_p of fuse	0.4 cal./g./°C.

$E_{calor.}$	3423.35 cal./°C.

Table XVII

(U) Heat of Combustion Experiments for P-BEP

	Experiment No.					
	1	2	3	4	5	6
Wt. P-BEP, g.[a]	0.634363	0.439734	0.508946	0.415395	0.534687	0.573994
Wt. 2-octanone, g.[a]	0.560928	0.575608	0.569071	0.435045	0.481840	0.505261
Wt. film, g.[a]	0.129521	0.116588	0.089470	0.093220	0.095263	0.095980
Wt. fuse, g[a]	0.002946	0.004205	0.005929	0.005137	0.005315	0.003993
Moles HNO_3 (X 10^4)	9.103	7.139	8.639	6.711	8.353	8.710
Moles HF (X 10^2)	1.339	9.278	1.074	0.8675	1.128	1.211
Mass, added platinum, g.	-7.843	0	0	0	0	0
T_i, °C.	22.72497	22.74632	22.72899	23.47351	22.92516	22.83212
T_f, °C.	25.18362	25.04498	25.04481	25.29597	25.02857	25.04332
$\Delta t_{corr.}$, °C.	0.04471	0.06795	0.06998	0.03845	0.06332	0.06318
$-\Delta E_c^\circ/M$, cal./g.[b]	3613.70	3627.90	3632.01	3623.25	3611.45	3627.80
$-\Delta E_c^\circ/M$, cal./g.	3618.6	3632.6	3634.5	3624.4	3614.0	3631.8

[a] Weighed in air against brass weights; values in grams.

[b] Uncorrected for residual solvent.

(C) The heat of formation depends on the selected value for HF (in 30 H_2O). For the present, the value adopted by the National Bureau of Standards in Technical Note 270-1 is employed to derive:

$$\Delta H f^{\circ}_{298} \text{ (P-BEP, s)} = -47.8 \pm 0.7 \text{ kcal./mole}$$

The uncertainty is taken as twice the overall standard deviation.

G. HEATS OF SOLUTION OF TVOPA AND P-BEP (U)

(U) The heats of solution of P-BEP and TVOPA in 2-octanone were measured in a Beckman 190B microcalorimeter. The calorimeter was originally designed by T. H. Benzinger and C. Kitzinger and is described in "Temperature: Its Measurement and Control in Science and Industry," C. M. Herzfeld, ed., Vol. III, Reinhold Publishing Co., New York, 1963, pp. 43-60.

(U) The mixing cell used was made of thin glass and is shown in Figure 6. Mercury was used to keep a vapor tight seal between components before mixing. P-BEP stuck to the glass and was easily covered by the mercury (solvent on both sides of the partition), while TVOPA was put in one side of the cell and the solvent in the other. Smooth mixing was accomplished by tumbling the cell end over end, which removed the mercury barrier between components.

(U) The final solutions were about 1% P-BEP or TVOPA in 2-octanone. Within experimental error of the combustion results, the heat of solution is taken to be the same as that of the 50% solutions used for the heat of combustion studies. The heat of solution results are given in Table XVIII and are consistent with the 2-3% precision expected of the calorimeter.

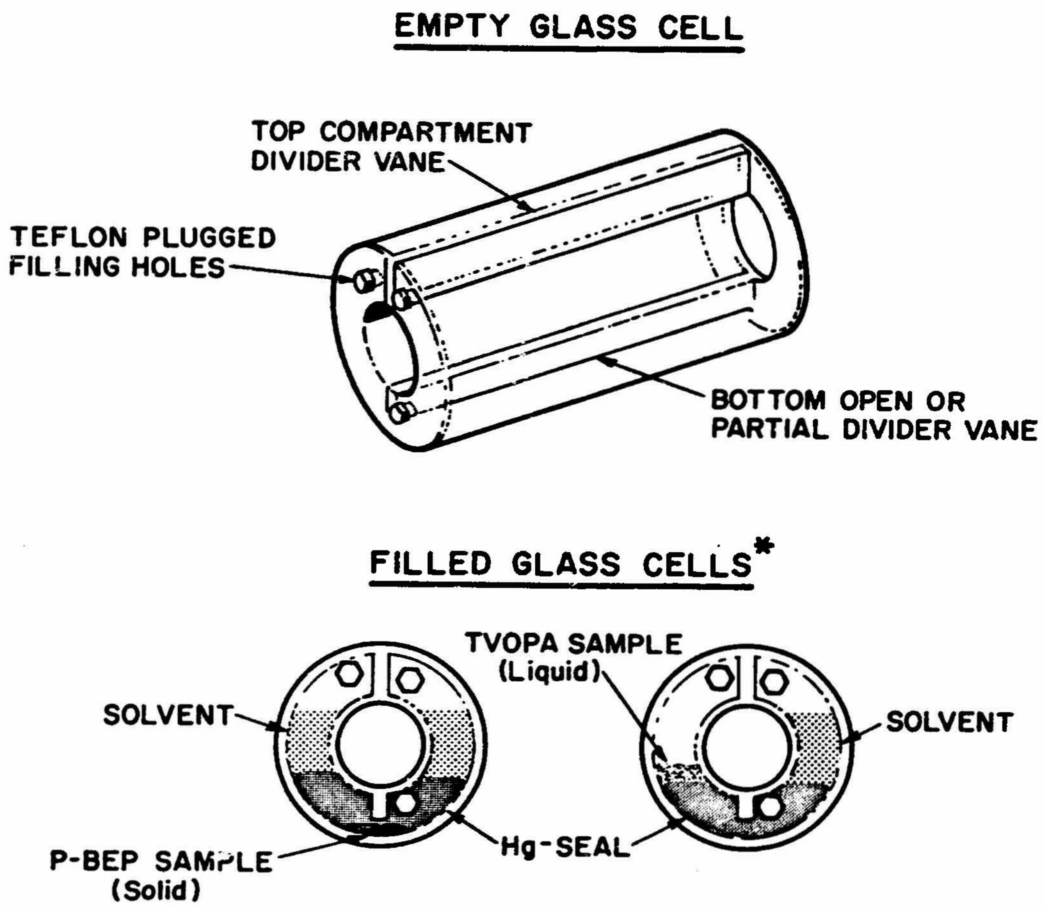
Table XVIII

(U) Heats of Solution of P-BEP and TVOPA in 2-Octanone

Material	Mass Sample g.	2-Octanone cc.	Measured Calories	ΔH solution cal./g.
P-BEP	0.1861	22.5	0.566	-3.04
P-BEP	0.1271	15.4	0.371	-2.92
TVOPA	0.0649	8.0	0.296	-4.55
TVOPA	0.0655	8.0	0.305	-4.66

H. EQUIPMENT AND TECHNIQUES (U)

(U) Significant improvements in equipment and procedures were made during the year. The platinum-lined combustion bomb heads were revamped by Parr Instrument Company to specifications



*PRIOR TO MIXING BY END OVER END ROTATION

(U) Fig. 6 - Mixing Cell

developed from experience at the Thermal Laboratory. These heads have been in service for some time and are a great improvement with respect to leakage under vacuum and corrosion due to inadequate seals. New heads for our nickel combustion bombs were machined at the Dow shops. These heads incorporate new needle valves of unique design and have proved to be highly serviceable.

(U) Also developed during the year were computer programs for the reduction of bomb calorimetric data to standard states. Most important of these is the program for C-H-O-N-F compounds which follows the outline given in NAVWEPS Report 8686, Technical Report 154 from U. S. Naval Propellant Plant, Indian Head, Maryland, by E. E. Baroody, G. J. Wynne, and M. F. Zimmer, August, 1964. These programs should give us increased accuracy in data reduction as well as saving manpower formerly occupied in hand calculations.

I. WORK IN PROGRESS (U)

1. Trifluoromethoxydifluoroamine, CF_3ONF_2 (C)

(C) A sample of trifluoromethoxy difluoroamine was synthesized and purified by the Synthesis Group (see next section of the report). The sample was analyzed by explosion with an excess of hydrogen in a platinum-lined bomb and determination of the amount of carbon monoxide produced. This analysis showed a carbon content about 99% of theory. Molecular weight measurements indicated a low molecular weight impurity. Infrared spectrum of the sample showed bands tentatively identified as due to FNO, CO_2, and N_2O. Currently, various techniques are under trial for upgrading the sample. Passage over MnO_2 and Ascarite removed FNO and CO_2. A molecular sieve technique was attempted for N_2O removal, but extensive sample decomposition resulted. Further work is planned on this compound as well as the related compounds CF_3NF_2 and $CF_2(ONF_2)_2$.

2. Crystalline Lithium-Doped Beryllium Hydride (C)

(C) Several experiments on the heat of hydrolysis of crystalline BeH_2 from Ethyl Corporation have been completed. Interpretation of the results depend upon analytical work not yet completed. Completion of this work is anticipated early in 1967.

J. SYNTHESIS (U)

1. General (U)

(C) Trifluoromethoxydifluoroamine, CF_3ONF_2, was prepared by the photochemical reaction of trifluoromethylhypofluorite, CF_3OF, and N_2F_4.

$$CF_3OF + N_2F_4 \xrightarrow[\text{Corex filter}]{h\nu} CF_3ONF_2 + NF_3$$

N_2F_4 was obtained from an outside source, and the CF_3OF was prepared by passing carbon monoxide and fluorine in a nitrogen stream over a silver fluoride catalyst at 400°C.

$$CO + F_2 \xrightarrow[400°C.]{AgF} COF_2 + CF_3OF$$

Any carbonyl fluoride, COF_2, contaminating CF_3OF was removed by filtering with a sintered glass filter.

A sample of bis(trifluoromethyl)peroxide, CF_3OOCF_3, was prepared by the photochemical reaction of CF_3OF for 12 hrs. without the Corex filter.

$$2\ CF_3OF \xrightarrow[12\ hrs.]{h\nu} CF_3OOCF_3 + F_2$$

2. Experimental

a. Preparation of Trifluoromethyl Hypofluorite, CF_3OF

A gas stream consisting of 47 parts fluorine, 8 parts carbon monoxide, and 45 parts nitrogen was passed over a bed of silver fluoride at 400°C. The product was trapped in liquid oxygen. Any COF_2 obtained as a by-product was removed by low temperature filtration.

b. Preparation of Trifluoromethoxydifluoroamine, CF_3ONF_2

About 5.8 g. (0.055 mole) of N_2F_4 and 5.8 g. (0.055 mole) of CF_3OF were placed into a 5 l. vessel and irradiated for 24 hrs. with ultraviolet light through a 9700 Corex glass filter (eliminates wave lengths below 260 millimicrons). The reaction mixture was washed with 50% NaOH then with 50% H_2SO_4. Wash solutions were drawn into the partially evacuated reactor. After the first wash, the product was vacuum transferred to allow removal of the solution, then it was vacuum transferred back into the reactor for the next wash. The material was then codistilled and chromatographed on a 21-ft. Kel-F tetramer column (25% oil on Chromosorb W) at -65°C.

c. Preparation of bis(Trifluoromethyl)Peroxide, CF_3OOCF_3

About 9.2 g. (0.087 mole) of CF_3OF was placed into a 5 l. flask and irradiated with ultraviolet light (without filter) for 14 hrs. The crude material was codistilled and chromatographed as described under Section (2) above.

SECTION III

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) The purpose of this research is to identify the reactive intermediates and end-products of the decomposition and combustion of a BeH_2 - NH_4ClO_4 - plastisol-grade nitrocellulose (PGNC) propellant. The objective is to obtain an understanding of the combustion mechanism for the purpose of increasing the combustion efficiency of this propellant.

(C) It was postulated that at high temperature one or more intermediates might have enough thermal stability to cause a reduced efficiency in the combustion process. It is a well known fact that many Isp caluclations are based on an equilibrium type distribution. It is also well known that many types of combustion deviate significantly from equilibrium in regard to flame temperature (22), species concentration (23, 24), energy of reaction (25, 26), and percentage of fuel which has been ionized (26). The ionization effect is reported to be valid for propellants containing metals as fuels. The deviation of combustion products from the equilibrium composition is shown in the recent work of Croomes (27). It should, therefore, be anticipated that the types and amounts of transitory species present in a propellant combustion deviate substantially from that calculated by equilibrium thermodynamics. The experimental verification of this deviation is a difficult problem. The technique employed in such a study must be capable of resolving the decomposition and combustion into measurable but separate steps. Furthermore, the technique should be capable of supplying energy to simulate the steps of combustion. Finally, the technique should be able to identify types and to measure the concentrations of material in microsecond time intervals.

(U) Recently, Nelson et al. (28 - 30) have shown the technique of flash heating (pyrolysis) to be well suited to the formation and detection of short-lived atomic and molecular species in the vapor phase The technique involves the heterogeneous flash heating of small grids or strips suspended in an absorption cell in such a manner that 95-98% of the background light first passes through the cell before entering the spectrograph used for detection. The sample-supporting grids or strips are efficiently heated by absorption of an intense light pulse from a source similar in design and operation to that employed in conventional flash photolysis experiments.

(U) The technique of heating by flash photolysis is especially amenable to studying the kinetics of free radical combustion reactions. The photoflash creates free radicals in copious amounts in a short period of time. The subsequent spectroflash timing and firing characteristics of the apparatus are admirably suited to record the absorption spectra of these radicals. To a high degree, the photolytic and pyrolytic effects of the photoflash approximate the conditions in a flame. Thus, the technique of flash heating can be applied to the study of the various stages of combustion from the initial decomposition of the fuel and oxidizer to the final steps of deflagration.

(U) The object of this research was to study the flash pyrolytic decomposition of each propellant ingredient in a vacuum to determine its mode of decomposition. After this study, each ingredient was studied in the presence of selected gaseous products known to be generated from other ingredients. Data obtained from such studies provided an intimate knowledge of the various chemical reactions occurring when transitory active intermediates react during combustion.

(C) Once the data on the decomposition of each ingredient was collected, binary combinations of the ingredients were flash heated; in this way, the kinetics of the BeH_2 - NH_4ClO_4, NH_4ClO_4 - PGNE and BeH_2 - PGNC system could be related to the decomposition of each ingredient alone.

B. EXPERIMENTAL (U)

(U) A block diagram of the flash heating apparatus presently employed in studying the deflagration of propellant is shown in Figure 7 (31). The apparatus is similar in design to that of Norrish and co-workers (32), consisting of (a) a photoflash lamp and its energy source, (b) a spectroflash lamp which can be triggered at a present delay, (c) a spectrographic means of analysis, and (d) a reaction cell. The schematic diagram of the system is shown in Figure 8. The reaction cell, as seen in Figure 9 along with the spectroflash lamp and collimator, possess a removable tapered joint at one end, allowing access to the cell when solids suspended on the light-absorbing graphite substrate are introduced. Evacuation of the cell and introduction of gases are accomplished by using the stopcock and tapered side arm. That portion of the reaction cell directly in the line of the photoflash and the windows at each end are made from quartz. The rest of the cell is pyrex.

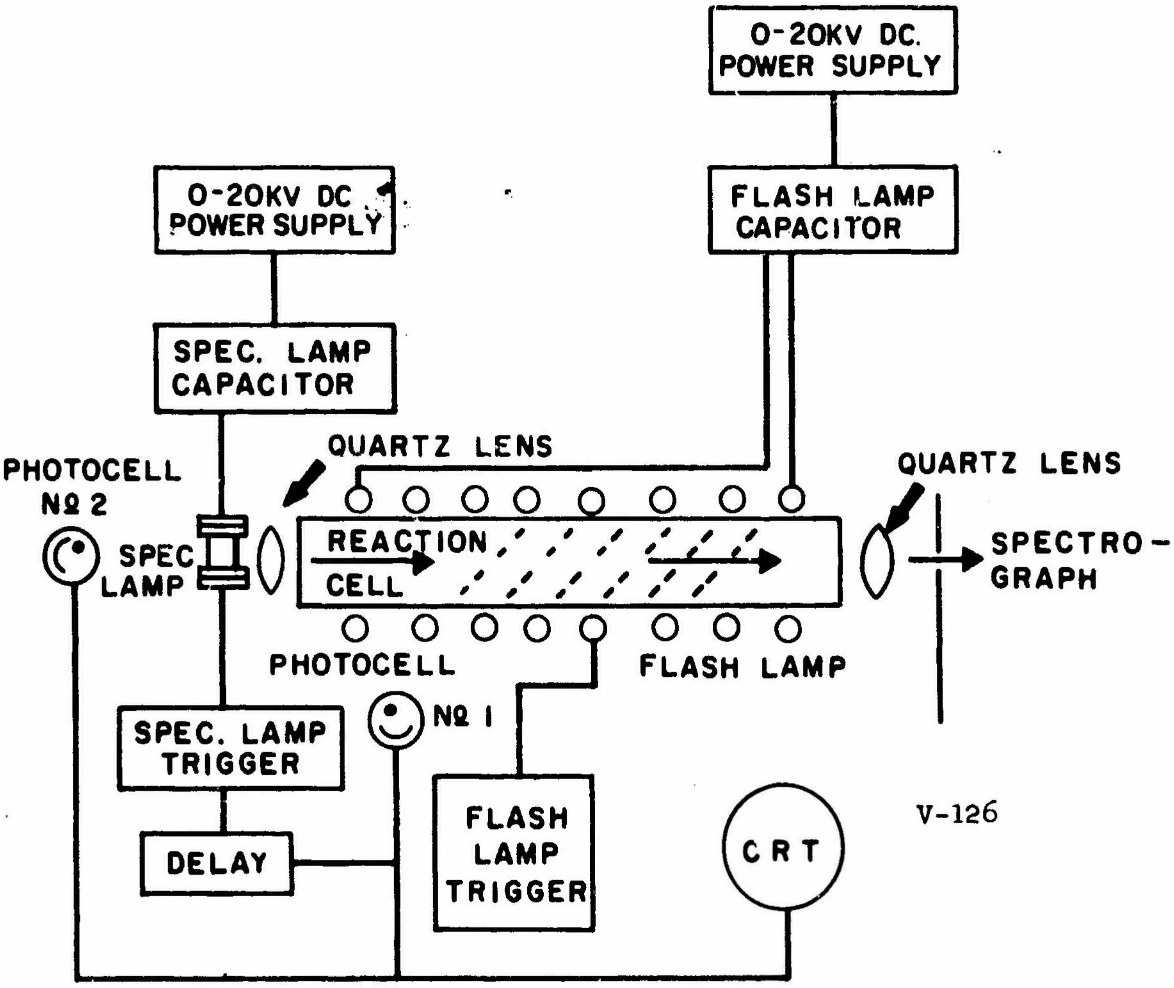
(U) The capacitance of the photoflash circuit is 30 microfarads. At the normal operating voltage of 10 KV, 1500 joules of energy are dissipated through the lamp in about 30 μsec. This energy has been sufficient to vaporize enough of the supporting graphite strips (m.p. = 3,727°C.) that the absorption spectrum of the CN radical has been observed in a nitrogen atmosphere. The spectroflash lamp is usually fired at 7.0-7.5 KV at 3.75 or 7.5 microfarads capacitance, depending upon the intensity of continuous radiation desired in a given spectral range.

(U) An alternative to the configuration shown in Figure 7 is also used. In this modification, the spectroflash is replaced by a high intensity xenon arc which is focused through the reaction cell onto the entrance slit of the spectrograph before and during the experiment. Typically, the spectroscopic plates at the exit end of the spectrograph are replaced by a photomultiplier tube behind a collimated slit. The spectrograph is aligned to focus a given wavelength of light from the xenon arc on the photomultiplier. This wavelength corresponds to the absorption bands of a particular species in the reaction cell. Since the species does not exist before the photoflash is fired, the photomultiplier sees the unattenuated light from the xenon arc. After the photoflash has been fired, the situation radically changes; the species is formed after a certain induction time and increases in concentration, depending upon its stability and reactivity with the environment, while absorbing larger amounts of light from the xenon arc. Correspondingly, the amount of light falling on the photomultiplier decreases and thus changes the photomultiplier current, which is recorded on an oscilliscope or a similar fast response device. This oscilliscope trace is essentially a time-resolved measurement of the concentration of the species under investigation.

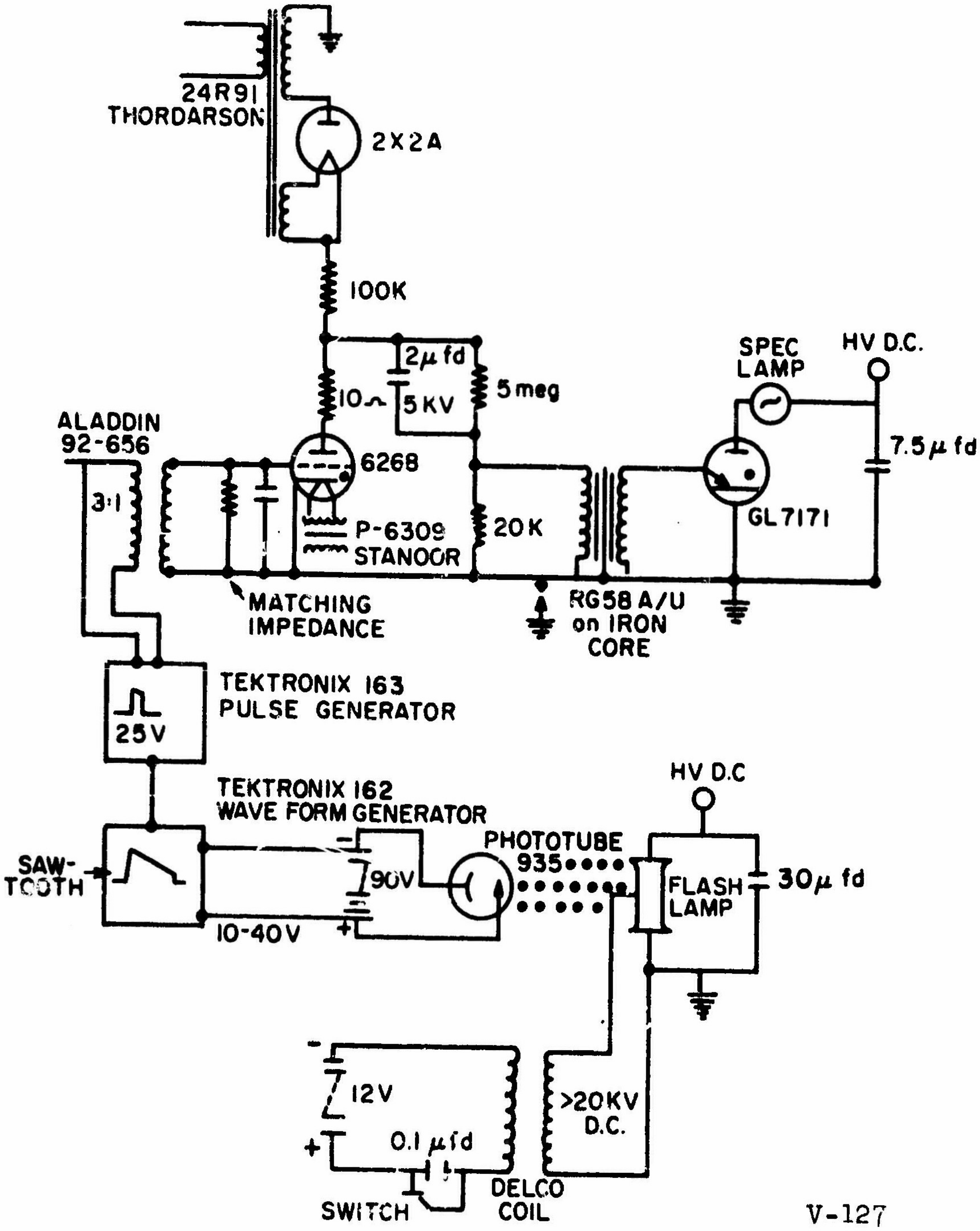
(U) The photometric technique described above gives instantaneous time resolution for only one species in a reaction system. The photographic technique, with its spectroscopic plate and time-delayed spectroflash, gives data for a number of species, but only at predetermined time delays. Once the existence and wavelength of a species have been determined by photographic means, the photometric technique is usually employed to obtain quantitative data.

(U) At the present time, a system has been constructed that will monitor simultaneously five different species (wavelengths). In order to have a consistent time relationship, the photoflash output and data at five wavelengths are simultaneously recorded on a 100 kilocycle tape recorder. Thus, the induction time and concentration of each species will be related to the initial photoflash and, likewise, to each other. The potential number of species monitored at one time is determined by the proximity of their absorption bands and the linear dispersion of the spectrograph.

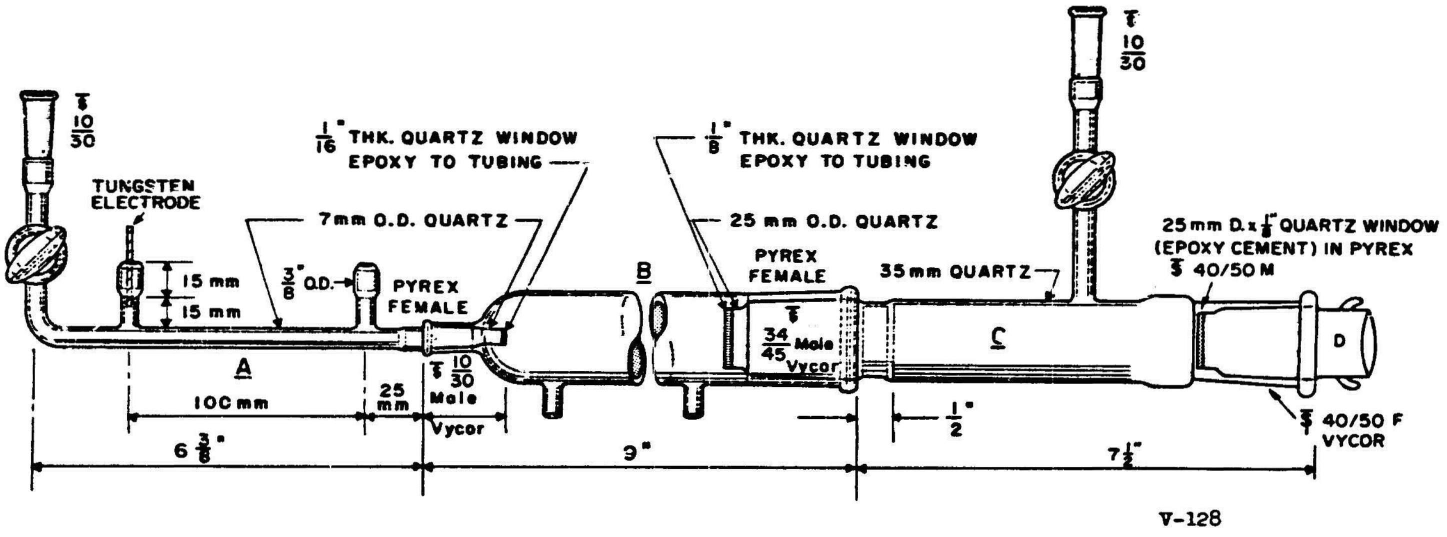
(C) The BeH_2 was a grade "A" sample obtained from Ethyl Corporation. Analysis showed the sample to be 96.66 weight % BeH_2. Free beryllium metal accounted for 2.68% of the sample with the remaining 0.66% being a mixture of $(t\text{-}C_4H_9)_2Be$, $(C_2H_5)_2Be$ and beryllium alkoxides of the above paraffins. The ammonium perchlorate was obtained from American Potash and Chemical Corporation. Its purity was at least 99 mole percent. The nitrocellulose and the plasticizers TMETN and DEGDN were propellant grade. All gases used in this study, with the exception of oxygen and nitrogen, were obtained from Matheson Company, Inc. and were used without further purification.



(U) Fig. 7 - Schematic Diagram of the Flash Heating Apparatus



(U) Fig. 8 - Electronics for Flash Heating Apparatus



(U) Fig. 9 - Reaction Cell for Flash Heating Studies

C. RESULTS OF BERYLLIUM HYDRIDE REACTION (C)

1. Flash Pyrolysis of Beryllium Hydride (C)

(C) The flash pyrolysis of beryllium hydride was carried out at 2477°K. ± 20°K. as determined from the intensity of two sets of iron lines added for this purpose. The work reported here was carried out in a vacuum, although a few runs were flashed in the presence of 50-500 mm. of nitrogen. The weight of the average sample flashed was about 40 mg. This was carried out by weighing a number of samples prior to flashing. If all 40 mg. of the BeH_2 (3.63×10^{-3} mole) decomposes to beryllium metal and hydrogen gas ($Be + H_2$), the pressure inside our 165 cc. reactor cell would be 4.25 atmos. at 2477°K. The pressure at room temperature would be 0.52 atmos. The actual pressure inside the cell would be higher during the flash, as there is a shock wave accompanying the rapid heating of the cell interior. The magnitude of this latter effect is not known.

(U) Most of the experiments described above were performed under vacuum conditions. Since wall effects can be severe under very low pressure, it is profitable to consider the mean free path under the experimental conditions. Initially, the vaporizing species flow almost unimpeded to the wall under essentially molecular flow conditions. However, it is believed that the gas density builds up rapidly in the reactor as sample is vaporized and true gas phase reactions quickly become dominant. When vaporization is complete, for example, it is estimated that a given molecule will suffer 4×10^9 molecular collisions for each centimeter of travel.

(C) The mean free path of the gaseous species BeH produced in the flash pyrolysis of BeH_2 can be estimated. The pyrolysis of BeH_2 yields BeH as a primary product via the proposed step:

$$BeH_2 \xrightarrow{h\nu} BeH + H$$

(C) Since repeated flashing of the same sample showed very little BeH or any species, it is assumed that all 40 mg. of the hydride is decomposed during the photoflash. The amount of sample yields 3.63×10^{-3} or 7.26×10^{-3} mole of gas as the maximum. Immediately upon flashing, the gas is confined in a volume 5.08 cm. long and 3.5 cm. in diameter. The 5.08 cm. is the length of the graphite strips holding the sample. The gas concentration in this volume is 8.95×10^{19} molecules per cc. The mean free path, l, can then calculated by using the equation (33):

$$l = \frac{1}{\sqrt{2}\,\pi\sigma^2 n}$$

where: σ is the molecular diameter; 1.341 Å was used for BeH (34)
n is taken as 4.97×10^{19} molecules/cc.

The mean free path for just the BeH (assuming no H and H_2 is present) is:

$$l = 2.51 \times 10^{-5} \text{ cm.}$$

The mean free path for the pyrolysis mixture of BeH and H can likewise be calculated. In this case, the value for σ is assumed to be:

$$\frac{0.5\sigma H_2 + \sigma BeH}{2} = \frac{0.37 + 1.3431 \text{ Å}}{2} = 0.856 \text{ Å}$$

and $n = 8.95 \times 10^{19}$ molecules per cc. The value for l in this case is 3.43×10^{-5} cm. As can be seen, the mean free path is quite small. A molecule will suffer approximately 2.9×10^9 to 4.0×10^9 collisions for every centimeter it travels.

(C) It is thought that the deactivation of species by the reactor wall is not an important feature of flash heating. The species BeH and BeH^+ (which is proposed as an intermediate) are only stable at high temperatures. It is highly unlikely that either species would survive a collision with the cold (~35°C.) reactor wall. The same cannot be said of H and H_2. However, as the spectra of these species were not observed, they do not enter into the kinetic analyses of the observed spectra. Husain and Norrish (35) state that, "The half life of NH (~70 µsec. maximum) was always negligibly small when compared with the time taken for diffusion from the center of the reaction vessel to the wall." Their reaction cell was 2.2 cm. I.D., much smaller than our 3.5 cm. I.D. The effects of the reactor wall on the gaseous species which are stable at room temperature were not ascertained.

(C) Two distinct regions of the absorption were observed when beryllium hydride was decomposed by flashing at 1500 joules. One was in the blue-green region around 5000 Å; the other in the ultraviolet at about 3000 Å. The upper wavelength absorption corresponds to the (0,0) band of the $^2\Pi \longleftarrow {}^2\Sigma$ ground state transition of BeH. The observed lines and their rotational designation are shown in Table XIV. The J_K values for the transition are given in half quantum values to conform to the literature references of Watson (36, 37).

(C) The lower region of absorption corresponds to the (0,1), (0,3), (1,3) and (1,4) bands of the $'\Sigma \longleftarrow {}'\Sigma$ system of BeH^+. The observed bands and their assignments are shown in Table XX.

(C) The unexpected presence of the charged species BeH^+ can be explained by the following series of reactions, with the first step being:

$$BeH_2 \xrightarrow[\Delta]{h\nu} BeH + H \qquad (1)$$

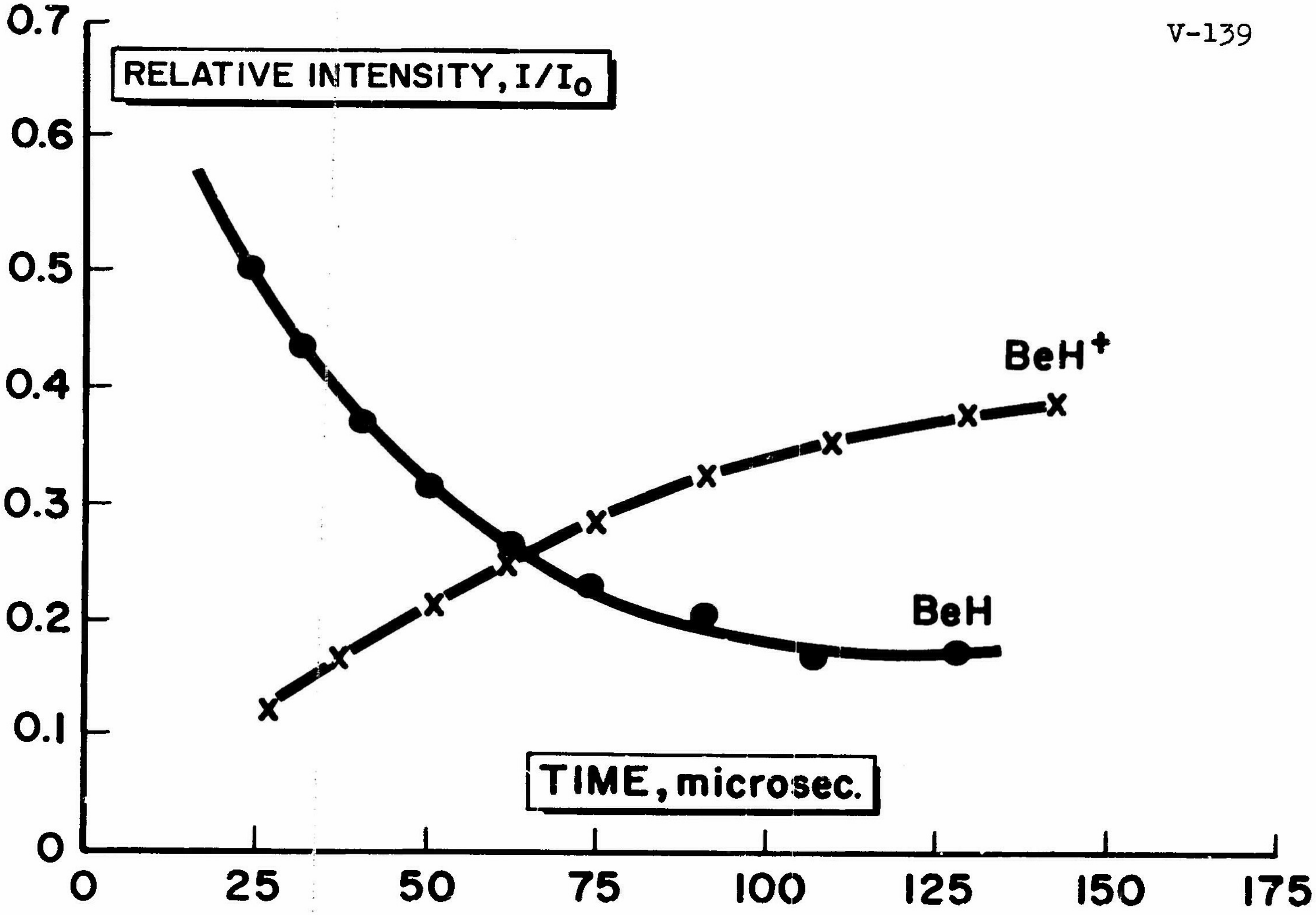
followed by the expected step:

$$BeH + BeH \longrightarrow 2\ Be + H_2 \qquad (2)$$

and

$$BeH + H \longrightarrow Be + H_2 \qquad (3)$$

V-139



(C) Fig. 10 - Decomposition of Beryllium Hydride at 2477 ± 20°K, which produce the metallic beryllium seen in the cell. The diatomic hydride could also lose an electron to form the charged species at the expense of 210.4 kcal./mole.

$$BeH \xrightarrow[\Delta]{h\nu} BeH^+ + e^- \qquad (4)$$

A more likely cause would be the charge transfer reaction:

$$BeH + H \longrightarrow BeH^+ + H^- \qquad (5)$$

which is only 180.6 kcal./mole endothermic. The high radical concentration as well as the extremely non-equilibrium conditions present during the photoflash would favor Reaction (5) over (4) as the mode of forming BeH^+.

(C) Spectroscopic studies, using photographic plates as the means of detection, show the species BeH to be formed immediately after the photoflash. At 140 μsec., this species is hardly detectable. The BeH^+, on the other hand, is first seen at 25 μsec. after the photoflash and increases in intensity beyond 150 μsec., the last data point in Figure 10.

(C) Photometric measurements, made by replacing the photographic plate with a photomultiplier tube as described in Section B., show the species BeH^+ to have a lifetime of about 2500 μsec., as shown in Figure 11. Under our experimental conditions, it can be said that the BeH^+ reactions are kinetically controlled, or else the steps:

$$BeH^+ + H^- \longrightarrow Be + H_2 \qquad (6)$$

and

$$BeH^+ + H \longrightarrow Be^+ + H_2 \qquad (7)$$

as well as (5) would lead to very low BeH^+ concentrations even at maximum. Additionally, if the system was thermodynamically controlled, step (6) and (7) would cause BeH^+ to disappear faster than does BeH, not the contrary, as illustrated in Figures 10 and 11.

(C) From observations in our laboratory, the presence of the charged ion BeH^+ seems to be the species which controls the combustion of BeH_2.

(C) An attempt was made to determine the ratio of BeH/BeH^+. This entailed a knowledge of the integrated absorption intensity of selected lines of each species as well as an estimate of the f-number of each species.

(C) The uncertainties in the calculation of the f-number rules out any valid calculation of the amounts of BeH and BeH^+ present during the decomposition of BeH_2. The integrated absorption intensities were determined with a microphotometer.

(C) An initial calculation with estimated f-numbers gave a BeH/BeH^+ ratio of 3 ± 1. This value was later discarded as the only known f-number for a charged hydride (H_2^+) was 0.3 (38), while our value was 0.005. The f-number for BeH was taken as 0.0015 which is consistent with 0.0012 reported by Penner (39) for OH.

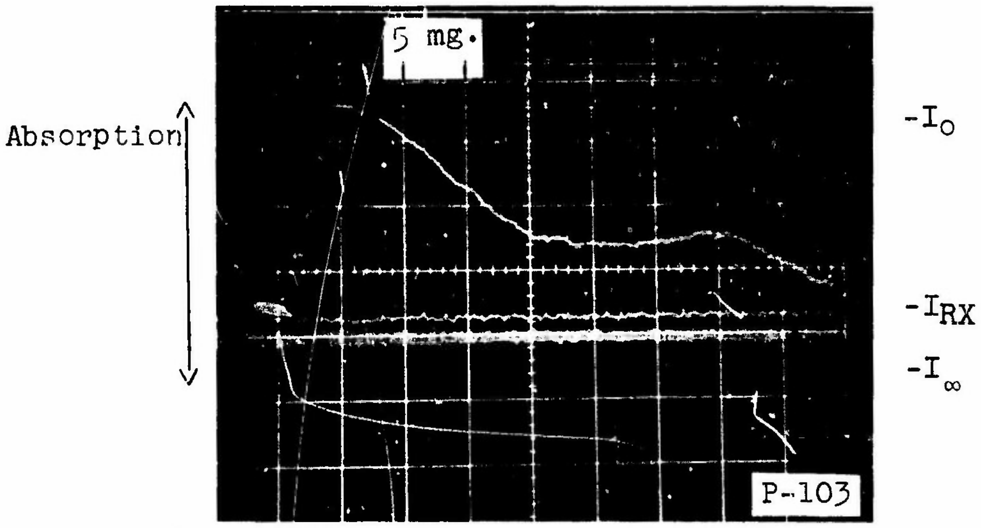
(C) The change in f-number from 0.005 to 0.3 for BeH^+ results in a change if concentration by a factor of 60, which is greatly beyond any experimental error. This attempt points up the need for a fundamental study of the spectra and energetics of the combustion of many rocket propellants.

(C) Thus, the greater stability of BeH^+ would account for some of the gaseous beryllium-containing product seen in the first 2500 μsec. being in a comparatively metastable state.

2. Flash Pryolytic Induced Reaction Between Beryllium Hydride and Oxygen (C)

(C) In any propellant containing ammonium perchlorate as an oxidizer, large amounts of oxygen, both atomic and molecular, are released during combustion. It is, therefore, prudent that the reaction between flash-pyrolyzed beryllium hydride and molecular oxygen should be studied. The overall reaction should be:

$$BeH_2 + O_2 \longrightarrow BeO + H_2O \tag{8}$$



(C) Fig. 11 - Oscilliscopic Traces of Lifetime of BeH^+ from 2834.7 Å line

I_o = Baseline with light off.

I_{RX} = Absorption due to 2751.8 Å line of BeH^+.

I_∞ = Baseline with light on - no absorption.

5 millisec./horizontal div.

Flash energy = 1500 joules.

Table XIX

(c) Observed Rotational Bands for 0-0 Transition of BeH in Absorption at 2477 ± 20°K.[a]

J_K[a]	$R(J_K)$, Å	$P(J_K)$, Å
1 1/2	4987.4	--
2 1/2	--	4997.5
3 1/2	4975.0	5003.7
4 1/2	--	5008.4
5 1/2[b]	--	5013.8
6 1/2	--	--
7 1/2	--	5020.0
8 1/2	--	5027.7
9 1/2	--	--
10 1/2	--	5037.0
11 1/2	--	5039.2
12 1/2	--	5041.7
13 1/2	--	5046.9
14 1/2	--	--
15 1/2	--	--
16 1/2	--	--
17 1/2	--	--
18 1/2	--	5064.2
19 1/2	--	--
20 1/2	--	--
21 1/2	--	--
22 1/2	--	--
23 1/2	--	--
24 1/2	--	5081.2
25 1/2	4862.5	--
26 1/2	--	--
27 1/2	--	--
28 1/2	--	5089.7

[a] Each line is an unresolved doublet, thus $R(J_K)$ for $J_K = 1/2$ corresponds to J transition of 0-1 and 0-2, while $P(J_K)$ for $J_K = 1\ 1/2$ would correspond to the J transition 0-1 and 1-2.

[b] $Q(5\ 1/2) = 4991.6$ Å.

Table XX

(C) Observed Rotational Bands[a] of BeH^+ in the Ultraviolet at 2477 ± 20°K.

	0-1		0-3		1-3		1-4	
J_K	R	P	R	P	R	P	R	P
1/2	--	--	--	--	--	--	3082.9	--
1/2	--	--	--	--	--	--	--	--
2 1/2	--	2885.8	--	--	--	--	--	3087.5
3 1/2	--	--	--	--	--	--	--	3090.6
4 1/2	--	--	--	3051.9	--	--	--	3093.7
5 1/2	--	--	--	--	--	--	--	--
6 1/2	--	--	--	3059.6	--	--	--	--
7 1/2	--	--	3044.7	3065.0	--	--	--	--
8 1/2	--	--	--	3068.9	--	2940.1	--	--
9 1/2	--	--	--	3075.1	--	--	--	--
10 1/2	--	2745.6	--	--	--	--	--	--
11 1/2	--	2751.8	--	3087.5	--	--	--	--
12 1/2	--	--	--	--	--	--	--	--
13 1/2	--	--	--	--	--	--	--	--
14 1/2	--	--	3071.2	--	--	--	--	--
15 1/2	--	--	3077.4	--	--	--	--	--
16 1/2	--	--	--	--	--	2994.4	--	--
17 1/2	--	--	--	--	--	--	--	--
18 1/2	--	--	--	--	--	--	--	--
19 1/2	--	--	--	--	--	3021.6	--	--
20 1/2	--	--	--	--	2983.3	--	--	--
21 1/2	--	--	--	--	--	--	--	--
22 1/2	--	--	--	--	3000.6	--	--	--
23 1/2	--	--	--	--	--	3065.0	--	--
24 1/2	--	--	--	--	--	--	--	--
25 1/2	2834.7	--	--	--	--	3087.5	--	--
26 1/2	--	--	--	--	3038.7	--	--	--
27 1/2	--	2912.2	--	--	3048.8	--	--	--
28 1/2	--	--	--	--	--	--	--	--
29 1/2	--	--	--	--	3059.6	--	--	--
30 1/2	--	2955.6	--	--	--	--	--	--

[a] Angstrom Units.

This study, with the fuel plus 20 mm. O_2, was made both with spectroscopic plates and with photomultipliers. The spectroscopic plates were used to detect a wide variety of transitory intermediates for the first 140 μsec., as it was desired to study initiation of the reactions in detail. The photomultipliers were used to study the lifetimes of three selected species (BeH^+, OH and BeO) up to several milliseconds.

(C) The data for the initiation of the reaction between BeH and BeH^+ with O_2 are seen in Figure 12. The gas phase temperature was 2495 ± 30°K., as calculated from the absorption of the OH lines. As seen in the figure, the concentration of BeO arises after the OH is already present in a large concentration. Also note that the BeH^+ is initially seen to have less intensity than the BeH, but later (~90 μsec.) it is the more intense hydride species. The time relationship between the intermediate and the BeO could be explained if the following steps for the BeH are allowed.

$$BeH_2 \xrightarrow[\Delta]{h\nu} BeH + H \qquad (1)$$

$$H + O_2 \longrightarrow OH + H \qquad (9)$$

$$BeH + O_2 \longrightarrow BeO + OH \qquad (10)$$

$$BeH + O \longrightarrow BeO + H \qquad (11)$$

and

$$BeH + OH \longrightarrow BeO + H_2 \qquad (12)$$

The BeH^+ species would undergo the same type of reaction but at a slower rate.

$$BeH^+ + O_2 \xrightarrow{e^-} BeO + CH \qquad (10a)$$

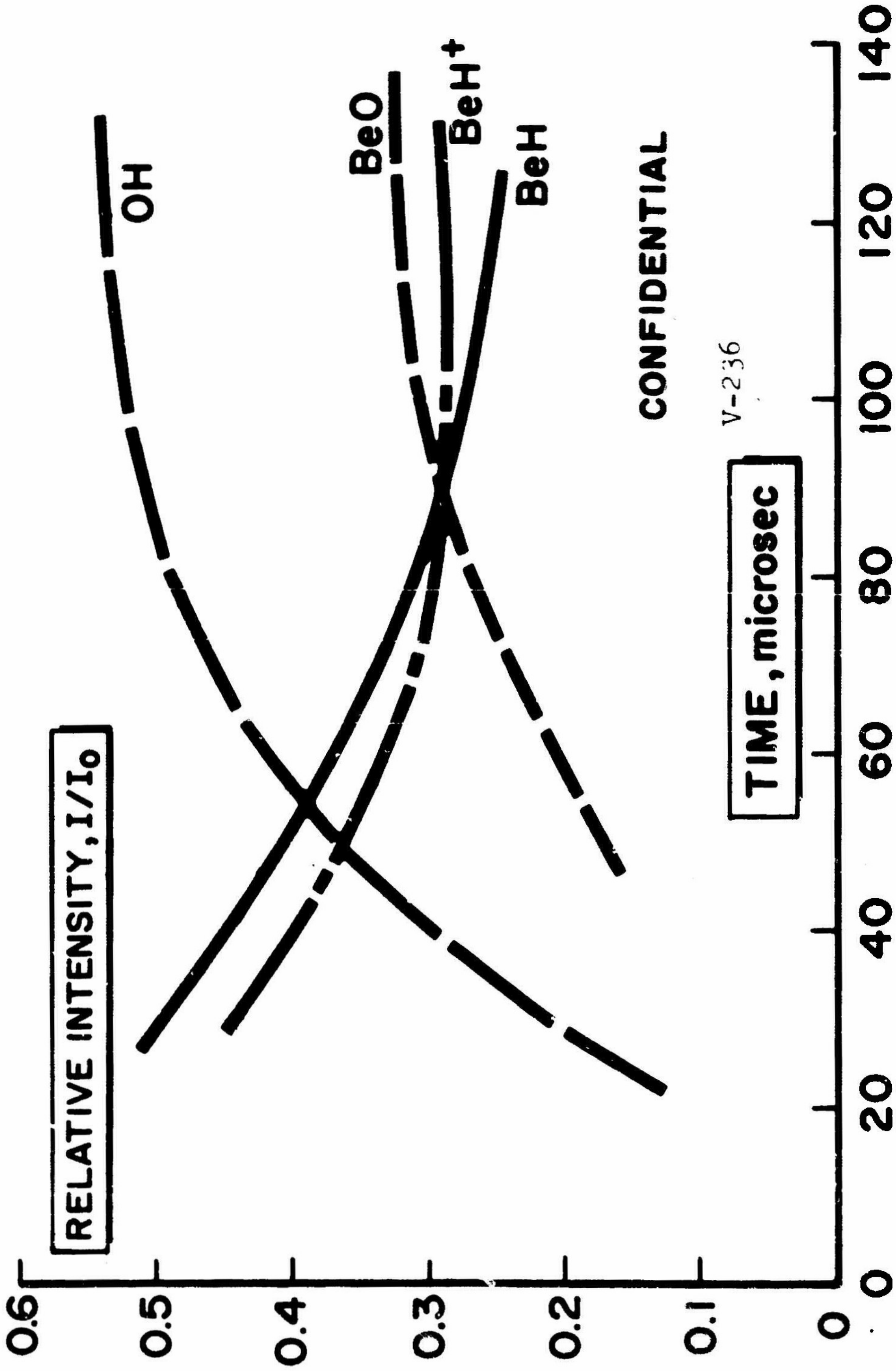
$$BeH^+ + O \xrightarrow{e^-} BeO + H \qquad (11a)$$

and

$$BeH^+ + OH \xrightarrow{e^-} BeO + H_2 \qquad (12a)$$

(C) An understanding of the energy transfer in combustion processes must be realized before an explanation of the actual mechansim of the loss and gain of an electron in the BeH^+ species can be postulated.

(U) An insight into this problem might be gained if a "Double Flash" pyrolytic unit were built. In such an apparatus, the intermediates formed from the photoflash would be subjected to a second flash before the spectroflash is fired to record the event. The light from this second flash would interact with the species formed from the first flash and excite them to higher electronic states and may even lead to ionization. The spectroflash would



(C) Fig. 12 - Reaction of Beryllium Hydride with Oxygen at 2477 ± 20°K.

record the various energy states of each species as a function of time. a number of such experiments would show the energy relationship between the species as a function of time and concentration. The two flash lamp energies could also be varied to supply data as a function of temperature. Such an apparatus would also yield data as to absorption data taken from a King furnace. The latter would give equilibrium data and the flash unit would yield kinetically controlled data.

(C) Photometric studies of the same system were accomplished by following the 2751.2 Å line of BeH^+, the 3089.1 Å line of OH, and, in some cases, the 3384 Å line of BeO. The latter line showed slight intensity variation and was not used for further work.

(C) A typical set of data is shown in Figure 13. The time history of BeH^+ is shown in the upper trace and the time history of the OH in the lower trace. The BeH^+ is seen in absorption until 350 millisecond (0.35 sec.). The long rise time of the BeO as compared to the BeH^+ and OH is also observed, indicating the latter two are precursors to the BeO.

3. Flash Pyrolytic Reaction Between Beryllium Hydride and Chloride (C)

(C) One of the pyrolysis products of NH_4ClO_4 is chlorine. For this reason the reaction between 40 mg. of flash pyrolyzed beryllium hydride and 140 mm. of chlorine was studied. The stoichiometry of the reaction is:

$$BeH_2 + 2\,Cl_2 \longrightarrow BeCl_2 + 2\,HCl \qquad (13)$$

(C) The system actually studied was chlorine-rich in a ratio of 2.5 moles of Cl_2/mole BeH_2. The products, when the BeH_2 was flashed at 1500 joules were BeCl, HCl, BeH, BeH^+, Cl_2, Cl_2^+ and Cl^+. The postulated reactions are:

$$BeH_2 \xrightarrow[\Delta]{h\nu} BeH + H \qquad (1)$$

$$BeH + Cl_2 \longrightarrow BeCl + HCl \qquad (14)$$

$$BeH + Cl \longrightarrow BeCl + H \qquad (15)$$

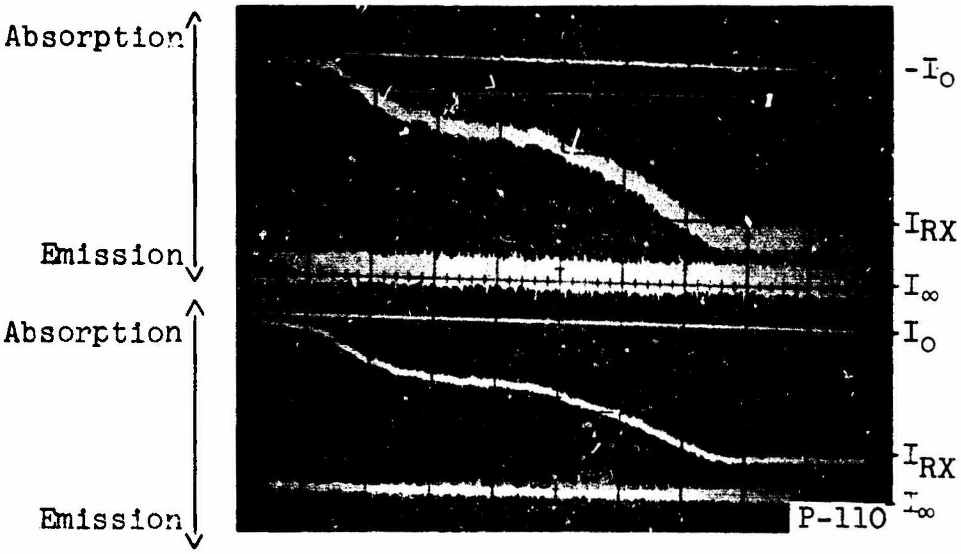
$$Cl_2 + H \longrightarrow HCl + Cl \qquad (16)$$

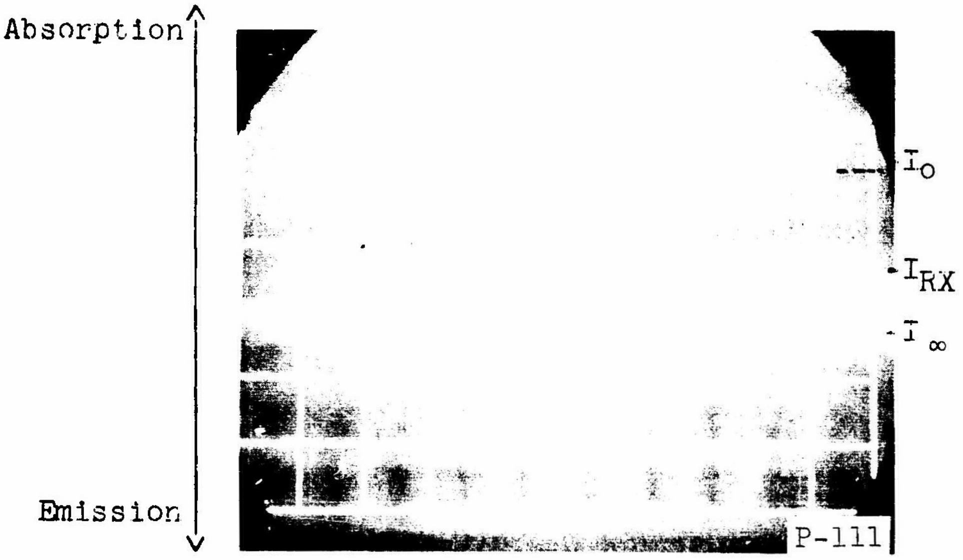
$$Cl_2 \xrightarrow{h\nu} 2\,Cl(Cl^+) \qquad (17)$$

and

$$BeCl + Cl \xrightarrow{M} BeCl_2 \qquad (18)$$

The BeH^+ undergoes reaction similar to (14) and (15) but at a slower rate.





(C) Fig. 13 - Oscilloscopic Traces of Time History of BeH^+, OH, and BeO from BeH_2 + 20 mm. O_2

Upper Photograph - BeH^+ - 2751.2 Å - upper trace
OH - 3089.1 Å - lower trace
Lower Photograph - BeO - 3389 Å
50 millisec./horizontal division

4. Reaction Between Beryllium Hydride and a Chlorine-Oxygen Mixture (C)

(C) The flash pyrolytic reaction between ~40 mg. of BeH_2 and a 2:1 mixture of Cl_2 and O_2 was studied at a flash energy of 1450-1560 joules. The transitory species recorded were BeH, BeH^+, Cl_2 HCl^+, HCl, Cl_2^+, Cl^+, OH, BeO, ClO. A few bands corresponding to BeCl were also indicated. Under our experimental conditions at 100 mm. of gas mixture, the preferred product was BeO almost to the exclusion of BeCl and its low temperature successor, $BeCl_2$. The reaction was studied for 180 μsec. Since only BeO was seen as a major product, no time versus intensity curves were drawn.

5. Pyrolytic Reaction Between Beryllium Hydride and Carbon Monoxide (C)

(C) Great amounts of carbon monoxide are formed by the combustion of a solid binder. To study the possibility of a high temperature reaction between this product and 28 mg. of BeH_2, the hydride was pyrolyzed in 150 mm. of CO. The most intense absorptions were due to BeH, BeH^+, and HCO. Indications are that under our experimental conditions the reaction between CO and BeH_2 is negligible. The CO is primarily a third body for the recombination of hydrogen atoms via:

$$BeH_2 \xrightarrow[\Delta]{h\nu} BeH + H \qquad (1)$$

$$H + CO \rightarrow HCO \qquad (19)$$

$$H + HCO \rightarrow H_2 + CO \qquad (20)$$

6. Pyrolytic Reaction Between Beryllium Hydride and Nitric Oxide (C)

(C) Nitric oxide is a product of both the decomposition of AP and the combustion of nitrocellulose. The combustion of PGNC alone yields about three moles of NO per mole of monomer unit. Additionally, the plasticizers TMETN and DEGDN yield three and two moles of NO, respectively, per mole of plasticizer when burned. The question naturally arises as to the influence of nitric oxide upon the decomposition product of beryllium hydride. The question of primary interest to the propellant industry is whether nitric oxide acts as an oxidizer at temperatures above 2300°K.

(C) The flash pyrolytic reaction between ~40 mg. of beryllium hydride and nitric oxide was studied both spectroscopically and photometrically in the temperature range 2000°-2700°K. at pressures up to 21 mm. NO. The only transitory species detected, in addition to the BeH and BeH^+, was HNO. The general appearance of the intensity vs. time trace of this species was that of a sine wave. The formation of HNO is attributed to the reaction:

$$H + NO \xrightarrow{M} HNO \qquad (21)$$

Its rapid disappearance is accounted for by:

$$H + HNO \longrightarrow H_2 + NO \qquad (22)$$

The main role played by nitric oxide in our experiments was that of a catalyst and third body for the recombination of hydrogen atoms.

D. RESULTS ON THE DECOMPOSITION OF AMMONIUM PERCHLORATE (U)

(U) Thermal decomposition of ammonium perchlorate was observed over the time interval 20-1000 μsec. after the initiating flash. The spectral range investigated was 2300-5000 Å. In order to verify the results observed, the flash photolytic decompositions of NO_2, ClO_2 and NH_3 were carried out.

(U) The first step in the pyrolysis of ammonium perchlorate has been reported to be a surface decomposition to gaseous ammonia and anhydrous perchlorate acid (40, 41). Our work indicated that at 20 μsec. after the flash, the two main bands are those of ClO_2 (2000 and 3360 Å) and OH (0-0 at 3064 Å, 1-1 at 3121 Å, and 2-2 at 3184 Å). The relative concentrations for selected radicals as a function of time are shown in Figure 14. These species, OH and ClO_2, could arrive from decomposition of perchloric acid. If the first step is:

$$NH_4ClO(s) \xrightarrow[\Delta]{h\nu} NH_3(g) + HClO_4(g) \qquad (23)$$

Then as far as perchloric acid is concerned, the second and succeeding steps could be:

$$HClO_4 \longrightarrow OH + (ClO_3) \longrightarrow ClO_2 + O \qquad (24)$$

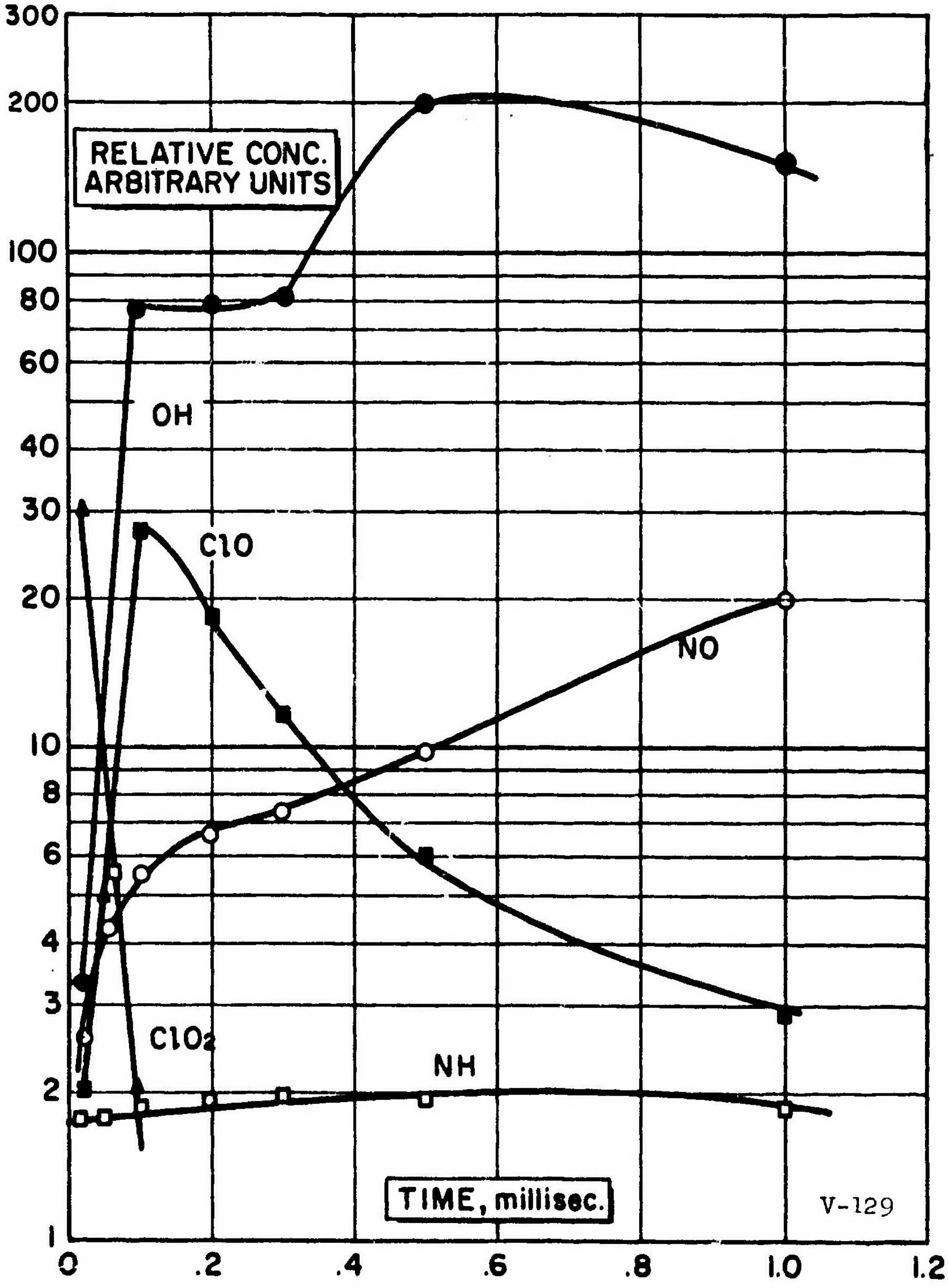
followed by:

$$ClO_2 \xrightarrow{h\nu} ClO + O \qquad (25)$$

$$ClO_2 + O \longrightarrow ClO + O_2 \qquad (26)$$

(U) In a few cases, O_2^+ and O_3 were observed. They are attributed to the high radical-radical reactions prevalent in adiabatic flash photolysis in the gas stage, coupled with the extremely nonequilibrium conditions existing just above the graphite strips. This volume, just above the strips, has a very high radical concentration. Bimolecular collisions are much more probable than diffusion into the less dense surroundings. Therefore, it is expected that many higher energy species would be observed than would be seen in ordinary flash photolysis. Even the well characterized OH is seen with ν'' (a rotational level of the lower electronic state) = 0, 1, and 2.

(U) Concurrent with the perchloric acid decomposition is the decomposition of ammonia. The first step is:



(U) Fig. 14 - Relative Radical Concentration Vs. Time in the Pyrolytic Decomposition of Ammonium Perchlorate

$$NH_3 \xrightarrow{h\nu} NH_2 + H \qquad (27)$$

The next two steps observed only under adiabatic conditions are (42):

$$NH_2 + NH_2 \longrightarrow NH_3 + NH \qquad (28)$$

$$NH_2 + H \longrightarrow NH + H_2 \qquad (29)$$

The NH radical has been observed at 3048, 3302, and 3360 Å. The relative concentration of NH seems to be independent of the other main species.

The ClO radical produced in Reactions (25) and (26), if left alone, decays by the following step:

$$ClO + ClO \longrightarrow Cl_2 + O_2 \qquad (30)$$

The same sort of collision accounts for the decay of OH.

$$OH + OH \longrightarrow H_2O + O \qquad (31)$$

$$O + O \xrightarrow{M} O_2 \qquad (32)$$

From the data obtained, the following reaction scheme is proposed for the deflagration of ammonium perchlorate:

$$NH_4ClO_4(s) \xrightarrow{h\nu} NH_3(g) + HClO_4(g) \qquad (23)$$

$$NH_3 \xrightarrow{h\nu} NH_2 + H \qquad (27)$$

$$NH_2 + O_2 \longrightarrow HNO + OH \qquad (33)$$

$$NH_3 + OH \longrightarrow NH_2 + H_2O \qquad (34)$$

$$NH_3 + O \longrightarrow NH_2 + OH \text{ (excited state)} \qquad (35)$$

O_2 + O coming from Reactions (24) through (26), and (30) through (32).

Additional steps for the rapid, almost explosive combustion are:

$$NHO \longrightarrow NO + H \qquad (36)$$

$$H + Cl_2 \longrightarrow HCl + Cl \qquad (37)$$

$$ClO + H \longrightarrow HCl + O \qquad (38)$$

$$NH_2 + O \longrightarrow OH + NH \qquad (39)$$

(U) The proliferation of species could then terminate by the following sequence of reactions:

$$HNO + HNO \longrightarrow N_2O + H_2O \qquad (40)$$

$$NH + NH \longrightarrow N_2H_2 \longrightarrow N_2 + H_2 \qquad (41)$$

$$NO + Cl \xrightarrow{M} NOCl \qquad (42)$$

$$NO + O \xrightarrow{M} NO_2 \qquad (43)$$

$$NO_2 + Cl \xrightarrow{M} NO_2Cl \qquad (44)$$

$$H + H \xrightarrow{M} H_2 \qquad (45)$$

$$H + OH \xrightarrow{M} H_2O \qquad (46)$$

$$H + Cl \xrightarrow{M} HCl \qquad (47)$$

$$Cl + Cl \xrightarrow{M} Cl_2 \qquad (48)$$

(U) A steady increase in the relative concentration of NO indicates that at high temperatures Reactions (42) through (44) are not thermodynamically favored or kinetically probable.

(U) No analyses of the gaseous products were attempted once the combustion was completed because this type of work is well-known and documented.

(U) It is of interest to note that the OH radical was observed as being excited (by the exothermicity of the reaction) to the $\nu'' = 2$ level. Similar excitation has been observed by Basco and Norrish (43). This, rather than the energetics of the reaction, indicates that transitions usually seen in emission are not those necessarily seen in absorption, or, if seen in absorption (44), not with the same distribution.

E. RESULTS OF REACTION BETWEEN BERYLLIUM HYDRIDE AND AMMONIUM PERCHLORATE (C)

(C) Mixtures of beryllium hydride and ammonium perchlorate were studied spectroscopically at flash energies of 1200-1600 joules. The composition of the mixtures was varied from a BeH_2/AP ratio of 1.0 to 0.5. It seemed to take more energy to decompose the mixture sufficiently to get adequate intensities than it took to decompose each component separately.

(C) The rate of decomposition of BeH_2 into BeH and BeH^+ seems to be constant and independent of the amount of NH_4ClO_4 present. The charged species BeH^+ was detected both in absorption and emission, indicating the non-equilibrium of the combustion. No positive evidence for BeCl was seen, showing either a very low concentration or an absence of BeCl and $BeCl_2$. This leads to the conclusion that BeH and BeH^+ react with the oxygenated species, including ClO, to form BeO almost to the total exclusion of BeCl and $BeCl_2$.

(C) In addition to the beryllium hydride reaction listed previously, the reaction:

$$BeH + ClO \longrightarrow BeO + HCl \qquad (49)$$

and

$$BeH^+ + ClO \longrightarrow BeO + HCl^+ \qquad (50)$$

would also account for the preference of BeO over BeCl as a reaction product.

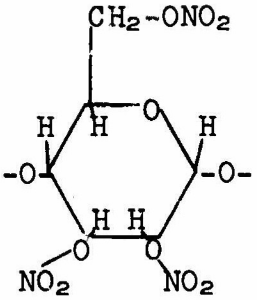
F. RESULTS OF THE DECOMPOSITION AND COMBUSTION OF BINDER MATERIALS (U)

(U) The binder material, in addition to being a matrix which incorporates the fuel and oxidizer, is itself a pseudofuel and potential oxidizer. The hydrocarbon skelton is the fuel portion and the active nitro groups are the oxidizer portion of the binder system. The particular binder system studied in this work contained plastisol grade nitrocellulose, and the plasticizers TMETN and DEGDN.

(U) The nitrocellulose was dissolved in ether. The solution was poured over the graphite strips and the solvent pumped off leaving a thin layer of nitrocellulose on the strips. The plasticizers were applied to the graphite strips as 50% solution of the plasticizer in ether. Flash energies varied from 100-1500 joules and analysis times from 50-300 μsec.

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

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



$$\xrightarrow[\Delta]{h\nu} (C_6H_7O_6) \longrightarrow H_2CO + (C_5H_5) + NO_2 \qquad (51)$$

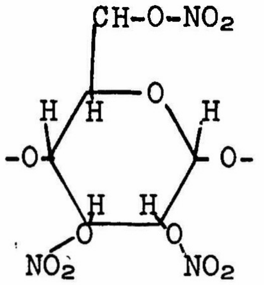
$$[C_5H_5O_5] \xrightarrow{\text{slow}} CH_3CHO + CO_2 + HCO + CO \qquad (52)$$

$$NO \longrightarrow NO + O \qquad (53)$$

$$2\ HCO + O \longrightarrow H_2O + 2\ CO \qquad (54)$$

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

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



$$\xrightarrow[\Delta]{h\nu} \underset{\text{I}}{[C_6H_7O_6]} + 3\ NO_2 \qquad (51)$$

$$NO_2 \longrightarrow NO + O \qquad (53)$$

$$\text{I} \xrightarrow{\Delta} H_2CO + [C_5H_5O_5] \xrightarrow{\text{slow}} CH_3CHO + CO_2 + HCO + CO \qquad (55)$$

$$HCO + O \xrightarrow{\text{slow}} CO + OH \qquad (56)$$

$$HCO + O_2 \longrightarrow CO_2 + OH \qquad (57)$$

$$CH_3CHO \longrightarrow CH_3 + HCO \qquad (58)$$

$$CH_3CHO \longrightarrow CH_4 + CO \qquad (59)$$

$$CH_4 + O \longrightarrow CH_3 + OH^- \qquad (60)$$

$$CH_3 + O \longrightarrow H_2CO + OH \qquad (61)$$

$$CH_4 + OH \dashrightarrow CH_3 + H_2O \qquad (62)$$

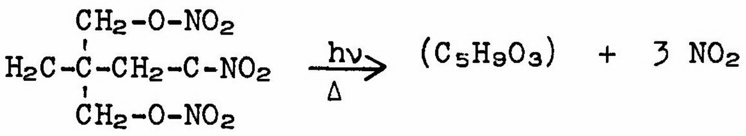
$$H_2CO + O \longrightarrow H_2O + CO \qquad (63)$$

$$NO + O \longrightarrow NO_2 \text{ (excited)} \qquad (64)$$

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

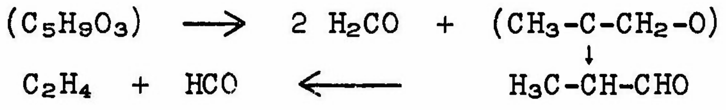
The plasticizer TMETN, when flashed with more than 1000 joules, yields C_2H_4, H_2CO and CO as products, the species of H_3CO and CO being predominant.

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



$$H_2C\text{-}\overset{CH_2\text{-}O\text{-}NO_2}{\underset{CH_2\text{-}O\text{-}NO_2}{C}}\text{-}CH_2\text{-}C\text{-}NO_2 \xrightarrow[\Delta]{h\nu} (C_5H_9O_3) + 3\ NO_2 \qquad (65)$$

$$NO_2 \longrightarrow NO + O \qquad (53)$$

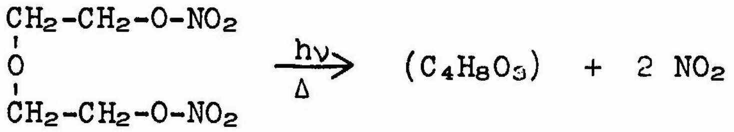


$$\begin{array}{ccccc} (C_5H_9O_3) & \longrightarrow & 2\ H_2CO & + & (CH_3\text{-}C\text{-}CH_2\text{-}O) \\ & & & & \downarrow \\ C_2H_4 + HCO & \longleftarrow & & & H_3C\text{-}CH\text{-}CHO \end{array} \qquad (66)$$

$$HCO + O \longrightarrow CO + OH \qquad (56)$$

$$2\ HCO \longrightarrow H_2CO + CO \qquad (54)$$

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



$$\begin{array}{l} CH_2\text{-}CH_2\text{-}O\text{-}NO_2 \\ O \\ CH_2\text{-}CH_2\text{-}O\text{-}NO_2 \end{array} \xrightarrow[\Delta]{h\nu} (C_4H_8O_3) + 2\ NO_2 \qquad (67)$$

$$NO_2 \longrightarrow NO + O \qquad (58)$$

$$(C_4H_8O_3 \longrightarrow CH_2\text{-}CHO + \text{-}O\text{-}CH_2\text{-}CH_2\text{-}O \longrightarrow 2\ H_2CO \qquad (68)$$

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

G. CONCLUSIONS (U)

(U) It has been demonstrated that the technique of flash photolysis/pyrolysis can yield significant data on the combustion process of solid propellants. An apparatus has been designed and built which offers a wide range of applicability while still adhering to the principle of simplicity in construction and operation.

(C) The decomposition of beryllium hydride is not a simple thermodynamic process existing between the hydride and its elemental constituents. The decomposition process is a kinetic phenomenon involving diatomic hydrides and atomic hydrogen as transitory intermediates. The charge transfer reaction in which the diatomic hydride is formed seems to be the step of greatest interest as the charged species seems to have the greater stability at temperatures in excess of 2000°C. All high temperature reactions involving BeH_2 must take into account the two diatomic hydrides and their reactions.

(U) The deflagration of ammonium perchlorate is essentially that of a mono-propellant as the product fuel, ammonia, is oxidized by the product oxidizer, anhydrous perchloric acid. The deflagration is a complex process involving many transitory species of very short lifetimes.

(U) The addition of a metal-containing fuel alters the deflagration of ammonium perchlorate. The metal oxide is the preferred product. If the fuel contains hydrogen, the products are HCl and the metal oxide with metal chloride.

(U) The binder materials burn in a way predictable from hydrocarbon combustion studies. The product of the $-NO_2$ groups are nitric oxide and O-atoms; only the latter show oxidizing power. The roles of the stable oxides CO and NO in the flame are reduced to being collisionally activated third bodies for the recombination of atoms.

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13. ABSTRACT

The ΔH_f was determined for Delta to be 2.5 ± 2.8 kcal./mole, and for NF_3, by two different methods, to average -31.6 ± 0.2 kcal./mole. Attempts to determine the heat of combustion of TVOPA were unsuccessful. Improvements in equipment and procedures are described. The heat of combustion of P-BEP in oxygen was determined to be 3629.0 cal./g. If the molecular weight is assumed to be exactly 100, based on the empirical formula, the derived heat of formation is -47.8 ± 0.7 kcal./mole. The heats of solution of TVOPA and P-BEP in 2-octanone were determined as -4.6 and -3.0 cal./g. respectively. Work on the identification and removal impurities in CF_3ONF_2 is continuing. The heat of hydrolysis of lithium-doped, crystalline Beane has been completed. In support of the thermal measurements, N_2F_4, NF_3, TVOPA and P-BEP were purified. CF_3ONF_2 and CF_3OOCF_3 were synthesized and then purified. The kinetics of decomposition and deflagration of a solid propellant containing Beane studied with a flash pyrolysis - kinetic spectroscopy apparatus above 2000°K. shows the existence of the subhydride and charged ion. Between 2200° and 2800°K., the subhydride is about three times that of the more stable ion. Reaction with O_2 is much slower with the ion than the subhydride. The study of the decomposition of NH_4ClO_4 shows the first step to be the dissociation to gaseous NH_3 and $HClO_4$. Subsequent reactions are the combustion of the various nitrogen species with the perchlorate species. Hydrogen, oxygen, and chlorine atoms also recombine to H_2, O_2, and Cl_2 by three body collisions. The reaction between Beane and NH_4ClO_4 produces the oxide only. The combustion of nitrocellulose and plasticizers TMETN and TEGDN is that which would be expected from hydrocarbon combustion studies.

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