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ANNUAL SUMMARY REPORT
Thermochemistry of Selected Compounds
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SUMMARY

It is the objective of this program to determine the heats of formation of selected chemical compounds related to rocket propulsion by applying the method of solution calorimetry. The work covered in this report includes calorimetric and analytical studies of two compounds - aluminum borohydride and SAP. The calorimetric study of aluminum borohydride concerned itself with the vapor phase reaction of aluminum borohydride with water vapor and the vapors of hydrochloric acid respectively. The hydrolyses were carried out at temperatures ranging from 0 to 40°C. It was found that at 0° or lower the production of pentaborane as an undesirable side product was minimized. In an attempt to determine the proper reaction conditions for the reaction of aluminum borohydride with water, water vapor, hydrochloric acid, or hydrochloric acid vapors such that well defined products could be formed in stoichiometric quantities, some 87 runs were performed. Many of these were run for analytical data only, some for thermochemical data only and others for both. From the analysis of these data, it appeared that the probability of the successful study of aluminum borohydride by the calorimetric method would be highest at the lower temperature. During the course of these studies that calorimeter has been operated adiabatically at 0, 25 and 40°C and is currently being operated isothermally at 0°C. As we sought the proper conditions for chemical reaction of this compound and simultaneously generated thermal data, we applied

this thermochemical data to calculations leading to a value for the heat of formation of aluminum borohydride. The values determined certainly must be considered as very preliminary since we had not obtained the optimum reaction conditions for the reaction.

From the thermochemical results of the reaction study of aluminum borohydride with hydrochloric acid (liquid phase) the heat of formation of aluminum borohydride was calculated to be $+5 \pm 10$ kcal/mole. From the thermochemical results of those studies in which the aluminum borohydride was allowed to react with the vapor existing above hydrochloric acid at 25°C , the calculation of the heat of formation yields a value of -8.8 ± 1.6 kcal/mole. A very preliminary value for the heat of formation derived from the data obtained from the reaction of aluminum borohydride with water vapor at 0°C yields a value of $+16$ kcal/mole.

Based on our analytical findings, our emphasis is on the continuation of the 0° water vapor-aluminum borohydride reaction.

Approximately 1.5 g. of SAP material was received from Aerojet General and 9 determinations of the heat of hydrolysis of this material were made. The results yielded a value for the ΔH of -54.4 ± 1.4 kcal/mole. The reaction products were analyzed as was the gaseous component liberated during this reaction. From the results of the analytical study, we are attempting to determine the equation for the reaction which has occurred in these runs. We also expect to repeat these experiments with the receipt of a pure sample of SAP.

I THE THERMOCHEMICAL STUDY OF ALUMINUM BOROHYDRIDE

It appeared from our early work that the hydrolysis of aluminum borohydride with hydrochloric acid at 40°C would offer to us the conditions for carrying out this reaction which would lead to well-defined reaction products and from which we may calculate the heat of formation of the compound, aluminum borohydride. The calorimeter was modified so that it would be capable of carrying out an adiabatic thermochemical study at the temperature of 40°C. This was accomplished with little loss, if any, to the accuracy of the measurements.

II METHOD OF ALUMINUM BOROHYDRIDE STUDIES

Ten hydrolyses studies of aluminum borohydride were performed by preparing a sample of the aluminum borohydride in a glass vial and submerging this in 200 cc of hydrochloric acid of various concentrations in a reaction bomb lined with tantalum. Upon reaching equilibrium in the calorimeter at 40°C, the aluminum borohydride sample was then brought in contact with the acid solution by a crushing mechanism. A violent reaction occurred, heat was liberated and measured. The hydrogen evolved was measured in a thermostated hydrogen evolution apparatus. The final solution was analyzed for aluminum and boron. The liberated gas was submitted for gas chromatographic and infrared analysis. From the infrared spectrogram one noted a carbon-hydrogen stretching frequency. This contaminant was noted also by other workers (Dr. D. Wagman of the National Bureau of

Standards and Dr. G. Sinke of Dow Chemical). The hydrogen analyses consistently ran low by approximately 15-20% as did the boron analyses. The boron to hydrogen ratio was in fair agreement with the theoretical ratio of these two materials. The aluminum value ran 2% low. The heat data generated in the 10 runs was fairly consistent, and if one uses the amount of boron formed or the amount of hydrogen evolved in this reaction as a means of determining the amount of aluminum borohydride that reacted then the heat of reaction is -290 ± 15 kcal/mole. Using these data in calculating the heat of formation of aluminum borohydride from this reaction heat and the known heats of formation of boric acid, aluminum chloride, hydrochloric acid and water one arrives at a heat of formation of approximately $+5 \pm 10$ kcal/mole. The value must be considered as preliminary since obviously the reaction products were not as well-defined as desired or in the proper stoichiometric quantities.

III THE HEAT OF REACTION OF ALUMINUM BOROHYDRIDE WITH THE VAPOR OF WATER AND/OR HYDROCHLORIC ACID

In those studies in which aluminum borohydride was allowed to react with hydrochloric acid solution, the violence of the reaction resulted in solid products appearing above the liquid level on the walls of the reaction vessel in addition to the products which were also dissolved in the acid solution. The prevention of this did not suggest itself with facility. To continue with that approach but to determine the amount of

material in solution and the amount of that adhering to the walls (above the solution) would appear to add to the uncertainty of the reaction heat and the calculation associated with it. We, therefore, sought to improve upon the method in an effort to reduce this level of uncertainty.

In this series of experiments, the aluminum borohydride was allowed to react with the vapor of hydrochloric acid or water existing in a closed reaction vessel. The source of this acid or water vapor was 2 cc of the liquid contained in a vial attached to the stem of the crushing mechanism of the bomb. 37% Hydrochloric acid was used as the liquid for the acid runs. The aluminum borohydride samples ranged in weight from .03 to .14 g. The material was fractionally distilled and contained in a small glass vial and sealed with a flame. The reaction vessel was sealed, evacuated and back-filled with hydrogen which had been saturated with hydrochloric acid vapor (or water vapor). Upon assembling in the calorimeter and upon reaching equilibrium, the reaction was initiated by crushing the vial containing the aluminum borohydride. Following each run, the contents of the bomb were analyzed for hydrogen, boron and aluminum. In the hydrogen analysis, the hydrogen was first passed through a soda-line trap to remove the hydrochloric acid vapor. The hydrogen was then bubbled through a water bubbler and collected in a flask over a volume of water thus displacing the water. This displaced water was collected and weighed. The aluminum was determined by EDTA method and the boron determined by the Mannitol Titration

Method. The aluminum recovery averaged approximately 98% again. The boron and the hydrogen once more were low this time by 10%. Calculating the heat of formation of aluminum borohydride from these runs, the value of -8.8 ± 1.6 kcal/mole was derived. In these calculations, the low boron and hydrogen analyses were not corrected; and therefore, this answer stands in error until the boron or hydrogen could be accounted for. Other difficulties with this method were related to the fact that the hydrochloric acid vapor reacted with the nickel containing lid of the reaction vessel thus introducing other metallic ions into the final wash solution prior to the analysis for aluminum and boron. We noted nickel in solution which interfered with the aluminum values; however, the nickel was removed by an electrolytic mercury cathode procedure. In continuing the investigation of the hydrolysis of aluminum borohydride with the vapors of hydrochloric acid or water, we attempted to seek the reasons for the low values of boron and hydrogen. We sought the assistance of the Olin-Mathieson Analytical Laboratories in New Haven, Conn.

As a check on our analysis for aluminum and boron, we asked the Olin Laboratories to analyze for these elements also in the solution resulting from one of our reactions. Their findings were essentially equal to those of ours. The mass spectrographic analysis of the evolved hydrogen showed a 0.1 mole % pentaborane found in the hydrogen.

To improve upon the boron analytical work, we changed from the Mannitol procedure to the Chapman Distillation which

is generally acknowledged as being more reliable. Repeating the analyses of boron and hydrogen where the reacting liquid was water rather than hydrochloric acid, the boron analyses appeared to be closer to the theoretical value. The hydrogen, however, was still low but to a less extent.

Upon lowering the temperature of this reaction, we carried out the hydrolysis at -80°C and submitted the evolved gas to mass spectrographic analysis. By comparison, the pentaborane found in this reaction was .06 mole % as compared with .1 mole % when the reaction was carried out at 25°C . The .06 mole % is approximately equal to the lower limit of detectability of the mass spectrometer. It appeared, therefore, that at a lower temperature the formation of the pentaborane would be minimized. However, -80°C appeared to be a temperature which would be somewhat difficult to maintain and operate calorimetrically. We, therefore, proceeded to determine at which temperature above -80°C we might carry out the calorimetric study. We carried out a series of reactions and analyzed for aluminum, boron, and hydrogen. We found no significant differences up to 0°C , but at 25°C we got lower values for boron and hydrogen. Therefore, 0°C appeared to be a preferable temperature at which to operate the calorimeter with no obvious difficulties presenting themselves.

The calorimeter was modified to operate adiabatically at 0° or slightly higher. Precooled water was continually run through the jacket. A heater was installed in the jacket of the

) calorimeter which was tripped by a relay when the differential temperature between the jacket and the reaction bucket and container exceeded a predetermined value. The adiabatic method was thus accomplished. Upon analyzing the heat data from several runs, the level of scatter was found to be higher than desired. Closer analysis showed that the cooling water entering the jacket varied as the ice in the precoolers melted and varied the temperature of the flowing water. Since the ΔT of a run is of the order of $.2^{\circ}\text{C}$ and in an effort to reduce the error introduced by the fluctuating inlet water temperature, a modification to the calorimeter was made to allow the study to be performed isothermally. In the original adiabatic method, two thermistors each in one arm of a Wheatstone bridge actuated a heater in the jacket when the difference in resistance between the two thermistors exceeded a predetermined value. As the water in the jacket warmed up because of the inlet temperature of the incoming water having increased by the stratification of temperature in the ice bath, the inner bucket containing the reaction vessel saw a higher temperature and its slope or heat transfer characteristics changed accordingly. This situation lead to slopes which varied. In the modified isothermal setup, one thermistor was placed in the outer jacket and the other thermistor was replaced with a resistor of a value equal to that of the thermistor at 0°C . By so doing, one arm of the Wheatstone bridge was held constant. The electronics involved allowed one to choose the ΔR desired between the control thermistor (or resistor in this case) and the resistance of the

thermistor in the water jacket. To test this modified method, two simulated runs were made one introducing electrical energy into the calorimeter and the other by measuring the heat of reaction of magnesium with hydrochloric acid contained in the reaction bomb. In both cases the slopes initially and finally were straight lines. In the simulated runs, the calorimeter temperature was adjusted such that a slight warming trend was obtained. Upon completion of the heat input (resulting in 0.2°C rise) and upon reaching final equilibrium a cooling trend was observed. The method then appears satisfactory for the study of the hydrolysis of aluminum borohydride. The samples have been prepared, and we are currently preparing for these runs.

IV THE HEAT OF HYDROLYSIS OF SAP

A sample weighing approximately 1.5 g. of the newly synthesized SAP compound from Aerojet General had been received and our initial objectives were to get preliminary heats of hydrolysis data on the material received. This initial sample was not of the highest purity desirable for calorimetric work, but the generation of the calorimetric data on this material was considered a useful exercise first to derive preliminary thermochemical data for this compound; and secondly to uncover any possible problem areas which might occur in the study of this compound. The heat of hydrolysis was measured in a reaction vessel containing approximately 100 cc of water. This reaction vessel sat in 2 liters of water and this was surrounded with circulating water jacket operated adiabatically. Samples of

SAP were prepared in a nitrogen drybox and weighed approximately .02 g. Nine determinations were run, the average heat was -54.4 ± 1.4 kcal/mole. Analytical analysis of the resultant solution has shown the anion to be quantitatively intact. The cation, however, had been shown to break down during this reaction yielding nitrogen gas as one of the products. The nitrogen determination was detected by the Olin-Mathieson Laboratory by mass spectrographic methods and found to exist at the level of .02 mole/mole of SAP reacted. We expect to rerun the calorimetric and the analytical runs upon receipt of a more pure sample.

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13 ABSTRACT Aluminum borohydride and SAP have been studied calorimetrically in an effort to derive their heats of formation. Much thermal and analytical data have been collected in this search for the proper reaction conditions which will yield the useful information sought. The SAP material has reacted quickly and completely with water and the thermal data were consistent. The aluminum borohydride hydrolysis is our preferred reaction but as yet the results are not as consistent as desired. These hydrolysis studies are currently being carried out isothermally at 0°C. The analytical support data is most useful and essential in this study.		

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