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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.

In recent years a number of experimental methods[1-8] and theoretical calculations[9-11] 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 Pasto[9] 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 values[10] 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 S^2 values indicate that spin contamination is not a problem (0.75 - 0.78)[12].

Table 1. DFT Calculated BDE's

	ΔE, kcal/mol	$<S^2>$	ZPE	BDE[16]
CH_3-H	101.7	0.753	9.4	104.9
CH_3CH_2-H	96.9	0.754	9.6	101.1
CH_3OCH_2-H	91.9	0.754	8.2	96.1(OH)
CH_3COCH_2-H	92.5	0.754	8.2	94.3(CHO)
$NCCH_2$-H	91.3	0.767	8.9	94.8
H_2NCH_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

$$X\text{-}CH_2\bullet + CH_4 \mapsto X\text{-}CH_3 + CH_3\bullet$$

	DFT	Ellison[16]	Bordwell[5]	Pasto[9]	Jensen[10]	log k_{rel}[8]	Creary[3]	Arnold[2]
X	**SE***	BDE*	**SE***	**SE***	**SE***	**azo**	σc	σα
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_3O	9.8	8.8(OH)	7.0	5.3	8.9(OH)	3.7	0.24	0.018
CH_3CO	9.2	10.6(CHO)		7.7(CHO)	9.5(CHO)	8.7	0.39(CO_2R)	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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References and Notes

1. Fisher, T.H., Meierhoefer, A.W. *J. Org. Chem.* **1978**, 43, 224.
2. Dust, J.M., Arnold, D.R. *J. Am. Chem. Soc.* **1983**, 105, 1221; Wayner, D.D.M.; Arnold, D.A. *Can. J. Chem.* **1985**, 63, 2378.
3. Creary, X., Mahrskeikh-Mohammad, M.E., McDonald, S. *J. Org. Chem.* **1987**, 52, 3254.
4. Agirbas, H., Jackson, R.A. *J. Chem. Soc. Perkin Trans. 2* **1983**, 739.
5. Bordwell, F.G., Zhang, X-M, Alnajjar, M.S. *J. Am. Chem. Soc.* **1992**, 114, 7623.
6. Jiang, X.K.; Ji, G.Z. *J. Org. Chem.* **1992**, 57, 6052.
7. Viehe, H.G.; Janousek, Z.; Merenyi, R. Ed. *Substituent Effects in Radical Reactions*, Reidel, 1986.
8. Timberlake, J.W. Ref. 7, pg. 271. These results are actually for a tertiary system.
9. Pasto, D.J., Krasnansky, R., Zercher, C. *J. Org. Chem.* **1987**, 52, 3062.
10. Lehd, M., Jensen, F. *J. Org. Chem.* **1991**, 56, 884.
11. Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. Ref. 7, pg. 1.
12. Three hybrid DFT methods were applied. Becke's three parameter functional[13] which has the form of $A*E_x^{Slater} + (1-A)*E_x^{HF} + B*\Delta E_x^{Becke} + E_c^{VWN} + C*\Delta E_c^{non\text{-}local}$, where the non-local correlation is provided by the LYP[14] expression (B3LYP). The constants, A.B, and C are those determined by Becke by fitting to the G1 molecular set. Becke's three parameter functional. For all calculations an extended Gaussian type basis set, 6-311+G(2d,2p) was used. The explanation and abbreviation of the basis sets are as in the GAUSSIAN computational package[15].
13. Becke, A.D. *J. Chem. Phys.* **1993**, 98, 5648.
14. Lee, C., Yang W. and Parr, R.G. *Phys. Rev. B* **1988**, 37, 785; Mielich, B., Savin, A., Stoll H. and Preuss, H. *Chem. Phys. Lett.* **1989**, 157, 200.
15. Frisch, M.J., Frisch A.E. and Foresman, J.B. *Gaussian 94 User's Reference*, Gaussioan, Inc., Pittsburgh, PA, 1995.
16. Berkowitz, J.; Ellison, G.B.; Gutman, D. *J. Phys. Chem.* **1994**, 98, 2744.
17. McMillen, D. F., Golden, D. M. Ann. Rev. Phys. Chem. **1982**, 33, 493.
18. Allyl values vary considerably. We have chosen an intermediate value from Roth, W. R., Bauer, F.; Beitat , A., Ebbrecht, T., Wüstefeld, M. *Chem. Ber.* **1991**, 124, 1453.

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