



Computation of Bond Dissociation Energies of Substituted Methanes with Density Functional Theory

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Abstract: Density functional theory has been used to calculate bond dissociation energies of substituted methanes and radical stabilization energies obtained are compared to other systems.
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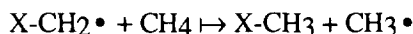
In recent years a number of experimental methods¹⁻⁸ and theoretical calculations⁹⁻¹¹ have been used to evaluate radical substituent effects. These have met with varying degrees of success and are not all mutually consistent. As levels of theory advance, undoubtedly calculated values of resonance stabilizations (SE) will improve. For example, the early work by Pasto⁹ shows reasonable correlation with experimental bond dissociation energies (BDE) but the magnitudes of the calculated SE's are too low by several kcal/mol. Jensen's values¹⁰ done at the 6-31G* level, more closely parallel BDE's but the SE's are still low.

With this in mind we have calculated the bond dissociation energies for a series of substituted methanes by Density Functional Theory [B3LYP/6-311 + G (2d,2p)]. Zero point energy corrections have been made and S² values indicate that spin contamination is not a problem (0.75 - 0.78)¹².

Table 1. DFT Calculated BDE's

	ΔE , kcal/mol	$\langle S^2 \rangle$	ZPE	BDE ¹⁶
CH ₃ -H	101.7	0.753	9.4	104.9
CH ₃ CH ₂ -H	96.9	0.754	9.6	101.1
CH ₃ OCH ₂ -H	91.9	0.754	8.2	96.1(OH)
CH ₃ COCH ₂ -H	92.5	0.754	8.2	94.3(CHO)
NCCH ₂ -H	91.3	0.767	8.9	94.8
H ₂ NCH ₂ -H	88.4	0.754	8.7	93.3 ¹⁷
CH ₂ =CHCH ₂ -H	82.9	0.778	8.5	87.6 ¹⁸

Table 2. Isodesmic Determination of Radical Stabilization



X	DFT SE*	Ellison ¹⁶ BDE*	Bordwell ⁵ SE*	Pasto ⁹ SE*	Jensen ¹⁰ SE*	log k _{rel} ⁸ azo	Creary ³ σ_c	Arnold ² σ_α
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH ₃	4.8	3.8	4.5	3.3	3.2	2.7	0.11	0.015
CH ₃ O	9.8	8.8(OH)	7.0	5.3	8.9(OH)	3.7	0.24	0.018
CH ₃ CO	9.2	10.6(CHO)		7.7(CHO)	9.5(CHO)	8.7	0.39(CO ₂ R)	0.06
NC	10.4	10.1	5.7	5.3	6.7	8.2	0.46	0.04
NH ₂	13.3	11.6	15.0	10.3	11.1			
CH ₂ =CH	18.8	17.3		7.8	12.6	9.6	0.67	
Correlation coefficient r for DFT SE vs other methods		0.985	0.819	0.841	0.942	0.865	0.962	0.767

* kcal/mol

The calculated BDE values are all several kcal/mol less than experimental values but the isodesmic relationship compensates for these differences and gives stabilization energies (SE) that are closer to experimental values than previous calculated values.

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