

Short Communications

Energy and Length of the Boron-Oxygen Bond

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A value around 120 kcal/mole has often been quoted in the literature for the single bond energy of the boron-oxygen bond. This value, apparently, is based on data for compounds, where boron is three-fold coordinated by oxygen. In such compounds, however, use is made of the empty fourth orbital of boron to form additional bonding. The quoted energy value is therefore larger than that of a true single boron-oxygen bond. The purpose of the present note is to survey the best values for the bond energy and bond length of: (1) The boron-oxygen single bond, (2) The normal boron-oxygen bond of three-fold coordinated boron, (3) The normal boron-oxygen bond of four-fold coordinated boron, (4) The boron-oxygen double bond.

(1) The energy of a hypothetical single boron-oxygen bond, $D(\text{B}-\text{O})$, can be estimated from the following formula according to Pauling¹:

$$D(\text{B}-\text{O}) = 0.5 [D(\text{B}-\text{B}) + D(\text{O}-\text{O})] + 23(X_{\text{B}} - X_{\text{O}})^2.$$

Taking the energy of a boron-boron single bond, $D(\text{B}-\text{B})$, equal to 65.5 kcal/mole² and that of an oxygen-oxygen single bond, $D(\text{O}-\text{O})$, equal to 33.2 kcal/mole¹ together with the electronegativity values $X_{\text{B}} = 2.0$ and $X_{\text{O}} = 3.5$ for boron and oxygen, respectively¹, the energy of the boron-oxygen bond comes out as 101 kcal/mole. This value, it must be emphasized, cannot be regarded as very accurate, the electronegativities being somewhat vaguely defined. The length of the hypothetical boron-oxygen single bond can be

estimated from the single bond radius of the elements³. By taking in account corrections for the electronegativity difference of boron and oxygen (see p. 229 in Ref.¹), the length of a single boron-oxygen bond is found to be 1.43 Å.

(2) The energy of the boron-oxygen bond of three-fold coordinated boron can be found with reasonable accuracy from experimental data. The most reliable result is probably obtained for the boron-oxygen bond in boric acid. The heat of formation of $\text{B}(\text{OH})_3(\text{g})$ from $\text{H}(\text{g})$, $\text{O}(\text{g})$ and $\text{B}(\text{g})$ is $\Delta H_{\text{f}}^{298} = -700.4$ kcal/mole. This value is derived from the following values, given in the literature: the heat of formation of $\text{H}_3\text{BO}_3(\text{g}) = -238.6$ kcal/mole,⁴ the heat of sublimation of $\text{B}(\text{c})$ to $\text{B}(\text{g}) = 128.0$ kcal/g atom,² the enthalpy of $\text{O}(\text{g})$ relative to $\frac{1}{2}\text{O}_2(\text{g}) = 59.2$ kcal/g atom¹ and the enthalpy of $\text{H}(\text{g})$ relative to $\frac{1}{2}\text{H}_2(\text{g}) = 52.1$ kcal/g atom.¹ Assuming a bond energy of 110.6 kcal/mole for the OH bond,¹ the bond energy of the boron-oxygen bond in this case is found to be: $(700 - 3 \times 110.6)/3 = 123$ kcal/mole.

The bond length of the boron-oxygen bond in crystalline $\text{B}(\text{OH})_3$ is 1.36 Å⁵ and is unlikely to differ much from this value in the gaseous phase.

(3) The energy of the boron-oxygen bond of boron in four-fold coordination by oxygen can only be roughly estimated. It is known, however, that a dilute solution of boric acid in water consists of mainly undissociated $\text{B}(\text{OH})_3$ molecules and that these react with OH^- ions to form the tetrahedral $\text{B}(\text{OH})_4^-$ ions⁶. The heat of this reaction:

$\text{B}(\text{OH})_3 \cdot \text{aq} + \text{OH}^- \cdot \text{aq} \rightarrow \text{B}(\text{OH})_4^- \cdot \text{aq}$
is -10.6 kcal/mole.⁷ By neglecting changes in hydration energy and taking the above value of 123 kcal/mole for each boron-oxygen bond in boric acid, we obtain for the energy of the boron-oxygen bond in four-fold coordinated boron:

$$(3 \times 123 + 10.6)/4 = 95 \text{ kcal/mole.}$$

This is only an approximate value. In support of it, however, it can be mentioned that the observed force constants of the boron-oxygen stretching vibrations for tetrahedrally and triangularly coordinated boron are 4.2 and 5.3 m dyn/Å, respectively.^{8,9} The ratio of these force constants, 0.79, is not far from the ratio of the corresponding bond energies given above ($95/123 = 0.77$).

The bond length of the boron-oxygen bond, when boron is tetrahedrally coordinated by oxygen, is usually about 1.47 Å¹⁰.

(4) Gaseous BO probably contains a boron-oxygen double bond. Recent estimates for the dissociation energy of this compound range around 170 kcal¹¹ and 185 kcal.¹² From the energy of formation given for BO, +5.8 kcal/mole,⁴ the energy of formation from the gaseous elements is found to be 181 kcal/mole. The length of this boron-oxygen double bond is 1.20 Å¹¹.

In B₂O₃(g) we have a structure (O=B—O—B=O angled about the central O), which contains boron-oxygen bonds of 1.36 Å and 1.20 Å.¹³ From the heat of formation of B₂O₃(g), 212.7 kcal/mole,⁴ together with the energy of 123 kcal for the 1.36 Å bond and the values for the formation of B(g) and O(g) quoted above, the boron-oxygen double bond is found to be 200 kcal/mole. A higher value is found from B₂O₃(g), assuming the structure O=B—B=O. Here the heat of formation is -104.8 kcal/mole,⁴ from which we find the boron-oxygen double bond energy equal to 207 kcal/mole. These values are somewhat higher than the value of 181 kcal/mole found for the double bond in gaseous BO.

(5) The results for the four different types of boron-oxygen bonds discussed above have been plotted as bond energy versus bond length in Fig. 1. The bond energies, D , are seen to be approximately represented by the following empirical equation (solid line in Fig. 1):

$$\log_{10} D = 3.5244 - 1.055r$$

where r is the bond length.

The bond energies given above indicate that the normal boron-oxygen bond of three-fold coordinated boron should have a double bond character somewhere around 25%. Pauling estimated from the bond lengths that the double bond character should be about 20%,¹ which is in fair agreement with the present estimate. Assuming 43% ionic character for the

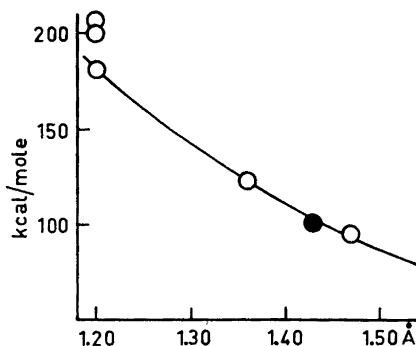


Fig. 1. Bond energy vs. bond length for some boron-oxygen bonds. Open circles represent experimental values, filled circle represents theoretical value for a hypothetical boron-oxygen single bond. Solid line corresponds to the empirical equation: $\log D = 3.5244 - 1.055r$

boron-oxygen bond,¹ a double bond character of 25% leaves us with a net charge on boron of +0.54 ($= 3 \times 0.43 - 3 \times 0.25$).

The boron-oxygen bond of boron in four-fold coordination appears to be about 6 kcal weaker than the single bond. A tentative explanation for the weakening can be given by assuming a decrease of about 0.1 unit in the electronegativity difference between boron and oxygen. A decrease of this magnitude would result in a loss of ionic resonance energy of:

$$(1.5^2 - 1.4^2) \times 23 = 6.7 \text{ kcal.}$$

The postulated change in the electronegativity difference can presumably be ascribed to the formal charge of -1 associated with boron in four-fold coordination. An electronegativity difference of 1.4 will correspond to 39% ionic character of the boron-oxygen bond¹. This leaves a net charge on boron of +0.56 ($= 4 \times 0.39 - 1.00$), which is practically the same as for boron in three-fold coordination.

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Hydrothermal Preparation of Compounds of the Type ABO_3 and AB_2O_4

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During the last few decades compounds of the type ABO_3 and AB_2O_4 have been extensively studied. Ceramic methods have been used for preparation.

We have investigated the applicability of hydrothermal methods for preparing $BaTiO_3$ and various other oxides. By reacting $Ba(OH)_2 \cdot 8H_2O$ with TiO_2 (anatase)

under hydrothermal conditions, $BaTiO_3$ is formed in the temperature range $380^\circ C - 450^\circ C$ and the pressure range 300–500 atm. Using freshly prepared $TiO_2 \cdot xH_2O$ and $Ba(OH)_2 \cdot 8H_2O$ tiny crystals of $BaTiO_3$ were formed in a 1 M NaOH solution, when treated in the pressure bomb for 70 h. The reaction did not take place in acid solution. The autoclaves used were in some cases of 20 ml volume and in others of about 100 ml volume. The autoclaves were lined with all silver tubing. Temperature was measured by a Pt-PtRh thermocouple connected to a Radiometer GVM 22 C galvanometer. The pressure was calculated from the percentage of fill of the autoclave and the temperature, using the values of density of water at different temperature and pressures determined by Kennedy.¹ The reaction product $BaTiO_3$ was identified from Guinier-powder patterns. A few single crystals large enough to be mounted on an X-ray goniometer were badly twinned.

Using the same method, the following compounds were prepared from the corresponding hydroxides and oxides: $CaTiO_3$, $SrTiO_3$, $CdTiO_3$, $PbTiO_3$, and $BaZrO_3$.

It is expected that bigger single crystals of $BaTiO_3$ and other compounds can be prepared from hydrothermal reactions by use of temperature gradient methods.

Preparation of $PbZrO_3$ from hydrothermal methods was unsuccessful. This was reported by Reed and Katz² too.

$CoAl_2O_4$ and $CoGa_2O_4$ were prepared under hydrothermal conditions from a mixture of the hydroxides. Preparation of the corresponding In-compound was unsuccessful. Ensslin and Valentiner³ could not prepare $CoIn_2O_4$ by using ceramic methods, and the existence of the compound is questionable.

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