OXIME BOND DISSOCIATION ENERGIES

The bond dissociation energies (BDE) of the O-H bond of oximes R_1R_2C=N-OH) are discussed in Chapter 2.1.1.2. The controversy associated with these values originates from conflicting experimental data coming from calorimetric and electrochemical experiments. Some of the conflicting data are listed in Table 1. The electrochemical method provides energies at least a couple of kcal mol^{-1} too large, sometimes much more than that. I described in the book some composite method computations (G3MP, G3, CBS-QB3 and CBS-ANO)[1] that suggest the BDE of acetone oxime is around 85 kcal mol^{-1}, consistent with the calorimetric results. These authors could not apply these expensive methods to other compounds and were forced to use UB3LYP, which underestimates the values of the BDEs.

Table 1. BDEs (kcal mol^{-1}) from calorimetric and electrochemical experiments and ONIOM-G3B3 computations.

R_1	R_2	Calorimetric	Electrochemical	ONIOM-G3B3
Me	Me	84.3[a]	95.8[b]	85.7
Ph	Ph	82.4[c]	89.0[b]	81.8
i-Pr	*i*-Pr	79.7[c]	87.7[d]	83.0

t-Bu *i*-Pr	82.6[c]	86.0[e]	83.0
t-Bu *t*-Bu	79.2[c]	84.2,[d] 82.6[e]	78.7
t-Bu 1-Ad	79.2[c]	81.7[d]	78.7
fluorenyl	82.0[c]	87.5[b]	80.4

[a]Ref. 2. [b]Ref. 3. [c]Ref. 1. [d]Ref. 4. [e]Ref. 5

Fu[6] has now applied the ONIOM-G3B3[7] approach to this problem. This is a clever way of attacking large molecules that require rather large computations to appropriately treat the quantum mechanics. So, each step of the G3B3 composite method is split into two levels: the high level is computed with the appropriate method from the G3B3 procedure, while the low level is treated with B3LYP. These resulting BDEs are listed in Table 1 and show remarkably nice agreement with the calorimetric results. These computed BDEs confirm that the electrochemical results are in error. Fu also computed the BDEs of some 30 other oximes for which electrochemical BDEs are available and for the large majority of these compounds, the electrochemical values are again too large.

Source: http://comporgchem.com/blog/?p=55