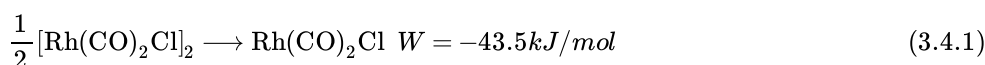


3.4: The Electrostatic-Covalent (ECW) Model for Acid-Base Reactions

The classification of Lewis acids and bases as hard and soft is a useful qualitative approach to rationalize their behavior. The ECW Model is a more quantitative model that describes and predicts the strength of Lewis acid – Lewis base interactions. The strength of the acid-base interaction is measured as the enthalpy of adduct formation, ΔH . Each acid is characterized by an E_A and a C_A . Each base is likewise characterized by its own E_B and C_B . The E and C parameters refer, respectively, to the electrostatic and covalent contributions to the strength of the bonds that the acid and base will form. These parameters have been empirically obtained by using enthalpies for adducts that *form only σ bonds between the acid and base as well as adducts that have no steric repulsion between the acid and base.*

$$-\Delta H = E_A E_B + C_A C_B + W$$

This equation reproduces and predicts the enthalpy change, ΔH , of a reaction between many acids and a bases. ΔH is a measure of strength of the bond between the acid and the base, both in the gas phase and in weakly solvating media. The W term represents a constant energy for cleavage of a dimeric acid or base. For example, the enthalpy of cleavage of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ by base B involves two steps. The first step is cleavage of the dimer, which is W:



The second step is the binding of B to the $\text{RhCl}(\text{CO})_2$ monomer. In another case, W is the enthalpy needed to cleave the internal hydrogen bonding of the H-bonding acid $(\text{CF}_3)_3\text{COH}$.

The calculation of the enthalpy of adduct formation for the reaction of pyridine, $\text{C}_5\text{H}_5\text{N}$ and bis(hexafluoroacetylacetonato)copper (II), $\text{Cu}(\text{HFacac})_2$, shows how these parameters are used. In this case $W = 0$ since neither the acid nor the base is a dimer. Selected parameters can be found at the Wikipedia page for the **ECW Model**

$$-\Delta H = E_A E_B + C_A C_B = (1.82)(1.78) + (2.86)(3.54) = 13.4 \text{ kcal/mol} = -56.1 \text{ kJ/mol}$$

$$\Delta H = -56.1 \text{ kJ/mol}, \quad \Delta H_{\text{measured}} = -56.1 \text{ kJ/mol}$$

However, the ΔH calculated for the reaction of Me_3B with Me_3N is less negative than that observed. This discrepancy is attributed to steric repulsion between the methyl groups on the B and N atoms. The difference between the calculated and observed values can then be taken as the amount of the steric effect, a value otherwise not attainable. Steric effects have also been identified with $(\text{CH}_3)_3\text{SnCl}$ and with $\text{Cu}(\text{HFacac})_2$. When π bonding contributes to the measured enthalpy, the enthalpy calculated from the E and C parameters will be less than the measured enthalpy and the difference provides a measure of the extent of the π bonding contribution.

A graphical presentation of this model clearly shows that *there is no single ranking order of Lewis acid or Lewis base strengths*, a point often overlooked, and emphasizes that the magnitude of acid and base interactions requires two parameters (E & C) to account for the interactions. A **Cramer-Bopp plot**^[7] using the three Lewis bases: acetonitrile, ammonia, and dimethyl sulfide illustrates that there is no unique ordering of Lewis base strengths. The Cramer-Bopp plot is a visual tool for comparing Lewis base strengths with the range of possible Lewis acid partners, and similar plots can be constructed to examine selected Lewis acids against the range of possible Lewis bases. These plots show that two properties are needed to completely define acid and base strength and that any attempt to define strength with one property or parameter is limited in its utility. For Drago's quantitative ECW model the two properties are electrostatic and covalent while for Pearson's qualitative HSAB theory the two properties are hardness and strength.

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