

Bond Lengths in Alkali Metal Oxides

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Bond length-bond strength correlations have been examined for oxygen bonded to Li, Na, K, and Rb. It is shown that, compared to those observed in ternary and other crystals, the bond lengths in the binary oxides are anomalously long by an amount that increases with atomic number. The effect closely parallels a corresponding diminishing of bond energies previously reported.

Introduction

In a recent investigation (1) of solid oxides it was observed that bond energies of the binary alkali metal oxides were anomalously low when compared with the values derived for the ternary and other oxides. The effect became larger with increasing atomic number (size) of the alkali atom. A corresponding effect has been identified for the binary alkali nitrides; this is so extreme that only Li_3N is stable under normal circumstances. These observations have been associated (2) with the increased metal-metal interactions to be found in cation-rich compounds. As bond lengths and bond energies are intimately interrelated, we also might expect to find anomalies in the observed bond lengths of the binary oxides. We have therefore undertaken a reexamination of bond lengths in ternary and other oxides with a particular view of determining what might be expected for the binary oxides if they behaved "normally."

Bond strength, v_{ij} , of a bond between atoms i and j is used in the Zachariasen (3, 4) sense, so that

$$\sum_i v_{ij} = z_j \quad (1)$$

where v_j is the formal valence of atom j .

As Zachariasen and others have discussed, v_{ij} so defined is generally a unique decreasing function of the bond length r_{ij} , and a number of analytical forms of this function have been proposed (5). The most commonly used expressions are (6)

$$v_{ij} = (R/r_{ij})^n \quad (2)$$

$$v_{ij} = \exp[(R' - r_{ij})/b] \quad (3)$$

where R , R' , n , and b are constant for a given pair of atoms i and j .

Allmann (7) and Brown and Shannon (8) among others, have determined parameters for Eqs. (2) and (3) that are appropriate for many metal atoms bonded to oxygen.

Zachariasen (3) emphasized that in some instances the effect of next-nearest (non-bonded) interactions might be to invalidate the strict applicability of bond length-bond strength correlations. Here we plan to investigate this effect for the binary alkali metal oxides which have the antiferroite structure in which each metal atom forms four equivalent bonds to oxygen and the

formal bond strength is unequivocally defined as $\nu = \frac{1}{4}$.

It is immediately apparent that the bond length in Na_2O is anomalously long when bond lengths in other compounds with Na in low coordination are examined. Well-refined structures of compounds (such as $\beta\text{-NaFeO}_2$) with Na in reasonably regular four coordination by oxygen are rare (other than metal-rich compounds, which we exclude for reasons given below). However, in $\text{Na}_2\text{TiSiO}_5$ (9), Na has four equidistant O neighbors at 2.307 Å and two more at 2.583 Å. Clearly for the four shortest bonds, $\nu < \frac{1}{4}$; accordingly for $\nu = \frac{1}{4}$ it is expected that $r < 2.307$ Å. In contrast in Na_2O (10) $r = 2.401$ Å. Alternatively consider $\text{NaOH} \cdot 4\text{H}_2\text{O}$ (11) in which Na forms five bonds to oxygen of almost equal lengths—the range is from 2.35 to 2.38 Å with a mean of 2.36 Å. Thus five bonds with a mean strength of 0.2 are all shorter than the bonds in Na_2O with a strength of 0.25.

A second piece of evidence that bond lengths in Na_2O are anomalous comes from theoretical calculations by Gibbs *et al.* (12). These workers, using *ab initio* molecular orbital methods, calculated bond lengths in the closed-shell molecular ions $M(\text{OH})_4^{n-}$ and $M(\text{OH})_6^{n-}$. For $M = \text{Na}, \text{Mg}, \text{Al},$ and Si [but excluding $\text{Na}(\text{OH})_4^{3-}$] the average absolute deviation between the calculated bond length and that observed in the corresponding solid oxides was 0.02 Å. On the other hand, the calculated bond length in $\text{Na}(\text{OH})_4^{3-}$ was 2.12 Å, shorter than the observed value in Na_2O by 0.28 Å.

Bond Strength–Bond Length Correlations

Brown and Shannon (8) determined the parameters in Eq. (2) so as to minimize the function

$$\delta^2 = \sum w_i (z_i - \sum_j \nu_{ij})^2 \quad (4)$$

where $z_i = 1$ for alkali atoms, the atoms j are oxygen, and w_i is a weight determined

by the precision of the measured bond lengths. We have carried out the same procedure (except for the use of unit weights) to determine the parameters of Eqs. (2) and (3). We deliberately sampled the literature independently taking only the results of good refinements of the structures of stoichiometric crystals taken from *Structure Reports* (13)—these are listed in the appendix. It is important to have as wide as possible a distribution of coordination numbers (and hence bond strengths) because in the limit of constant bond strength the parameters in Eqs. (2) and (3) are not determinable. The number of independent metal atoms in the structures used for the final analyses were for Li—54, for Na—35, for K—38, and for Rb—13.

Particularly in the case of the sodium oxides, it was immediately apparent that the data consisted of two populations. One of these comprised the many metal-rich compounds (i.e., those for which the metal/non-metal ratio exceeded unity) whose structures were determined mainly by Professor R. Hoppe and his collaborators. These consistently had bond lengths longer than predicted from the data for the other compounds. Anticipating our conclusion, that in cation-rich compounds bond lengths are abnormally long due to cation–cation interactions, the data for these compounds were not used in the subsequent analysis.

Table I lists the parameters derived by us, by Allmann (7) and by Brown and Shannon (8). The agreement is only fair although as shown in Fig. 1 for Na, the results overlap in the range of observed bond lengths as is only to be expected. Also in the range of observed bond lengths, the curves representing Eqs. (2) and (3) are virtually indistinguishable and as both equations gave almost identical root mean square deviations [δ in Eq. (4)], for simplicity, only Eq. (2) is used in what follows.

Part of the reason for the discrepancies between the parameters found by different

TABLE I
BOND LENGTH-BOND STRENGTH PARAMETERS FOR
ALKALI METAL OXIDES

	Li	Na	K	Rb	Source
R	1.369	1.777	1.869	—	Brown and Shannon (8)
n	3.9	5.6	5.0	—	Eq. (2)
R	1.311	1.592	1.450	—	This work
n	3.68	4.16	2.96	—	Eq. (2)
R'	1.292	1.661	1.84	—	Allmann (7)
b	0.478	0.439	0.478	—	Eq. (3)
R'	1.164	1.332	1.126	—	This work
b	0.50	0.615	0.88	—	Eq. (3)
R	1.448	1.687	1.887	1.902	$n = 4.82$, Eq. (2)

workers is to be found in the fact that alkali metal-oxygen bonds are weak and hence unusually susceptible to small perturbations; Brown and Shannon found the largest value of δ for Na and K of the 25 elements bonded to oxygen that they examined. Indeed they remarked that for bonds to K that n refined to 4.3, "but $n = 5.0$ gives as good agreement." Figure 2 demonstrates that the curve $\delta(n)$ is indeed a very shallow minimum for the case of Na-O bonds. (Note that in deriving the curve in Fig. 2 R was optimized for each value of n separately.) For most bond length-bond strength correlations n is between 4 and 6 (6, 8) so we also calculated R using the mean ($n = 4.82$) of all the values found by

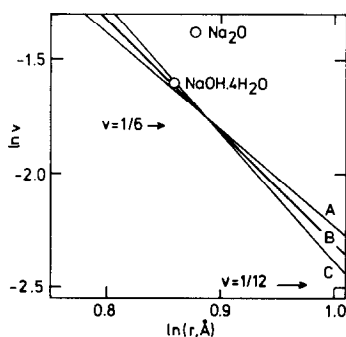


FIG. 1. Bond length-bond strength relationships for sodium-oxygen bonds according to Eq. (2). (A) this work; (B) $n = 4.82$; (C) Ref. (8). The diagram covers the range of observed bond lengths.

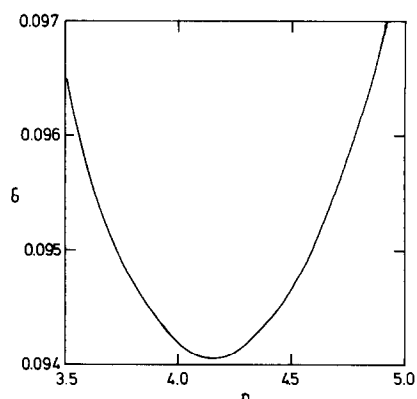


FIG. 2. The mean square deviation, δ in Eq. (4), as a function of the exponent n in Eq. (2).

Brown and Shannon. That this might be appropriate is suggested by the observation (8, 14) that when bond lengths to oxygen of first row (Li-N) and second row (Na-S) atoms are fitted to Eq. (2) with constant values of R and n for each row, n is now well defined and close to the above value. We found in fact for the Rb data that we could not reliably determine n , so $n = 4.82$ was assumed.

Bond Lengths in the Binary Oxides

Table II lists bond lengths calculated for $\nu = \frac{1}{4}$ using the various derived expressions. They are reasonably constant (in the case of Na the largest deviation from the mean is 0.05 Å) indicating that the values are not

TABLE II
OBSERVED (IN SOLID M_2O) AND CALCULATED BOND
LENGTHS IN ALKALI METAL OXIDES FOR $\nu = \frac{1}{4}$

Li	Na	K	Rb	Source
1.953	2.276	2.466	—	Brown and Shannon, Eq. (2)
1.954	2.269	2.502	—	Allmann, Eq. (3)
1.912	2.185	2.346	—	This work, Eq. (2)
1.911	2.227	2.316	—	This work, Eq. (3)
1.923	2.249	2.518	2.544	This work, Eq. (2), $n = 4.82$
1.931	2.241	2.430	2.544	Mean of above entries
1.999	2.403	2.792	2.925	Observed in M_2O

very sensitive to the method of derivation. Also listed are the values observed in anti-fluorite structure oxides. The most important point is that the observed values are larger by an amount smoothly increasing from almost zero in Li_2O to about 0.4 Å in Rb_2O . We have also plotted the experimental point for Na_2O in Fig. (1); clearly it lies off the calculated lines (in contrast to $\text{NaOH} \cdot 4\text{H}_2\text{O}$ which is normal).

The inescapable conclusion to be drawn from these results, especially when they are combined with the observations cited in the introduction, is that the bonds in the binary alkali metal oxides are longer than normal bonds of the same strength. It is clear too that the origin of the bond length increase is metal-metal interaction (rather than oxygen-oxygen interaction). In K_2O , for example, the shortest K . . . K distance is 3.22 Å (compare the shortest distance of 4.63 Å in the metal); likewise the shortest O . . . O distance is 4.56 Å (to be compared with O . . . O distances in, e.g., silicates that are about 2.6 Å).

These results show also that bond length-bond strength correlations are not exact relationships even though they are often a very useful diagnostic (15). The effect of next-nearest neighbor interactions will be greatest for large atoms forming a large number of weak bonds which is why the correlations are not very good for the alkali metal-oxygen bonds. Conversely the effect of next-nearest neighbors will be least for atoms (such as Si and P) that form a small number of strong bonds although even here it has been argued that bond lengths are affected by nonbonded repulsions (16, 17). To take an admittedly extreme case, the bond strength sum at O in Rb_2O is calculated to be $\Sigma v = 1.10$ using the parameters of Table I. Here we can use the deviation from the expected value of $\Sigma v = 2.0$, not as evidence that the structure is incorrect (6) or that O is really OH (15), but as evidence that next-nearest neighbor interactions are important.

Finally, it should be remarked that the increased bond lengths in the binary oxides should not be ascribed to the unusually high coordination number (eight) of oxygen as the bond length in Li_2O is essentially "normal." It is clear anyway from a study (18) of mixed anion compounds that it is the bond strength and not coordination number that primarily determines bond lengths.

Appendix

The following are the compounds whose structures were used to determine the bond length-bond strength relationships. Following each compound is an abbreviated reference of the form: journal, volume, page. Journal abbreviations are SR = *Structure Reports*, AC = *Acta Crystallographica*, JMS = *Journal of Molecular Structure*, ZA = *Zeitschrift für anorganische und allgemeine Chemie*, and PSJ = *Journal of the Physical Society of Japan*.

Li compounds: Li_2WO_4 SR,45A,257; LiNbO_3 SR,42A,260; CsLiWO_4 SR,46A,272; LiBO_2 SR,29,386; $\text{Li}_2\text{B}_4\text{O}_7$ SR,45A,281; LiB_3O_5 SR,44A,228; $\text{LiAlSi}_4\text{O}_{10}$ SR,46A,390; Li_2SiO_3 SR,43A,297; Li_4SiO_4 SR,45A,360; Li_2CO_3 SR,45A,400; LiPO_3 SR,42A,329; LiH_2PO_3 SR,42A,330; $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ SR,46A,311; Li_3PO_4 SR,46A,399; Li_2SO_4 SR,42A,367; LiSO_3F SR,44A,266; LiRbSO_4 SR,46A,346; $\text{LiCsSO}_3 \cdot 2\text{H}_2\text{O}$ SR,45A,325; $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ SR,43A,293; $\text{Li}(\text{H}_2\text{O})_3\text{ClO}_4$ SR,41A,362; $\text{LiNaGe}_4\text{O}_9$ SR,34A,259.

Na compounds: $\text{Na}_2\text{W}_2\text{O}_7$ SR,41A,255; NaClO_3 SR,43A,293; NaBrO_3 SR,43A,293; NaClO_2 SR,42A,389; NaHSO_4 SR,45A,330; KNaSO_4 SR,46A,348; NaNbO_3 SR,42A,261; NaClO_4 SR,45A,355; $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ SR,41A,361; $\text{LiNaGe}_4\text{O}_9$ SR,34A,259; Na_2GeO_3 SR,18,447; $\text{Na}_2\text{TiSiO}_5$ SR,44A,300; Na_2SiO_3 SR,32A,448; NaAsO_3 SR,19,443; $\text{Na}_2\text{S}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ SR,46A,364; $\text{Na}_2\text{MgSiO}_4$ AC,B37, 1483; NaHSiO_3 AC,B37,789; $\text{NaPd}(\text{SO}_3)_4 \cdot 2\text{H}_2\text{O}$ AC,B37,19.

K compounds: KIO_2F_2 SR,42A,200; KClO_3 SR,44A,291; KNaSO_4 SR,46A,348; KH difluorofumarate JMS,69,59; KH difluoromaleate JMS,69,59; $\text{KH}(\text{IO}_3)_2$ SR,43A,295; KClO_4 SR,43A,293; $\text{K}_2\text{PO}_3\text{F}$ SR,45A,299; K methyloxalate SR,44B,17; KCO_2H AC,B36,1940; KSnO_3 SR,35A,222; KPO_3 SR,42A,355; $\text{KH}_5(\text{PO}_4)_2$ SR,38A,307; $\text{K}_2\text{S}_4\text{O}_6$ SR,45A,343; $\text{K}_2\text{S}_3\text{O}_6$ SR,45A,342; KHSO_4 SR,41A,342; $\text{K}_2\text{Cr}_3\text{O}_{11}$ SR,45A,250; K_2PbO_2 SR,44A,194; K_2ZrO_3 SR,35A,222.

Rb compounds: LiRbSO_4 SR,46A,346; Rb_2SO_4 SR,40A,262; Rb_2CO_3 SR,46A,305; RbNO_3 SR,45A,292; Rb_2PbO_3 SR,43A,349; Rb_2ZrO_3 ZA,375,264; Rb_2SnO_3 ZA,375,264; RbAuO_2 SR,35A,216; $\text{Rb}_2\text{TiGe}_3\text{O}_9$ SR,42A,243; $\text{Rb}_2\text{Ge}_4\text{O}_9$ SR,42A,243; LiRbSO_4 SR,46A,346.

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