Bond valence and bond energy

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ABSTRACT

The relationship between bond valence and structural energy has never been fully explored, although several predictive models have assumed some simple relationship between the two. Some of these models relate energy only to bond valence, while others also take into account other factors, such as bond character. We examined periodic trends in bond dissociation energies as a function of their ionicity, covalency, and metallicity, defined in terms of the electronegativity values of the atoms involved. A statistical model was optimized to describe these trends, allowing us to generate rough bond energy vs. bond valence curves. The shapes of these curves vary dramatically as a function of bond character, and are strongly influenced by the lone-pair bond-weakening effect. The curve shapes can be used to rationalize several chemical trends, including the preferred structures of compounds with different bond types, the prevalence of peroxide and persulfide minerals, preferred bond lengths in oxides, and the pKᵰ values of (hydr)oxy-acids. The last is perhaps the most important, because some valence-based acidity models are in current use, despite the fact that some aspects of their rationale are unclear.

Keywords: Bond valence, energy, ionicity, metallicity, covalency, lone-pair bond-weakening effect, acidity

INTRODUCTION

The bond-valence model (BVM) is a standard tool in inorganic chemistry for rationalizing known structures and vetting proposed structures. The fact that the BVM can distinguish between more or less probable structures implies that there must be some systematic relationship between bond valence and structural energy, but the nature of that relationship has proven elusive.

Even so, it is fairly common to simply assume a particular form of the relationship. For example, some schemes for relating energy and stability to bond valence implicitly include the assumption that the energy for a given bond valence is invariant across bond types. The Structure Prediction Diagnostic Software (SPuDS) uses deviations from ideal bond-valence sums to calculate a “global instability index,” which has been successfully used to predict the most stable geometries of compounds with the perovskite structure (Lufaso and Woodward 2001). Multi-Site Complexation (MUSIC) is a popular type of surface complexation model in which the acidity constants (pKᵰ values) for oxide surface groups are fixed using a quantitative structure activity relationship (QSAR) that relates pKᵰ values to deviations from the ideal sums incident to surface oxygen atoms (Hiemstra et al. 1996).

Others have challenged the idea that energy cost for a given bond-valence deviation is consistent across bond types. Adams and Rao (2009, 2014), for example, developed a molecular mechanics force field in which energy cost was assumed to be proportional to the square of bond-valence deviation, but the scaling factors were different between bond types. Wander and Bickmore (2016) created a very accurate, valence-based potential energy model for the Al-Si-H-O system, which required differing, and non-linear bond valence-energy relationships for various bond types. Bickmore et al. (2004, 2006a, 2006b) showed that the MUSIC model would be more accurate if pKᵰ estimates were made by taking into account both bond character (ionicity vs. covalency) and bond valence considerations. However, the relationship between pKᵰ values and bond character was much more pronounced for species with low coordination numbers for the central cation.

That bond valence cannot be the only consideration for predicting reaction energies should have been obvious from the start, given that Pauling’s (1932) calibration of his electronegativity scale was based on the fact that single (1.0 v.u.) bonds of different types have widely disparate dissociation energies. For example, the bond dissociation energy of the covalently bonded F₂(g) is 158.67 kJ/mol, while more metallically bonded Cs₂Br₂ has a bond dissociation energy of 43.919 kJ/mol, and the ionic bond bonded CsF₂(g) has a dissociation energy of 517.1 kJ/mol. All three of these molecules are held together with a single bond, but their bond dissociation energies vary by more than a factor of 10 (Wander et al. 2015).

We suggest that bond dissociation energies (also called “bond energies”) like these represent the simplest point to begin working out the main features of the relationship between bond valence and energy. That is, if we can collect examples where both the bond valence and bond energy are known, we can begin to see if they can be rationalized in terms of periodic trends related to bond character. Clearly, other considerations (e.g., steric effects