BOND DISSOCIATION ENTHALPIES OF HYDROCARBONS

We suggest that the experimental deprotonation energy (DPE) of cyclohexane is in doubt. G2MP2 predicts the DPE of cyclohexane is 414.5 kcal mol^{-1}, a figure significantly higher than the experimental[1] value of 404 kcal mol^{-1}. Given that the deviation between the G2MP2 computed DPE and experiment is about 2 kcal mol^{-1}, we suggest that cyclohexane should be re-examined.

In a recent *JACS* article,[2] Kass calls into question the experimental bond dissociation energies (BDE) of the small cycloalkanes. With his experimental determination of the BDE of both the vinyl and allylic positions of cyclobutene, Kass can compare experimental and computed BDEs for a range of hydrocarbon environments, as listed in Table 1. The two composite methods G3 and W1 provide excellent BDE values for the small alkanes, one acyclic alkene, and the small cyclic alkenes. These composite methods appear to accurately predict BDEs of hydrocarbons.

However, the small cyclic alkanes are dramatic outliers. The well-accepted experimental BDEs of cyclopropane, cyclobutane, and cyclohexane are 3-5 kcal mol^{-1} lower than those predicted by the composite methods.

Given the strong performance of the computational methods, and the difficulties associated with experimental determinations of BDEs, Kass suggests that the BDEs of these cycloalkanes are in error. Further experiments are deserved.

Table 1. Computed and experimental BDEs (kcal mol^{-1}) of some simple hydrocarbons.

	G3[a]	W1[a]	Expt.
Methane	104.2	104.3	105.0±0.1[b] 104.9±0.2[c]
Ethane	101.2	101.2	100.5±0.3[b] 101.1±0.4[c]
$(CH_3)CH_2$	98.9	98.4	98.1±0.7[b] 97.8±0.5[c]
$CH_3CH_2CH_2CH_3$	98.8	98.8	98.3±0.5[b] 98.3±0.5[c]
Z-2-butene (allyl)	86.0	87.0	85.6±1.5[d]
Cyclopropene (vinyl)	109.6	109.8	106.7±3.7[e]
Cyclopropene (allyl)	100.4	100.4	90.6±4.0[f]

Cyclobutene (vinyl)	111.9	112.4	112.5±2.5[a]
Cyclobutene (allyl)	90.6	91.7	91.2±2.3[a]
Cyclopentene (allyl)	84.2	85.0	82.3±1.1[g]
Cyclohexene (allyl)	83.9		85±1[h]
Cyclopropane	109.2	109.0	106.3±0.3[b] 106.3±0.3[c]
Cyclobutane	100.5	99.9	96.8±1.0[b] 96.5±1.0[c]
Cyclopentane	96.4	96.9	95.6±1.0[b] 96.4±0.6[c]
Cyclohexane	100.0		99.5±1.2[b] 95.5±1.0[c]

[a]Ref. 2. [b]Ref. 3. [c]Ref. 4. [d]Ref. 5. [e]Ref. 6. [f]Ref. 7. [g]Ref. 8. [h]Ref. 9

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