Trivalent Ion Hydrolysis Reactions: A Linear Free-Energy Relationship Based on Density Functional Electronic Structure Calculations

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Metal ion hydrolysis is fundamental in aqueous chemistry because of the influence of coordinating hydroxide ions on reaction rates; examples include enhanced labilization of coordinating water molecules in hydrolyzed complexes[1] and stabilization of oxidized products in electron-transfer reactions involving hydrolyzed reductants.[2] Moreover, the role of metal hydrolysis reactions in defining a baseline for establishing trends in metal−ligand binding has motivated efforts toward comprehensive integration of $M^{z+}{}_xOH_y$ stability constants.[3−5]

The hydrolyzing ability of a metal ion is roughly proportional to the charge to ionic radius ratio (Z^m/r^n),[6] however, charge/size ratios are often poor indicators of pK_{11},[7] especially for the trivalent ions. Charge/size correlations can be improved by grouping cations into categories based on criteria such as hardness, electronegativity, or the presence of partly filled d orbitals.[3a,8] These criteria are to some extent ad hoc, and, furthermore, none of these approaches has completely succeeded in correlating the hydrolysis constants of all the trivalent ions.[5a] In addition, it is not obvious how to extend many of the more sophisticated empirical methods to polynuclear species or oxide surfaces.[9] In this study, density functional electronic structure calculations of the acidities of trivalent metal ions are used to develop a linear free energy relationship which correlates the relative values of the hydrolysis constants of the common trivalent metal ions: Al^{3+}, Sc^{3+}, Ti^{3+}, Mn^{3+}, V^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, and Y^{3+}.

Previous computational approaches to metal ion hydrolysis[10] have generally focused on a single ion and have involved the explicit calculation of solvent effects to relate the gas-phase deprotonation energy of the complex to the hydrolysis constant. This approach depends on successful calculation of the balance of large offsetting contributions to the free energy of the hydrolysis reaction. In our study, density functional electronic structure calculations are used to correlate pK_{11} for a series of trivalent ions. Density functional theory (DFT)[11] has been shown to reliably reproduce the structures, frequencies and energetics of a broad range of transition metal clusters[12,13] and has also been used with success in the study of aquo ions.[14] The deprotonation of the trivalent $M(H_2O)_6{}^{3+}$ ion in the gas phase is chosen as a structural model for the hydrolysis reaction in solution. Calculated deprotonation energies are correlated against the measured pK_{11}. This energy is a more sensitive indicator of hydrolyzing tendency than the total energy of the aquo complex which has been used in a previous study.[15] There are two hypotheses to be tested through these calculations. The first is that solvent effects will tend to cancel for the series of trivalent ions. Neglect of differential solvation effects is also implicit in previous empirical approaches, all of which have focused on aspects of the metal−OH, metal−H_2O bonding as revealed through the electronic structure of the metal. The second hypothesis is that electronic structural effects, such as covalency, hardness, and partial filling of d shells, will be accounted for in the DFT calculations, eliminating the need to sort ions into groups having similar electronic structural characteristics before a good correlation of relative hydrolysis constants can be obtained. To test these hypotheses, DFT calculations were performed on $M(H_2O)_6{}^{3+}$ and $M(OH)(H_2O)_5{}^{2+}$ complexes for the trivalent metals listed above. The ions are, for the most part, hexacoordinated in aqueous solution. Sc^{3+} and Y^{3+} have coordination numbers higher than six,[16] but they are treated as $M(H_2O)_6{}^{3+}$ ions to eliminate the systematic size-dependence for removal of a proton from a gas-phase cluster and to maintain equality in the cancellation of solvent effects.

The calculations were done using the program system DGauss[17] on Silicon Graphics computers. The geometries were optimized using analytic gradient methods at the local level with the potential fit of Vosko, Wilk, and Nusair.[18] Second derivatives were calculated analytically at the same level. Final energies for the optimal LDFT structures were calculated at the gradient-corrected level with Becke's exchange functional[19] and Perdew's correlation functional.[20] The optimizations were done with the DZVP2 basis sets where possible (Al, Fe, Ti, V, Sc, Cr, Mn, O, H) and with

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(7) We use the notation pK_{xy} to mean $-\log K_{xy}$, where $K_{xy} = [M^{z+}{}_x(OH)_y{}^{(xz-y)+}][H^+]^y/[M^{z+}]^x\gamma_{MOH}{}^{(xz-y)+}\gamma_{H^+}{}^y/\gamma_{Mz+}{}^x a_{H_2O}{}^y$ as defined in ref 3, p 10. pK_{11} therefore refers to the first hydrolysis constant of the mononuclear species.

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Table 1. Calculated Acidities (kcal/mol) and Experimental $pK_{11}{}^a$

	ΔE_{H+}	pK_{11}	R(M$-$OH$_2$)	θ(MOH)
Al^{3+}	32.2	5.0[3]	190.7/187.6[23a]	138.0
Sc^{3+}	29.6 (43.3)[b]	4.3$-$4.8[5]	211.1/207[23a]	177.4
Ti^{3+}	18.7	1.3[25]$-$2.23	200.1/202.8[23b]	179.9
V^{3+}	20.3	2.3[3]	204.8 × 2/200.7[23c]	135.0
			204.9 × 2/200.7	
			205.0 × 2/200.7	
Cr^{3+}	24.8	3.6[25]$-$4.33	196.5/196.3[23a]	128.6
Mn^{3+}	8.9	0.7[3]	192.6 × 2/199.1[23a]	122.1
			193.4 × 2/199.1	
			211.0 × 2/199.1	
Fe^{3+}	15.8	2.2[3]	201.3/199.4[23d]	179.1
Ga^{3+}	31.5	2.6[3]$-$4.327	197.4/194.5[23a]	124.0
Y^{3+}	45.0 (72.0)[b]	7.7[3]	229.8/234 × 6; 252 × 3[23e]	178.0

^{a} M$-$O bond distance in M^{3+}(H$_2$O)$_6$ calc/expt in pm; MOH bond angle in M^{3+}(H$_2$O)$_6$(OH)$^-$ in degrees. ^{b} Values in parentheses refer to ΔE_{H+} for heptaaquo and octaaquo ions.

the DZVP basis set (Ga, Y) otherwise.[17,21] All calculations were carried out for the high-spin case for complexes with occupied d orbitals and optimized without symmetry constraints.

All ions except for Mn(H$_2$O)$_6{}^{3+}$ have nearly T_h symmetry. The hexaaquo Mn^{3+} ion has a significant distortion with four short and two long bond lengths. The M$-$O bond lengths predicted by LDFT are shorter than the Hartree$-$Fock values previously reported[22] and also shorter than those calculated using gradient-corrected DFT.[10c,14b] Perhaps fortuitously, they are in closer agreement with experimental bond lengths as determined in cesium alums[23] and, for Al^{3+}, in agreement with core-valence correlated MP2 calculations.[24] To calculate the proton binding energies, a proton was removed from the optimized M(H$_2$O)$_6{}^{3+}$ structure, and the M(OH)(H$_2$O)$_5{}^{2+}$ ion was optimized.

The proton binding energy, ΔE_{H+}, is defined as

$$\Delta E_{H+} = (E\{M(OH)(H_2O)_5{}^{2+}\} + ZPE\{M(OH)(H_2O)_5{}^{2+}\}) - (E\{M(H_2O)_6{}^{3+}\} + ZPE\{M(H_2O)_6{}^{3+}\}) \quad (1)$$

where $(E,ZPE)\{M(OH)(H_2O)_5{}^{2+}\}$; $(E,ZPE)\{M(H_2O)_6{}^{3+}\}$ are the electronic energies and zero-point energies of the optimized complexes, respectively. This yields an energy ΔE_{H+} at 0 K which is a positive quantity and corresponds to the acidity of M(H$_2$O)$_6{}^{3+}$; the larger the value, the more difficult it is to remove the proton from the M(H$_2$O)$_6{}^{3+}$ complex.

Values for ΔE_{H+} are given in Table 1. Figure 1 shows the correlation between the calculated acidities and the solution pK_{11}.[3,4b,5,25] The correlation is good for all ions except Ga^{3+}. Experimental determinations of the pK_{11} for Ga^{3+} show an anomalously large ionic strength dependence, with values ranging between 0.4 to >4.3.[5b,4b] The recent value of 3.8 taken from the compilation of Richens[5c] is more consistent with our results than lower values previously reported. The correlation is 0.993 without Ga and 0.978 with Ga, showing that to a very high degree of consistency the hydrolysis constants correlate well with the gas-phase acidity. This suggests that for these species the solvent
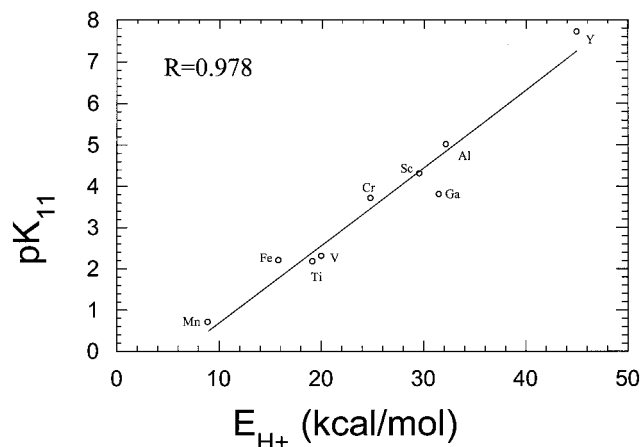
Figure 1. pK_{11} vs ΔE_{H+} ($\Delta E_{H+} = E\{M(OH)(H_2O)_5{}^{2+}\} - E\{M(H_2O)_6{}^{3+}\}$).

effects are approximately constant and that the dominant effects are the changes in energies of the isolated hexa-coordinated ions. It also suggests that DFT theory is capturing whatever electronic structural aspects are giving rise to the relative basicities of the M$^{3+}-$OH$^-$ interactions. The high values of ΔE_{H+} for the higher coordinated Sc^{3+} and Y^{3+} in Table 1 underscore the need to choose the coordination spheres consistently in the gas phase.

Previous results include an HF/6-31G* value[26] for Al^{3+} of 46 kcal/mol without zero point effects as compared to our nonzero point corrected value of 40.1 kcal/mol. For Fe^{3+}, Martin et al.[10c] obtained values of 29.2 kcal/mol (B3LYP/6-31G*), 25.4 kcal/mol (B3LYP/6-31+G*), and 28.1 kcal/mol (B3LYP/6-31++G**) as compared to our value of 23.8 kcal/mol. (We obtain 19.9 at the B3LYP/DZVP2 level). Thus, it is important to use a consistent level of calculation when making the correlations.

Over 20 years ago, Baes and Mesmer[3c] suggested that if quantum mechanics were at a more advanced state, it might be possible to compute the stabilities of hydrolysis products directly, rather than by relying on a comparative chemical approach. In this work, we have shown that DFT calculations of the gas-phase hexaaquo ion deprotonation energies do provide a reasonable basis for understanding the relative aqueous acidities of the trivalent ions. The DFT ab initio approach is probably the most successful means of correlating trivalent hydrolysis reactions to date. The coherence of the calculated values also lends additional credence to the measured experimental values which can be highly uncertain because of the interference of polynuclear species, among other reasons (see discussion of Mn^{3+} hydrolysis by Siskos et al.).[27] This provides further confidence, motivation, and means for developing a more fundamental understanding, through DFT calculations, of the electronic structural effects which promote or inhibit hydrolysis. In addition, the success of the calculations performed here should carry over to the prediction of acid$-$base reactions involving polynuclear species and surfaces where bonding relationships are more complex.

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