Heat of Reaction of Nitrogen Trifluoride with Elemental Boron

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Heat evolved in the reaction of nitrogen trifluoride with crystalline elemental boron has been measured in a bomb calorimeter. The heat of reaction calculated from these data is −239.7 ± 1.2 kcal. mole^{-1}. Derived heat of formation of nitrogen trifluoride is −30.4 ± 1.2 kcal. mole^{-1}.

CONVENTIONAL oxygen bomb combustion of boron and boron-containing compounds has yielded results which are often ambiguous and difficult to interpret. For example, recent values for the heat of formation of boric oxide derived from combustion of boron in oxygen have ranged from −281 kcal. mole^{-1} (*2*) to −336 kcal. mole^{-1} (*3*). Much of the difficulty can be traced to the formation of glassy boric oxide as a combustion product which inhibits complete combustion. In addition, there is the probable formation of one or more sub-oxide species and their hydrates which complicate the interpretation of experimental results.

The recent developments in fluorine bomb calorimetry by Hubbard and his co-workers (*4*) have solved these problems by the combustion of boron in fluorine to give gaseous boron trifluoride. However, the apparatus and techniques necessary for the safe handling of elemental fluorine are still beyond the scope of the small thermochemical laboratory.

This article presents the results of an investigation of the use of nitrogen trifluoride as a calorimetric oxidant for boron. Nitrogen trifluoride gives the volatile boron trifluoride reaction product and also may be handled safely with conventional apparatus.

EXPERIMENTAL

Apparatus. The calorimeter was a Parr Model 1200 operated isothermally with the jacket temperature maintained at 27.5° C. The combustion bomb was a Parr Model 1003, made entirely of Monel to reduce corrosion. Temperature measurements were made with a platinum resistance thermometer in conjunction with a G-2 Mueller bridge.

Materials. The crystalline boron was obtained from American Potash and Chemical Corp. and had the following elemental analysis: 0.07% Fe; 0.02% Si; 0.28% Ti; 0.07% Cu; 99.56% B (by difference). Nitric acid oxidation followed by titration in the presence of mannitol indicated 99.4% boron. X-ray examination showed primarily the β-rhombohedral modification. The combustion samples were prepared in the form of pellets under 25,000 p.s.i. pressure in a KBr pellet press.

The NF_3 was obtained from Air Products, Inc. and further purified by fractional condensation. A typical mass spectrometric analysis of the purified material gave: 0.2% CO_2 or N_2O; 0.2% CF_4; 0.2% NO; 99.4% NF_3 (by difference).

Calibration. The calorimeter was calibrated with benzoic acid (NBS Standard Sample 39 h.). The mean of seven calibration experiments gave 24878.5 cal. ohm^{-1} as the energy equivalent of the standard calorimeter with a standard deviation of the mean of ±7.4 cal. ohm^{-1} or ±0.03%. All energies are expressed in terms of the defined calorie equal to 4.184 (exactly) joules.

Procedures. The pelleted combustion samples were supported in the bomb on fused calcium fluoride disks. These disks cracked from thermal shock during combustion but usually did not separate. The samples were ignited by 3 mil platinum fuse wire placed in direct contact with the sample. The combustion bomb with sample in place was evacuated to $\sim 10^{-4}$ mm. Hg. To assure complete removal of moisture it was found necessary to heat the bomb to 90° to 100° C. for an hour while pumping. Nitrogen trifluoride was introduced into the evacuated bomb to give the desired initial pressure. Experiments were made over the range from 2 to 9 atm. absolute pressure of NF_3.

Product Analyses. Completeness of combustion was determined from the amount of unburned sample recovered after combustion. The average percentage combustion in the experiments to obtain thermochemical data was 95%. The analysis for unburned boron was complicated in all experiments by a small amount (of the order of 2 or 3% of the initial sample) of BF_3 retained on the bomb surfaces in the form of a nonvolatile, moisture-sensitive white solid, believed to be a metal fluoride-BF_3 adduct. Attempts to positively identify the material were not successful. The nonvolatile combustion residues were separated into water soluble and insoluble portions. The insoluble portion, which contained the unburned boron, was oxidized with nitric acid to convert the boron to boric acid. The fluoride ion was precipitated as calcium fluoride. Interfering metal ions were removed as the insoluble hydroxides and the boric acid titrated in the presence of mannitol. The soluble portion, containing the BF_3 adduct was analyzed in the same manner except for the nitric acid oxidation step.

Excess NF_3 was used in all the runs and about 1% of this excess decomposed to the elements. To determine the amount of fluorine formed from decomposition, the reaction gases were passed through acidic KI solution and the released iodine was titrated with standard thiosulfate.

In preliminary experiments, the condensable reaction product gases were collected and separated by high vacuum techniques. Mass spectrometric and infrared analyses showed no boron containing compounds other than BF_3.

RESULTS

It is not practical to present results of all of the experiments in detail, but data from a typical experiment at 3 atm. initial NF_3 pressure are shown in Table I. The correction to standard states was found to be less than 0.5 cal. and was not included in the reduction of data. No correction was made for the formation of the small amount of BF_3 adduct formation; however, the error introduced by neglecting this correction was estimated from the heat of formation of KBF_4 and from the relative stabilities of metal fluoride-BF_3 adducts to be less than the uncertainty of this experimental results. No discernible trend was observed in runs with varying amounts of the BF_3 adduct.

Sixteen combustion runs were made, giving a mean $\Delta E_c^0/M$ (boron crystal) of −22177 cal. gram^{-1} with a

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Table I. Data from Typical Combustion Experiment

m (sample), gram[a]	0.1458
ΔR_c, ohm	0.12910
E (calor.)($-\Delta R_c$), cal.	−3211.8
E (cont.)($-\Delta R_c$), cal.	−3.3
ΔE (NF_3 decomp.), cal.	−14.8
$\Delta E_c^0/M$ (sample), cal. gram^{-1}	−22153
Correction for 0.44% impurities, cal. gram^{-1}	24
$\Delta E_c^0/M$ (boron crystal), cal. gram^{-1}	−22227

[a] Mass of sample corrected for incomplete combustion.

standard deviation of the mean of ±57 cal. gram^{-1}. The correction for the 0.44% impurities was made on the basis of combustion of the elements to the stable fluorides. The value of $\Delta E_c^0/M$ (boron crystal) corresponds to the idealized reaction

$$B(c) + NF_3(g) = BF_3(g) + \tfrac{1}{2} N_2(g)$$

For this reaction, using 10.82 as the atomic weight for boron, the standard change in internal energy, $\Delta E^0_{298.15}$, is -240.0 ± 1.2 kcal. gram-atom^{-1} and the standard heat of reaction, $\Delta H^0_{298.15}$, is -239.7 kcal. gram-atom^{-1}. The uncertainty is expressed as twice the standard deviation of the mean.

Using the heat of formation of BF_3 (*4*) of −270.10 kcal. mole^{-1}, the derived heat of formation of NF_3 is -30.4 ± 1.2 kcal. mole^{-1}. This value is in substantial agreement with the value of Armstrong, Marantz, and Coyle (*1*), −29.7 ±1.8 kcal. mole^{-1}.

NOMENCLATURE

m = mass in vacuo, grams
ΔR_c = corrected resistance change, ohms
E (calor.) = energy equivalent of standard calorimeter, calories ohm^{-1}
E (cont.) = energy equivalent of calorimeter contents, calories ohm^{-1}
ΔE (NF_3decomp.) = energy change for NF_3 decomposition, calories
M = gram formula weight

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LITERATURE CITED

(1) Armstrong, G.T., Marantz, S., Coyle, C.F., *J. Am. Chem. Soc.* **81**, 3798 (1959).
(2) Eggersgluess, W., Monroe, A.G., Parker, W.G., Trans. Faraday Soc. **45**, 661 (1949).
(3) Todd, B.J., Miller, R.R., J. Am. Chem. Soc. **68**, 530 (1946).
(4) Wise, S.S., Margrave, J.L., Feder, H.M., Hubbard, W.N., J. Phys. Chem. **65**, 2157 (1961).

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