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Gas phase Lewis acidity and basicity scales for boranes, phosphines and amines based on the formation of donor–acceptor complexes

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ABSTRACT

Gas phase Lewis acidity is analyzed in a set of substituted boranes by their hydride affinity, while Lewis basicity is estimated in a set of phosphines and amines through their proton affinity. Acidity and basicity trends are also evaluated from the bond energy of borane–NH_3, phosphine–BH_3/BF_3 and amine–BH_3/BF_3 adducts, respectively. The relationship between the Lewis acidity/basicity estimations and other chemical reactivity descriptors is explored by the use of both global and local parameters. Intrinsic measures of electron-accepting/electron-releasing capability, like the vertical electron affinity and the vertical ionization energy, correlate with the acidity/basicity scales based on small basic/acidic counterparts, namely the hydride/proton affinity scales. The molecular electrostatic potential and the Fukui function provide detailed information on the charge deficiency/excess and electronic redistribution along the molecules, as well as a guide to identify the effect of the substituents on the acidity/basicity of these sets of molecules. We also discuss some difficulties in locating the true minima on the potential energy surface of some aromatic Lewis acids and bases, as well as of some of their acid–base complexes.

1. Introduction

A major issue in chemistry is the acid–base reactivity. Although acids and bases have been largely studied in solution, their gas phase reactions are relevant to obtain an accurate understanding of the intrinsic reactivity of each kind of species since they appear in many chemical reactions [1]. The acidity of boranes and the basicity of phosphines and amines have been largely studied by experimental [2] and theoretical methods [3].

Between 1923 and 1938, Lewis generalized the definition of acids and bases as acceptors and donors of electron pairs, respectively. The Lewis definition is intimately related with the Octet Rule, since electron deficient species show an acidic reactivity pattern, whereas bases consistently have lone electron pairs [1b,4]. According to this definition, electron deficient species, like boranes and the proton, act as Lewis acids when they react with electron pair donors, while species with lone electron pairs, like phosphines and amines, behave as Lewis bases towards electron deficient species. Usually, a Lewis acid reacts with a Lewis base and they form an adduct. Unlike the Arrhenius [5] and Brönsted–Lowry concepts [6], where the reference acid is the proton, or the Lux–Flood definition that deals with the oxide ion (O^{2-}) as the reference species [7], in the Lewis context there is not a single reference acid or base. In this sense, the Lewis acidity and basicity scales are not unique, although the proton basicity scale remains as a special case due to its great relevance in chemistry.

The gas phase Lewis basicity can be estimated by the proton affinity (PA), defined as the negative of the enthalpy of the protonation reaction of a basic species, B: + $H^+ \rightarrow BH^+$. In the same way, a gas phase Lewis acidity scale comes from the hydride affinity (HA), defined as the negative of the enthalpy of the reaction between an acid and the hydride ion, A+:$H^- \rightarrow AH^-$. In the literature [1c], for the Lewis bases, the negative of the Gibbs free energy of the protonation reaction is named the gas-phase basicity (GB). On the other hand the gas-phase acidity (GA) is defined as the Gibbs free energy for the dissociation reaction, $HX \rightarrow H^+ + X^-$, in this way, the negative of the free energy of the reaction between a Lewis acid and the hydride ion does not have a standard name. In the experiments where the constant equilibrium is measured, such as those that involve the ion–molecule interactions, the connection with the thermodynamics is direct through the Gibbs free energy [8], for this reason the calculated values of the Gibbs free energies of the reactions between a Lewis base/acid and the proton/hydride ion acquire a relevant place. In this paper we focus our discussion on the PA and HA values, but for the sake of completeness we also report the corresponding Gibbs free energy values.

Other scales can be obtained by changing the reaction partner. For example, the basicity can be tested using different reference acids, like BH_3 or BF_3, while acids can react with NH_3 as a reference base. The gas phase stability of these donor–acceptor complexes is

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a basicity/acidity measure. In order to include the thermal effects on the stability of the adducts, we compute the enthalpy and the Gibbs free energy for the reaction of formation of the donor–acceptor complexes at 298 K. Except where it is explicitly commented, the discussion is based on the molecular energy, ΔE, without any thermal contribution since trends are essentially similar for the other quantities. Several of the acid–base complexes that we study are commonly used in many chemical processes; e.g. amine–borane and phosphine–borane adducts act as reducing agents, hydrogen storage materials, inorganic precursors in polymerizations, stabilizers, and protecting groups [9].

The ionization energy (IE) measures the energy needed to remove one electron from a chemical species and the electron affinity (EA) refers to the ability of an atom or molecule to accept one electron. These quantities have been used as the simpler estimates of basicity and acidity, respectively [10]. On the other hand, the prediction of the chemical behavior of a molecule, considering only their intrinsic properties is a major goal of chemistry. For the Lewis bases and acids, two factors are very interesting, the identification of both electron deficient sites and places with electrons in excess and the prediction of those locations that are more susceptible to be polarized when the system is exposed to an external perturbation (usually this perturbation comes from the presence of another molecule). The former comes from the molecular electrostatic potential (MEP), which represents the interaction energy between the chemical species and a positive point charge located at a specific position in space [11]. The latter is associated with the Fukui function, a quantity defined in the Density Functional Theory (DFT) framework [12], which identifies electron donor and acceptor sites within a chemical species. The Fukui function, $f(\mathbf{r}) = (\partial\rho(\mathbf{r})/\partial N)_v$, is a discontinuous function with respect to integer number of electrons, this discontinuity is very important in chemical reactivity theory. The acceptor Fukui function, $f^+(\mathbf{r})$, predicts the reactivity of the system in front of a nucleophile (Lewis base or electron donor), whereas the donor Fukui function, $f^-(\mathbf{r})$, does the same with an electrophile (Lewis acid or electron acceptor). In order to include the electronic relaxation effects, a finite differences approximation for both Fukui functions, $f^+(\mathbf{r}) \approx \rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})$ and $f^-(\mathbf{r}) \approx \rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})$, is preferred over the molecular orbital approximation [12b,c]. Here N and ρ_N represent the number of electrons and the electron density of the species of interest, respectively. A way to rationalize the acid–base reactions is through the hard–soft acid–base model (HSAB model). This model states that a hard acid prefers to react with a hard base and a soft acid prefers a soft base [12c].

In this work, the Lewis acid set consists in a group of boranes, X_nBH_{3-n}, with several kinds of substituents. Electron attractor and donor groups are considered in the set. Some substituents (X = OH, F) present high electronegativity and also have atoms with lone electron pairs that can conjugate with the boron atom. We consider substituents whose positive inductive effect may lower the acidity at the boron site (electron donors, like the methyl group) and those that increase the Lewis acidity due to a negative inductive effect and without electronic conjugation capability (electron acceptors, like the trifluoromethyl group). Aromatic groups such as C_6H_5 and C_6F_5 provide a combination of inductive and resonance effects; for this substituents the steric factor may be also relevant. In order to evaluate the Lewis acidity of this borane set, we estimate the gas phase acidity with both the hydride affinity and the bond energy of the borane–ammonia adducts.

The gas phase Lewis basicity is evaluated in a set of substituted amines and phosphines, L_nYH_{3-n}, where Y is the nitrogen or phosphorous atom, and L = H, OH, F, Me, CF_3, C_6H_5, and 2,4,6-trimethylphenyl group ($C_6H_2Me_3$). This set of substituents covers several features that may increase or lower the basicity due to inductive, resonance and steric effects, or even to a combination of them. Those effects reflect in the electronic structure of the Lewis bases and also in the interaction energy of the bases with charged or neutral Lewis acids, like the proton, BH_3 and BF_3. From these interactions one gets the proton affinity, BH_3 and BF_3 basicity scales.

2. Methods

The electronic structure of the Lewis acids and bases is computed with the GGA-type density functional BLYP (Becke88 exchange [13] and Lee–Yang–Parr correlation [14] contributions). A triple-ζ GTO split valence Pople basis with additional diffuse and polarization functions, 6-311++g(3df,3pd), is used. It has been reported that GGA functionals provide a better performance for the Pople's basis over the Dunning's correlation consistent basis set for properties that include energies and gradients, despite that the latter have a slightly larger number of basis functions [15]. For the sake of comparison, for some complexes, we also report reaction energies with the MP2/6-311++g(3df,3pd) method. Except where it is commented our discussion is based on the BLYP/6-311++g(3df,3pd) results. In the literature one can find very accurate values for the hydride affinity and the interaction energy of the borane–NH_3 adducts for some compounds included in this work [16], even when the values obtained with the CCSD(T)/CBS method [16c] are more accurate than our estimations, the trends are preserved. The values for the enthalpy reaction (ΔH) and the Gibbs free energy (ΔG) are computed at 298 K. In this work we do not estimate the basis set superposition error since this correction is expected to be small for a large basis set.

The graphical analysis of the molecular electrostatic potential is made over an isosurface of the molecular electron density with a value of 0.001 au, which encompasses more than 95% of the molecular electronic charge; moreover the volume included within this surface is consistent with the van der Waals radii of the atoms in a molecule [17]. Both Fukui functions are calculated by the finite differences approach and they are plotted over an electrostatic potential molecular surface that mimics covalent radii of the atoms [18]. This molecular surface corresponds to an isosurface of the molecular electrostatic potential with a constant value of 0.3 au for every neutral species. The analysis of the electrostatic potential and the Fukui functions is made with the gOpenMol 3.00 program [19]. All the electronic properties are computed with the quantum chemistry package NWChem 5.1.1 [20].

3. Results and discussion

3.1. Boranes acidity

Methylboranes, $(CH_3)_nBH_{3-n}$, are weaker Lewis acids than BH_3, while trifluoromethylboranes, $(CF_3)_nBH_{3-n}$, are stronger. Lewis acidity towards the hydride ion decreases by 2 kcal/mol in phenylboranes, but it considerably increases with pentafluorophenyl substituents (up to 35 kcal/mol) due to the negative inductive effect of fluorine atoms. Hydroxyl and fluoride substituents show a different pattern. Even when these groups are very electronegative, the hydride affinity decreases for the series of hydroxyboranes and fluoroboranes, respect to BH_3 (Table 1). In the literature, it has been pointed out that this behavior could be due to the conjugation between the lone electron pairs of the substituents and the empty p-orbital of the boron atom [16c,21]. This kind of conjugation has been assumed to be opposite to the negative inductive effect of the substituent [22]. In this respect, Brinck and coworkers observed that the electrostatic potential is consistent with the electronegativity of the halogens, rather than with the conjugation [23]. The analysis of the MEP shows that the boron atom on the fluoroboranes becomes more positive than that of BH_3 as the