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Note

ON ENTHALPIES OF HYDRATION, IONIZATION POTENTIALS, AND THE SOFTNESS OF IONS

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In a recent paper House et al. [1] showed that for 30 monoatomic metal cations the standard molar enthalpy of hydration is linearly correlated with the total ionization energy, *IE*

$$\Delta_{\mathrm{hyd}} H^0(\mathrm{kcal\ mol}^{-1}) = 0.822\ IE(\mathrm{kcal\ mol}^{-1}) - 2.56 \qquad (1)$$

with a correlation coefficient of 0.9896. It should be noted, however, that for certain ions (e.g., Cu^+, Ag^+, Tl^+) the deviations from the correlation (i.e., the calculated minus the experimental quantity) are positive, whereas for others (e.g., Na^+, Ca^{2+}) they are negative. It is also noteworthy that the ion Hg^{2+} was excluded from the correlation; if included it would have shown a large positive deviation.

It appears that the correlation expressed by eqn. (1) obscures a much more important fact concerning the cations, namely their properties as soft or hard Lewis acids [2]. Already Ahrland [3,4] has pointed out that the difference between the standard molar enthalpy of hydration of a cation and the total energy of ionization required to produce it is a good measure of the relative softness of the ion. (A corresponding relationship exists for the standard molar enthalpy of hydration and the electron affinity for an anion.) This relationship was developed further by the present author [5,6], who has presented extensive tables of the softness parameters of ions, and has suggested instances where they can be used [5,7].

The suggestion is that a large part of the energy expended by the ionization of an atom (or radical) is returned when the ion produced interacts with the dipoles of the solvent. Figure 1 shows a schematic representation of this idea for both a cation and an anion, for the particular solvent water. Since the most extensive set of data for the standard molar enthalpy of solvation is available for the solvent water, and since the hydrogen ion has a special relationship to this solvent (Fig. 2), the softness parameter scale for cations (M^{m+}) was defined as [5]

$$\sigma_M = [\sigma_A(M^{m+}) - \sigma_A(H^+)]/\sigma_A(H^+) \qquad (2)$$

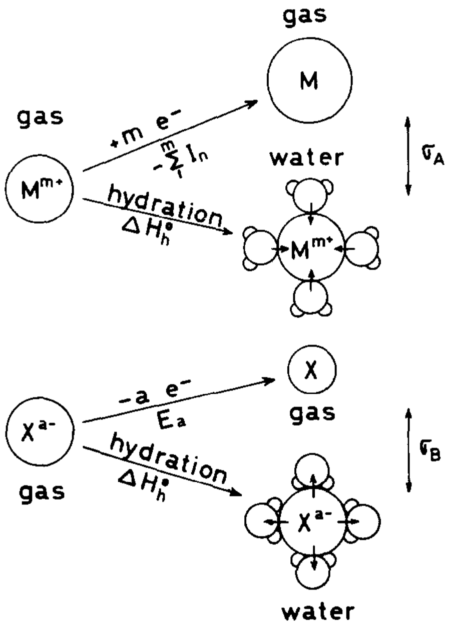

Fig. 1. A schematic representation of the formation of gaseous and aqueous cations and anions from the corresponding neutral atoms (radicals).

where

$$\sigma_A(M^{m+}) = \left[\sum_{i=1}^{m} I_i + \Delta_{\text{hyd}} H^0 \right] / m \tag{3}$$

and $\sum_{i=1}^{m} I_i = IE$. These expressions lead to negative values for the softness parameters of ions known to be hard Lewis acids and to positive values for those known to be soft.

Notes to Table 1.

[a] Unless otherwise noted, the values of $\Delta_f H^0$ of M(g), M^{m+}(g), and M^{m+}(aq) required for the calculations are from ref. 8.

[b] The $\Delta_{\text{hyd}} H^0$ value was calculated from a semiempirical equation of S.I. Drakin and A.V. Mikhailov [12]; Ag^+ generally behaves as if it had a much more positive σ_M.

[c] $\Delta_f H^0$ of NH_4(g) from ref. 13.

[d] $\Delta_f H^0$ of UO_2^+(g) from ref. 9.

[e] $\Delta_f H^0$ of M(g) and M^{m+}(g) from ref. 14.

[f] $\Delta_f H^0$ of UO_2^{2+} from ref. 15.

[g] $\Delta_f H^0$ of M(g) and M^{m+}(g) from ref. 9.

[h] $\Delta_f H^0$ of Bi^{3+}(aq) from ref. 10.

[i] $\Delta_f H^0$ of Zr^{4+}(aq) and Hf^{4+}(aq) from ref. 16.

[j] From ref. 7.

TABLE 1

Softness parameters of cations [a]

Ion	σ_M	Ion	σ_M
H^+	0.00	Y^{3+}	−0.71 [e]
Li^+	−1.02	La^{3+}	−0.75 [e]
Na^+	−0.75	Ce^{3+}	−0.72 [e]
K^+	−0.58	Pr^{3+}	−0.63 [e]
Rb^+	−0.53	Nd^{3+}	−0.58 [e]
Cs^+	−0.54	Pm^{3+}	−0.53 [e]
Cu^+	−0.22	Sm^{3+}	−0.36 [e]
Ag^+	+0.18 [b]	Eu^{3+}	−0.19 [e]
Au^+	+0.44 [b]	Gd^{3+}	−0.66 [e]
In^+	−0.47 [b]	Tb^{3+}	−0.64 [e]
Tl^+	+0.20	Dy^{3+}	−0.50 [e]
NH_4^+	−0.60 [c]	Ho^{3+}	−0.53 [e]
UO_2^+	−0.38 [d]	Er^{3+}	−0.57 [e]
$(CH_3)_4N^+$	+0.81 [j]	Tm^{3+}	−0.43 [e]
$(C_6H_5)_4As^+$	+7.32 [j]	Yb^{3+}	−0.27 [e]
Be^{2+}	−0.63	Lu^{3+}	−0.64 [e]
Mg^{2+}	−0.41	Ac^{3+}	−0.67 [g]
Ca^{2+}	−0.66	U^{3+}	−0.54 [g]
Sr^{2+}	−0.64	Np^{3+}	−0.45 [g]
Ba^{2+}	−0.66	Pu^{3+}	−0.45 [g]
Ra^{2+}	−0.58	Am^{3+}	−0.44 [g]
V^{2+}	−0.10	Cm^{3+}	−0.71 [g]
Cr^{2+}	−0.24	Ti^{3+}	−0.54 [b]
Mn^{2+}	−0.15	V^{3+}	−0.29 [b]
Fe^{2+}	−0.16	Cr^{3+}	−0.10 [b]
Co^{2+}	−0.11	Mn^{3+}	+0.33 [b]
Ni^{2+}	−0.11	Fe^{3+}	+0.29
Cu^{2+}	+0.38	Co^{3+}	+0.50
Zn^{2+}	+0.35	Ga^{3+}	+0.29
Cd^{2+}	+0.58	In^{3+}	+0.48
Hg^{2+}	+1.27	Tl^{3+}	+1.07
Sn^{2+}	+0.29	Sb^{3+}	+0.63 [b]
Pb^{2+}	+0.41	Bi^{3+}	+0.82 [h]
Pd^{2+}	+0.48	Ce^{4+}	−0.10 [e]
Pt^{2+}	+0.33 [b]	Zr^{4+}	−0.43 [e,i]
Sm^{2+}	−0.62 [e]	Hf^{4+}	-0.61 [e,i]
Eu^{2+}	−0.62 [e]	Th^{4+}	−0.57
Yb^{2+}	−0.56 [e]	Pa^{4+}	−0.46 [g]
UO_2^{2+}	−0.27 [f]	U^{4+}	−0.38 [g]
Al^{3+}	−0.31	Np^{4+}	−0.22 [g]
Sc^{3+}	−0.52	Pu^{4+}	−0.21 [g]

Notes to Table 1 on preceding page.

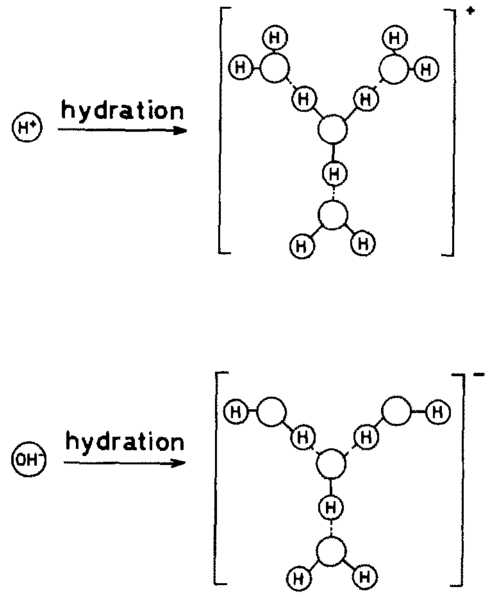

Fig. 2. A schematic representation of the hydration of the hydrogen and hydroxide ions.

Similarly, values of σ_x, the softness parameters of anions (X^{x-}), are obtained from:

$$\sigma_x = \left[\sigma_B(X^{x-}) - \sigma_B(OH^-)\right]/\sigma_A(H^+) \tag{4}$$

where the hydrated hydroxide anion, which strongly resembles the hydrated hydrogen cation (Fig. 2), is taken as the reference, and

$$\sigma_B(X^{x-}) = \left[-EA + \Delta_{hyd}H^0\right]/x \tag{5}$$

and EA is the electron affinity of the atom or radical producing the anion. Here, again, the softness parameters of anions that are soft Lewis bases are positive and those that are hard are negative. Thus, when the enthalpy of interaction between ions of opposite charge is made to be proportional to the negative value of the product of the softness parameters of these ions, the observed preference for soft–soft and hard–hard interactions over soft–hard interactions is recovered.

Table 1 presents the values of the softness parameters of cations, σ_M, recalculated with more recent input data [6] than those employed for the values published originally [5]. It also includes values that have been calculated for a few more ions from more recently available data for $\Delta_{hyd}H^0$ or IE. Table 2 lists the softness parameters of anions, with some new values calculated from more recent electron affinity and $\Delta_{hyd}H^0$ data added to the original list [5].

It is suggested that these measures of the Lewis softness and hardness of

TABLE 2

Softness parameters for anions [a]

Ion	σ_x	Ion	σ_x
OH^-	0.00	NO_3^-	+0.03 [j]
F^-	−0.66	ClO_3^-	+0.03 [i]
Cl^-	−0.09	BH_4^-	+2.00 [c]
Br^-	+0.17	BF_4^-	−0.30 [j]
I^-	+0.50	ClO_4^-	−0.30 [i]
SH^-	+0.65 [b]	ReO_4^-	−0.40 [k]
SeH^-	+0.44 [b]	HCO_2^-	−0.33 [l]
CN^-	+0.41 [c]	$CH_3CO_2^-$	−0.22 [l]
N_3^-	+0.66 [d]	$B(C_6H_5)_4^-$	6.86 [q]
I_3^-	+0.87 [e]		
CNO^-	+0.71 [f]	S^{2-}	+1.09 [m]
SCN^-	+0.85 [f]	CO_3^{2-}	−0.50 [n]
BO_2^-	−0.94 [g]	SO_4^{2-}	−0.38 [o]
NO_2^-	+0.15 [h]		
ClO_2^-	+0.12 [i]	PO_4^{3-}	−0.78 [p]

[a] Unless otherwise noted, the values of $\Delta_f H^0$ of X(g), X^{x-}(g) required for the calculations are from ref. 8, and $\Delta_{hyd} H^0$ of X^{x-}(g) is from ref. 11.

[b] The value for $\Delta_f H^0$ of X(g) from ref. 17.

[c] *EA* of CN(g) from ref. 18.

[d] *EA* of N_3(g) from ref. 19.

[e] $\Delta_f H^0$ of I_3^-(g) from ref. 20 and that of I_3(g) from ref. 21.

[f] *EA* of CNO(g) and CNS(g) from ref. 22.

[g] All the data from ref. 10.

[h] *EA* of NO_2(g) from ref. 23.

[i] $\Delta_f H^0$ of X(g) and of X^-(g) from ref. 24.

[j] *EA* of NO_3 from refs. 8, 25.

[k] $\Delta_f H^0$ of ReO_4(g) and of ReO_4^-(g) from ref. 26.

[l] *EA* of RCO_2(g) from ref. 27.

[m] $\Delta_f H^0$ of S^{2-}(g) from ref. 9.

[n] $\Delta_f H^0$ of CO_3^{2-}(g) from the Madelung term of the lattice energy from ref. 28, multiplied by 0.9 to account for the repulsion term.

[o] $\Delta_f H^0$ of SO_4^{2-}(g) from ref. 9 and *EA* of SO_4(9) from ref. 29.

[p] *EA* of PO_4(g) and $\Delta_f H^0$ of PO_4^{3-}(g) from ref. 29 and data in ref. 8.

[q] Ref. 7.

ions are of greater value than the ability to estimate approximate standard molar enthalpy of hydration according to eqn. (1).

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