

# Low-Level Models for the Determination of Acid Strength

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Given the central role of pH in chemistry and other related fields, understanding acidity and the thermochemical components responsible for it is crucial. There are still many common misconceptions regarding the factors affecting acid strength. For example, many text books still assert that the addition of more oxygen atoms to the central atom of an oxyacid increases acid strength due to a polarizing effect that withdraws electron density from the H-X bond, thereby weakening it. In fact, for many oxy- as well as carboxylic acids there are negligible effects on bond strength. In the hydrohalogenic acids, it is found that the more polar the bond, the stronger the bond. Bond strength can be used as a factor for evaluating acidity, but other factors such as the stability of the conjugate base play an important role as well. Recently in the literature it was suggested that the sum of the bond dissociation energy (BDE) and electron affinity (EA) may be used as a predictor for acid strength. This correlates well with pKa for the hydrohalogenic acids but not for carboxylic acids and some oxyacids. Both BDE and EA are defined for the gas phase, but most acid/base reactions occur in aqueous solution, and hydration is a significant effect as well.

In this work, we use low-level *ab initio* calculations to evaluate factors associated with deprotonation, including hydration trends and effects on BDE and EA for hydrohalogenic acids. Relative electron densities were also analyzed. Hydration energy was found to increase with decreasing electron density on the halogen atom with decreasing number of available atomic shells. This may be associated with the smaller, more electronegative halogen having better orbital overlap with the water molecule, thus delocalizing the electron and lowering the energy. This effect may also be responsible for the more electronegative halo-substituted acetic acids being the stronger acids.