Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2016

SUPPLEMENTARY INFORMATION FOR

A Guide to the Selection of Switchable Functional Groups for CO_2-Switchable Compounds

A. K. Alshamrani, J. R. Vanderveen and P. G. Jessop

Contents

1. Derivations of equations in Scenario 1

1.1 Derivation of equation 9 (pH of amine/water mix)

$$K_{aH} = \frac{[B]_{aq}[H_3O^+]_{aq}}{[BH^+]_{aq}}$$

For the rest of the derivations in water, the subscript “aq” will be dropped for simplicity.

$K_w = [H_3O^+]\,[OH^-]$

charge balance in water: $[BH^+] + [H_3O^+] = [OH^-]$

$[BH^+] = [OH^-] - [H_3O^+]$

$[BH^+] = K_w/[H_3O^+] - [H_3O^+]$

initial conc of base = $[B]_0 = [B] + [BH^+]$

$[B]_0 = K_{aH}[BH^+]/[H_3O^+] + [BH^+]$

$[B]_0 = K_{aH}(K_w/[H_3O^+] - [H_3O^+])/[H_3O^+] + K_w/[H_3O^+] - [H_3O^+]$

$[B]_0 = K_{aH}K_w/[H_3O^+]^2 - K_{aH} + K_w/[H_3O^+] - [H_3O^+]$

$[B]_0[H_3O^+]^2 = K_{aH}K_w - K_{aH}[H_3O^+]^2 + K_w[H_3O^+] - [H_3O^+]^3$

$0 = \mathbf{[H_3O^+]^3} + [B]_0\mathbf{[H_3O^+]^2} + K_{aH}\mathbf{[H_3O^-]^2} - K_w\mathbf{[H_3O^+]} - K_{aH}K_w$

$0 = \mathbf{[H_3O^+]^3} + \mathbf{[H_3O^+]^2}(K_{aH} + [B]_0) - K_w\mathbf{[H_3O^+]} - K_{aH}K_w$

1.2 Derivation of equation 10 (%protonation of amine/water mix)

$$K_{aH} = \frac{[B][H_3O^+]}{[BH^+]}$$

initial conc of base = $[B]_0 = [B] + [BH^+]$

fraction protonated = $[BH^+]/[B]_0$

fraction protonated = $[BH^+]/([B] + [BH^+])$

fraction protonated = $[B][H_3O^+]/K_{aH}([B] + [B][H_3O^+]/K_{aH})$

fraction protonated = $[H_3O^+]/K_{aH}(1 + [H_3O^+]/K_{aH})$
fraction protonated = $[H_3O^+]/(K_{aH} + [H_3O^+])$
% protonation = $[H_3O^+]/(K_{aH} + [H_3O^+])$ x 100%

1.3 Calculation of pK_{aH} required at very low $[B]_0$

In the special case of very low $[B]_0$ in the absence of CO_2, $[H_3O^+] = 1 \times 10^{-7}$ M
Therefore for 5% protonation:
$0.05 = 1 \times 10^{-7}/(K_{aH} + 1 \times 10^{-7})$
$0.05K_{aH} + 5 \times 10^{-9} = 1 \times 10^{-7}$
$0.05K_{aH} = 0.95 \times 10^{-7}$
$K_{aH} = 0.95 \times 10^{-7}/0.05$
$pK_{aH} = 5.7$

In the special case of very low $[B]_0$ under 1 bar of CO_2, the pH is the same as that of pure water under 1 bar of CO_2. That can be calculated as follows:

$K_w = [H_3O^+][OH^-]$
$K^*_{a1} = [H_3O^+]_{aq}[HCO_3^-]_{aq}/([H_2CO_3]+[CO_{2(aq)}])$
$K_H = ([H_2CO_3]+[CO_{2(aq)}]) / P_{CO2}$
Charge balance: $[H_3O^+] = [OH^-] + [HCO_3^-]$

$K^*_{a1} = ([H_3O^+][HCO_3^-])/(K_H P_{CO2})$
$K^*_{a1}K_H P_{CO2} = [H_3O^+][HCO_3^-]$
$[HCO_3^-] = K^*_{a1}K_H P_{CO2}/[H_3O^+]$
$[H_3O^+] = K_w/[H_3O^+] + K^*_{a1}K_H P_{CO2}/[H_3O^+]$
$[H_3O^+]^2 = K_w + K^*_{a1}K_H P_{CO2}$
$[H_3O^+] = (K_w + K^*_{a1}K_H P_{CO2})^{0.5}$

at 25 °C and 0.1 MPa of CO_2
$[H_3O^+] = (1\times10^{-14}\ M^2 + 4.365\times10^{-7}\ M \cdot 0.342\ M/MPa \cdot 0.1\ MPa)^{0.5}$
$= 1.2218 \times 10^{-4}$ M (pH = 3.9)

Therefore for 95% protonation, using equation 10:

$$\%\ \text{protonation} = \frac{[H_3O^+]}{[H_3O^+] + K_{aH}} \times 100\%$$

$0.95 = 1.2218 \times 10^{-4}/(K_{aH} + 1.2218 \times 10^{-4})$
$0.95K_{aH} + 1.1607 \times 10^{-4} = 1.2218 \times 10^{-4}$
$0.95K_{aH} = 6.109 \times 10^{-6}$
$K_{aH} = 6.109 \times 10^{-6}/0.95 = 6.43 \times 10^{-6}$
$pK_{aH} = 5.2$

1.4 Derivation of equation 11 (pH of amine/water mix under CO_2)

$K_w = [H_3O^+][OH^-]$
$K^*_{a1} = [H_3O^+]_{aq}[HCO_3^-]_{aq}/([H_2CO_3]+[CO_{2(aq)}])$

$K_{aH} = [B][H_3O^+]/[BH^+]$

$K_H = ([H_2CO_3]+[CO_{2(aq)}]) / P_{CO2}$

Charge balance: $[H_3O^+] + [BH^+] = [OH^-] + [HCO_3^-]$
Mass balance: $[B]_o = [B] + [BH^+]$

$K^*_{a1} = ([H_3O^+][HCO_3^-])/(K_H P_{CO2})$
$K^*_{a1}K_H P_{CO2} = [H_3O^+][HCO_3^-]$
$[HCO_3^-] = K^*_{a1}K_H P_{CO2}/[H_3O^+]$

$[B]= K_{aH}\,[BH^+]/[H_3O^+]$
$[B]_o = [BH^+] + K_{aH}[BH^+]/[H_3O^+]$
$[B]_o = [BH^+](1 + K_{aH}/[H_3O^+])$
$[B]_o = [BH^+]([H_3O^+]/[H_3O^+] + K_{aH}/[H_3O^+])$
$[B]_o = [BH^+]([H_3O^+] + K_{aH})/[H_3O^+]$
$[BH^+] = [H_3O^+][B]_o/([H_3O^+]_{aq}+ K_{aH})$

$[H_3O^+] + [BH^+] = [OH^-] + [HCO_3^-]$
$[H_3O^+] + [H_3O^+][B]_o/([H_3O^+] + K_{aH}) = K_w/[H_3O^+] + K^*_{a1}K_H P_{CO2}/[H_3O^+]$
multiply both sides by $([H_3O^+] + K_{aH})$
$[H_3O^+]([H_3O^+]+ K_{aH}) + [H_3O^+][B]_o = ([H_3O^+] + K_{aH})K_w/[H_3O^+] + ([H_3O^+] + K_{aH})K^*_{a1}K_H P_{CO2}/[H_3O^+]$
$[H_3O^+]^2 + [H_3O^+]K_{aH} + [H_3O^+][B]_o = K_w + K_{aH}K_w/[H_3O^+] + K^*_{a1}K_H P_{CO2} + K_{aH}K^*_{a1}K_H P_{CO2}/[H_3O^+]$
$[H_3O^+]^2 + [H_3O^+](K_{aH} + [B]_o) = K_w + K^*_{a1}K_H P_{CO2} + K_{aH}K_w/[H_3O^+] + K_{aH}K^*_{a1}K_H P_{CO2}/[H_3O^+]$
multiply both sides by $[H_3O^+]$
$[H_3O^+]^3 + [H_3O^+]^2(K_{aH} + [B]_o) = (K_w + K^*_{a1}K_H P_{CO2})[H_3O^+] + K_{aH}K_w + K_{aH}K^*_{a1}K_H P_{CO2}$
$[H_3O^+]^3 + [H_3O^+]^2(K_{aH} + [B]_o) - (K_w + K^*_{a1}K_H P_{CO2})[H_3O^+] - K_{aH}K_w - K_{aH}K^*_{a1}K_H P_{CO2} = 0$
which is equation 11
if $P_{CO2} = 0$ then this simplifies to
$[H_3O^+]^3 + [H_3O^+]^2(K_{aH} + [B]_o) - K_w[H_3O^+] - K_{aH}K_w = 0$
which is equation 9

2. Derivations of equations in Scenario 2

2.1 Derivation of equation 12

$$K_{aH} = \frac{[B][H_3O^+]}{[BH^+]}$$

$K_w = [H_3O^+]_{aq}\,[OH^-]_{aq}$
charge balance in water: $[BH^+] + [H_3O^+] = [OH^-]$
$[BH^+] = [OH^-] - [H_3O^+]$
$[BH^+] = K_w/[H_3O^+] - [H_3O^+]$
solubility of base = S = $[B] + [BH^+]$
$S = [B] + [B][H_3O^+]/K_{aH}$
$S = [B]\,(1 + [H_3O^+]/K_{aH})$
$S = S_0\,(1 + 10^{-pH}/10^{-pKaH})$
$\log S = \log S_0 + \log\,(1 + 10^{pKaH-pH})$

2.2 Derivation of equation 13

$K_b = [BH^+]\,[OH^-]\,/\,[B]$
$K_w = [H^+]\,[HO^-]$

Charge balance: $[H^+] + [BH^+] = [HO^-]$

$K_w / [OH^-] + [BH^+] = [OH^-]$
$K_w + [BH^+] [OH^-] = [OH^-]^2$
$K_w + [B] K_b = [OH^-]^2$
$[OH^-] = (K_w + [B] K_b)^{0.5}$

$S_0 = [B]$ at saturation
$S_{aq} = [B] + [BH^+] = S_0 + K_b [B] / [OH^-]$
$= S_0 (1 + K_b / (K_w + [B] K_b)^{0.5})$
$= S_0 (1 + K_b / (K_w + S_0K_b)^{0.5})$

2.3 Derivation of equation 16

$$K_{aH} = \frac{[B][H_3O^+]}{[BH^+]}$$

fraction protonated = $n_{BH+}/n_{B0} = [BH^+]/[B]_0$
$= [B][H_3O^+]/K_{aH}[B]_0$

$$\text{fraction protonated} = \frac{S_0[H_3O^+]}{[B]_0K_{aH}}$$

$$\%\text{ protonation} = \frac{S_0[H_3O^+]}{[B]_0K_{aH}} \text{ x } 100\%$$

2.4 Derivation of equation 17

at system midpoint: % protonation = 50%

$0.5 = S_0[H_3O^+]/[B]_0K_{aH}$
$[B]_0K_{aH}/2S_0 = [H_3O^+]$
$\log[H_3O^+] = \log K_{aH} + \log([B]_0/2S_0)$
$pH = pK_{aH} – \log([B]_0/2S_0)$

2.5 Derivation of equation 18

$$K_{aH} = \frac{[B][H_3O^+]}{[BH^+]}$$

$K_w = [H_3O^+] [OH^-]$
charge balance in water: $[BH^+] + [H_3O^+] = [OH^-]$
$[BH^+] = [OH^-] - [H_3O^+]$
$[BH^+] = K_w/[H_3O^+] - [H_3O^+]$
$S_0 = [B]$
$[BH^+] = S_0[H_3O^+]/K_{aH}$
$K_w/[H_3O^+] - [H_3O^+] = S_0[H_3O^+]/K_{aH}$
$K_w - [H_3O^+]^2 = S_0[H_3O^+]^2/K_{aH}$
$K_w = [H_3O^+]^2 + S_0[H_3O^+]^2/K_{aH}$
$K_w = [H_3O^+]^2 (1 + S_0/K_{aH})$
$[H_3O^+]^2 = K_w/(1 + S_0/K_{aH})$
$[H_3O^+] = K_w^{0.5}/(1 + S_0/K_{aH})^{0.5}$

2.6 Derivation of equation 20 (pH in the presence of CO_2)

Assume that there is some precipitated neutral B and no precipitated salt.
$S_0 = [B]$
$K_{aH} = [B][H_3O^+]/[BH^+] = S_0[H_3O^+]/[BH^+]$
$K_w = [H_3O^+]\,[OH^-]$
charge balance in water: $[BH^+] + [H_3O^+] = [OH^-] + [HCO_3^-]$
mass balance: $[B]_0 = [BH^+] + [B] + n_{ppt}/V$
or $[B]_0 = [BH^+] + S_0 + n_{ppt}/V$
fraction protonated = $n_{BH+}/n_{B0} = [BH^+]/[B]_0$
$K_H = [\text{“}H_2CO_3\text{”}]/P_{CO2}$
$K^*_{a1} = [HCO_3^-][H_3O^+]/[\text{“}H_2CO_3\text{”}]$
$K^*_{a1}K_H = [HCO_3^-][H_3O^+]/P_{CO2}$
$K^*_{a1}K_HP_{CO2} = [HCO_3^-][H_3O^+]$

$[BH^+] + [H_3O^+] = [OH^-] + [HCO_3^-]$
$S_0[H_3O^+]/K_{aH} + [H_3O^+] = K_w/[H_3O^+] + K^*_{a1}K_HP_{CO2}/[H_3O^+]$
$[H_3O^+](1 + S_0/K_{aH}) = (K_w + K^*_{a1}K_HP_{CO2})/[H_3O^+]$
$[H_3O^+]^2 = (K_w + K^*_{a1}K_HP_{CO2})/(1 + S_0/K_{aH})$

$$[H_3O^+] = \sqrt{\frac{K_w + K^*_{a1}K_HP_{CO2}}{1 + S_0/K_{aH}}}$$

2.7 Derivation of equation 21 (% protonation in presence of CO_2)

$K_{aH} = S_0[H_3O^+]/[BH^+]$
fraction protonated = $[BH^+]/[B]_0 = S_0[H_3O^+]/[B]_0K_{aH}$

$$\text{fraction protonated} = \frac{S_0\sqrt{\dfrac{K_w + K^*_{a1}K_HP_{CO2}}{1 + S_0/K_{aH}}}}{[B]_0K_{aH}}$$

$$\%\ \text{protonation} = \frac{S_0\sqrt{\dfrac{K_w + K^*_{a1}K_HP_{CO2}}{1 + S_0/K_{aH}}}}{[B]_0K_{aH}} \times 100\%$$

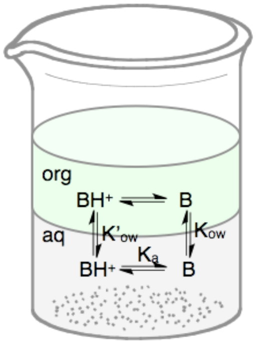
or

$$[B]_0 = \frac{S_0\sqrt{\dfrac{K_w + K^*_{a1}K_HP_{CO2}}{1 + S_0/K_{aH}}}}{P_{prot}K_{aH}}$$

where P_{prot} is the fraction protonated

3. Derivations of equations in Scenario 3

3.1 Derivation of equation 25



$$K_{aH} = \frac{[B]_{aq}[H_3O^+]_{aq}}{[BH^+]_{aq}}$$

$$K_P = \frac{[B]_{org}}{[B]_{aq}}$$

$$K'_P = \frac{[BH^+]_{org}}{[BH^+]_{aq}}$$

$$D = \frac{[B]_{org} + [BH^+]_{org}}{[B]_{aq} + [BH^+]_{aq}}$$

$$D = \frac{K_P[B]_{aq} + K'_P[BH^+]_{aq}}{[B]_{aq} + [B]_{aq}[H_3O^+]_{aq}/K_{aH}}$$

$$D = \frac{K_P[B]_{aq} + [B]_{aq}K'_P[H_3O^+]_{aq}/K_{aH}}{[B]_{aq} + [B]_{aq}[H_3O^+]_{aq}/K_{aH}}$$

Multiply top and bottom by $K_{aH}/[B]_{aq}$

$$D = \frac{K_P K_{aH} + K'_P[H_3O^+]_{aq}}{K_{aH} + [H_3O^+]_{aq}}$$

3.2 Derivation of equation 26

$$K_{aH} = \frac{[B]_{aq}[H_3O^+]_{aq}}{[BH^+]_{aq}}$$

$$K_P = \frac{[B]_{org}}{[B]_{aq}}$$

$$K'_P = \frac{[BH^+]_{org}}{[BH^+]_{aq}}$$

initial moles of base = $n_0 = [B]_{org}V_{org} + [B]_{aq}V_{aq} + [BH^+]_{org}V_{org} + [BH^+]_{aq}V_{aq}$

$V_{rat} = V_{org}/V_{aq}$

$$\text{fraction protonated} = \frac{n_{BH+}}{n_0} = \frac{[BH^+]_{org}V_{org} + [BH^+]_{aq}V_{aq}}{[B]_{org}V_{org} + [B]_{aq}V_{aq} + [BH^+]_{org}V_{org} + [BH^+]_{aq}V_{aq}}$$

$$= \frac{[BH^+]_{aq}K'_PV_{org} + [B]_{aq}[H_3O^+]_{aq}V_{aq}/K_{aH}}{[B]_{aq}K_PV_{org} + [B]_{aq}V_{aq} + [BH^+]_{aq}K'_PV_{org} + [B]_{aq}[H_3O^+]_{aq}V_{aq}/K_{aH}}$$

$$= \frac{[B]_{aq}[H_3O^+]_{aq}K'_PV_{org}/K_{aH} + [B]_{aq}[H_3O^+]_{aq}V_{aq}/K_{aH}}{[B]_{aq}K_PV_{org} + [B]_{aq}V_{aq} + [B]_{aq}[H_3O^+]_{aq}K'_PV_{org}/K_{aH} + [B]_{aq}[H_3O^+]_{aq}V_{aq}/K_{aH}}$$

Cancel out $[B]_{aq}$ and multiply top and bottom by K_{aH}/V_{aq}

$$\text{fraction protonated} = \frac{[H_3O^+]_{aq}(K'_PV_{rat} + 1)}{K_{aH}(K_PV_{rat} + 1) + [H_3O^+]_{aq}(K'_PV_{rat} + 1)}$$

$$\text{\% protonation} = \frac{[H_3O^+]_{aq}(K'_PV_{rat} + 1)}{K_{aH}(K_PV_{rat} + 1) + [H_3O^+]_{aq}(K'_PV_{rat} + 1)} \times 100\%$$

3.3 Derivation of equation 27

at the midpoint, % protonation = 50%. Put this into equation 20 and rearrange.

$K_{aH}(K_PV_{rat} + 1) + [H_3O^+]_{aq}(K'_PV_{rat} + 1) = 2[H_3O^+]_{aq}(K'_PV_{rat} + 1)$
$K_{aH}(K_PV_{rat} + 1) = [H_3O^+]_{aq}(K'_PV_{rat} + 1)$
$[H_3O^+]_{aq} = K_{aH}(K_PV_{rat} + 1)/(K'_PV_{rat} + 1)$
$\log[H_3O^+]_{aq} = \log K_{aH} + \log(K_PV_{rat} + 1) – \log(K'_PV_{rat} + 1)$
$pH = pK_{aH} - \log_{10}(K_PV_{rat} + 1) + \log_{10}(K'_PV_{rat} + 1)$

3.4 Derivation of equation 28

$$K_{aH} = \frac{[B]_{aq}[H_3O^+]_{aq}}{[BH^+]_{aq}}$$

$$K_P = \frac{[B]_{org}}{[B]_{aq}}$$

$$K'_P = \frac{[BH^+]_{org}}{[BH^+]_{aq}}$$

initial moles of base = $n_0 = [B]_{org}V_{org} + [B]_{aq}V_{aq} + [BH^+]_{org}V_{org} + [BH^+]_{aq}V_{aq}$

$K_w = [H_3O^+]_{aq}[OH^-]_{aq}$
$V_{rat} = V_{org}/V_{aq}$
charge balance in water:
$[BH^+]_{aq} + [H_3O^+]_{aq} = [OH^-]_{aq}$
$[BH^+]_{aq} = [OH^-]_{aq} - [H_3O^+]_{aq}$
$[BH^+]_{aq} = K_w/[H_3O^-]_{aq} - [H_3O^+]_{aq}$

To save space, we will use “H^+” to represent “H_3O^+” and note that $[H^+]$ is the aqueous phase concentration of H_3O^+.

$[B]_0 = [B]_{org}V_{rat} + [B]_{aq} + [BH^+]_{org}V_{rat} + [BH^+]_{aq}$
$[B]_0 = [B]_{aq}K_PV_{rat} + [B]_{aq} + [BH^+]_{aq}K'_PV_{rat} + [BH^+]_{aq}$
$[B]_0 = [B]_{aq}(K_PV_{rat} + 1) + [BH^+]_{aq}(K'_PV_{rat} + 1)$
$[B]_0 = K_{aH}[BH^+]_{aq}(K_PV_{rat} + 1)/[H^+] + [BH^+]_{aq}(K'_PV_{rat} + 1)$
$[B]_0 = K_{aH}(K_w/[H^+]_{aq} - [H^+]_{aq})(K_PV_{rat} + 1)/[H^+] + (K_w/[H^+]_{aq} - [H^+]_{aq})(K'_PV_{rat} + 1)$
$0 = K_{aH}(K_w/[H^+]_{aq} - [H^+]_{aq})(K_PV_{rat} + 1)/[H^+] + (K_w/[H^+]_{aq} - [H^+]_{aq})(K'_PV_{rat} + 1) - [B]_0$
$0 = (K_{aH}K_w/[H^+]^2 - K_{aH})(K_PV_{rat} + 1) + (K_w/[H^+]_{aq} - [H^+]_{aq})(K'_PV_{rat} + 1) - [B]_0$

multiply by $[H^+]^2$
$0 = (K_{aH}K_w - K_{aH}[H^+]^2)(K_PV_{rat} + 1) + (K_w[H^+] - [H^+]^3)(K'_PV_{rat} + 1) - [B]_0[H^+]^2$
$0 = K_{aH}K_w(K_PV_{rat} + 1) - K_{aH}[H^+]^2(K_PV_{rat} + 1) + K_w[H^+](K'_PV_{rat} + 1) - [H^+]^3(K'_PV_{rat} + 1) - [B]_0[H^+]^2$
$0 = - [H^+]^3(K'_PV_{rat} + 1) - K_{aH}[H^+]^2(K_PV_{rat} + 1) - [B]_0[H^+]^2 + K_w[H^+](K'_PV_{rat} + 1) + K_{aH}K_w(K_PV_{rat} + 1)$
$0 = - [H^+]^3(K'_PV_{rat} + 1) - [H^+]^2\{K_{aH}(K_PV_{rat} + 1) + [B]_0\} + [H^+]K_w(K'_PV_{rat} + 1) + K_{aH}K_w(K_PV_{rat} + 1)$
$0 = - [H^+]^3(K'_PV_{rat} + 1) - [H^+]^2\{K_{aH}K_PV_{rat} + K_a + [B]_0\} + [H^+]K_w(K'_PV_{rat} + 1) + K_{aH}K_w(K_PV_{rat} + 1)$
$0 = [H^+]^3(K'_PV_{rat} + 1) + [H^+]^2\{K_{aH}K_PV_{rat} + K_a + [B]_0\} - [H^+]K_w(K'_PV_{rat} + 1) - K_{aH}K_w(K_PV_{rat} + 1)$

Derivation of equation 29

$$K_{aH} = \frac{[B]_{aq}[H_3O^+]_{aq}}{[BH^+]_{aq}}$$

$$K_P = \frac{[B]_{org}}{[B]_{aq}}$$

$$K'_P = \frac{[BH^+]_{org}}{[BH^+]_{aq}}$$

$K^*_{a1}= [H_3O^+]_{aq}\,[HCO_3^-]_{aq}\,/([H_2CO_3]+[CO_{2(aq)}])$

$K_H = ([H_2CO_3]+[CO_{2(aq)}]) / P_{CO2}$

initial moles of base = $n_0 = [B]_{org}V_{org} + [B]_{aq}V_{aq} + [BH^+]_{org}V_{org} + [BH^+]_{aq}V_{aq}$

$K_w = [H_3O^+]_{aq}[OH^-]_{aq}$
$V_{rat} = V_{org}/V_{aq}$
charge balance in water:
$[BH^+]_{aq} + [H_3O^+]_{aq} = [OH^-]_{aq} + [HCO_3^-]_{aq}$
$[BH^+]_{aq} = [OH^-]_{aq} + [HCO_3^-]_{aq} - [H_3O^+]_{aq}$
$[BH^+]_{aq} = K_w/[H_3O^+]_{aq} + [HCO_3^-]_{aq} - [H_3O^+]_{aq}$
$[BH^+]_{aq} = K_w/[H_3O^+]_{aq} + K^*_{a1}([H_2CO_3]+[CO_{2(aq)}])/[H_3O^+]_{aq} - [H_3O^+]_{aq}$

To save space, we will use “H^+” to represent “H_3O^+” and note that $[H^+]$ is the aqueous phase concentration of H_3O^+.

$[B]_0 = [B]_{org}V_{rat} + [B]_{aq} + [BH^+]_{org}V_{rat} + [BH^+]_{aq}$
$[B]_0 = [B]_{aq}K_PV_{rat} + [B]_{aq} + [BH^+]_{aq}K'_PV_{rat} + [BH^+]_{aq}$
$[B]_0 = [B]_{aq}(K_PV_{rat} + 1) + [BH^+]_{aq}(K'_PV_{rat} + 1)$
$[B]_0 = K_{aH}[BH^+]_{aq}(K_PV_{rat} + 1)/[H^+] + [BH^+]_{aq}(K'_PV_{rat} + 1)$
$[B]_0 = K_{aH}(K_w/[H^+] + K^*_{a1}([H_2CO_3]+[CO_{2(aq)}])/[H^+] - [H^+])(K_PV_{rat} + 1)/[H^+] + (K_w/[H^+] + K^*_{a1}([H_2CO_3]+[CO_{2(aq)}])/[H^+] - [H^+])(K'_PV_{rat} + 1)$
$[B]_0 = K_{aH}(K_w/[H^+] + K^*_{a1}K_HP_{CO2}/[H^+] - [H^+])(K_PV_{rat} + 1)/[H^+] + (K_w/[H^+] + K^*_{a1}K_HP_{CO2}/[H^+] - [H^+])(K'_PV_{rat} + 1)$
$0 = K_{aH}(K_w/[H^+] + K^*_{a1}K_HP_{CO2}/[H^+] - [H^+])(K_PV_{rat} + 1)/[H^+] + (K_w/[H^+] + K^*_{a1}K_HP_{CO2}/[H^+] - [H^+])(K'_PV_{rat} + 1) - [B]_0$
$0 = (K_{aH}K_w/[H^+]^2 + K_{aH}K^*_{a1}K_HP_{CO2}/[H^+]^2 - K_{aH})(K_PV_{rat} + 1) + (K_w/[H^+] + K^*_{a1}K_HP_{CO2}/[H^+] - [H^+])(K'_PV_{rat} + 1) - [B]_0$
multiply by $[H^+]^2$
$0 = (K_{aH}K_w + K_{aH}K^*_{a1}K_HP_{CO2} - K_{aH}[H^+]^2)(K_PV_{rat} + 1) + (K_w[H^+] + K^*_{a1}K_HP_{CO2}[H^+] - [H^+]^3)(K'_PV_{rat} + 1) - [B]_0[H^+]^2$
$0 = K_{aH}K_w(K_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2} (K_PV_{rat} + 1) - K_{aH}[H^+]^2(K_PV_{rat} + 1) + K_w[H^+](K'_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}[H^+](K'_PV_{rat} + 1) - [H^+]^3(K'_PV_{rat} + 1) - [B]_0[H^+]^2$

$$0 = - [H^+]^3(K'_PV_{rat} + 1) - K_{aH}[H^+]^2(K_PV_{rat} + 1) - [B]_0[H^+]^2 + K_w[H^+](K'_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}[H^+](K'_PV_{rat} + 1) + K_{aH}K_w(K_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}(K_PV_{rat} + 1)$$

$$0 = - [H^+]^3(K'_PV_{rat} + 1) - [H^+]^2\{K_{aH}(K_PV_{rat} + 1) + [B]_0\} + [H^+]\{K_w(K'_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}(K'_PV_{rat} + 1)\} + K_{aH}K_w(K_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}(K_PV_{rat} + 1)$$

$$0 = [H^+]^3(K'_PV_{rat} + 1) + [H^+]^2\{K_{aH}(K_PV_{rat} + 1) + [B]_0\} - [H^+]\{K_w(K'_PV_{rat} + 1) + K_{aH}K^*_{a1}K_HP_{CO2}(K'_PV_{rat} + 1)\} - K_{aH}K_w(K_PV_{rat} + 1) - K_{aH}K^*_{a1}K_HP_{CO2}(K_PV_{rat} + 1)$$

4. Additional information concerning Scenario 1

4.1 Experimental Methods

The pK_{aH} values of DBU, 2-IME, and PYPO were experimentally determined as follows. A standard solution (0.1 M) of the compound in distilled water was titrated by 0.1 M HCl at 30 ˚C, and the pH was continuously recorded after addition of HCl. The pK_{aH} was taken as the pH at the half-equivalence point.

pH measurements of base solutions were performed in the following manner. Vials and centrifuge tubes were washed with deionized water (from a Millipore purification system, 18.2 MΩ) until the wash water had a pH within 0.2 units of 7. Stock solutions of base (10 mM, 100 mM, and 1000 mM) were prepared by accurately weighing out the base in a washed and dried vial, dissolved into DI water, and then transferred, with rinses, into a 100 mL glass volumetric flask. The contents of the volumetric flask were then diluted to volume. Three polypropylene 50 mL centrifuge tubes were washed with the DI water and then washed with a 5 mL portion of the base solution. Afterward, 25 mL of the base solution was added to each tube. Each tube of solution was covered with a screw cap and placed into a water bath with a temperature of 30.0 °C. All pH measurements were taken with a pH probe (Orion 4 Star benchtop pH meter equipped with an Orion Ag/AgCl glass probe (Thermo Scientific)). After 10 minutes, the tubes were removed from the bath and the pH of the each solution was measured 3 times in quick succession. The average measured pH of the solutions was determined by first calculating the average measured pH of each individual solution, then calculating the average pH between solutions. The tubes were placed back into the bath and CO_2 was passed slowly through the base solutions using a needle for sufficient time to obtain a constant pH. The necessary time varied with concentration and strength of the base, and was determined by measuring the pH every 20 min. A hole was created in the screw caps to prevent over-pressurization. The fully carbonated solutions were removed from the water bath and the pH of each solution was measured 3 times in quick succession. The average measured pH of the solutions was determined by first calculating the average measured pH of each individual solution, then calculating the average pH between solutions.

4.2 Tables of Theoretical Data

Table S1. The theoretical pH values for solutions of bases having specified pK_{aH} values and specified concentrations in water at 25 ˚C in the absence of CO_2.

$[B]_0$, mM	pK_{aH}= 5	pK_{aH}= 6	pK_{aH}= 7	pK_{aH}= 8	pK_{aH}= 9	pK_{aH}= 10	pK_{aH}= 11	pK_{aH}= 12	pK_{aH}= 13
0.001	7.02	7.14	7.46	7.80	7.97	8.00	8.00	8.00	8.00
0.01	7.15	7.51	7.98	8.43	8.80	8.96	8.99	8.99	9.00
0.1	7.525	8.00	8.49	8.98	9.43	9.79	9.97	9.99	9.99
1	8.00	8.5	8.99	9.498	9.98	10.43	10.79	10.96	10.99
10	8.505	8.99	9.50	9.99	10.49	10.98	11.43	11.79	11.96
100	9.00	9.50	9.99	10.50	10.99	11.49	11.98	12.43	12.84
1000	9.50	9.99	10.50	10.99	11.50	11.99	12.49	12.98	13.43

Table S2. The theoretical % protonation values for solutions of bases having specified pK_{aH} values and specified concentrations in water at 25 ˚C in the absence of CO_2.

$[B]_0$, mM	pK_{aH}= 5	pK_{aH}= 6	pK_{aH}= 7	pK_{aH}= 8	pK_{aH}= 9	pK_{aH}= 10	pK_{aH}= 11	pK_{aH}= 12	pK_{aH}= 13
0.001	1	7	26	61	92	99	100	100	100
0.01	0.70	3	10	27	62	92	99	100	100
0.1	0.30	1	3	10	27	62	92	99	100
1	0.1	0.32	1	3	10	27	62	92	99
10	0.03	0.1	0.32	1	3	10	27	62	92
100	0.01	0.03	0.1	0.32	1	3	10	27	62
1000	0.003	0.01	0.03	0.1	0.32	1	3	10	26

Table S3. The theoretical pH values for solutions of bases having specified pK_{aH} values and specified concentrations in water at 25 ˚C in the presence of 0.1 MPa CO_2.

$[B]_0$, mM	pK_{aH}= 5	pK_{aH}= 6	pK_{aH}= 7	pK_{aH}= 8	pK_{aH}= 9	pK_{aH}= 10	pK_{aH}= 11	pK_{aH}= 12	pK_{aH}= 13
0.001	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91	3.91
0.01	3.93	3.93	3.93	3.93	3.93	3.93	3.93	3.93	3.93
0.1	4.06	4.08	4.08	4.08	4.08	4.08	4.08	4.08	4.08
1	4.67	4.79	4.8	4.8	4.8	4.8	4.8	4.8	4.8
10	5.33	5.7	5.8	5.8	5.8	5.8	5.8	5.8	5.8
100	5.88	6.3	6.7	6.8	6.8	6.8	6.8	6.8	6.8
1000	6.40	6.9	7.3	7.7	7.8	7.8	7.8	7.8	7.8

Table S4. The theoretical % protonation values for solutions of bases having specified pK_{aH} values and specified concentrations in water at 25 ˚C in the presence of 0.1 MPa of CO_2.

$[B]_0$, mM	pK_{aH}= 5	pK_{aH}= 6	pK_{aH}= 7	pK_{aH}= 8	pK_{aH}= 9	pK_{aH}= 10	pK_{aH}= 11	pK_{aH}= 12	pK_{aH}= 13
0.001	94	99	100	100	100	100	100	100	100
0.01	92	99	100	100	100	100	100	100	100
0.1	90	98	100	100	100	100	100	100	100
1	68	94	99	100	100	100	100	100	100
10	32	69	94	99	100	100	100	100	100
100	12	32	69	94	99	100	100	100	100
1000	4	12	32	69	94	99	100	100	100

Table S5. The pK_{aH} values required for bases to have specific % protonation values in water at 25 ˚C under air or 0.1 MPa of CO_2, assuming that the base and its bicarbonate salt are both fully soluble.

$[B]_0$, mM	% P In absence of CO_2				% P In presence of 0.1 MPa CO_2			
	5	10	20	30	95	90	80	70
	pK_{aH}				pK_{aH}			
0.001	5.83	6.26	6.81	7.16	5.19	4.879	4.52	4.28
0.01	6.44	7.06	7.71	8.11	5.21	4.88	4.53	4.29
0.1	7.5	8.05	8.7	9.15	5.36	5.02	4.65	4.41
1	8.43	9.05	9.7	10.11	6.09	5.74	5.34	5.05
10	9.43	10.05	10.7	11.11	7.08	6.73	6.33	6.04
100	10.43	11.05	11.7	12.11	8.08	7.73	7.33	7.04
1000	11.42	12.05	12.7	13.11	9.08	8.73	8.33	8.04

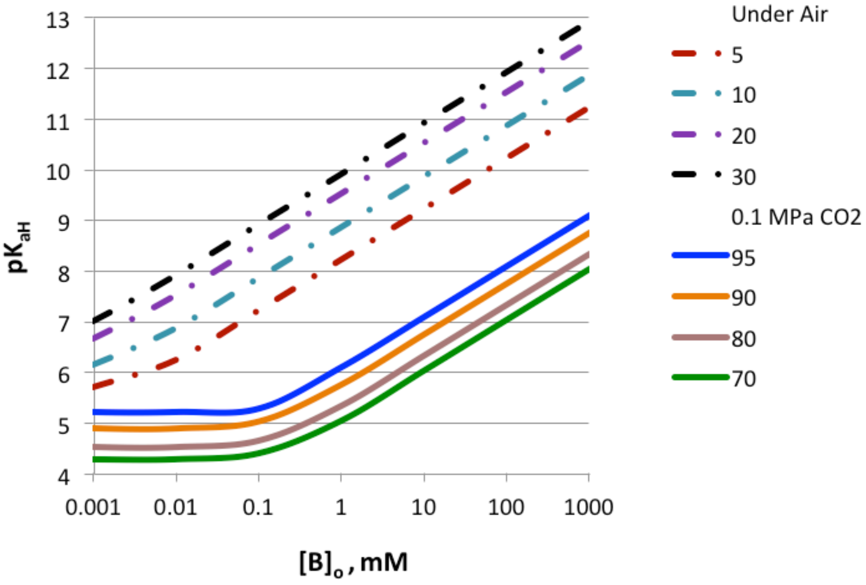


Figure S1. The pK_{aH} required for a base to have a specified % protonation when mixed with water at 30 ˚C. The dashed lines show the required pK_{aH} to obtain the specified % protonation in the absence of CO_2. The solid lines show the pK_{aH} required to obtain the specified % protonation values in the presence of 0.1 MPa of CO_2.

Table S6. The pK_{aH} values required for bases to have specific % protonation values in water at 30 ˚C under air or 0.1 MPa of CO_2, assuming that the base and its bicarbonate salt are both fully soluble.

$[B]_0$, mM	% P In absence of CO_2				% P In presence of 0.1 MPa CO_2			
	5	10	20	30	95	90	80	70
	pK_{aH}				pK_{aH}			
0.001	5.73	6.14	6.65	7.01	5.21	4.89	4.53	4.3
0.01	6.28	6.89	7.54	7.95	5.23	4.91	4.55	4.31
0.1	7.26	7.88	8.54	8.95	5.3	5.05	4.68	4.43
1	8.26	8.88	9.54	9.94	6.12	5.78	5.37	5.077
10	9.26	9.88	10.54	10.95	7.11	6.77	6.36	6.065
100	10.26	10.88	11.54	11.95	8.11	7.77	7.36	7.065
1000	11.26	11.88	12.54	12.95	9.11	8.77	8.36	8.065

Table S7. The pK_{aH} values required for bases to have specific % protonation values in water at 60 ˚C under air or 0.1 MPa of CO_2, assuming that the base and its bicarbonate salt are both fully soluble.

$[B]_0$, mM	% P In absence of CO_2				% P In presence of 0 .1 MPa CO_2			
	5	10	20	30	95	90	80	70
	pK_{aH}				pK_{aH}			
0.001	5.27	5.63	6.05	6.35	5.32	5	4.65	4.41
0.01	5.56	6.11	6.73	7.14	5.34	5.02	4.66	4.43
0.1	6.45	7.1	7.72	8.19	5.54	5.2	4.83	4.57
1	7.45	8.07	8.72	9.13	6.34	5.99	5.59	5.3
10	8.45	9.07	9.72	10.13	7.34	6.98	6.58	6.29
100	9.45	10.07	10.72	11.13	8.34	7.99	7.59	7.29
1000	10.45	11.07	11.72	12.13	9.34	8.99	8.58	8.29

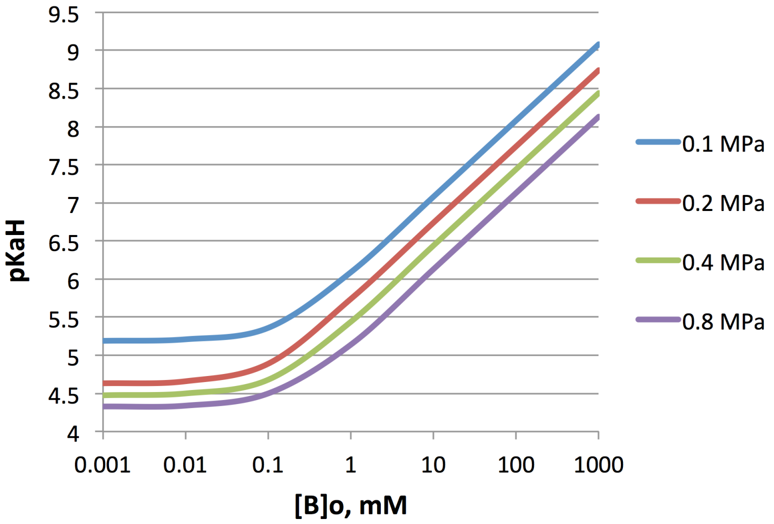


Figure S2. The pK_{aH} required for a base to have 95 % protonation when mixed with water at 25 ˚C under the specified pressure of CO_2.

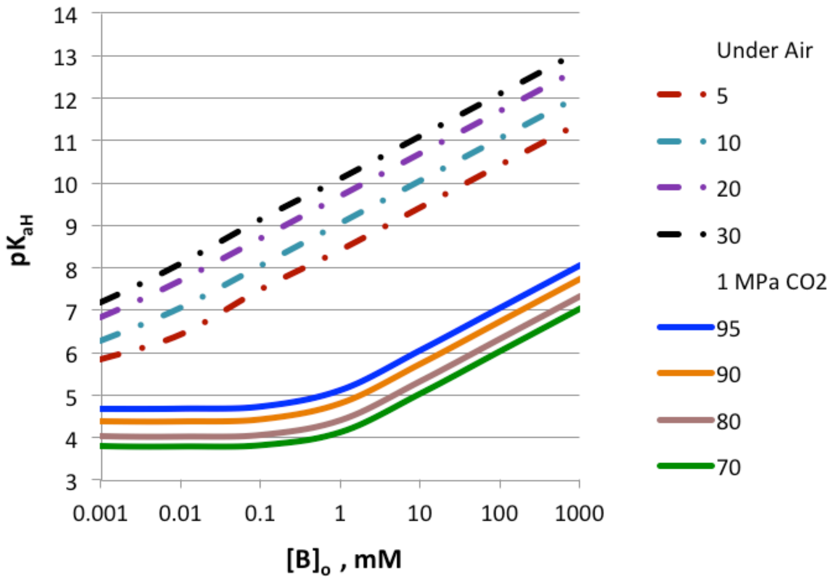


Figure S3. The pK_{aH} required for a base to have a specified % protonation when mixed with water at 25 ˚C. The dashed lines show the required pK_{aH} to obtain the specified % protonation in the absence of CO_2. The solid lines show the pK_{aH} required to obtain the specified % protonation values in the presence of 1 MPa (10 bar) of CO_2.

Table S8. The pK_{aH} values required for bases to have specific % protonation values in water at 25 ˚C under air or 1 MPa of CO_2, assuming that the base and its bicarbonate salt are both fully soluble.

$[B]_0$, mM	% P In absence of CO_2				% P In presence of 1 MPa CO_2			
	5	10	20	30	95	90	80	70
	pK_{aH}				pK_{aH}			
0.001	5.83	6.26	6.81	7.16	4.69	4.365	4.012	3.78
0.01	6.44	7.06	7.71	8.11	4.7	4.37	4.02	3.79
0.1	7.5	8.05	8.7	9.15	4.75	4.42	4.06	3.82
1	8.43	9.05	9.7	10.11	5.14	4.8	4.41	4.13
10	9.43	10.05	10.7	11.11	6.08	5.73	5.33	5.04
100	10.43	11.05	11.7	12.11	7.08	6.73	6.33	6.04
1000	11.42	12.05	12.7	13.11	8.08	7.73	7.33	7.04

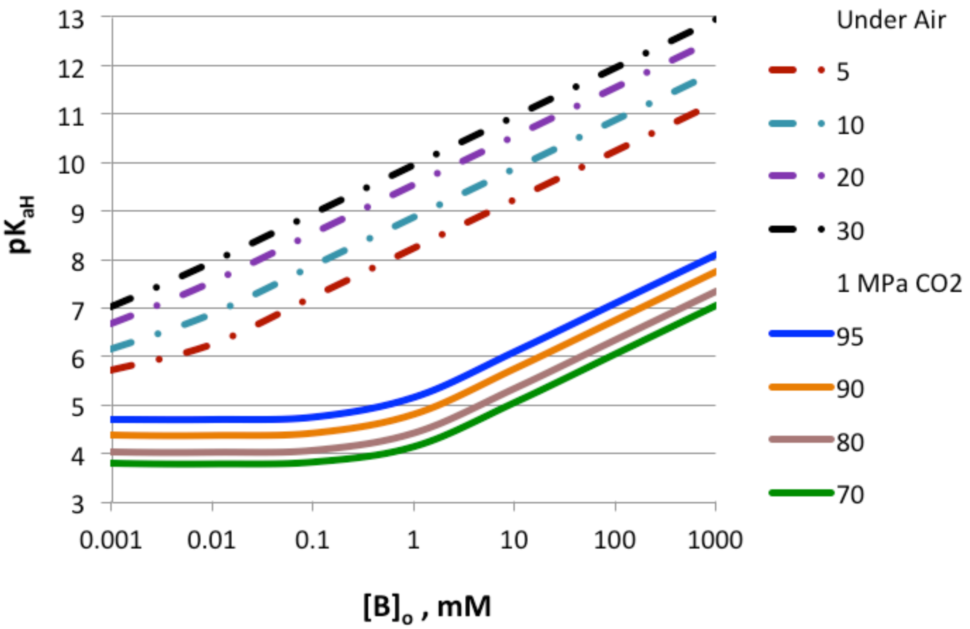


Figure S4. The pK$_{aH}$ required for a base to have a specified % protonation when mixed with water at 30 °C. The dashed lines show the required pK$_{aH}$ to obtain the specified % protonation in the absence of CO$_2$. The solid lines show the pK$_{aH}$ required to obtain the specified % protonation values in the presence of 1 MPa (10 bar) of CO$_2$.

Table S9. The pK$_{aH}$ values required for bases to have specific % protonation values in water at 30 °C under air or 1 MPa of CO$_2$, assuming that the base and its bicarbonate salt are both fully soluble.

[B]$_0$, mM	% P In absence of CO$_2$				% P In presence of 1 MPa CO$_2$			
	5	10	20	30	95	90	80	70
	pK$_{aH}$				pK$_{aH}$			
0.001	5.73	6.14	6.65	7.01	4.71	4.381	4.03	3.8
0.01	6.28	6.89	7.54	7.95	4.71	4.39	4.04	3.8
0.1	7.26	7.88	8.54	8.95	4.76	4.44	4.08	3.84
1	8.26	8.88	9.54	9.95	5.17	4.83	4.44	4.16
10	9.26	9.88	10.54	10.95	6.11	5.77	5.36	5.07
100	10.26	10.88	11.54	11.95	7.11	6.77	6.36	6.07
1000	11.26	11.88	12.54	12.95	8.11	7.77	7.36	7.07

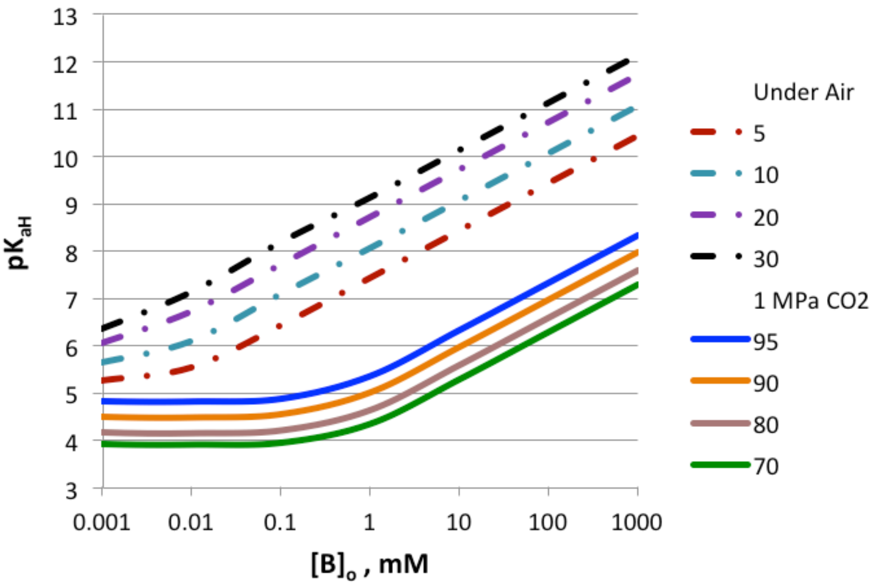


Figure S5. The pK_{aH} required for a base to have a specified % protonation when mixed with water at 60 ˚C. The dashed lines show the required pK_{aH} to obtain the specified % protonation in the absence of CO_2. The solid lines show the pK_{aH} required to obtain the specified % protonation values in the presence of 1 MPa of CO_2.

Table S10. The pK_{aH} values required for bases to have specific % protonation values in water at 60 ˚C under air or 1 MPa of CO_2, assuming that the base and its bicarbonate salt are both fully soluble.

$[B]_0$, mM	% P In absence of CO_2				% P In presence of 1 MPa CO_2			
	5	10	20	30	95	90	80	70
	pK_{aH}				pK_{aH}			
0.001	5.27	5.63	6.05	6.35	4.82	4.494	4.142	3.91
0.01	5.56	6.11	6.73	7.14	4.83	4.5	4.15	3.92
0.1	6.45	7.1	7.72	8.19	4.89	4.57	4.21	3.96
1	7.45	8.07	8.72	9.13	5.37	5.03	4.64	4.36
10	8.45	9.07	9.72	10.13	6.34	5.99	5.59	5.3
100	9.45	10.07	10.72	11.13	7.34	6.99	6.59	6.3
1000	10.45	11.07	11.72	12.13	8.34	7.99	7.59	7.3

5. Additional information concerning Scenario 2

5.1 Calculation of the S_0 value of $CyNMe_2$ in water

The solubility of $CyNMe_2$ in water is 1.4 wt% at 25 ˚C; this value was obtained by interpolation of the data of Stephenson.[1] This corresponds to a concentration of ~0.11 M if one assumes that a 1 kg solution has a volume of 1 L. Using equation 13, one can calculate that in this case S_0 and S are identical to several digits. Therefore S_0 = ~0.11 M

5.2 pK_{aH} values required

Table S11. The theoretical pH values of the aqueous phase of a base/water mixture in the absence of CO_2 as a function of the pK_{aH} of the base and $[B]_0$, the number of moles of base added to the system per litre of solution, at 25 °C. For each base, S_0 is assumed to be 0.01 M.

$[B]_0$, mM	pK_{aH}= 5	pK_{aH}= 6	pK_{aH}= 7	pK_{aH}= 8	pK_{aH}= 9	pK_{aH}= 10	pK_{aH}= 11	pK_{aH}= 12	pK_{aH}= 13
0.001	7.02	7.14	7.46	7.80	7.97	8.00	8.00	8.00	8.00
0.01	7.15	7.51	7.98	8.43	8.79	8.96	9.00	9.00	9.00
0.1	7.52	8.00	8.49	8.98	9.43	9.79	9.97	10.00	10.00
1	8.00	8.5	9.00	9.49	9.98	10.43	10.79	10.96	11.00
10	8.50	9.00	9.50	10.00	10.50	11	11.5	12	12.5
100	8.50	9.00	9.50	10.00	10.50	11	11.5	12	12.5
1000	8.50	9.00	9.50	10.00	10.50	11	11.5	12	12.5

Table S12. The pK_{aH} required for a base to have 5% protonation when mixed with water under air or a 95% protonation in water under 0.1 MPa CO_2, for incompletely soluble bases having an S_0 value of 1, 10 or 100 mM, at 25 °C.

$[B]_0$, mM	P= 5% under air			P= 95% under 0.1 MPa CO_2		
	S_0= 100 mM	S_0= 10 mM	S_0= 1 mM	S_0= 100 mM	S_0= 10 mM	S_0= 1 mM
0.001	5.83	5.83	5.83	5.19	5.19	5.19
0.01	6.44	6.44	6.44	5.21	5.21	5.21
0.1	7.5	7.5	7.5	5.36	5.36	5.36
1	8.43	8.43	8.4	6.09	6.09	6.09
10	9.43	9.4	10.4	7.08	7.08	7.08
100	10.4	11.4	12.4	8.08	8.08	8.78
1000	12.4	13.4	14.4	9.08	9.78	10.78

6. Additional information concerning Scenario 3

Table S13. The pK_{aH} values required for bases to have specific % protonation values in a biphasic water:organic mixture at 25 °C, assuming V_{rat}=0.5 and $\Delta logK_P$=2.8. These values were used to create the plot shown in Figure 16.

$[B]_0$, mM	5% protonation under air			95% protonation under 1 bar CO_2		
	pK_{aH} at given $logK_P$			pK_{aH} at given $logK_P$		
	$logK_P$=-1	$logK_P$=1	$logK_P$=3	$logK_P$=-1	$logK_P$=1	$logK_P$=3
0.001	5.87	6.87	8.53	5.23	6.23	7.94
0.01	6.48	7.47	8.96	5.25	6.24	7.95
0.1	7.46	8.45	9.91	5.39	6.39	8.03
1	8.46	9.45	10.91	6.13	7.12	8.59
10	9.46	10.45	11.91	7.12	8.11	9.57
100	10.46	11.45	12.91	8.12	9.11	10.57
1000	11.46	12.45	13.91	9.12	10.11	11.57

7. References

[1] R. M. Stephenson, *J. Chem. Eng. Data* **1993**, *38*, 634.