

Calculation of pKa

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To determine the pK_a of the protonated species ($AH^+ \rightarrow A + H^+$ reaction) we use the isodesmic equation with aniline [1, p.413]:

$$pK_a = pK_a^{\text{ref}} + \frac{\Delta G_{\text{gas}} - \Delta G_{\text{gas}}^{\text{ref}} + \Delta G_{\text{solv}} - \Delta G_{\text{solv}}^{\text{ref}}}{T \ln 10}, \quad (1)$$

where “ref” means a reference system (aniline),

$$\Delta G_{\text{gas}} = G_{\text{gas}}(A) - G_{\text{gas}}(AH^+), \quad (2)$$

is the differential Gibbs energy (or free energy) in the vacuum (gas phase), and

$$\Delta G_{\text{solv}} = G_{\text{solv}}(A) - G_{\text{solv}}(AH^+), \quad (3)$$

is the differential solvation energy. DFT calculations with CAM-B3LYP functional and 6-31G* basis set give $\Delta G_{\text{gas}} = 9.18$ eV for aniline and 8.28 eV for ATAOPV. Using SMD solvation model [4] we get $\Delta G_{\text{solv}} = 2.72$ eV for aniline and 3.60 eV for ATAOPV. Thus $pK_a - pK_a^{\text{ref}} = -0.72$. The reported pK_a values for aniline vary from 4.6 [2] to 4.9 [3]. Therefore the pK_a of the protonated species is about 4.0.

References

- [1] C J Cramer, Essentials of computational chemistry: theories and models (Wiley, 2004)
- [2] W P Jencks, F H Westheimer, Aqueous pKa Values (ACS), [dx.doi.org/2200/20061121124513540T](https://doi.org/10.1021/bk-1969-0211)
- [3] Handbook of chemistry and physics, <http://www.hbcpnetbase.com>
- [4] A V Marenich, C J Cramer, D G Truhlar, Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions, J Phys Chem B 113, 6378 (2009)