Introduction to ECW Acid-Base Model

Unlike the qualitative Pearson's HSAB model (Hard Soft Acid-Base model,) the quantitative ECW model can be used to correlate and predict the enthalpies of adduct formation and to obtain enthalpy changes for displacement or exchange reactions involving many Lewis acids and bases. Unlike all other acid-base models, graphical displays of the ECW model clearly show that there is no one order of acid or base strengths, and illustrates that two parameters are needed for each acid and base to provide an order of acid or base strength. The ECW model can also provide a measure of steric strain energy or pi bonding stabilization energy accompanying adduct formation, which is not possible with any other acid-base model.

References:

(1) Vogel, G.C.; Drago, R. S. *J. Chem. Ed.,* 1996, 73, 8, 701

(2) Drago, R. S. Applications of Electrostatic-Covalent Models in Chemistry, Surfside: Gainesville, FL, 1994.

(3) https://en.m.wikipedia.org/wiki/ECW_model

A general acid–base reaction between a Lewis acid (A) and a Lewis base (:B) yielding the adduct (A:B) can be represented by:

$$A + :B \rightarrow A:B \qquad \Delta H$$

where ΔH is the enthalpy for the adduct formation. Enthalpies for a multitude of Lewis acid and base adduct formations have been measured. Enthalpies for these adduct formations can be reproduced and predicted using two-term, four parameter equation:

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (1)$$

where the parameters have the following meaning:

E: a measure of the tendency of the acid or base to undergo electrostatic interactions, (reported in this document in units of $(kcal/mol)^{1/2}$)

C: a measure of the tendency of the acid or base to undergo covalent interactions, (reported in this document in units of $(kcal/mol)^{1/2}$)

The W term represents a constant energy for a process that precedes the adduct formation between the acid and base. (See examples.)

The enthalpies used to obtain the parameters were from adduct formations *where only σ bonding between acid and base exists, and there is no steric repulsion between acid and base.* The enthalpies were measured in the gas phase, or poorly solvating solvents, which have minimal contributions from solvation energies. For adducts where these conditions are met, the calculated E & C enthalpy changes for adduct formation are typically within +/- 0.3 to 0.5 kcal of the measured values (1,2).

Example 1: (no processes needed to precede adduct formation, W = 0.)

$I_2 + C_5H_5N \rightarrow C_5H_5N{:}I_2$

I_2 $E_A = 0.50$ $C_A = 2.00$

C_5H_5N $E_B = 1.78$ $C_B = 3.54$

$-\Delta H_{calc} = E_AE_B + C_AC_B + W = [(0.50)(1.78)] + [(2.00)(3.54)]$

$\Delta H_{calc} = -8.0$ kcal/mol (in close agreement with $\Delta H_{measured} = -7.8$ kcal/mol)

Example 2: (dissociation of acidic dimer precede adduct formation)

$\frac{1}{2}[(CO)_2RhCl]_2 + (CH_2)_4S \rightarrow (CO)_2RhCl{:}\,S(CH_2)_4$

$(CH_3)_4S$ $E_B = 0.26$ $C_B = 4.07$

$\frac{1}{2}[CO)_2RhCl]_2$: $E_A = 4.32$ $C_A = 4.13$ $W = -10.39$ kcal/mol $(CO)_2RhCl$

-2W = (the dissociation energy of dimer) = 20.8 kcal/mol $[(CO)_2RhCl]_2$

The dissociation energy of this dimer cannot be obtained by any other means.

Determining energies terms like this is a valuable asset of an ECW analysis.

$-\Delta H_{calc} = E_AE_B + C_AC_B + W = [(4.32\,(0.26)] + [(4.13)\,(4.07)] + -10.39$

$\Delta H_{calc} = -7.5$ kcal/mol (in close agreement with $\Delta H_{measured} = -7.6$ kcal/mol)

Example 3: (intramolecular hydrogen bonding in acid must be broken before adduct formation)

$(CF_3)_3COH + NH_3 \rightarrow (CF_3)_3COH{:}\ NH_3$

$(CF_3)_3COH$ $E_A = 3.06$ $C_A = 1.88$ $W = -0.87$ kcal/mol

$-W$ = (energy for breaking intramolecular hydrogen bonding) = 0.87 kcal/mol)

NH_3 $E_B = 2.31$ $C_B = 2.04$

$-\Delta H_{calc} = E_AE_B + C_AC_B + W = [(3.06)\ (2.31)] + [(1.88)\ (2.04)] + -0.87$

$\Delta H_{calc} = -10.0$ kcal/mol (This is a prediction of an enthalpy that has not been measured.)

Distinguishing Features of ECW

Comparison of ΔH of adduct formation calculated with ECW to the measured enthalpy changes of adduct formation can provide quantitative insights into the following, which is not possible with any other acid-base models.

- Steric hindrance
- π bonding stabilization in coordination complexes

Example 1: steric effects:

$B(CH_3)_3 + N(CH_3)_3 \rightarrow B(CH_3)_3{:}N(CH_3)_3$

$B(CH_3)_3$ $E_A = 2.90$ $C_A = 3.60$

$N(CH_3)_3$ $E_B = 1.21$ $C_B = 5.61$

$\Delta H_{measured} = -17.62$ kcal/mol $\Delta H_{calculated} = -23.7$ kcal/mol

(reduction in measured ΔH due to Steric hindrance)

Steric strain energy = $\Delta H_{measured} - \Delta H_{calculated} = 6.1$ kcal/mol

(steric strain estimated from hydrocarbon structurally analogous to adduct = 7.8 kcal/mol)

Example 2: π bonding stabilization

$Rh_2(but)_4$ (but = butyrate) + $C_5H_5N \rightarrow C_5H_5N{:}Rh_2(but)_4$

$Rh_2(but)_4$ $E_A = 1.81$ $C_A = 2.61$

C_5H_5N $E_B = 1.78$ $C_B = 3.54$

$\Delta H_{measured} = -16.6$ kcal/mol $\Delta H_{calculated} = -12.5$ kcal/mol

(increase in measured ΔH due to π bonding to C_5H_5N)

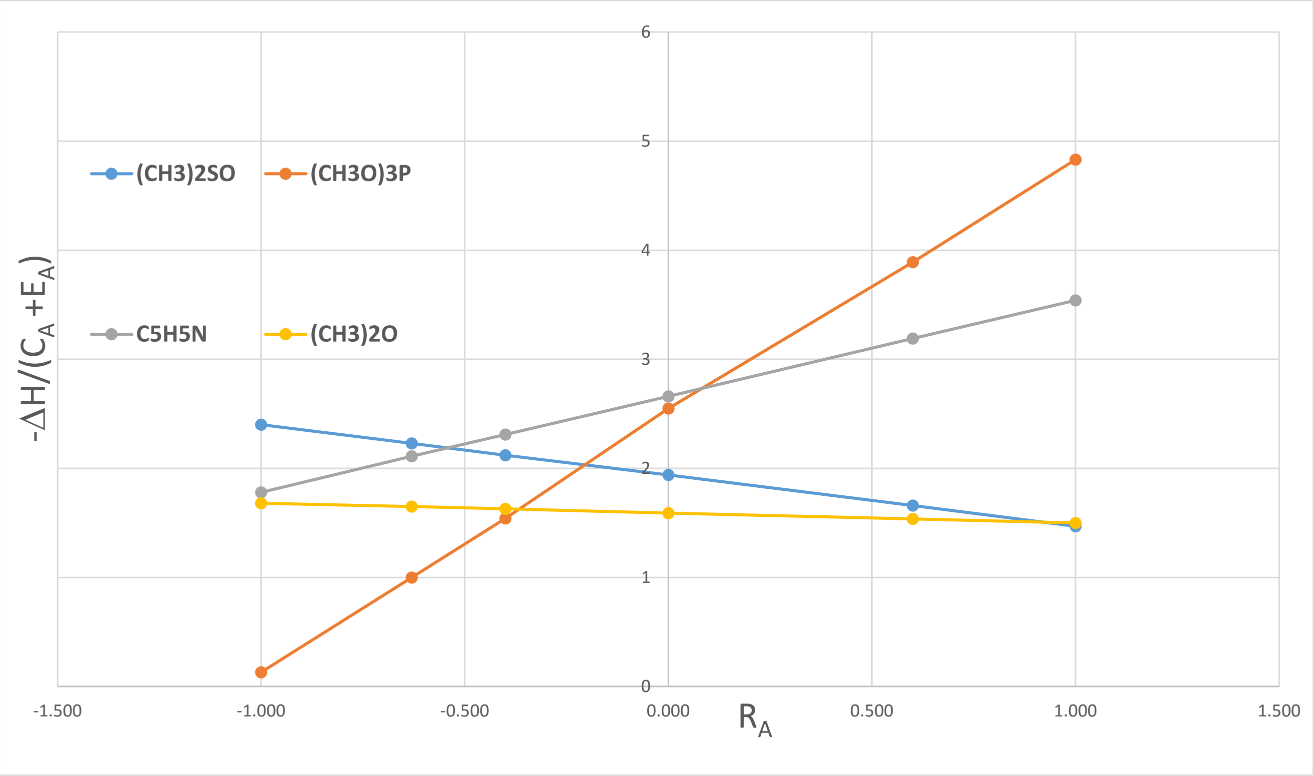
π stabilization = $\Delta H_{measured} - \Delta H_{calculated} = -4.1$ kcal/mol

Graphical Display of ECW:

Rearranging and factoring equation 1 (where W = 0,) yields the equation below;

$$\frac{-\Delta H}{E_A+C_A} = \frac{C_B-E_B}{2}\,(R_A) + \frac{C_B+E_B}{2} \qquad \text{Where } (R_A) = \frac{C_A-E_A}{C_A+E_A}$$

This equation shows that a plot of $\frac{-\Delta H}{E_A+C_A}$ vs R_A is linear with a slope of $(C_B - E_B)/2$ and an intercept of $(C_B + E_B)/2$. The order of the interactions of the 4 bases displayed in the "Cramer-Bopp" plot below varies with R_A of the acid, which depends on *both* E and C parameters of the acid. The plot can be constructed using the relationships that at $R_A = 1$, $-\Delta H / (C_A + E_A) = C_B$ and at $R_A=-1$, $-\Delta H / (C_A + E_A) = E_B$ This plot for the 4 bases shown below clearly illustrates that there is *no inherent order of base strengths for all acids.* ECW is a quantitative model that uses two parameters for each acid (and each base) and can provide the order of base strengths toward any acid (Ra = 1 to -1). Models with one parameter for each acid cannot provide relative base strengths for acids with a wide range of E&C R_A values , (ex. donor numbers, pK_b, or hard/soft).



Factoring equation 1 differently yields a form of the above equation that a plot of $\frac{-\Delta H}{E_B+C_B}$ vs R_B determines relative acid strengths for bases with R_B = 1 to -1. These plots clearly show that there is no one order of base strengths or acid strengths, a concept often misunderstood.

Other Aspects of the ECW model

Since the fundamental value of E or C is unknown for any acid or base, in order to obtain a unique set of parameters four standards must be set. The E_A and C_A values of I_2 were set at 0.50 and 2.00, respectively and the E_B for $CH_3C(O)N(CH_3)_2$ was set at 2.35 and C_B for $(C_2H_5)_2S$ was set at 2.35. These standard parameters impose electrostatic–covalent contributions to the adduct bond providing a model consistent with the Pauling and Mulliken bonding descriptions. *The ability of the current E and C parameters to calculate enthalpies that accurately reproduce the measured enthalpies and predict additional enthalpies is not affected by the choice of the standard.* The detailed matrix formulation shows how to change the standard parameters (2). One may impose any model one choses by selecting four values as dictated by the transformation matrix given in the reference. The parameters can be transformed to fit any suitable model which is useful.

As discussed in references, due to increasing enthalpy data that became available since the EC equation was first proposed the parameters have been improved. *Mixing E and C numbers from the literature prior to 1990 with current improved parameters will result in incorrect calculations and is to be avoided.*

Enthalpies measured in the gas phase and poorly solvated solvents are not abundant due to the limited solubility of many acids and bases in poorly solvated solvents and the difficulty in making these measurements. This has limited the number of acids and bases that can be assigned E and C parameters. However, with the available set of E, C, and W parameters, the enthalpies of adduct formation of over 2000 adducts can be predicted. For displacement reactions: A:B + :B’ -> A:B’ + :B or A:B + A’ -> A’:B + A over 180, 000 enthalpies can be predicted and for exchange reaction: A:B + A”:B” -> A:B” + A”:B the number is nearly 2,000,000.

Extension of the ECW Model

Besides correlating and predicting enthalpies of adduct formation for Lewis and bases, the E_B and C_B parameter have been used as a reference scale of donor strength for analysis of physicochemical properties accompanying adduct formation(1). For example, the shift of the phenol OH stretching frequency, $\Delta\upsilon_{OH}$, that occurs upon adduct formation with 21 donors was analyzed by

$$\Delta\upsilon_{OH} = E_A{}^* E_B + C_A{}^* C_B + W^*$$

The asterisks indicate that the phenol parameters ($E_A{}^* = 167$, $C_A{}^* = 109$, $W^* = -224$) are those for frequency shifts and not those for enthalpies, and the correlation indicates the shifts are dominated by σ donor-acceptor interactions. Similar correlations have been found with other spectroscopic shifts (NMR, EPR, UV-vis, IR, etc.) accompanying adduct formation(2). A few correlations dealing with free energy changes associated with adduct formation have been analyzed and provide insight.