t-BUTYL RADICAL AND ANION

Two interesting questions are addressed in a focal-point computational study of *t*-butyl radical and the *t*-butyl anion from the Schaefer group.[1] First, is the radical planar? EPR and PES studies from the 1970s indicate a pyramidal structure, with an inversion barrier of only 0.64 kcal mol^{-1}. The CCSD(T)/cc-pCVTZ optimized structure of *t*-butyl radical shows it to be pyramidal with the out-of-plane angle formed by one methyl group and the other three carbons of 22.9°, much less than the 54.7° of a perfect tetrahedron. Focal point analysis give the inversion barrier 0.74 kcal mol^{-1}, in outstanding agreement with experiment.

Second, what is the electron affinity (EA) of the *t*-butyl radical? Schleyer raised the concern that the alkyl anions may be unbound, and suggested that the electron affinity of *t*-butyl radical was -9.6 kcal mol^{-1}; in other words, the anion is thermodynamically unstable. This focal-point study shows just how sensitive the EA is to computational method.

The HF/CBS value of the EA is -39.59 kcal mol^{-1} (unbound anion), but the MP2/CBS value is +41.57 kcal mol^{-1} (bound anion!). The CCSD/aug-cc-pVQZ value is -8.92 while the CCSD(T)/aug-cc-pVQZ value is +4.79 kcal mol^{-1}. The estimated EA at CCSDT(Q)/CBS is -1.88 kcal mol^{-1}, and inclusion of correction terms (including ZPE and relativistic effect) gives a final estimate of the EA as -0.48 kcal mol^{-1}, or a very weakly unbound *t*-butyl anion. It is somewhat disconcerting that such high-level computations are truly needed for some relatively simple questions about *small* molecules.

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