

Abstract

Water addition to molecular oxides has been studied using quantum chemistry. First, the formation and stability of Sc and Ge oxides was investigated in order to verify the applicability of the approach. Second, model oxides in the sequences Sc-Mn and Al-Ar were used to investigate the reactivity toward water addition. Addition of water to M=O groups was found exothermic if the coordination on M was less than four. When the coordination was saturated, the M=O units were seen to drive the deprotonation of the M-OH units, and thus causing the acidic properties of the hydroxide. For Al(OH)₃·6 H₂O, two types of complexes were observed. Either a four-coordinated anionic structure, with proton loss on the Al-OH₂ unit, or a six-coordinated cationic complex was formed. The use of six water ligands was found to constitute a minimum solvation model for a M(III) hydroxide.

Hydrolysis of M-O-M bridges was in general (for oxyhydroxides of 3d, 3p and 4p elements) found to be endothermic processes, but involving only small reaction enthalpies (± 40 kJ/mol) for M(IV) to M(VII). This is of relevance to the water induced degradation of protective chromium oxide scales, but most profoundly, to the hydrolysis of P-O-P bridges in oligophosphates. This reaction displayed a near-zero energetics, which questions the concept of "high-energy compounds" attributed to the biological oligophosphates, such as ATP.

Keywords: aluminum, silicon, phosphorous, sulfur, chlorine, argon, scandium, titanium, vanadium, chromium, manganese, gallium, germanium, arsenic, selenium, bromine, oxides, hydroxides, acids, water, hydrolysis, solvation, complexes, energetics, quantum chemistry, DFT.

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