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FINAL REPORT

Thermochemistry of Selected Compounds
Nonr-3608(00) (U)

by
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November 14, 1961 - November 15, 1966

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SUMMARY

It has been the objective of this program to determine the heats of formation of selected chemical compounds related to rocket propulsion by applying the methods of calorimetry. The calorimetric techniques included combustion, solution, and reaction calorimetry. The accomplishments of the program are presented in chronological order and rather than repeat the details of all phases of the work, references are made to the appropriate quarterly, semi-annual, or annual report.

Thermochemical studies were made on the following elements and compounds: Lithium Aluminum Boron, LiAl, AlB_2, $LiAlH_4$, Aluminum Hydride, Li_3AlH_6, B_2O_3 (Crystalline), B_2O_3 (Amorphous), H_3BO_3, BCl_3, Aluminum Borohydride, and Fluorammonium Perchlorate.

Section I.

Our initial objective was to determine the heat of formation of the alloy LiAl. Our first attempts were by combustion calorimetry under pressurized oxygen. Aluminum lithium and the alloy LiAl were combusted in an oxygen atmosphere, and the heat evolution measured. The products were also analyzed, and it was frequently noticed that complete combustion was not attained. Attempts at achieving 100% combustion were not entirely satisfactory and for that reason the calorimetric approach was changed to solution calorimetry in which the solvent was hydrochloric acid. Complete reactions were easily obtained, and the generated heat easily measured. The heat of formation of

the compound was assigned the value of -15 kcal/mole (for details see reference 1).

Solubility tests were run for boron, aluminum diboride, and dodecaboride to determine if a suitable solvent could be found which would allow solution calorimetric methods to be employed in determining the heats of formation of these binary compounds. Boron powder dissolved satisfactorily in an acidic potassium periodate solution at 30°C. This solvent was without apparent affect on either AlB_2 or AlB_{12}. Thirty solvent systems were included in the study, none of which proved feasible as a solvent for the borides even at elevated temperatures. A survey of the literature in addition to several private communications was made in search of boride solvent information; no solvents were found. It is concluded that the heats of formation of aluminum diboride and aluminum dodecaboride must be determined by methods other than acid solution calorimetry (see reference 1). The method which would most likely be successful in studying the compound AlB_2 and AlB_{12} is that of fluorine combustion. An apparatus was constructed for the handling of fluorine and the loading of the reaction vessel with fluorine. As part of the study to determine the heat of formation of AlB_2 by fluorine combustion, it was necessary to establish a satisfactory furnace configuration within the bomb which would withstand the energetic combustion. The configuration adopted utilized CaF_2 coated aluminum

disks and crucibles and was found to withstand the thermal shock without shattering. The material designated as AlB_2 when purchased was found to be AlB_{12} plus free aluminum. Upon removal of the aluminum, we continued our studies on the AlB_{12} at fluorine temperatures of 125 psi. 100% combustion was achieved. Since the purity of the material was far below our requirements, we acquired no quantitative data by our fluorine studies (see reference 2).

Section II.

As a preliminary study to determine the heat of formation of the new complex Li_3AlH_6, it was decided to determine the heat of formation of lithium aluminum hydride. To do so, the heats of solution of lithium aluminum and lithium aluminum hydride in hydrochloric acid were measured. From this data, the heat of formation of the compound was calculated to be -24.67 ± 2.21 kcal/mole (see references 2 and 3). The heat of formation of the reaction motors material Li_3AlH_6 was determined by measuring the heats of solution of lithium aluminum and Li_3AlH_6 in 4N HCl at 25°C. The heat of formation was found to be -79.39 ± 3.45 kcal/mole (see reference 2).

The heats of formation of the aluminum hydrides designated as Olane-58 prepared by the Olin Company and Dowane-1451 prepared by Dow Chemical Corporation was determined by measuring the heats of solution of these compounds and aluminum

in 6N HCl at 75°C. Collecting the data to 25°C yielded the following results: Olane-58, the heat of formation was -4.6 ± 1.6; for Dowane-1451, the heat of formation was found to be -2.5 ± 3.7 (see reference 2).

Section III.

The heats of formation of the compounds B_2O_3 (Amorphous), B_2O_3 (Crystalline), and BCl_3 (Liquid) were sought. From the measurements of the heats of solution of B_2O_3 (Amorphous), B_2O_3 (Crystalline), H_3BO_3, and BCl_3 (Liquid) the necessary calculations were made employing also auxiliary data. The heat of formation of BCl_3 (Liquid) was calculated to be -101.04 ± .39 kcal/mole. The heat of formation of B_2O_3 (Crystalline) was found to be -303.63 ± .42. That of B_2O_3 (Amorphous) was found to be -299.30 ± .43. The energy of transformation, therefore, from crystalline to amorphous was found to be + 4.33 kcal/mole ± 0.06 (see references 4,5, and 6).

Section IV. - Studies of Aluminum Borohydride

Investigators of the thermochemical study of the hydrolysis of the aluminum borohydride have met with difficulties which prevent the gathering of consistent heat data (see references 7, 8, and 9). Rulon and Mason[7] observed in their hydrolysis studies, the formation of undesirable brown products and inconsistent heat data although a few of their runs were free of colored products. Kilpatrick[10] noted only a partial hydrolysis of aluminum borohydride and indicated that the complete hydrolysis was to be achieved only slowly. Brown and Brown[11] pointed out the benefit of a catalyst in the hydrolysis

of the borohydride ion. In our search for the proper conditions under which the hydrolysis of aluminum borohydride should be carried out, we have investigated the hydrolysis at temperatures ranging from -80°C to +40°C. The reactions studied were between aluminum borohydride both in the liquid and vapor state and water or hydrochloric acid both in the liquid and vapor state. Analysis of the products following each of the reactions indicated that the most reliable reaction would be between aluminum borohydride vapor and water vapor at 1°C. For many of the reactions in which aluminum borohydride vapor was reacted with the vapors of water at 1°C, the products were analyzed for aluminum, boron, and gaseous hydrogen. It should be noted here that mass spectrographic analysis was made of the hydrogen resulting from the hydrolysis studies both at 25°C and 1°C. The hydrogen generated from the 25°C run contained a significant amount of diborane; whereas, at 1°C the amount was almost negligible. Accordingly, the boron and hydrogens were low for the 25°C run and at the 1°C level the boron and hydrogens came up to close to theoretical values. Although we have made many runs of the hydrolysis of aluminum borohydride at 1°C, we have never been able to achieve the level of reproducibility desirable for proper thermochemical calculations leading to a value for the heat of formation for the compound. We will, however, present a value for this figure based on our results later on in the report. For some of the details of this earlier work see reference 12.

ANALYTICAL RESULTS OF ALUMINUM BOROHYDRIDE HYDROLYSIS REACTIONS

The Olin-Mathieson Company has offered to us the mass spectrographic facilities for the analysis of the hydrogen evolved for the aluminum borohydride hydrolyses, and we have utilized these services to unravel some of the complexities of this particular reaction. The hydrolysis of aluminum borohydride at 25°C with the vapors of water has resulted in the formation of 98.87 mole % hydrogen and 1.13 mole % diborane. At 1°C, the reaction produced 99.97 mole % hydrogen and 0.03 mole % pentaborane. The data reconfirmed our earlier results also by Olin that at the 25°C level, a significant amount of diborane or pentaborane is formed and at the lower temperature (1°C) an insignificant amount of pentaborane is formed. Averaging 45 runs of the hydrolysis of aluminum borohydride with the vapors of water at 1°C, the heat of reaction was calculated to be -238 kcal/mole. Calculating the heat of formation of aluminum borohydride from this plus auxiliary data, yields a value of -17 ± 7 kcal/mole.

SUBSTITUTED AMMONIUM PERCHLORATE STUDIES

Hydrolysis studies have been carried out on fluorammonium perchlorate and the heat of reaction has been determined to be -54.4 ± 1.4 kcal/mole. Mass spectrographic analysis performed by the Olin Company of the gas evolved upon solution of the substituted ammonium perchlorate has identified the gas to be diatomic nitrogen. A 0.5293 gm. sample of SAP yielded 13.8 cc.

diatomic nitrogen. In our analytical studies of the first sample received, the dissolution of the material in water yielded the calculated theoretical amount of the fluoride ion and the perchlorate ion. The amount of nitrogen found by mass spectrographic analysis is too low to account for all of the nitrogen as would be calculated theoretically. We have found no solutions to the reasons for this low value. The nitrogen analyses were carried out on two different samples and two different batches of the material yielding both the low value reported.

CONCLUSIONS

This report highlights the work accomplished under this contract, and the appropriate references covering the details of the experimental work are made. It can be seen from the results of the work that the conditions under which the hydrolysis of aluminum borohydride is performed directly influence the reaction, its kinetics and products. It is a complex reaction, and we have come very close to a stoichiometric reaction.

The dissolution of fluorammonium perchlorate in water again appears to be a complex reaction with regard to the final state of the nitrogen. We are not able to account for all of the nitrogen, and a stoichiometric reaction cannot be proposed at this time. The heat data, on the other hand, appears to be very consistent and reproducible. This is in contrast to the heats of hydrolysis of aluminum borohydride

which has considerable scatter. In our final runs of the hydrolysis of aluminum borohydride at 1°C, the aluminum, boron, and hydrogen as measured analytically are generally close to the theoretically calculated amount.

REFERENCES

(1) Annual Technical Report, November 14, 1961-November 14, 1962, Nonr-3608(00) - Naticnal Research Corporation, Ludwig G. Fasolino, "Thermodynamic Properties of Selected Compounds".

(2) Semi-Annual Technical Summary Reports, January 1, 1963-June 30, 1963, July 1, 1963-December 31, 1963; National Research Corporation - Nonr-3608(00).

(3) Fasolino, J. Chem. Eng. Data 9, No. 1, January, 1964.

(4) Annual Report - Nonr-3608(00), November, 1963-November, 1964, National Research Corporation.

(5) J. Chem. Eng. Data 10, No. 4, October. 1965.

(6) J. Chem. Eng. Data 10, No. 4, October, 1965.

(7) Rulon and Mason, J. Am. Chem. Soc. 73, 5991, (1951).

(8) Donald Wagman, National Bur. Standards, Washington, private communication.

(9) G. Sinke, Dow Chemical Co., private communication.

(10) Kilpatrick, J. Phys., Chem. 57, 385 (1953).

(11) Brown and Brown, J. Am. Chem. Soc. 85, 1493, (1962).

(12) Annual Summary Report - Nonr-3608(00), November, 1964-November, 1965, National Research Corporation.

(13) Quarterly Letter Report, Nonr-3608(00), November, 1965-February, 1966.

(14) Quarterly Letter Report, Nonr-3608(00), February, 1966-May, 1966.

(15) Quarterly Letter Report, Nonr-3608(00), May, 1966-August, 1966.