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

QUARTERLY PROGRESS REPORT AFRPL-TR-66-176
(1 July 1966 to 30 September 1966)

October 1966

NOV 22 1966

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

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

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Report Nr. T-202-3Q-66

QUARTERLY PROGRESS REPORT (U)
(1 July 1966 to 30 September 1966)

October 1966

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MIDLAND, MICHIGAN

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FOREWORD

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

This is the third quarterly report, covering the work performed during 1 July 1966 through 30 September 1966. The Dow report number is T-202-3Q-66.

The work was performed by 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.

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

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

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SECTION I

SUMMARY

(C) The heat of combustion of 1,2,3-[1,2-bis(difluoroaminoethoxy)]propane, TVOPA, in oxygen has been determined to be -1613 ± 3.5 kcal./mole. From this value and from previous data, the $\Delta H f^{\circ}_{298.15}$ is calculated to be -217.4 ± 3.5 kcal./mole. Work in progress includes the heat of combustion of P-BEP, poly-[bis(difluoroamino)epoxy propane], by a similar technique. Trifluoromethoxydifluoramine has been synthesized and purified, and the heat of explosion of this compound is being determined.

(C) Additional studies on the combustion kinetics of the decomposition of beryllium hydride have been made. The combustion reaction of beryllium hydride with nitrous oxide has been investigated. Emphasis was placed on the study of oxygen combustion of Beane. The reaction was followed by monitoring the BeH^+ and OH radical absorption lines with our recording apparatus.

SECTION II

THERMOCHEMISTRY

A. HEAT OF COMBUSTION OF TVOPA, 1,2,3-tris[1,2-bis(Difluoroaminoethoxy]propane (C)

1. Introduction (U)

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

Table I

(U) Variation of Chloride Content with Sample Treatment

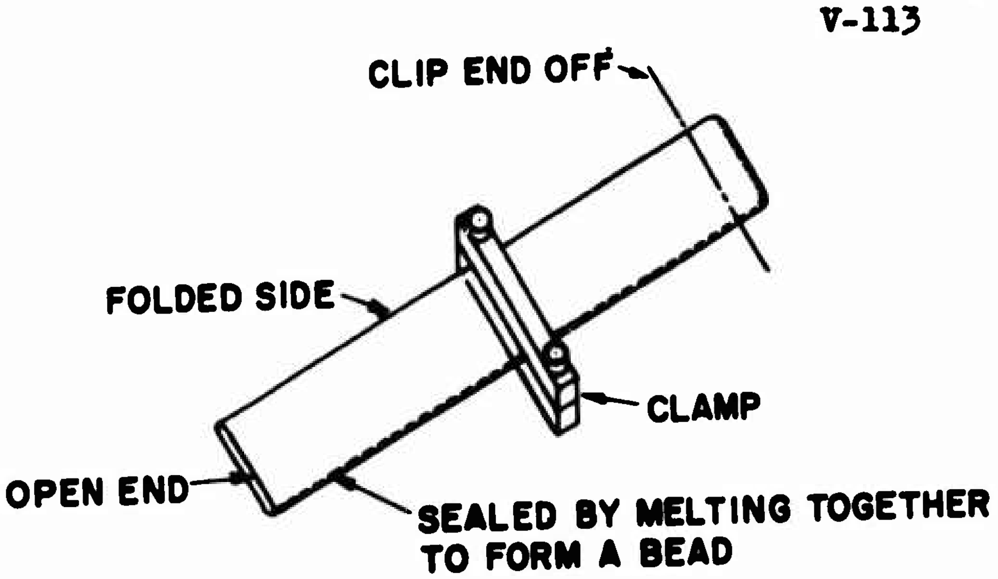
Treatment of Sample[a]	mg. Chloride/ g. Sample
Pumped on for ~3 hrs. at 25°C.	21 to 27
Warmed to 50°C. while pumping ~2 hrs.	6 to 13
Pumped at 25°C. over weekend, 3 days	2 to 3

[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 1, 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. 1 - 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 recovered 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 II and of the polyester film in Table III.

Table II

(U) Heat of Combustion of 2-Octanone

	Sample 1 $-\Delta^{\circ}_{c}/M$ (cal./g.)		Sample 2[a] $-\Delta^{\circ}_{c}/M$ (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	Ave.	9,367.7
	= ±2.0 cal./g.		= ±1.9 cal./g.

[a] This sample contained about 0.3% water.

Table III

(U) Heat of Combustion of Polyester Film

$-\Delta^{\circ}_{c}/M$ (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 (1).

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

Table IV

(U) Results of Analyses of Bomb Washings

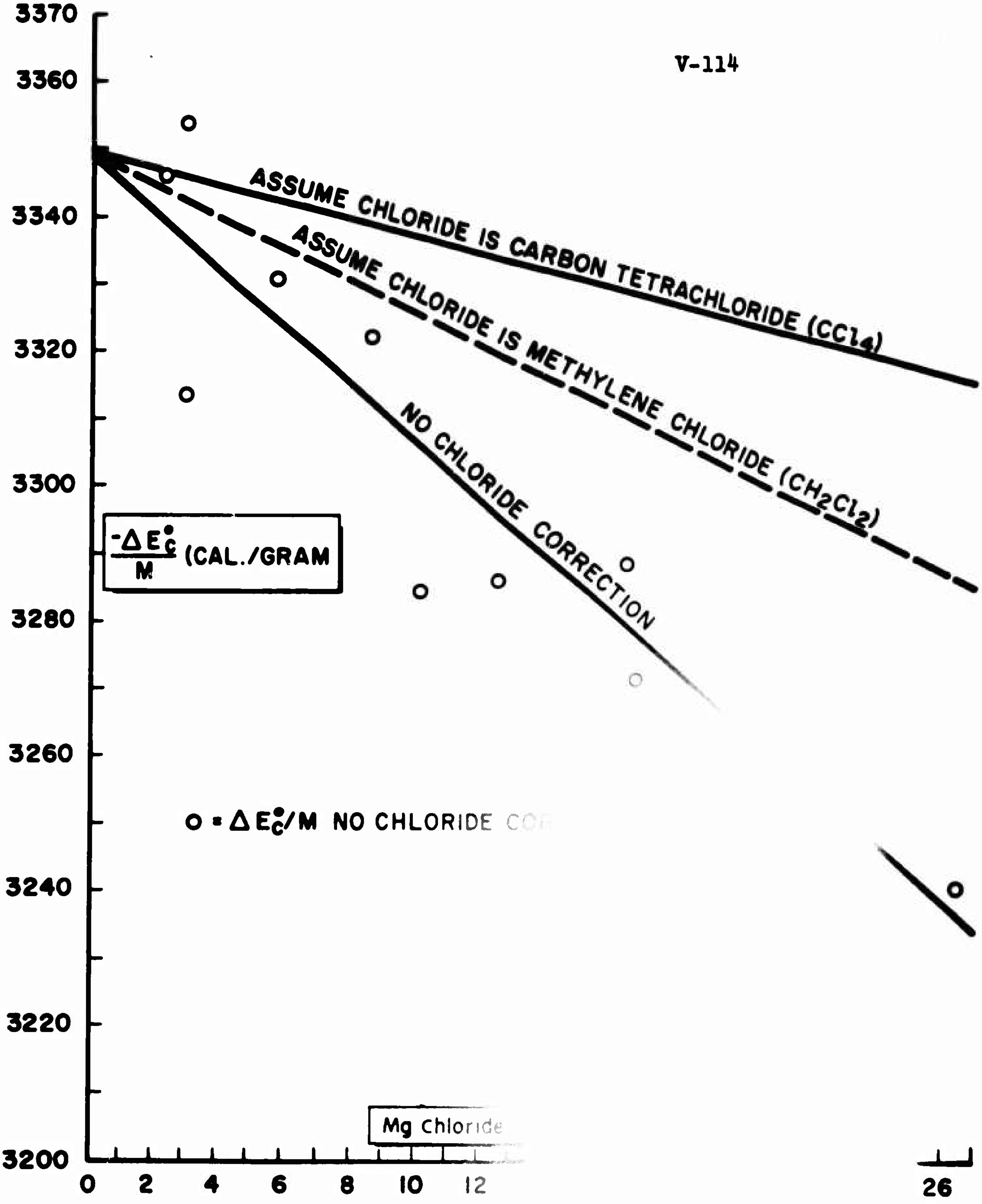
Experiment No.	Fluoride %	Chloride %	Nitrogen %
1	92.9	16.2	13.2
2	96.8	11.6	10.9
3	98.0	8.1	12.0
4	98.4	7.1	10.0
5	99.7	4.1	12.0
6	99.8	11.8	12.2
7	97.8	12.4	12.1
8	97.7	1.5	9.3
9	96.3	1.8	11.4
10	99.4	1.1	11.2
11	100.2	4.1	11.0
12	100.0	10.1	11.4

(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 I).

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

(C) For calculation of the "Washburn corrections," the following data were taken from the Rohm & Haas report (2): 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 $-\Delta^{\circ}_{c}/M$ for each combustion experiment corrected for the CH_2Cl_2 left in the TVOPA was calculated (Table V). A plot (Figure 2) of these $-\Delta E^{\circ}_{c}/M$ 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 $-\Delta E^{\circ}_{c}/M$ values are corrected for chloride assuming it is all CH_2Cl_2, a trend in $-\Delta E^{\circ}_{c}/M$ with chloride is still apparent. Even a correction


V-114
3370
3360
3340
3320
3300
3280
3260
3240
3220
3200
$\frac{-\Delta E_c^\circ}{M}$ (CAL./GRAM
ASSUME CHLORIDE IS CARBON TETRACHLORIDE (CCl4)
ASSUME CHLORIDE IS METHYLENE CHLORIDE (CH2Cl2)
NO CHLORIDE CORRECTION
○ = ΔE°c/M NO CHLORIDE CO
Mg Chloride
0
2
4
6
8
10
12
26

assuming the chloride was all present as CCl_4 would not completely eliminate the trend in $-\Delta^{\circ}_{c}/M$ 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 V). In order to obtain a zero chloride value for $-\Delta E^{\circ}_{c}/M$ a straight line fit was made by a least squares treatment to the data plotted in Figure 2 and listed in Table V. The intercepts of these lines at zero chloride content were for $\Delta E^{\circ}_{c}/M$ = 3,348.9 ± 3.7, -3,348.9 ± 3.8, -3,348.6 ± 3.9 cal./g. The standard deviations of the respective $-\Delta^{\circ}_{c}/M$ values in Table V from the least squares lines were calculated from the equation $\sigma = \Sigma X_1/n(n-2)$. 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 $\Delta E^{\circ}_{c}/M$ 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 $\Delta E^{\circ}_{c}/M$ values vary linearly with the chloride content from none to 25 mg. chloride per gram of sample.

Table V

(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 $\Delta H^{\circ}_{c} = -1623$ kcal./mole reported by Rohm & Haas (2) 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 $-\Delta E^{\circ}_{c}/M$ extrapolation to zero chloride content.

B. WORK IN PROGRESS (U)

(C) The heat of combustion of poly[bis(difluoroamino)epoxypropane], P-BEP, is being run by a technique similar to that used for TVOPA. Preliminary results include analyses that indicate some loss of fluorine since the original analysis by Shell Development Company.

(C) A dry box facility for beryllium compounds is now operative. We are awaiting a sample of alane-terminated beryllium hydride polymer from Rocketdyne.

(C) The heat of explosion of CF_3ONF_2 and hydrogen is being investigated. Preliminary results indicate complete reaction to CO_2, N_2, and HF.

(U) Exploratory work has shown that nitrogen trifluoride mixtures with octafluorocyclobutane and/or tetrafluoroethylene explode and give quantitative conversion to CF_4, N_2, and F_2. The octafluorocyclobutane is attractive as an ignition promoter for compounds which ordinarily might not react with NF_3. The products, CF_4 and N_2, are stable, unassociated gases, which is an advantage over the highly associated HF produced when H_2 is used as an igniter.

C. SAMPLE PURIFICATION AND SYNTHESIS (U)

1. Purification (U)

(C) During this quarter, a final 4 g. of TVOPA, 1,2,3-tris-[1,2-bis(difluoroamino)ethoxypropane, was purified by the procedure described in our Second Quarterly Report (3) and delivered to the Thermal Research Laboratory. The purification of P-BEP, poly[bis-(difluoroamino)-epoxypropane], by a similar procedure is being continued. About 5 g. has been prepared for the Thermal Research Laboratory.

2. Synthesis (U)

a. General (U)

(U) The synthesis and purification of CF_3ONF_2 have advanced to the point where material of >99% purity has been isolated. Recently, a gas chromatographic purification procedure has been developed in which passage of partially purified CF_3ONF_2 through a 21-foot Kel-F tetramer column (25% oil on Chromosorb W) at -65°C. yielded CF_3ONF_2 that was not contaminated by CF_3OOCF_3. A previous attempt to remove CF_3OOCF_3 by passing a 0.2 g. sample through a 21-foot TCP column (25% TCP on Chromosorb W) from -30° to -70°C. gave little separation. About 30 g. of CF_3OF also was prepared during this quarter for starting material.

(U) About 4 g. of CF_3ONF_2 was delivered to the Thermal Research Laboratory during this quarter.

b. Experimental (U)

(U) The reaction used to synthesis CF_3ONF_2 was approximately the same described previously (3), but the procedure used in the purification has been revised. Crude CF_3ONF_2 was first washed with 50% H_2SO_4 to remove some of the N_2O and N_2F_4 which may have been present. This crude material was then washed with 50% NaOH to remove CO_2, NO, NO_2, and SiF_4. To remove CF_4, NF_3 and remaining N_2O most effectively, codistillation was used. The removal of CF_3OOCF_3 from CF_3ONF_2 was accomplished by vapor phase chromatography through a 21-foot Kel-F tetrameter column (25% oil on Chrmosorb W) at -65°C. CF_3ONF_2 of >99% purity resulted. Recently, 1 g. of CF_3ONF_2 was purified by this procedure.

SECTION III

(U) COMBUSTION KINETICS

A. INTRODUCTION (U)

(C) The study of the combustion characteristics of a beryllium hydride propellant has been continued. During this period additional studies of the decomposition of BeH_2 have been made. The combustion reaction of BeH_2 and NO has been investigated. The major task undertaken during this time has been the study of the oxygen combustion of beryllium hydride. The reaction was followed by monitoring one absorption line of BeH^+ and one of the OH radical.

B. EXPERIMENTAL PROCEDURES (U)

(C) The procedure reported in our two earlier reports (3, 4) was used to study the decomposition of BeH_2 as well as its reaction with NO. The procedure utilizes a pre-set spectroscopic lamp delay to give point-by-point data over a wide range of absorption.

(U) The system utilized in our time-resolved photomultiplier circuit is quite different, and warrants a description. The first task is to find at least one absorption line of each specie to be studied which is intense enough to be seen above the gross fog on the spectroscopic plate. The next problem is to determine the width of the line in angstroms and translate it into millimeters of width. This is accomplished by determining the plate factor (number of angstroms photographed per millimeter length of spectroscopic plate) for the particular grating setting. Our plate factors lie between 7.4 Å/mm. and 7.5 Å/mm. An absorption line of 0.2 Å width would require a slit of only 0.027 mm. width. In addition to cutting such a narrow slit in the copper mask, which is placed in the exit end of the spectrograph instead of the spectroscopic plate, the additional problem of translating the wave length differences of two absorption lines into linear differences of the copper strip is also difficult. This is done by measuring the actual linear distance of the two lines of an exposed spectroscopic plate and using this difference as soon as one of the slits for one of the lines has been made.

(U) The problem can be defined as simply cutting two 0.02-0.03 mm. wide slits in a copper sheet 1 in. x 10 in. x 0.125 in. to within an accuracy of 0.01 mm. The accuracy with which the slits are made is quite critical since light will leak in around the absorption line if the slits are too wide. This leakage of light will cause the photomultiplier to react as if the absorption line were weak (giving only a slight change in current). The precision of the slit width is not as critical in emission spectroscopy, since one is measuring a narrow beam of light superimposed on a on a non-emitting background. Only the emission line is seen even if the slit is several times as wide as the emission line. However, in absorption spectroscopy the criterion is to make the slit even narrower than the full absorption line. Thus, the light above the wings of the absorption line is negated.

(U) The correct linear distance between slits also requires great accuracy. This distance determines the wavelength spread of the absorption line. One absorption line can be made to coincide with one of the slits by turning the grating. The coincidence of the second line with the second slit is strictly a function of the workmanship employed in preparing the masks.

(C) The 2751.8 Å line of BeH^+ was chosen because of its proximity to the 2752.77 Å line of mercury. The mercury emission line was used to line up the grating so that the 2752.77 Å mercury line fell on the slit we propose to use for the 2750.1 Å line. By using an absorption line close to that of the mercury calibration line, the inherent error in the gear train of the spectrograph is minimized, as the distance through which the grating must be turned is quite small. The indirect means of lining up the grating and exit slits can be useful for aligning one absorption line and one slit. Since the other slit is a fixed distance from the fiducial slit, it will coincide with the absorption line only if the mask was properly prepared and precise measurement taken and accurate placement of the slits employed.

(U) In this laboratory a novel system is employed to prepare slits and masks. First, the distances between the desired lines recorded on the spectroscopic plate are carefully measured (with our linear comparator). The distance is measured from the low wavelength side of the higher wavelength line to the upper wavelength side of the lower line. Next, the width of the line (in mm.) is measured. The center of the spectroscopic plate is next lined up with the center of the copper mask. The approximate position of each line to be monitored is scribed across the copper mask as viewed through the plate. Then 3/8 in. holes are drilled in the copper using the scribe marks as centers. The copper mask is then transferred back to the linear comparator for the rest of the operation.

(U) Double edged razor blades are broken in two along their long axis. The blades are then cut to 1 in. lengths (width of the copper mask). One razor blade is glued over the farther half of one of the 3/8 in. holes with Dow Corning RTV 731 after being carefully lined up perpendicular to the edge of the mask with the aid of the cross-hairs in the microscope of the linear comparator. The second razor blade is aligned parallel to the first and separated from it by a distance equal to one-half the width of the absorption line under consideration. In the case of the 2751.8 Å line, this distance is 0.020 mm. The second razor blade is then glued making a completed slit 3/8 in. and 0.020 mm. wide. The sharp edges of the razor blades make ideal slit jaws as they have converging edges facing the radiation to minimize diffraction, as required by the laws of physics.

(U) When one slit is finished, the whole mask is moved laterally, while still on the carriage of the linear comparator, to a distance corresponding to the nearer edge of the second absorption line. The above steps are repeated for preparing the second slit.

(C) The mask presently being used worked very well in the first attempt, attesting to the accuracy of its construction. It was employed to monitor the BeH^+ and OH peaks in three systems: BeH_2 decomposition in vacuum, $BeH_2 + O_2$, and BeH_2 + NO.

(C) The BeH_2-O_2 combustion was studied at approximately 0.1, 10, 20, and 50 mm. of oxygen. The BeH_2 decomposition was studied in vacuum and at 50 mm. of argon. The reaction between BeH_2 and NO was attempted at 21 mm. pressure of NO. Larger samples of BeH_2 were flashed in these runs to insure sufficient intensity. The average weight is about 0.04 gm.

(C) A second copper mask is almost completed. It will be used to monitor the 2751.8 Å line of BeH^+, the 3089.1 Å line of OH, and 3383 Å line of BeO simultaneously.

(C) Under construction are masks to monitor the BeH, BeO species, and the BeH^+-BeO-BeH species. The latter mask should prove helpful in determining the ratio of intensities of BeH and BeH^+ as well as their induction times.

(U) The data, i.e., photomultiplier outputs, are recorded on an oscilloscope or on the tape recorder, depending upon the lifetime of the species and their intensity changes during the reaction. The recorded data are then played back into an oscilloscope and the trace photographed for a permanent record. When the three-slit masks are complete, all data will be recorded on the tape recorder to give one continuous time-history of the reaction.

(C) The masks can be used to study the reaction between BeH_2 and any material which will yield BeH^+ and OH, and BeH-BeO-BeH^+ as products respectively. Such materials as NO_2, CO_2, AP, and ClO_2 could be studied in reactions with BeH_2 utilizing the copper masks available in this laboratory.

C. RESULTS AND DISCUSSION (U)

1. Beryllium Hydride Decomposition (U)

(C) As reported in our previous quarterly reports, BeH_2 decomposed to BeH and BeH^+, according to absorption spectral evidence. In addition, H_2 and Be metal are detected as products after the decomposition is complete. From the above evidence, we conclude the first step in the decomposition of BeH_2 is:

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

(C) The recombination of hydrogem atoms accounts for part of the hydrogen seen at the conclusion of the reaction. Additional reactions involving BeH are:

$$BeH + H \rightarrow Be + H_2 \qquad (2)$$

and

$$BeH + BeH \rightarrow Be + H_2 \qquad (3)$$

This can account for the Be metal and H_2 gas produced.

(C) It was assumed the BeH^+ was formed from the reaction:

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

This reaction is calculated to be endothermic by 210.34 kcal. (Data from JANAF Tables for all species except BeH^+ which was calculated for us by the Dow Thermal Research Laboratory).

(C) Reaction (4) produces an electron as a result of the interaction of radiation upon BeH. A second reaction could be written for the formation of BeH^+ which is just as plausible and thermodynamically more favorable.

$$BeH + H \rightarrow BeH^+ + H^- \quad \Delta Hr = +180.55 \text{ kcal.} \qquad (5)$$

(U) Many charge transfer reactions are known in high temperature chemistry of hydrocarbon system. CH^+ is a well known product of the flash photolytic decomposition of acetylene.

(C) The slower rate of disappearance of BeH^+ when observed on our spectroscopic plates as compared to that of BeH could be explained when one considers the various steps in which each hydride species participate. As seen above, BeH can react by (2), (3), (5), and possibly (4). BeH^+ on the other hand can disappear by the reaction:

$$BeH^+ + H^- \rightarrow Be + H_2 \quad \Delta Hr = -304 \text{ kcal.} \qquad (6)$$

or

$$BeH^+ + H \rightarrow Be^+ + H_2 \quad \Delta Hr = -35.14 \text{ kcal.} \qquad (7)$$

or even remotely by the step:

$$BeH^+ + BeH^+ \rightarrow 2\,Be^+ + H_2 \quad \Delta Hr = +38.96 \text{ kcal.} \qquad (8)$$

Once BeH is formed in the flash, it would react rapidly with itself and with the hydrogen atoms formed by steps (2) through (5) in the volume immediately around each graphite strip. The BeH^+ is then being formed in this rapidly expanding hot gas volume. As this hot gas volume expands, the species in it are removed farther from each other. Since BeH^+ reacts bimolecularly and since each reactant is being sped outward from the strips, the chance of two particles colliding and reacting is becoming more remote as each microsecond passes.

(C) In our apparatus, it is safe to say that the BeH^+ reactions are kinetically controlled. Thermodynamic considerations would lead to low BeH^+ concentrations even at maximum concentrations. The BeH^+ would also disappear at a rate faster than that of BeH or, at best, would disappear at a rate parallel to that of BeH. However, our photographic work shows the BeH^+ intensity to be rising while that of BeH is falling, indicating the faster rate of disappearance of BeH. The inclusion of steps (5) through (7) is logical in light of the extreme temperature (~2500°K.) obtained in such a short time (25-35 μsec.). The tape recorder-photomultiplier circuit will cast further light on the BeH-BeH^+ equilibrium.

2. Beryllium Hydride and Nitrous Oxide (C)

(C) The BeH_2 was flashed in 21 mm. of NO. The system was over-oxidized in NO according to the equation:

$$BeH_2 + 2\,NO \rightarrow BeO + H_2O + N_2 \qquad (9)$$

(C) The reaction was observed from 10 to 485 μsec. after the photoflash. The data were recorded on Kodak 103-O and 103-F spectroscopic plates. In a few cases, a few OH lines were observed, whose intensity and lack of reproducibility led us to attribute their existence to the slight outgassing of air and water absorbed on the cell walls. The main reaction intermediate was HNO. It is believed that this was formed in the following way:

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

$$H + NO \xrightarrow{M} HNO \qquad (10)$$

and possibly by:

$$BeH + NO \rightarrow Be + HNO \qquad (11)$$

The corresponding BeH^+ reaction for (11) would be:

$$BeH^+ + NO \rightarrow Be^+ + HNO \qquad (12)$$

The rapid disappearance of HNO is attributed to:

$$HNO + H \rightarrow H_2 + NO \qquad (13)$$

(C) The presence of NO tended to cause the BeH^+ to disappear at a slower rate than when BeH_2 is flashed in a vacuum. The same effect has been noted when argon or nitrogen was added to the cell.

(C) Our conclusion is that the nitric oxide serves only as a third body to the recombination of hydrogen atoms and is not an oxidizer to BeH_2 under our experimental conditions.

3. Photometric Observations of Beryllium Hydride-Oxygen Reaction (C)

(C) The oxidation of BeH_2 by O_2 was studied under four different pressures of oxygen. The pressures were 0.1, 10, 20, and 50 mm. respectively.

(C) Studies on the vacuum decomposition of BeH_2 have been instituted using a photomultiplier to follow the intensity of a BeH^+ absorption line. As seen from Figure 3, the lifetime of BeH^+ is about 22 milliseconds when the 2751.8 Å line of the P branch of the (0, 1) transition of the $'\Sigma-'\Sigma$ ground state electronic absorption system is followed. Figure 4 shows the lifetime of BeH^+ when the $R_{25\frac{1}{2}}$ line at 2834.7 Å of the same transition is followed. The further reduction in absorption of Figure 4 was caused by the movement of the light source. This movement is caused by the shock wave resulting from the air heated by the flash. The problem was solved by supporting the light source independently of the flash apparatus.

(U) As pointed out above, during a flash, there is always some OH present. This is caused by absorption of water and air from the cell walls. The problem is minimized by drying the glassware in an oven at 125°C.

(C) Figure 5 shows the absorption spectrum of the 2751.8 Å BeH^+ line and the 3089.1 Å OH line recorded simultaneously resulting from the decomposition of BeH_2 in vacuum.

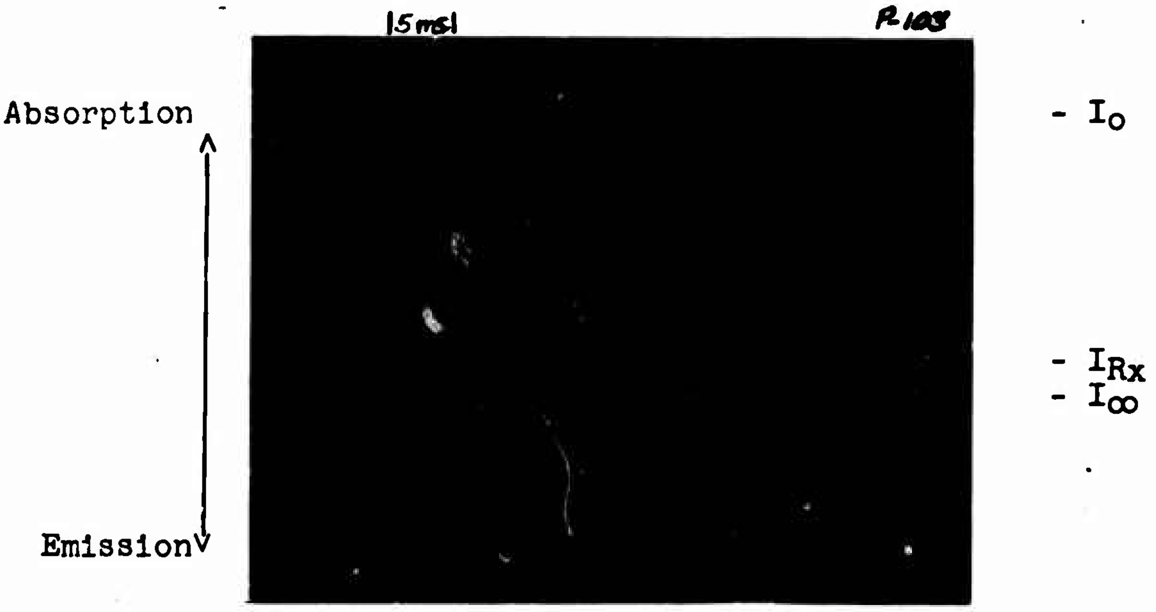
(C) It is noted that the OH line is usually present even when no oxygen containing compound is added to the cell. This absorption is an indication of background oxygen. The upper (BeH^+) trace was recorded at 1/100 the sensitivity of the lower (OH) trace.

(C) The same two absorption lines for BeH_2 in 0.1 mm. oxygen can be seen in Figure 6. The BeH^+ shows total absorption out to at least 50 milliseconds. The OH readical is seen to disappear much more rapidly and is essentially gone at 30 milliseconds.

(C) Figures 7, 8, and 9 show the absorption spectra of BeH^+ and OH resulting from a 1500 joule flash upon BeH_2 with 10, 20, and 50 mm of O_2 respectively. The most striking feature of these three figures is that the lifetime and intensity of the OH radical approaches that of the fuel, BeH^+, as the oxygen pressure is raised. This tends to show that to a large degree the step:

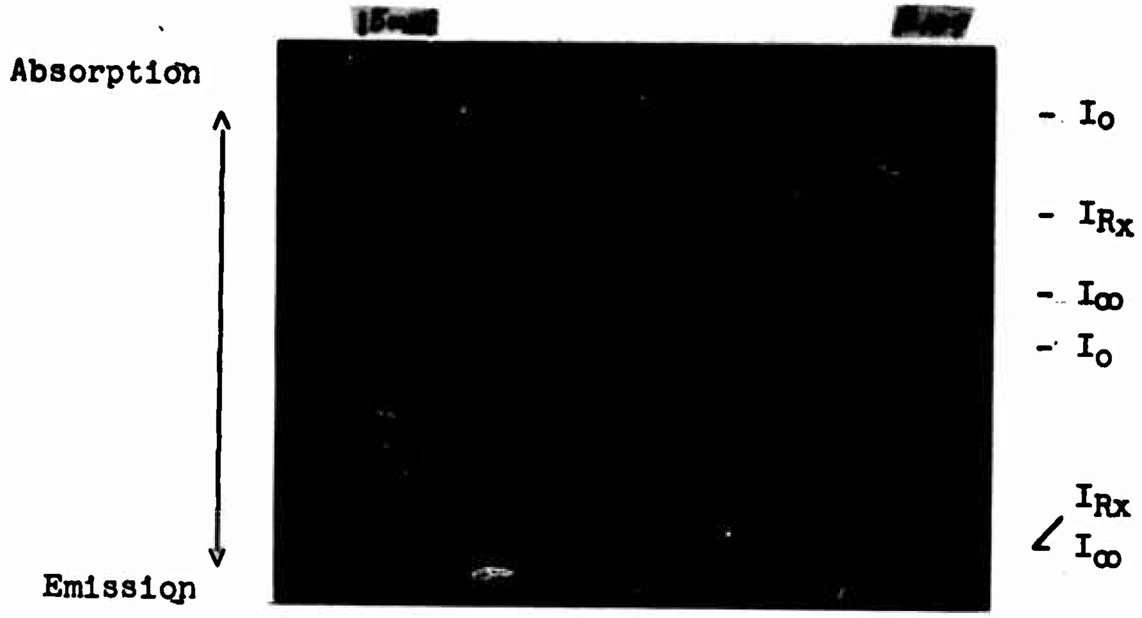
$$BeH^+ + O_2 \xrightarrow{e^-} BeO + OH \qquad (14)$$

(C) Fig. 3 - Lifetime of BeH^+ from 2751.8 Å Line



(C) Fig. 4 - Lifetime of BeH^+ from 2834.7 Å Line

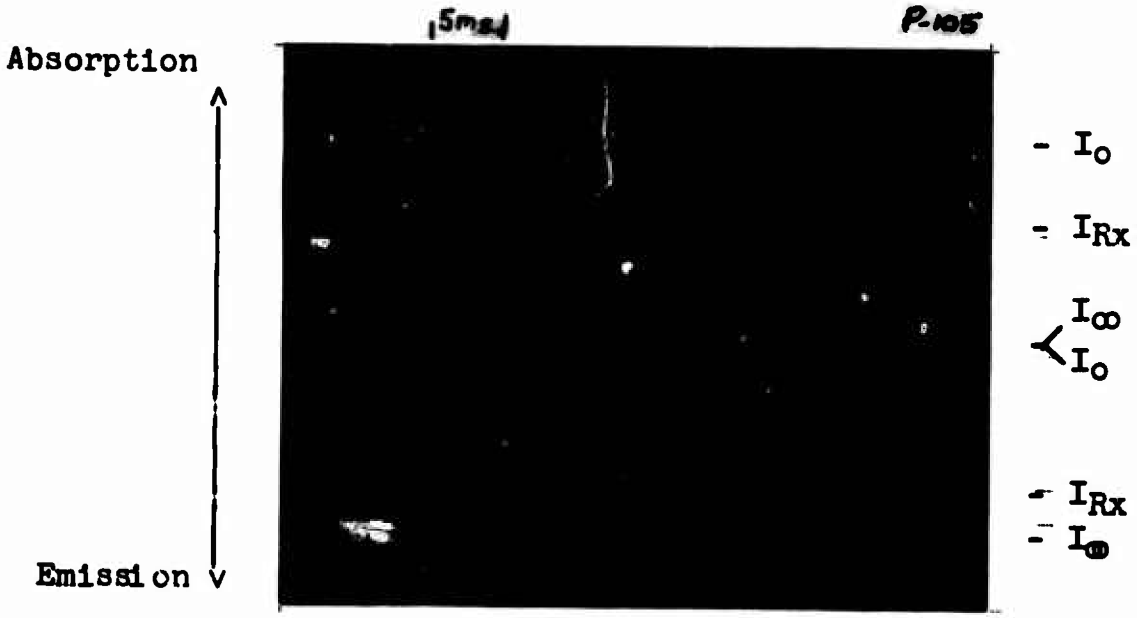
I_o = Baseline with light off.
I_{Rx} = Absorption due to 2751.8 Å line of BeH^+
I_∞ = Baseline with light on - no absorption.
5 millisec./horizontal div.
Flash energy = 1500 joules



(C) Fig. 5 - Absorption of BeH^+ and OH

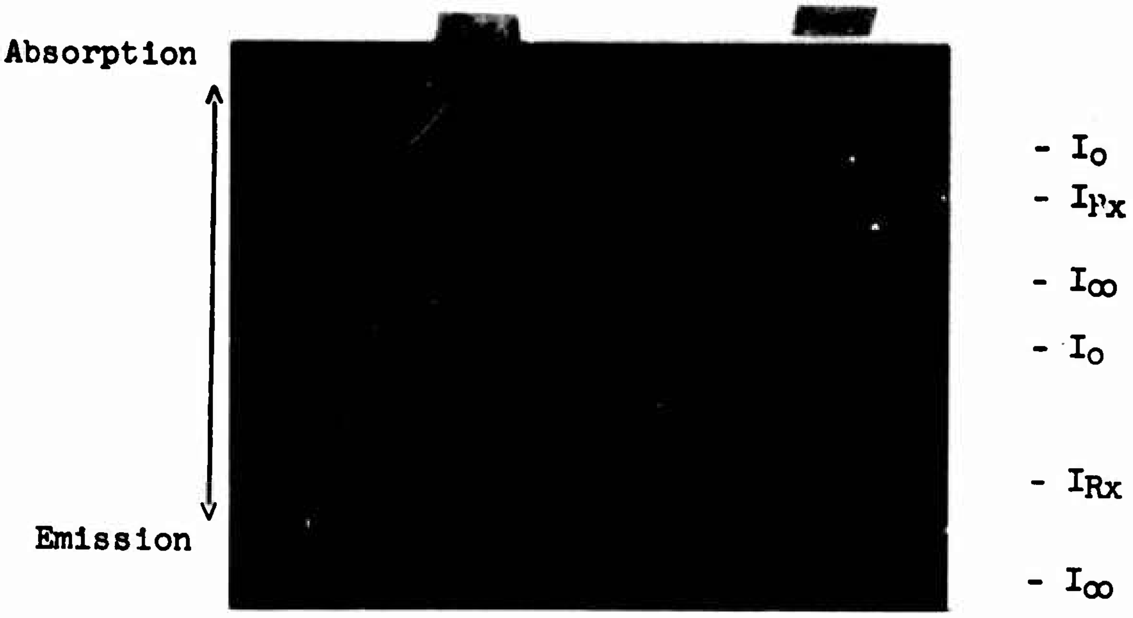
Upper trace 2751.2 Å line of BeH^+.

Lower trace 3089.1 Å line of OH.



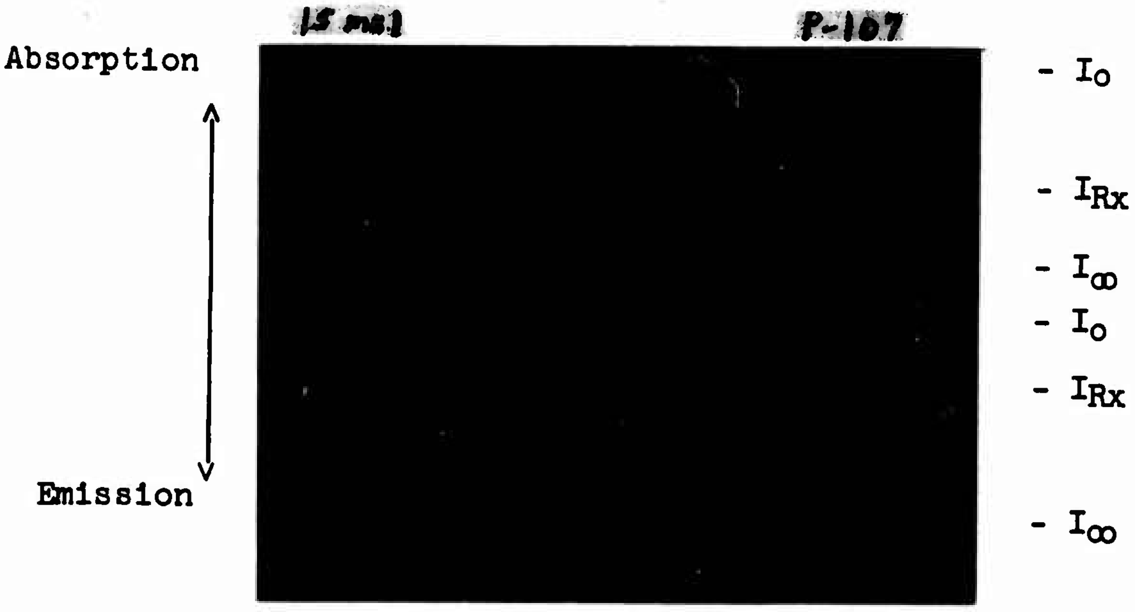
(C) Fig. 6 - Absorption of BeH^+ and OH from BeH_2-O_2

P_{O_2} = 0.1 mm. (Same as Figure 5).



(C) Fig. 7 - Absorption of BeH^+ and OH from BeH_2 + 10 mm. O_2

Dips on traces caused by flucuating light source.

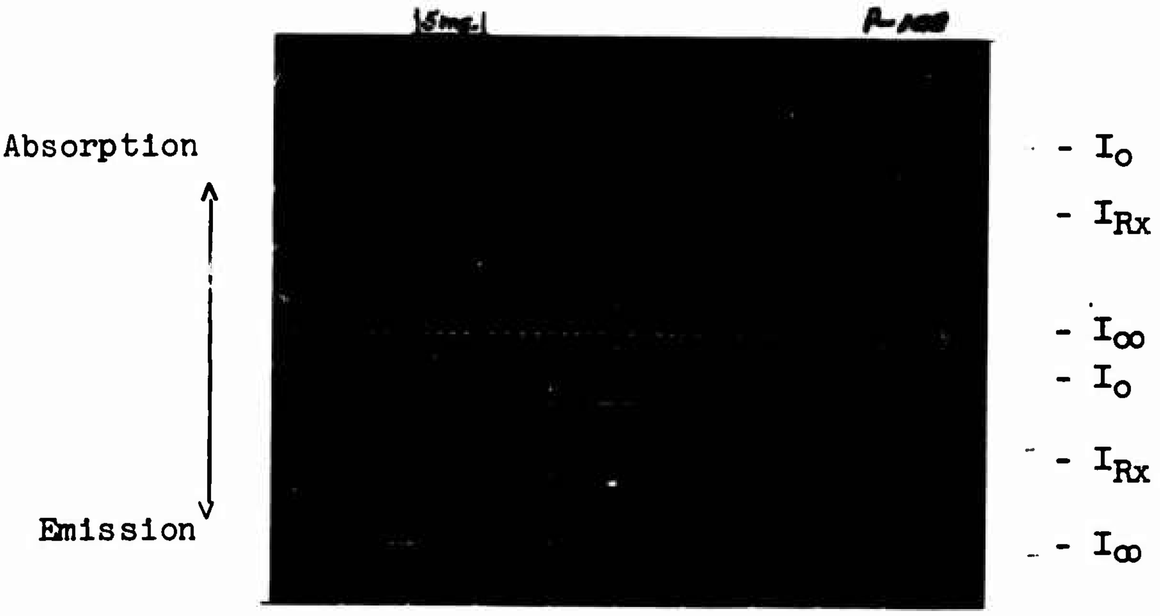


(C) Fig. 8 - Absorption of BeH^+ and OH from BeH_2 + 20 mm. O_2

is fast and efficient, and the OH concentration is proportional to the O_2 content. The implication is that the combustion of BeH_2 is carried out through the BeH^+ species rather than through BeH_2 per se. As soon as a third mask is completed the role of BeH will be studied to determine if it is only a precursor to BeH^+ or if it also plays the role of a fuel.

D. FUTURE WORK (U)

(C) The last quarter of the contract will be spent in studying the systems BeH_2-O_2; BeH_2-AP; and BeH_2-NO with the photometric technique with emphasis on the BeH-OH-BeH^+ interaction.



(C) Fig. 9 - Absorption of BeH^+ and OH from BeH_2 + 50 mm. O_2

SECTION IV

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13 ABSTRACT

The heat of combustion of TVOPA, in oxygen has been determined to be -1613 ±3.5 kcal./mole. From this value and from previous data, the $\Delta H_{f\,298.15}^{\circ}$ is calculated to be -217.4 ± 3.5 kcal./mole. Work in progress includes the heat of combustion of P-BEP by a similar technique. Trifluoromethoxydifluoramine has been synthesized and purified, and the heat of explosion of this compound is being determined.

Additional studies on the combustion kinetics of the decomposition of Beane have been made. The combustion reaction of Beane with nitrous oxide has been investigated. Emphasis was placed on the study of oxygen combustion of Beane. The reaction was followed by monitoring the appropriate radical absorption lines with our recording apparatus.

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NF Compounds						
Combustion Kinetics						
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