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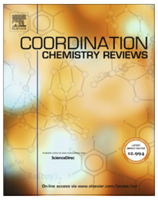

Review

Chemistry is about energy and its changes: A critique of bond-length/bond-strength correlations

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ABSTRACT

The current usage of bond-length/bond-strength (BLBS) correlations, namely, that a shorter bond must be associated with larger dissociation energy and/or force constant, is appraised. The numerous exceptions to these rules are noted. The originators of these rules considered them as useful empirical correlations, but in the course of time these relationships have often been painted as laws. As shall be seen, each exception to these rules can be explained by some effects, like strain, steric effects, dispersion stabilization, hybridization defects, bond ionicity, orbital shrinkage, and so on. As such, when the number of special reasons that can be invoked for failures of the BLBS rules, is close to the number of the exceptions to these rules, one must conclude that such correlations cannot be considered as anything even close to physical laws. Indeed, it is often the exceptions to the rules that point to interesting bonding aspects and/or reorganization processes. We argue against disregarding bond dissociation energies or related energy quantities in this context. While the various reorganization processes involved in determining these energy quantities may complicate the BLBS correlations appreciably, compared to the properties that probe structures only close to equilibrium, their consideration cannot be avoided if we want to extract chemical sense from the notion of a bond strength.

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1. Introduction

The relationships between bond lengths and "bond strengths" have preoccupied the chemical community for decades, leading to the basic tenet that shorter bonds are also stronger bonds. Thus, as soon as it became possible to determine bond lengths, chemists tried to find links between the bond length and other properties, which may be associated with "bond strength", e.g., bond dissociation energies (BDE), the force constant (k_e) of the bond, its bond multiplicity (N_B), its interatomic electron density (ρ_B), and so on. While there is no compelling fundamental basis for the existence of such relations, still this search for significance has generated a family of bond-length/bond-strength (BLBS) correlations, which have proven to be extremely useful for chemists, and some of them

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have gained the status of laws rather than as useful-intuitive correlations.

Once in a while it is important to examine the rules or laws that guide our chemical intuition, and this is what this essay attempts to do. Thus, we shall first introduce various types of the BLBS relations derived over the years, and try to trace their origins. Subsequently, we shall point out cases that deviate from these correlations, and where possible we discuss the reasons for the deviations. As shall be seen, the number of special effects causing these deviations equals the number of the deviations, and hence, it is doubtful that BLBS correlations can really be considered as "rules/laws". Furthermore, even though the thermochemical BDEs do not always correlate with respective bond lengths, we question the suggestions that there may exist a unique definition of "bond strength" that can replace the BDE.

We will also consider recent views that bond dissociation energies are not suitable measures of "bond strength", and one should concentrate instead exclusively on local force constants. While this seemingly simplifies matters, it takes away most of the chemical significance of any bond-strength definition.

2. Bond-strengths and force constants

Kraka, Larsson and Cremer (KLC) have addressed these issues in a comprehensive review in 2010 [1], and our considerations here rely on their broad treatment. To appreciate the problematic issues of the term "bond strength", let us look at the most common representation of how the energy of a diatomic molecule changes with the interatomic distance (Fig. 1). This is a Morse curve, which has a minimum energy at an equilibrium distance R_e, and which at $R = \infty$ converges to a finite energy value D_e, which is the bond dissociation energy (BDE), without the zero-point energy correction. It is very clear that at face value, the "bond strength" is associated with the D_e quantity, which is the thermodynamic quantity that determines reaction energies when this bond is broken and replaced by another one. The D_e or BDE measures the strength of the bond A-B vis-à-vis its separate fragments, A + B.

The expression of a Morse curve is given in Eq. (1):

$$\mathrm{E}(R) = D_e\{1 - \exp[-\mathrm{a}(R - R_e)]\}^2 \tag{1}$$

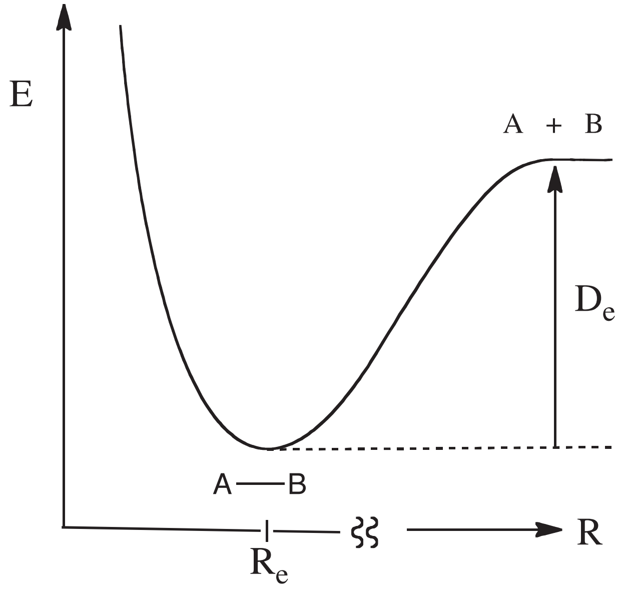

Fig. 1. A Morse curve for the dissociation of a bond A-B.

Transforming the coordinate R to a dimensionless coordinate leads to:

$$n = \exp[-a(R - R_e)] \ (a\text{in units of } 1/\text{Å}) \tag{2}$$

In this expression, $n = 1$ corresponds to $R = R_e$, and $n = 0$ to $\mathrm{R} = \infty$. The reader will immediately recognize that Eq. (2) is virtually identical to the expression of bond order (BO) used by Pauling [2–4].

Plugging Eq. (2) into the Morse function in Eq. (1), we get the following simple energy expression as a function of n:

$$E(n) = D_e(1 - n)^2 \tag{3}$$

This function is a parabola having a minimum energy at $n = 1$ ($R = R_e$). The depth of this minimum is D_e relative to the value of $E(n)$ at $n = 0$ (corresponding to $R = \infty$). Taking the second derivative of $E(n)$ leads to:

$$\mathrm{d}^2E(n)/\mathrm{d}n^2|_{n=1} = 2D_e \tag{4}$$

In the sense that the second derivative measures the curvature/steepness of the potential energy along the given coordinate, then Eq. (4) defines a generalized 'force constant' of a bond. Thus, using the common bond-energy/bond-length curves leads to the conclusion, that for bonds describable by Morse curves, the force constant and the D_e(BDE) of these bonds are one and the same quantity.

Indeed, the usual expression of a used in the Morse function links k_e and D_e, as follows:

$$a = (k_e/2D_e)^{1/2} \tag{5}$$

Thus, by deriving n with respect to R, we find that the second derivative is the force constant k_e at the minimum of the well:

$$\mathrm{d}^2E(\mathrm{R})/\mathrm{d}R^2 = \left[\mathrm{d}^2E(\mathrm{n})/\mathrm{d}n^2\right]\left(\mathrm{d}^2n/\mathrm{d}R^2\right)|_{\mathrm{R=Re}} = k_e \tag{6}$$

Within this framework D_e and k_e appear to be in a way synonymous, though measuring curvatures in different coordinate systems. We will, however, see below that these relationships do not hold once we move beyond such simplified treatments.

Before proceeding to the description of the various BLBS correlations, it is important to stress that although it is intuitive to consider that as R_e becomes shorter, k_e and D_e become larger, or vice versa, such a direct relationship is not apparent, at least to the present authors, from either the original or the transformed Morse curves, nor to the best of our knowledge from any fundamental theory.

3. BLBS-type relationships

3.1. Badger's rule and its various analogs

As recounted by KLC [1], the search for empirical relationships, between the bond length and the corresponding stretching frequency or force constant, dates back to the 1920s [5]. The search has gradually widened and has led by now to approximately 60 different expressions which link force constants, bond lengths, bond dissociation energies and bond multiplicities. The reader is highly recommended to consult this paper, which gives an overview of the topic [1].

Badger was the first to formulate a widely applicable relationship between the force constant of a bond (k_e) and it bond length (R_e) [6]. He noted that there are three factors, which could be employed to estimate the strength of chemical bonds, the BDE, the inter-nuclear distance (R_e) and the force constant of the bond (k_e). Since the BDE was frequently unobtainable with any desired accuracy, Badger decided to focus on R_e and k_e and seek "*what relations might exist between them*". He noted that a variety of mole-