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Abstract

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THE NATURE OF THE GREEN GLOW AND THE COMPOSITION OF THE PRODUCTS OF BORON COMBUSTION AT A TEMPERATURE OF 3100°K

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Until recently the composition of boron-containing combustion products had not been fully established. A flame in the presence of boron emits an intense band spectrum in the region 3700-6800 Å ([1]). These “fluctuation bands” have been attributed to various molecules: BO ([2]), B_2O_3 ([3]), H_3BO_3 ([4]). In 1958 A. A. Mal’ tsev and V. M. Tatevskii ([5]) proposed that the fluctuation bands belong to the BO_2 radical. This point of view is supported by the work of Kaskan and Millikan ([6]), as well as by the works of A. A. Mal’ tsev, V. K. Matveev, and V. M. Tatevskii ([7–9]).

In order to establish the nature of the fluctuation bands and the composition of the products of boron combustion, we developed a method based on the study of the dependence of absorption in the 5470 Å band on the concentration of oxygen, water, and hydroxyl during an explosion in a bomb with central ignition.

The spectra of explosions were studied on an apparatus by means of which simultaneous recording of the absorption spectrum and the explosion pressure could be carried out. In the work a steel spherical bomb with central ignition was used ([10]). Light from the source—a mercury lamp SVDSh-500—passed through quartz windows in the bomb and was focused on the entrance slit of a DMR-1 monochromator. To avoid superposition of the explosion radiation on the absorption spectrum, the radiation of the lamp was modulated by a rotating disk at a frequency of about 2500 cps, placed between the bomb and the mercury lamp. At the exit of the monochromator a photomultiplier FEU-18 was installed, the signal from which, after amplification, was fed to an electronic oscilloscope (for visual observation) and to a loop oscillograph (for recording). During the experiment, the intensity of the source radiation transmitted through the bomb, as well as the explosion pressure, was continuously recorded on the drum of the loop oscillograph. A membrane indicator IGI ([10])* served as the pressure transducer.

Mixtures of CO, O_2, H_2, and Ar were burned in the bomb. According to a

Fig. 1

Figure 1: Fig. 1

known method (^{11}), the temperature T_e and the composition of the combustion products at the moment when the maximum pressure P_e was reached were calculated. Small additions of diborane (from 0.1 to 0.3 mole per 100 moles of the initial mixture) were introduced into the initial mixtures; these had almost no effect on the magnitude of the maximum pressure P_e, and hence on the concentrations of oxygen, water, and hydroxyl. For mixtures of different initial composition, the dependence of absorption in the 5470 Å band on the amount of diborane added was studied. The absorption was measured at the moment when the maximum explosion pressure was reached. Figure 1 gives the oscillogram of the pressure and spectral absorption of an explosion in one of the experiments. The figure shows the pressure curve 1; the amplitude of the sinusoidal curve 2 is proportional to the intensity of the light transmitted through the bomb; the separate loop (curve 3) is us—

was used to mark the instant of ignition of the combustible mixture by a spark from an induction coil.

In mixtures with diborane additives, at the instant of maximum pressure the following boron-containing products may exist: B_2O_3, B_2O_2, BO, BO_2,

Fig. 1

HBO_2. The concentrations of these products are related to one another by four equations for equilibrium constants and one material-balance equation.

$$B_2O_3 \rightleftarrows B_2O_2 + \tfrac{1}{2}O_2, \quad K_1 = \frac{m_{B_2O_2} \cdot m_{O_2}^{1/2}}{m_{B_2O_3}} \cdot A; \tag{1}$$

$$B_2O_2 \rightleftarrows 2BO, \quad K_2 = \frac{m_{BO}^2}{m_{B_2O_2}} \cdot A^2; \tag{2}$$

$$BO_2 \rightleftarrows BO + \tfrac{1}{2}O_2, \quad K_3 = \frac{m_{BO} \cdot m_{O_2}^{1/2}}{m_{BO_2}} \cdot A; \tag{3}$$

$$HBO_2 + OH \rightleftarrows BO_2 + H_2O, \quad K_4 = \frac{m_{BO_2} \cdot m_{H_2O}}{m_{HBO_2} \cdot m_{OH}}; \tag{4}$$

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$$2m_{0\,\mathrm{B_2H_6}} = a = 2m_{\mathrm{B_2O_3}} + 2m_{\mathrm{B_2O_2}} + m_{\mathrm{BO}} + m_{\mathrm{BO_2}} + m_{\mathrm{HBO_2}}, \tag{5}$$

where

$$A = \sqrt{\frac{P_0 T_e}{100 T_0}}. \tag{6}$$

Here m denotes the number of moles of the product calculated per 100 moles of the initial mixture; $m_{0\,\mathrm{B_2H_6}}$ is the number of moles of diborane per 100 moles of the initial mixture; P_0 and T_0 are the initial pressure and temperature; a is the number of gram-atoms of boron per 100 moles of the initial mixture. On the left-hand sides of equations (1)–(4) stand the values of K_p. A is the conversion coefficient from partial pressures to numbers of moles.

The initial and final compositions of the mixtures investigated (not counting boron) are given in Table 1. The initial composition was calculated in such a way that in explosions of all mixtures the same final temperature, $T_e = 3080°\mathrm{K}$, was reached. We assumed that the fluctuation bands belong

either $\mathrm{B_2O_3}$, or $\mathrm{BO_2}$. Using the system of equations (1)–(5), one can express a through the concentration of each of the products $m_{\mathrm{BO_2}}$ or $m_{\mathrm{B_2O_3}}$:

$$a = \left(1 + \frac{K_3}{A m_{\mathrm{O_2}}^{1/2}} + \frac{1}{K_4}\cdot\frac{m_{\mathrm{H_2O}}}{m_{\mathrm{OH}}}\right) m_{\mathrm{BO_2}} + \frac{2K_3^2}{K_2}\cdot\frac{1}{m_{\mathrm{O_2}}}\left(1 + \frac{A m_{\mathrm{O_2}}^{1/2}}{K_1}\right) m_{\mathrm{BO_2}}^2, \tag{7}$$

$$a = 2\left(1 + \frac{K_1}{A m_{\mathrm{O_2}}^{1/2}}\right) m_{\mathrm{B_2O_3}} + \frac{\sqrt{K_1 K_2}}{A^{3/2} m_{\mathrm{O_2}}^{1/4}}\left[1 + \left(\frac{1}{K_4}\cdot\frac{m_{\mathrm{H_2O}}}{m_{\mathrm{OH}}} + 1\right)\frac{A m_{\mathrm{O_2}}^{1/2}}{K_3}\right] m_{\mathrm{B_2O_3}}^{1/2}. \tag{8}$$

Table 1

$P_0 = 500$ mm Hg, $T_0 = 293°\mathrm{K}$, $T_e = 3080°\mathrm{K}$

Experiment No.	$m_0\mathrm{H_2}$	$m_0\mathrm{O_2}$	$m_0\mathrm{CO}$	$m_0\mathrm{Ar}$	$m_0\mathrm{N_2}$	$m_{\mathrm{H_2}}$	m_{H}	$m_{\mathrm{H_2O}}$
2,2	2,651	16,123	47,000	33,505	0,721	0,235	0,367	1,749
2,3	6,121	16,560	42,368	34,270	0,681	0,602	0,588	4,455
2,4	9,404	16,864	37,660	35,437	0,638	0,964	0,774	7,099
10,2	6,096	25,990	32,599	34,581	0,735	0,298	0,414	4,448
10,4	19,579	27,382	17,500	34,863	0,676	1,081	0,788	16,035

Experiment No.	m_0H_2	m_0O_2	m_0CO	m_0Ar	m_0N_2	m_{H_2}	m_H	m_{H_2O}

Experiment No.	m_{OH}	m_{O_2}	m_O	m_{CO}	m_{CO_2}	m_{NO}	m_{N_2}
2,2	0,968	2,631	0,904	23,802	23,197	0,165	0,695
2,3	1,541	2,602	0,900	21,508	20,861	0,165	0,599
2,4	1,940	2,574	0,895	19,175	18,495	0,158	0,500
10,2	2,205	10,765	1,829	10,969	21,631	0,327	0,572
10,4	4,139	10,446	1,802	5,948	11,551	0,303	0,522

Note. The composition is given in moles per 100 moles of the initial mixture.

For each of the mixtures in Table 1, diborane additions a were selected experimentally such that the absorption in all the mixtures would be the same (here, as below, only the absorption at the moment of maximum explosion pressure is meant). Table 2 gives the experimental values of a at which the absorption in all mixtures is the same. The optical density is 0.434.

Table 2

Mixture No.	a	m_{H_2O}/m_{OH}
2,2	0,159	1,807
2,3	0,200	2,89
2,4	0,258	3,659
10,2	0,159	2,035

It follows from Table 2 that a linear dependence exists between the experimental values of a and the ratio m_{H_2O}/m_{OH}:

$$a = 0.0544\,\frac{m_{H_2O}}{m_{OH}} + 0.0497. \tag{9}$$

This dependence is shown in Fig. 2. At the same time, no dependence is observed between the experimental values of a and m_{O_2}.

Let us compare the data of Table 2 and the experimental dependence (9) with the theoretical expressions (7) and (8). The experimental conditions are such that, for all values of a, m_{O_2}, and m_{H_2O}/m_{OH}, the absorption is the same. If the absorption is due to BO_2, then m_{BO_2} in (7) is constant, and if the absorption is due to B_2O_3, then $m_{B_2O_3}$ in (8) is constant. The experimental dependence (9) corresponds to the theoretical expression (7) in the case when the spectrum

Fig. 2

Figure 2: Fig. 2

is due to the BO_2 radical and when the main combustion products of diborane are BO_2 and HBO_2. In this case equation (7) takes the form

$$a = \frac{m_{BO_2}}{K_4} \cdot \frac{m_{H_2O}}{m_{OH}} + m_{BC_3}, \tag{10}$$

which fully corresponds to the experimental equation (9). From comparison of (9) and (10) one can determine K_4 and the absolute concentration m_{BO2} and m_{HBO2}: $K_4 = 0.9$.

On the other hand, the experimental dependence (9) in no case satisfies equation (8). This means that the observed spectrum cannot be ascribed to the molecule B_2O_3. The absence of any relation between the experimental values of a and the oxygen concentration m_{O2} also indicates this. The experimental dependence (9) likewise cannot be explained if one assumes that the spectrum is due to the molecule BO or B_2O_2.

Fig. 2

Thus, the results of the present work confirm the conclusions of A. A. Maltsev and V. M. Tatevskii, Kaskan and Millikan concerning the assignment of the fluctuation bands to the BO_2 radical.

It has been established that the principal boron-containing combustion products under the experimental conditions at 3080°K are HBO_2 and BO_2.

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Note: Figure translations are in progress. See original paper for figures.