

## Recent Developments in Lewis-Acid Base Chemistry

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Ever since the Lewis model of acid-base interactions was first proposed there has been an interest in ways to either qualify or quantify this chemistry [1], particularly since the Lewis model makes acid-base interactions one of the three basic types of chemical interactions.

A common approach to this problem is to treat the acid base interaction as simply the formation of a sigma bond between the acid and base. From Mulliken's work [2], we see that the wavefunction for the sigma bond can be described as a product of both electrostatic and covalent terms. Klopman [3] used perturbation theory to show the importance of both charge controlled and frontier controlled effects in the transition state of an acid-base displacement reaction.

Ahrland, Chatt, and Davies first pointed out that there seemed to be three distinct types of metals, and grouped them accordingly into class (a), class (b), and borderline metals. This idea of different classes of electron acceptors was further developed by Pearson [4] into the current and widely used hard soft acid base (HSAB) theory - "hard acids prefer to coordinate to hard bases and soft acids prefer to coordinate to soft bases." While this theory has seen many successes [5], it also received a great deal of criticism. Some of this criticism stemmed from the fact that it was purely an empirical division, while there were also criticisms because it did not always give correct predictions. To help explain cases where HSAB did not correctly predict the observed result, Pearson included another intrinsic quantity which he called the implicit strength, and proposed the following correlation:

$$\log K = S_A S_B + \sigma_A \sigma_B$$

where S's represent the implicit strength factors, and  $\sigma$ 's are hard-soft parameters.

In 1983, working with Parr, Pearson [6] gave HSAB a firmer theoretical foundation by expounding on the initial work of Mulliken, and by making use of the then newly developed density functional theory to provide an absolute definition for hardness.

$$\eta = 1/2(\delta\mu/\delta N)_Z = -1/2(\delta X/\delta N)_Z = 1/2(\delta^2 E/\delta N^2)_Z$$

where  $\eta$  is the absolute hardness,  $\mu$  is the chemical potential, X is the absolute electronegativity, Z is the nuclear charge, N is the number of electrons, and E is the ground-state electronic energy. Through this definition, HSAB has been brought one step closer to quantification.

Shortly after the proposal of HSAB theory, Drago [7] devised an equally controversial quantification of acid base interactions which related the change in enthalpy of an acid base interaction to the ability of the acid and the base to undergo both electrostatic and covalent interactions with one another. This led to tables of E (for electrostatic) and C (for covalent) parameters which, although set on an arbitrary scale (with the acid  $I_2$  having an E and C value of 1), could successfully predict the enthalpy change of acid base interactions for the set of acids and bases described. While this theory has some shortcomings including difficulties dealing with solvent effects, and currently no direct method to describe interactions which involve the formation of more than a simple sigma bond, its basis is theoretically sound.

Both approaches conclude that there is no single reference acid (or base) which can provide an inherent order of basicity (or acidity); however, there have been frequent attempts to

do just that, for example, donor and acceptor numbers [8,9]. The desire to have a single acidity or basicity order is understandable since one-parameter correlations are invariably easier to analyze, present, and modify to include new species. With this in mind, Drago has recently [10] provided a means by which one can produce single term acid-base parameters based upon the E and C parameters for the reference and the assumption that the acids or bases being studied will all have approximately the same C/E ratio. These parameters allow for some insight into the kinds of interactions that can be important when studying new systems.

## References

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