

Theoretical studies on aluminate and sodium aluminate species in models for aqueous solution: $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, and $\text{NaAl}(\text{OH})_4$

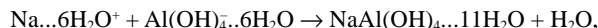
J.A. TOSSELL

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742, U.S.A.

ABSTRACT

Ab initio quantum mechanical calculations were performed on $\text{Al}(\text{OH})_3$, $\text{Al}(\text{OH})_4^-$, $\text{NaAl}(\text{OH})_4$ and related species with varying numbers of explicit water molecules to elucidate the structural, spectral and energetic properties of the possible species. We find that $\text{Al}(\text{OH})_3$ reacts with H_2O in the gas-phase with an exoergicity of 24.1 kcal/mol to produce $\text{Al}(\text{OH})_3\text{H}_2\text{O}$, which has shorter Al-OH distances, larger Al-OH stretching frequencies, and a 15 ppm larger Al NMR shielding than does $\text{Al}(\text{OH})_4^-$. When the first hydration spheres of these species are included the Al NMR shieldings becomes very similar, but the O and H NMR parameters and the IR and Raman spectra still show significant differences. The hydration energy of $\text{Al}(\text{OH})_3\text{H}_2\text{O}$ is determined from a “supermolecule” calculation on $\text{Al}(\text{OH})_3\text{H}_2\text{O}\dots 6\text{H}_2\text{O}$, whereas that for $\text{Al}(\text{OH})_4^-$ is obtained using the supermolecule calculation on $\text{Al}(\text{OH})_4^-\dots 6\text{H}_2\text{O}$ plus an evaluation of the electrostatic Born hydration energy of the supermolecule. The calculated energy change for the acid dissociation reaction, $\text{Al}(\text{OH})_3\text{H}_2\text{O}\dots 6\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_4^-\dots 6\text{H}_2\text{O} + \text{H}^+$, is +297.9 kcal/mol in the gas phase but only +2.3 kcal/mol in aqueous solution, due to the strong hydration of H^+ and $\text{Al}(\text{OH})_4^-\dots 6\text{H}_2\text{O}$. Using quantum mechanically calculated entropies for the unhydrated species, $\text{Al}(\text{OH})_3\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_4^-$, plus the experimental hydration entropy of H^+ , the $-T\Delta S$ term for this reaction is calculated as about +11.8 kcal/mol. Adding in calculated zero-point energies and room temperature enthalpy corrections gives a free energy change of +0.5 kcal/mol. Thus pKa for the acid dissociation of $\text{Al}(\text{OH})_3\text{H}_2\text{O}$ is near zero at room T , and $\text{Al}(\text{OH})_4^-$ will be dominant except under very acidic conditions.

Properties are also calculated for the bare close-contact ion pair $\text{NaAl}(\text{OH})_4$ and for hydrated forms of both a close-contact and a solvent-separated ion pair, $\text{NaAl}(\text{OH})_4\dots 10\text{H}_2\text{O}$ and $\text{NaAl}(\text{OH})_4\dots 11\text{H}_2\text{O}$. In accord with previous calculations on silicate anions and ion pairs, formation of an unhydrated close-contact ion pair increases the shielding of the Al in $\text{Al}(\text{OH})_4^-$, while reducing the Al-O symmetric stretching frequency. The calculated energy change at 298 K in aqueous solution for the ion pair formation reaction,



is +17.6 kcal/mol, close to the value determined experimentally. After addition of calculated zero-point energies, enthalpy corrections, and calculated entropy changes we obtain a ΔG value of +1.7 kcal/mol for this reaction, giving a log K around -1, consistent with significant ion pair formation. The $\text{NaAl}(\text{OH})_4\dots 11\text{H}_2\text{O}$ species is a solvent-separated ion pair with full hydration of both its Na^+ and $\text{Al}(\text{OH})_4^-$. Its calculated Al NMR shielding and Al-O symmetric stretching frequencies are very similar to those for $\text{Al}(\text{OH})_4^-\dots 6\text{H}_2\text{O}$, whereas its Na NMR shielding is about 5 ppm smaller than that of $\text{Na}(\text{OH}_2)_6^+$, although its Na electric field gradient (and consequently its line-width) are larger. Thus it appears that Na NMR may be the best technique for characterizing this ion pair.