

Calculating the Acidity of Silanol Groups on Silicate Oligomers and Silicate Surfaces

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Calculated gas-phase deprotonation energies, obtained at the 6-31 G* Hartree-Fock and higher levels, for Si(OH)₄ and a series of related molecules, are shown to correlate well with experimental aqueous pK_a values. When approximate values of hydration energies are incorporated agreement of calculation and experiment is even better. Calculated deprotonation energies also correlate well with oxygen under-bondings evaluated using Brown's bond-length based approach and with electrostatic

potentials at the proton site evaluated using phenomenological charge models. Calculations on silicate oligomers yield lower deprotonation energies, consistent with greater acidity, and these deprotonation energies can also be interpreted using a bond-length based model. The approach is general enough that it can be used to describe pK_as of different order, such as pK_a1, 2 and 3 for H₃PO₄ or pK_a0 for the protonation of Si(OH)₄ and other neutral silicates.