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WADD TECHNICAL REPORT 60-782
PART III

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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

PART III. MASS SPECTROMETRIC STUDIES OF THE MOLECULES BC_2 IN THE VAPOR ABOVE THE SYSTEM BORON-CARBON

GEORGES VERHAEGEN
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UNIVERSITY OF BRUSSELS

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AERONAUTICAL SYSTEMS DIVISION

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DIRECTORATE OF MATERIALS AND PROCESSES
CONTRACT No. AF 61(052)-225
PROJECT No. 7350

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, with Mr. F. W. Vahldiek acting as Project Engineer.

This report covers work conducted from March 1960 to March 1961.

WADD Technical Report 60-782, Part I and Part II, have already been published, Part V and Part VI are in preparation, with Part IV to follow when it becomes available.

The authors wish to acknowledge the aid and encouragement of Professor Paul Goldfinger and useful conversations with Dr. Jean Drowart.

ABSTRACT

The molecules BC_2 and B_2C have been identified in the vapor effusing from graphite Knudsen cells containing boron.

The atomization energy $D_o^o(B\text{-}C\text{-}C) = 297 \pm 7$ kcal/mole.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Directorate of Materials and Processes

MASS SPECTROMETRIC STUDIES OF THE MOLECULE BC_2 IN THE VAPOR ABOVE THE SYSTEM BORON-CARBON*

by Georges Verhaegen, Fred E. Stafford** and Marcel Ackerman***

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The vapors of extremely refractory materials are known to contain important quantities of molecular species(1) whose concentration increases with temperature. In particular, many polyatomic gaseous molecules containing carbon are known including several metallic carbides(2). An extreme-

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(1) M.G. Inghram and J. Drowart in High Temperature Technology, Proceedings of a Symposium, Mc Graw Hill, New York (1960)

(2) W.H. Chupka, J. Berkowitz, C.F. Giese, M.G. Inghram, J. Phys. Chem. 62, 611 (1958).

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ly refractory system of special theoretical interest because of its simplicity is that containing boron and carbon. This system has been studied previously by Chupka[3] who observed B_2 and measured its dissociation energy. In the present

(3) W.A. Chupka, quoted by Inghram and Drowart. ref. (1)

study, we have identified the gaseous species BC_2 and calculated ΔH_0° for the reaction

$$BC_2(g) = B(g) + 2C(s) \qquad (1)$$

When SiC was added tothe system $BCSi^+$ was observed and BSi^+ was identified tentatively.

The experimental arrangement is that used previously in this laboratory.[4] A mixture of powdered graphite and boron was placed in a graphite crucible over which a thin

(4) M. Ackerman, F.E. Stafford, J. Drowart. J. Chem. Phys. 33, 1784 (1960).

Ta radiation shield fitted snugly. The effusing molecular beam was severely collimated and ionised by electrons with energy up to 70 eV. An 8 inch, 60° sector, single focusing mass spectrometer was used to analyse the ions and a secondary electron multiplier to detect them. Samples were prepared by heating the finely powdered elements <u>in situ</u> at 1700°C for 12 to 18 hours.

The species containing B observed were B^+, B_2C^+ and BC_2^+. In addition C^+ and C_3^+ also were measured. When SiC was added, $BCSi^+$, BSi^+, SiC_2^+, Si_2C^+, Si^+, Si_2^+, SiC^+ were observed.

Measurements of $I(B^+)/I(BC_2^+)$ were taken in four different experiments and cover a temperature range from 2014° to 2470°K.

Enthalpy changes were calculated from experimental intensities using the formula :

$$-RT\ln K_{eq} = \Delta F_T^\circ = \Delta H_0^\circ + T\,\Delta\left[(F_T^\circ - H_0^\circ)/T\right] \quad (2)$$

where $-(F_T^\circ - H_0^\circ)/T$ is the free energy function[5]. Parameters

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(5) K.S. Pitzer, Quantum Chemistry, Prentice-Hall, New York, 1953, page 277.

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used in calculating the free energy function of $BC_2(g)$ were taken by analogy with BO(g) and $C_2(g)$. The molecule is assumed to be linear B-C-C, with a B-C distance of 1.2 A and C-C of 1.3A. Vibration frequencies were calculated[6] to be 1380, 660 (doubly degenerate) and 2270 cm^{-1}.

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(6) G. Herzberg, Infrared and Raman Spectra, Van Nostrand, New York, 1945, Page 173.

Only the ground electronic state was considered and was assumed to be two-fold degenerate. Free energy functions for B(g) and C(s) were taken from Stull and Sinke[7]. The activity of carbon was taken to be unity.

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(7) D.R. Stull and G.C. Sinke, American Chemical Society, Washington, D.C. 1956.

Use of eq. (2) to reduce the experimental points gives ΔH_0° for reaction (1) equal to -42 kcal/mole. No trend with either temperature or time is observed. The arithmetic average deviation of the points is $\pm$ 1 kcal/mole but due to possible systematic errors the total uncertainty is estimated to be $\pm$ 7 kcal/mole. Using this enthalpy change, the average measured ratio of ionic intensities, $I(B^+)/I(BC_2^+)$ at the lowest temperature, 2014° K, is 38; and at the highest temperature, 2470° K, is 6.3.

The experimental points log $I(B^+)/I(BC_2^+)$ were plotted as a function of 1/T. Calculation of the slope by the method of least squares and correction for ΔC_p yield $\Delta H_0^\circ = -51 \pm 15$ kcal/mole. This value is considered less accurate than the "third law" result. The agreement between the two however is within experimental error.

The measured appearance potentials (B_2C^+ = 10.0 $\pm$ 1, BC_2^+ = 10.5 $\pm$ 1 eV) indicate that BC_2 and B_2C both are parent peaks.

Combining $\Delta H_0^\circ = -42$ kcal/mole for reaction (1) with ΔH_0° (vap) (C_2) = 196.9 (8) and ΔH_0°(vap)(C) = 169.6 kcal/mole, we obtain $D_0^\circ(B - C_2)$ = 155 $\pm$ 7 and D_0°(B-C-C) = 297 $\pm$ 7 kcal/mole. Preliminary calculations for the species BCSi give D°_{298} (B-CSi)= 155 $\pm$ 15 and D°_{298} (B-C-Si) = 258 $\pm$ 15 kcal/mole.

8. J. Drowart, R.P. Burns, G. De Maria and M.G. Inghram. J. Chem. Phys. 31, 1131 (1959).
R.L. Altman, J. Chem. Phys. 32, 615 (1960)
E. Clementi, Astrophys. J. 133, 309 (1961).

If $D_0^\circ(B\text{-}C_2)$ is compared to D_0° of other molecules(9) containing boron e.g. BF(196 kcal/mole), BO(175 kcal/mole),

9. A.G. Gaydon, Dissociation Energies, Chapman and Hall, London (1953).

BCl(118 kcal/mole) or BN(92 kcal/mole) we see that the $B\text{-}C_2$ bond is very strong, being almost as stable as B-O. The B-CSi bond is of the same magnitude as $B\text{-}C_2$.

Because of the relative abundance of the molecules and the possibility of interesting correlations, these measurements are being extended to other systems.