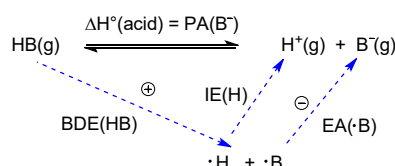


Acid and base strength variations: rationalization for cyclic amine bases and acidic aqua cations

*^a Helgard G. Raubenheimer and *^a Selwyn F. Mapolie

Supporting Information

Thermochemical cycle for simple acid dissociation



Scheme S1 Thermochemical cycle for proton dissociation in the gas phase: BDE = bond dissociation energy, EA(\cdot B) = electron affinity of the radical \cdot B.

Simple electronegativity relationships

Pauling, 1932–1960^{1–3} used a thermochemical approach – defined in molecular VB terms.

$$D_{A-B} = (D_{A-A} + D_{B-B})/2 + C(\chi_A - \chi_B)^2 \quad (s1)$$

$$D_{A-B} = (D_{A-A} \times D_{B-B})^{1/2} + C(\chi_A - \chi_B)^2 \quad (s2)$$

(D = bond dissociation energy; C is a constant depending on the energy units used.)

The greater the difference between the electronegativities of atoms A and B (χ_A and χ_B respectively) the more the single bond between A and B is stabilized compared to the average strength of the homonuclear bonds A–A and B–B. The constant, C, equals 1 for bond energies expressed in eV bond⁻¹ and 96.5 for bond enthalpies in units of kJ mol⁻¹.⁴

- Revised by Allred.⁵
- Schomaker and Stevenson⁶ proposed that electronegativity difference between two atoms influence heteronuclear bond distances (Å) according to eq. (s3).

$$r_{A-B} = r_A + r_B - 0.09 (\chi_A - \chi_B) \quad (s3)$$

(r_A and r_B are covalent radii in Å; $\chi_A > \chi_B$)

Mulliken, 1934–1935^{7–8} originally based his equation on atomic properties.

$$\chi_A = \frac{(IE)_A + (EA)_A}{2} \quad (EA > 0) \quad (s4)$$

(IE = ionization energy; EA = electron affinity)

The relationship refers to the attraction of atom A for its own valence shell electrons as well as for electrons from outside the atom (during electron attachment).

- Extended by Hinze and Jaffé.⁹

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Different dominant factors for binary hydrides

The gas-phase acidity order for p-block binary hydrides in all periods increases from left to right and from top to bottom in periodic group 15–17, and is dominated, respectively, by *electron attraction* and changes in *bond-strength* (Table 1).

The proton affinity, on the other hand, decreases from left to right in a particular period but like acidity, increases down groups 16 and 17. Thanks to the peculiar, almost constant ionization energies of NH₃, PH₃, and AsH₃ despite increasing size of the central atoms,¹ the *covalent bonds* formed between the cationic radicals CXH_3^+ (X = N, P, As) and CXH in the appropriate thermodynamic cycle (Scheme 1), determine the decreasing order of base strength in group 15 (predicted by the rules in Table 1). In the other groups, the steadily decreasing ionization energy of the neutral hydride members, drives their increasing basicity. The dominance of *electron attraction* in influencing the PAs down group 16 and of bond strength in group 15, is quantitatively illustrated in Example S1.

Example S1 Dominant energies (kJ mol⁻¹) in the thermochemical cycle (Scheme 1 in main text) for the basicity of group 15 and group 16 binary hydrides (energy values taken from Ref. 2 below differ somewhat from those in Ref. 3).

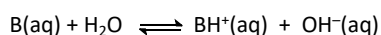
Group 15	IE(PH ₃ ; 962) < IE(NH ₃ ; 979) -----	17 kJ mol ⁻¹ advantage for PH ₃ (lower)
	BAE(CXPH_3^+ and CXH ; 427) < BAE(CXNH_3^+ and CXH ; 535)---	108 kJ mol ⁻¹ advantage for NH ₃ (negative values are used in the thermochemical cycle)
		91 kJ mol ⁻¹ overall advantage for NH ₃
		BAE dominant (bond formation)
Group 16	IE(H ₂ S; 1004) < IE(H ₂ O; 1218)-----	214 kJ mol ⁻¹ advantage (lower) for H ₂ S
	BAE(H ₂ SC X^+ and CXH ; 405) < BAE (H ₂ O CX^+ and CXH ; 598)-----	193 kJ mol ⁻¹ advantage for H ₂ O
		21 kJ mol ⁻¹ overall advantage for H ₂ S
		IE dominant (electron attraction)

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Equilibrium constants for bases and acids

The ionization of a base B in water



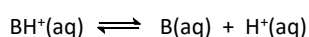
is quantified by the equilibrium constant K_b with

$$K_b = \frac{a_{\text{BH}^+} \times a_{\text{OH}^-}}{a_{\text{B}} \times a_{\text{H}_2\text{O}}}$$

It may be assumed that $a_{\text{H}_2\text{O}} = 1$ (like a pure liquid) because H₂O is the solvent in a dilute solution, simplifying the expression to

$$K_b = \frac{a_{\text{BH}^+} \times a_{\text{OH}^-}}{a_{\text{B}}}$$

It is common practice to not only compare the strength of a series of bases by their K_b values but also by the $\text{p}K_a$ values of their conjugate acids. For the above generic example the ionization of the conjugate acid of the base B, BH⁺ in water



has the equilibrium constant

$$K_a = \frac{a_{\text{B}} \times a_{\text{H}^+}}{a_{\text{BH}^+}}$$

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$$pK_a = -\log K_a = -\log \frac{a_B \times a_{H^+}}{a_{BH^+}}$$

Owing to the well-known relationships between K_a and K_b and pK_a and pK_b , the lower the pK_a value the stronger the acid and the weaker its conjugate base.

Drago's analysis of amine basicity

Drago and coworkers¹ established the type of chemical interaction responsible for the partial reversal in base strength progression in the $\text{Me}_n\text{NH}_{3-n}$ amine series when comparing the gas phase to aqueous solution.

Their semi-empirical parametrization analysis depends on the well-known E,C-type correlation (eq. s5)^{2,3} with gas-phase entropy changes for acid-base reactions. The additional parameter W was introduced to incorporate a constant

$$-\Delta H = E_A E_B + C_A C_B - W \quad (\text{s5})$$

(A = acid, B = base; E = electrostatic and C = covalent contribution)

contribution from a selected acid to each base in the ensemble,⁴ but is of no significance to this discussion. The work was supplemented by INDO/1-type calculations.

It was found that an increase in n for the acid $\text{H}(\text{H}_2\text{O})_n^+$ ($n = 0-6$), not only reduces its acidity but effects changes in the detailed intermolecular chemical interaction during protonation. A complete reordering of the original gas-phase basicity may result. Following Cramer and Bopp,⁵ the conclusions are clearly and quantitatively portrayed in a 'Great E & C plot' (Fig. 5 in Ref. 1). In general: the covalent term $C_A C_B$ dominates in the gas phase; with an increase in n , the fractional contribution by electrostatic (charge-dipole) interaction plays an ever bigger role and influences discrimination between the bases.

The reversal in gas-phase donor order that occurs in bulk water ($n \geq 6$) is thus accommodated without invoking solvation effects such as hydrogen bonding between NH units and solvent H_2O molecules, diverse entropy influences or gross dielectric effects.

Take note that the nature of $\text{H}(\text{H}_2\text{O})_n^+$ in pure water is not yet properly understood⁶ despite many theoretical and simulating gas-phase studies. It has been experimentally indicated that the single positive charge influences up to six water molecules and that interaction with additional water molecules cannot be observed (at least not by IR-measurements) in bulk water.^{7,8}

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Dehydration enthalpy correlation

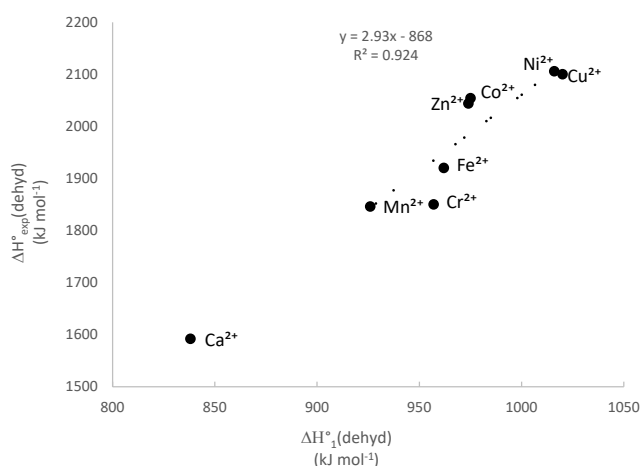
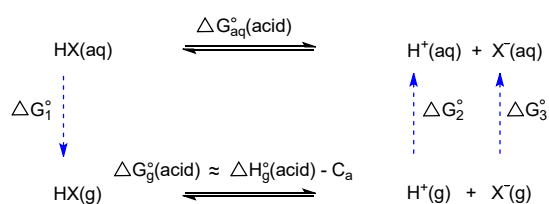


Fig. S1 Correlation between the total experimental dehydration enthalpies, $\Delta H^{\circ}_{\text{exp}}(\text{dehyd})$, of the hydrated cations $\text{M}^{2+}(\text{aq})$ and the secondary sphere dehydration enthalpies, $\Delta H^{\circ}_1(\text{dehyd})$, of the aqua cations $\text{M}(\text{H}_2\text{O})_n^{2+}$ ($\text{M} = \text{Ca}$ to Zn). [Data from Table 7 in main text.]

The strength of hydrohalic acids in water



Scheme S2 Free energy cycle for the ionization of hydrohalic acids; $T\Delta S_{\text{g}}^{\circ}(\text{acid}) > 0$, C_a is a constant.

The acids HCl–HF are essentially completely ionized in water and their relative strengths are only of theoretical interest. The main thermodynamic cycle in Scheme S2 applies.

A subtle interplay of thermodynamic factors and particularly solvent effects, leads to the conclusion that the relative acid strength ranking in the gas phase (dominated by homolytic bond rupture) is maintained in solution. The most important discriminatory interactions with water and thermodynamic contributions to $\Delta G_{\text{aq}}^{\circ}(\text{acid})$ in Scheme S2 are accounted for by ΔG_3° (ion hydration). The hydration enthalpy change in the final step becomes less favourable with larger anions whereas the entropy contribution is more favourable the larger the anion; the former change dominates in the HX acid series. The large change in hydration free energy of the $\text{H}^+(\text{g})$ ions, ΔG_2° , is constant in this series and does not influence the strength variation in water.

As can be seen from the independent treatments by Bell¹ and Dasent,² the two large enthalpy changes in the thermodynamic cycle – associated, respectively, with homolytic HX(g) bond rupture in the secondary cycle (Scheme S1) on the one hand and $\text{H}^+(\text{g})$ and $\text{X}^-(\text{g})$ hydration (ΔH_2° and ΔH_3° in the extended primary cycle) on the other – nearly cancel but the net effect causes an enthalpy turn-about of gas-phase acid strength in the condensed phase, showing HBr to be stronger than HI. The increasingly positive $T\Delta S_3^{\circ}$ contribution by the numerically small but nevertheless significant change in the entropy of hydration, ΔS_3° , from HF to HI, establishes the final and normal progression according to which, theoretically, HBr is predicted to be weaker than HI in aqueous medium.

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Problems

1. (i) Explain the influence of:
 - (a) ring size
 - (b) Me-substitution
 on the hybridization, Pauli repulsion and effective electronegativity of the nitrogen lone pair orbitals in cyclic amine bases.

(ii) The gas-phase basicity (PA) of unsubstituted cyclic amines decrease with ring size. Explain, by constructing an appropriate thermochemical cycle, which energy is decisive in determining strength variation.

(iii) In aqueous medium, the gas phase strength variation is partially reversed. Describe in terms of an extended thermochemical cycle whether enthalpy or entropy changes are dominant in determining the reversal.
2. (i) Pyridine (py) has a PA of 930 kJ mol⁻¹ against the 954 kJ mol⁻¹ of piperidine (pip). Predict qualitatively, and give your reasoning, whether *electron attraction* or the *homolytic bond energy* (between H₅C₅N $\dot{\text{C}}$ or H₁₀C₅N $\dot{\text{C}}$ and H $\dot{\text{C}}$ radicals) is the dominant strength-determining factor in the appropriate thermochemical cycle (draw the cycle).

(ii) Use the following information to substantiate your answer to (i):
 IE(pyr) = 893, IE(pip) = 775 kJ mol⁻¹;
 BDE(pyH⁺) = 511, BDE(pipH⁺) = 417 kJ mol⁻¹.
3. Derive the equation {BAE($\dot{\text{C}}$ B + $\dot{\text{C}}$ H) = PA + IE(amine) – 1312.6} used to calculate BAE values in Table 4 of the main text; start with Scheme 1.

4. The gas-phase base strength of $\text{py} < \text{pip}$ is maintained in aqueous solution. When, however, pyridine and ammonia is compared, the gas-phase basicity order $\text{py} > \text{NH}_3$ is reversed in solution.
- Draw an appropriate generic thermodynamic cycle to take solvation effects into account during protonation of these bases in water.
 - Motivate which step determines the reversal in strength.
 - Explain whether enthalpy or entropy change in this step (ii) is expected to play a dominant role in the strength reversal.
5. Enthalpy changes for the hydration of period 4 aqua dications show a double-humped curve. Describe qualitatively the form of the curve and rationalize the rather similar curve obtained for the corresponding entropy changes.