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AN ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF THE BORON OXIDE MOLECULE B_2O_3

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The problem of the structure of oxygen compounds of boron has long attracted the attention of investigators. A large number of works have been devoted to the study of the structure of glassy and crystalline boron oxide (see, for example, the monograph (1)). However, the literature still lacks experimental data on the configuration and geometrical parameters of the B_2O_3 molecule in the gas phase. The acquisition of such data is of great interest for elucidating regularities in the structure of molecules of the type X_2Y_3, and is also necessary for calculating the thermodynamic functions and equilibrium constants of certain gas reactions by the methods of statistical thermodynamics.

The purpose of the present investigation is to determine the geometrical structure of the B_2O_3 molecule in the vapor by the electron-diffraction method. The work was carried out on the electron-diffraction apparatus of Moscow State University for investigating molecules of difficultly volatile compounds, equipped with a high-temperature evaporator (with heating of the ampoule by electron bombardment) and a sector device (2). A preparation of boron oxide obtained by prolonged dehydration of boric acid (of "chemically pure" grade) in vacuum was used. Before the electron-diffraction patterns were taken, the boron oxide loaded into the evaporator ampoule was melted and dehydrated for a long time in high vacuum (directly in the electron-diffraction apparatus). Evaporation of boron oxide was carried out at temperatures of the order of 1500–1800°, from a molybdenum ampoule, and also from a tungsten ampoule with a molybdenum head; identical results were obtained in this way*. The electron-diffraction photographs of the vapors were taken on diapositve photographic plates coated with black ink (protection from radiation of the evaporator), using one- and two-petal s^2- and s^3-sectors, at different accelerating voltages for the electrons ($\lambda = 0.0428$–0.0562 Å), with exposures varied from several seconds to 1–2 min.

From boron oxide vapor, 7 series of electron-diffraction patterns were obtained (3 photographs in each series) suitable for photometry; of these, several series were measured visually, and the rest were processed photometrically. The interpretation of the electron-diffraction patterns was carried out by two methods—

Fig. 1. Radial distribution curve $D(r)$ for the boron oxide molecule

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the radial distribution method in the version of J. Karle and I. Karle (3-5), and the method of successive approximations (6) using the photometric data. The methods of processing and interpreting the electron-diffraction patterns have been described in detail in previous communications from our laboratory (2,7). It should be noted that carrying out the present investigation was associated with overcoming many experimental difficulties and was performed over the course of several years.

The radial distribution curve $D(r)$, constructed from the experimental data, is shown in Fig. 1. The initial region of the intensity curve—

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* Tantalum ampoules were not used because of strong corrosion under the conditions of our experiments.

···region ($s = 0$–4 Å^{-1}), inaccessible to experimental determination, was extrapolated by the theoretical curve $I(s)$ for the group of atoms O—B = O with the values: r(B—O) = 1.36 Å, r(B = O) = 1.20 Å, and r(O ... O) = 2.56 Å, since they make the principal contribution to the scattering by the B_2O_3 molecule (see below). As is seen from Fig. 1, the curve $D(r)$ has only two sharply expressed peaks at $r = 1.28$ and 2.56 Å.

Fig. 1. Radial distribution curve $D(r)$ for the boron oxide molecule

The interpretation of the electron-diffraction patterns obtained and of the curve $D(r)$ is impossible without information on the composition of boron oxide vapor, since the molecules B_2O_3, B_4O_6, and BO_2 may have similar scattering patterns (see in more detail ([8])). In ([9]) a reference was made to an unpublished mass-spectrometric study by Bredt, who found that at 1300° the principal component of boron oxide vapor is the monomer B_2O_3. To verify these data we undertook a mass-spectrometric study of the composition of the products of evaporation of boron oxide ([10]), the results of which confirmed Bredt' s data and proved close to the soon-published measurements of Inghram, Porter, and Chupka ([11]). On the basis of mass-spectrometric studies of the vapor composition ([10,11]) and determinations of the molecular weight of the vapor ([12]), which indicate the presence of B_2O_3 molecules in boron oxide vapor, the electron-diffraction data obtained by us can be interpreted. We note that in the intensity distribution of the scattered electrons on electron-diffraction patterns of boron oxide and boron sulfide ([13]) a great similarity is observed, permitting one to assume an analogous structure for the molecules of these compounds.

We tested the following models of the B_2O_3 molecule:

From consideration of the curve $D(r)$ (Fig. 1) it follows that the bipyrami-

Models of the B_2O_3 molecule: (I), (II), (III), (IV), and (V)

Figure 2: Models of the B_2O_3 molecule: (I), (II), (III), (IV), and (V)

dal model of B_2O_3 (I) is unsuitable. As in the case of boron sulfide (^{13}), the curve $D(r)$ of the B_2O_3 molecule has two clearly expressed peaks, and the value $r_2 = 2.56$ Å for the second peak is twice the value $r_1 = 1.28$ Å for the first peak; obviously, with these parameters it is impossible to construct a bipyramid. Similar considerations also compel rejection of models (II)–(IV). These conclusions are also confirmed by calculations by the method of successive approximations. Thus, Fig. 2 presents the theoretical curve for the bipyramidal model of B_2O_3 with $r(B—O) = 1.36$ Å, $\angle OBO = 84°$, and $\angle BOB = 78°$, as well as theoretical curves 2-4, corresponding to models (II)–(IV), which in the scattering-angle region under consideration have no similarity to the experimental curve.

Let us consider the question of the correspondence of the curve $D(r)$ to model (V). The first peak at 1.28 Å may be interpreted as a composition of two close peaks corresponding to the interatomic distances $B_{(2)}—O_{(1)}$ and $B_{(2)} = O_{(4)}$*, not resolved by the curve $D(r)$ separately; the second peak at 2.56 Å should be assigned to the interatomic distance $O_{(1)} \dots O_{(4)}$. Since the value of the interatomic distance r_2 is twice as large as r_1, this inevitably leads to the conclusion that the group of atoms $O—B = O$ has a linear structure. The ratio of the areas of the two peaks of the curve $D(r)$, equal to 2.7, is close to the theoretical value for model (V), 2.5, whereas for the other models a sharp discrepancy is observed.

In interpreting the radial-distribution curve, the question arises why the curve $D(r)$ has no peaks in the region of larger interatomic distances. From analysis of the theoretical curve $I(s)$ for model (V), it was found that the main pattern of the electron-diffraction photograph–the alternation of even intense maxima and intensity steps (low-intensity maxima) on the outer side of these maxima (see the experimental curve in Fig. 2)–is determined by the sum of three harmonics corresponding to the interatomic distances $B_{(2)}—O_{(1)}$, $B_{(2)} = O_{(4)}$, and $O_{(1)} \dots O_{(4)}$. Consequently, the amplitudes of the three remaining harmonics, corresponding to the interatomic distances $B_{(1)} \dots B_{(3)}$, $B_{(2)} \dots O_{(5)}$, and $O_{(4)} \dots O_{(5)}$, are small in comparison with the amplitudes of the first three harmonics. This means that the amplitudes of thermal vibrations of these unbonded pairs of atoms are sufficiently large. Such a conclusion appears natural, since in model B_2O_3 of type (V) one may expect large deformation vibrations of the valence angle of the central oxygen atom at the high temperatures of our experiments, which should lead to smoothing of the peaks on the curve $D(r)$ in the region $r > 3$

* The number of interatomic distances of each of these types in the B_2O_3 model under consideration is the same; therefore the value r_1 is equal to the half-sum of the distances $B_{(2)}—O_{(1)}$ and $B_{(2)} = O_{(4)}$.

Fig. 2. Theoretical intensity curves for various models of boron oxide and the experimental curve

Figure 3: Fig. 2. Theoretical intensity curves for various models of boron oxide and the experimental curve

Å. It is interesting to note that on the curve $D(r)$ of boron sulfide [13] peaks corresponding to unbonded pairs of atoms were observed; this can be explained by the larger nuclear charge of the sulfur atom and the lower temperature of the experiments in the study of the B_2S_3 molecule, owing to which the conditions for diffraction by unbonded pairs of atoms proved more favorable than in the B_2O_3 molecule.

Fig. 2. Theoretical intensity curves for various models of boron oxide and the experimental curve.

Let us turn to the method of successive approximations. Theoretical curve 5 for model (V), with parameter values $r(B_{(2)}—O_{(1)}) = 1.36$ Å, $r(B_{(2)} = O_{(4)}) = 1.20$ Å, and $\angle BOB = 95°$, agrees satisfactorily with the experimental curve (see Fig. 2), except that on the outer side of the 2nd maximum there are two intensity steps instead of one. Complete agreement of the theoretical curve with the experimental one is obtained when larger vibration amplitudes of the above-mentioned unbonded pairs of atoms are taken into account; the corresponding curve 6 is shown in Fig. 2. Thus, the data obtained by the method of successive approximations are in full agreement with the data of the radial-distribution method.

Since the angle BOB is determined by interatomic distances for which the radial-distribution curve has no clear peaks, it is difficult to decide on the exact value of this angle. To determine this angle the following procedure was used. By the method of successive approximations, theoretical intensity curves were constructed for various values of this parameter (without taking vibrational factors into account), and it was determined at what value of the angle BOB the best agreement of the curves $I(s)$ with the experimental one is obtained. Naturally, without taking into account the amplitudes of thermal vibrations of the atoms, complete agreement of these curves cannot be expected; however, having obtained in this way an acceptable agree-

···in what follows, when vibrational factors are taken into account, it is easier to achieve agreement between the theoretical curve and the experimental one. Thus it was found that the BOB angle is approximately 95°; we adopted this value as the most probable one, without analyzing the possible error.

Thus, the electron-diffraction data obtained by us are best fitted by a planar angular model of B_2O_3 with a linear arrangement of the bonds $O—B = O$ and with the following parameter values:

1) $r(B—O) = 1.36 \pm 0.02$ Å;

2) $r(\mathrm{B=O}) = 1.20 \pm 0.03$ Å;

3) $\angle\mathrm{BOB} = 95^\circ$.

It should be noted that the B_2O_3 model of type (V) agrees well with literature data on boron–oxygen bond lengths. The distance $r(\mathrm{B—O}) = 1.36$ Å, within the experimental error, coincides with the length of the B—O bond in molecules of boric esters according to electron-diffraction data, and with the length of the B—O bond in boric acid H_3BO_3 and its salts according to X-ray data ([14]). The distance $r(\mathrm{B=O}) = 1.20$ Å coincides with the bond length in the BO molecule according to spectroscopic data ([14]). The oxygen valence angle of 95° corresponds to experimental data and theoretical concepts concerning the magnitude of this angle in compounds of a similar type. The results of our investigation agree with the study of the infrared spectrum of boron oxide vapors ([15]), which testifies in favor of a planar structure of the B_2O_3 molecule.

Our earlier investigation ([1,3]) of the geometry of the B_2S_3 molecule, which is a structural analogue of the B_2O_3 molecule, confirms the interpretation and the results of the electron-diffraction study of the boron oxide molecule.

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