sciendo

On the thermodynamics of homolytic C—H bond cleavage in linear and branched alkanes: Comparison of DFT and composite G4 and G4(MP2) methods

Dagmar Štellerová, Vladimír Lukeš

Institute of Physical Chemistry and Chemical Physics, Slovak University of Technology in Bratislava, Radlinského 9, SK-812 37 Bratislava, Slovakia
dagmar.stellerova@stuba.sk

Abstract: This work provides a systematic theoretical study on gas-phase bond dissociation enthalpies for homolytic C—H bond cleavage in linear and branched alkanes. Quantum chemical calculations were performed using the density functional theory (DFT) and *ab initio* composite (G4(MP2), G4) methods. In case of DFT calculations, the M06-2X and B3LYP functionals combined with 6-311++G**, aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ basis sets were covered. In linear molecules, the best agreement with experiment was observed for B3LYP/aug-cc-pVQZ. In both composite approaches, as the number of C atoms increases, the BDE values are affected by the systematic error of the method. For example, G4 BDE of terminal —CH3 group of hexane is 422.6 kJ · mol^{-1} while for undecane it is 415.5 kJ · mol^{-1}. On the contrary, the composite methods are in better agreement with experiments compared to the DFT approaches for simple branched hydrocarbons.

Keywords: alkanes, chemical accuracy, DFT, G4(MP2), radical mechanism

Introduction

The bond dissociation enthalpy (BDE) is a measure of a chemical bond's strength; therefore, this quantity does not depend on a reaction path. It can be defined as the standard enthalpy change when X—Y is homolytically cleaved while providing radical fragments X$^{\bullet}$ and Y$^{\bullet}$. Although the enthalpy change is temperature-dependent, it is often evaluated at standard temperature conditions (298.15 K). Generally, BDEs are useful quantities in investigating the thermodynamics of chemical processes (Rimarčík et al., 2011; Bordwell et al., 1994; Denisov and Tumanov, 2005).

Experimentally deriving BDEs for larger molecules is not realistic. These measurements are suitable for simple and rather small model molecules while requiring a great deal of experience. Three commonly applicable techniques can be used to determine BDEs measured in solution or in gas-phase (Berkowitz et al., 1994). In this context, methods of chemical radical kinetics and equilibrium, various calorimetric and electrochemical methods including the acidity / electron affinity cycle, generation of radicals by pyrolysis or photolysis combined with spectrometric determination of energy levels can be mentioned (Blanksby and Ellison, 2003). Nevertheless, bond dissociation enthalpy investigation is still challenging, and it is subject to considerable experimental errors and uncertainties. Accuracy of many BDE experimental values, especially those dating back to before 1970, is within ±4—10 kJ · mol^{-1} (Darwent, 1970). Therefore, these BDEs can be especially unreliable and have been subject to later revisions (Luo, 2007). For example, experimentally determined BDE of C—H bonds for benzene in 1965 was 430.54 kJ · mol^{-1} (Trotman-Dickenson, 1965), while the currently accepted value is 472(2) kJ · mol^{-1} (Ervin and DeTuri, 2002). A similar situation arose for phenol over a period of 20 years, where O—H BDEs ranging from 358.6 to 380.6 kJ · mol^{-1} were reported in literature (Mulder et al., 2005). On the other hand, experimental accuracy of small molecules is very high. For example, experimental BDE for the hydrogen molecule is 435.780 kJ · mol^{-1} (Balakrishnan et al., 1992).

Because the experimental BDE values are highly dependent on the size of the molecule under investigation, as well as on the methodology and experimental technique, theoretical calculations play a very important role in their investigation. Since the thermodynamics of radical reactions is minimally affected by the environment, the calculations in the gas phase offers plausible results. In case of simple aromatic molecules, the description of the thermodynamics of homolytic X—H bond cleavage for X = O, S, N at the DFT level is in sufficient agreement with the experiment (Klein et al., 2006; Barckholtz et al., 1999) using functionals B3LYP and M06-2X (Lee et al., 1988; Becke, 1988; Zhao and Truhlar, 2008). Paradoxically, *ab initio* BDE calculations can result in large deviations from the experiment due to spin contamination of radicals. This problem does not arise only for the CCSD(T) approach (Raghavachari

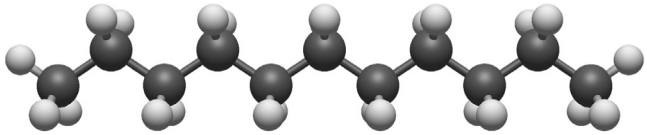

Fig. 1. Optimal *all-trans* M06-2X/6-311++G** geometry of undecane ($\mathbf{C_{11}H_{24}}$) molecule.

et al., 1989), which is very challenging and practically applicable only for small molecules in a large base of atomic orbitals. A certain compromise solution has been introduced by the Gaussian-*n* (G*n*) family of composite approaches (Pople et al., 1989; Curtiss et al., 1990, 1991, 1998, 2007). These approaches combine methods with a high level of theory and a small basis set with methods employing lower levels of theory with larger basis sets. With the development of computer technology, the G4 and G4(MP2) methods have recently gained great popularity in the calculation of thermodynamic quantities of chemically interesting polyatomic molecules (Kováčová, 2024; Rayne and Forest, 2011). This implies a natural need

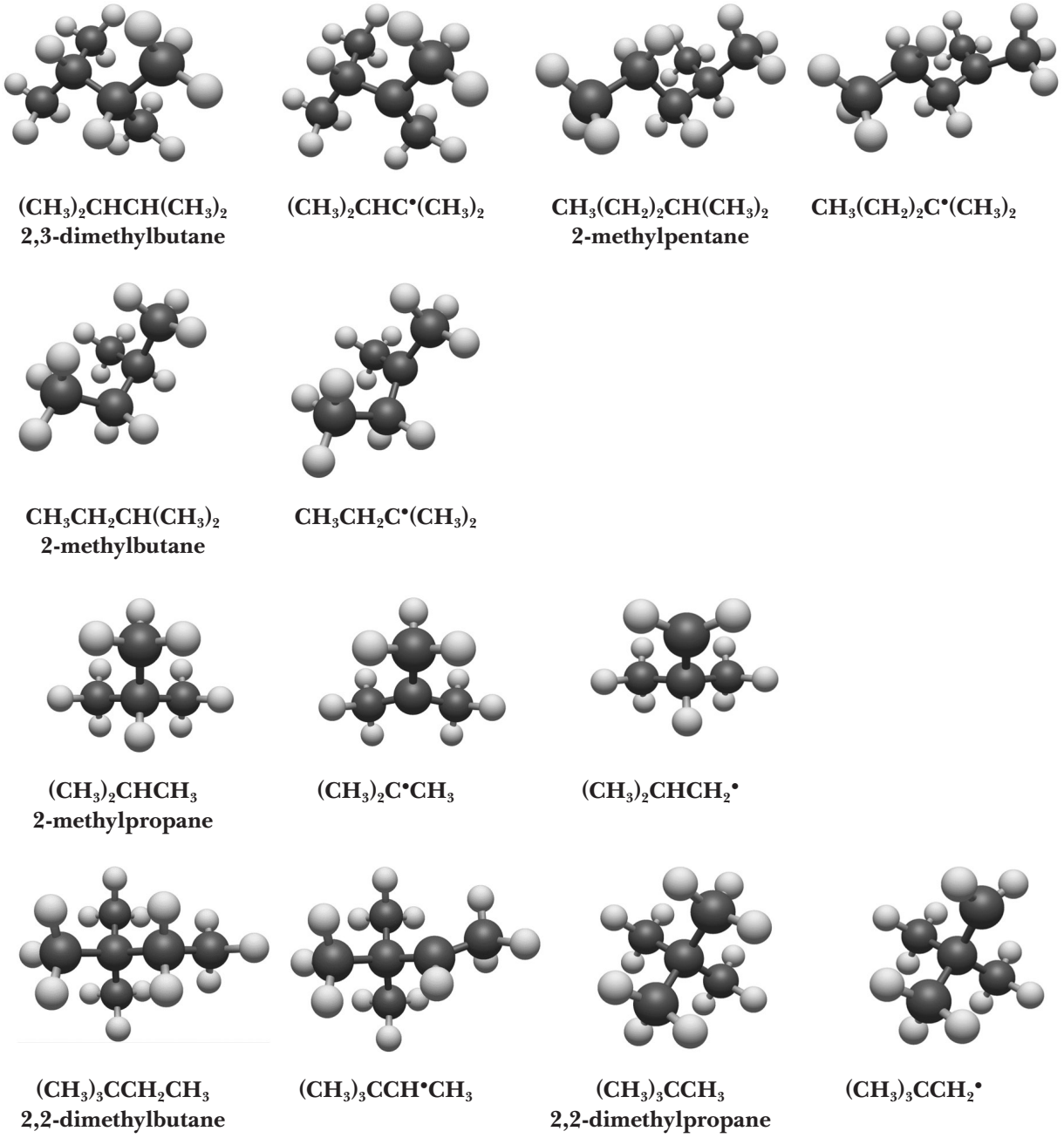

Fig. 2. Optimal M06-2X/6-311++G** geometries of studied branched hydrocarbons and their radical forms.

for a better understanding of the computational reliability of the above approaches with respect to standard DFT approaches.

Since the main purpose of this work is to validate G4 and G4(MP2) methods, systematic computations of linear and simple branched alkanes were performed (see Fig. 1 and Fig. 2). This set of molecules represents an optimal testing system for possible induction effect of methyl groups on thermodynamic hydrogen atom abstraction. Moreover, radicals of these molecules play a key role in oxidation reactions in industrial processes and chemical laboratories and the energetics of these reactions were studied experimentally more than 30 years ago.

Partial aims of this theoretical paper include: (1) to optimize and discuss the gas-phase geometries of molecules; (2) to calculate selected C—H bond dissociation enthalpies by two standardly used hybrid functionals in combination with 6-311++G** basis set of atomic orbitals; (3) to compare 6-311++G** results with calculations of aug-cc-pVNZ (where N = D, T and Q) basis sets; (4) to perform G4 and G4(MP2) calculations of the studied molecules; and (5) to compare the obtained results with available experimental data.

Computational Details

All calculations were performed using default settings of the Gaussian 16 program package (Frisch et al., 2016). Four theoretical approaches, i.e., density functional theory (DFT) 3-paramenter hybrid B3LYP functional, DFT M06-2X hybrid functional, and G4(MP2) and G4 composite *ab-initio* methods, were used to obtain optimal geometries of parent and radical structures. With B3LYP and M06-2X functionals, Pople's triple zeta 6-311++G** (Hariharan and Pople, 1973; Rassolov et al., 1998) and Dunning's (Dunning, 1989) correlation-consistent augmented (aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ) basis sets were applied. Since radical formation does not depend on the presence of a solvent (difference $< 5\ kJ \cdot mol^{-1}$), gas-phase optimalization was performed at room temperature (298.15 K). Total gas-phase enthalpy of the hydrogen atom used to calculate BDEs is $-1306\ kJ \cdot mol^{-1}$ (Rimarčík et al., 2010). The optimized structures were confirmed to be real minima by vibrational analysis (no imaginary frequencies). The Avogadro program (Hanwell et al., 2012) was used to design and visualize the studied species.

Results and Discussion

Structures of studied hydrocarbons

Gas-phase calculations were carried out for saturated linear and branched alkanes together with their corresponding radical forms (Fig. 1 and Fig. 2). Within linear hydrocarbons, molecules with the carbon chain of $n = 1$ up to $n = 11$ (see Fig. 1) were studied. Homolytic cleavage was performed at terminal methyl C—H bond of the molecules. For each of them, apart from tetrahedral methane geometry, *all-trans* conformation of dihedral angles has been set. The distance between all neighboring carbons was 1.53 Å, shortened to 1.49 Å for terminal C—C bond in radicals. Bond angles of terminal methyl moiety H—C—H were in range of 107.6 ° to 109.5 ° and 117.6 ° to 120.0 ° for parent and radical conformations, respectively.

As for branched hydrocarbons, 6 small molecules have been selected, namely 2-methylpropane, 2,2-dimethylpropane, 2-methylbutane, 2,2-dimethylbutane, 2,3-dimethylbutane and 2-methylpentane (see Fig. 2). Initial conformation arrangements of branched alkanes were divided from the geometries of linear structures. For the 2-methylpropane and 2,2-dimethylpropane, cleavages of hydrogen from primary carbon have been carried out. Similarly to above mentioned linear structures, the abstraction caused change in H—C—H angles from 107.8 ° to 118.0 ° in 2-methylpropane and 108.0 ° to 118.0 ° in 2,2-dimethylpropane. Geometry of 2,2-dimethylbutane challenged retraction of H atom from secondary carbon. The orientation of C_1—C_2—C_3—C_4 remained planar for both parent and radical conformations. The rest of the branched alkanes went through cleavage of hydrogen from tertiary carbon. The values of dihedral angles defined by H—C—$C^{(\bullet)}$—C atoms slightly titled in parent molecules vary from –4 ° in 2,3-dimethylbutane to 15 ° in 2-methylpropane in their radical forms.

HAT of primary C—H bonds in linear alkanes

In general, quantum-chemical calculations may provide different reaction enthalpies depending on the choice of computational approach, i.e., the type of approximation and the basis set used. To assess the reliability of different theoretical approaches, HAT for homolytic cleavage of C—H terminal methyl groups in linear hydrocarbons was performed. First, the calculations were carried out at the B3LYP/6-311++G** and M06-2X/6-311++G** levels of theory with the results collected in Tab. 1. For both methods, BDE values vary in agreement with the experimental values with the increasing methylene moiety up to butane. In case of higher hydrocarbons (pentane to undecane), the BDE values remain unchanged, with the values of $420.5\ kJ \cdot mol^{-1}$ for B3LYP and $415.0\ kJ \cdot mol^{-1}$ for M06-2X, using the 6-311++G** basis of atomic orbitals. The induction effect along the sigma bonds was present as an explanation. Higher alkanes do

Tab. 1. Experimental (Luo, 2007) and theoretical C—H BDE values of studied hydrocarbons at different levels of theory. Corrected values are in parentheses. All values are in $kJ \cdot mol^{-1}$.

Radical	B3LYP				M06-2X				G4	G4(MP2)	Exp.
	6-311++G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	6-311++G**	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ			
$CH_3^{\bullet}$	437.5 (433.6)	431.7 (433.4)	438.2 (433.6)	439.0 (433.6)	429.1 (434.6)	423.5 (435.0)	430.4 (434.7)	432.2 (435.2)	441.5 (435.4)	443.7 (436.4)	439.3 ±0.4
$C_2H_5^{\bullet}$	418.1 (419.9)	412.8 (419.5)	418.4 (419.9)	419.1 (419.9)	412.8 (419.3)	407.6 (419.2)	413.4 (419.4)	415.1 (419.8)	425.5 (420.9)	427.1 (422.0)	420.5 ±1.3
$C_3H_7^{\bullet}$	421.1 (422.0)	416.1 (421.9)	421.5 (422.0)	422.1 (422.0)	415.6 (422.0)	408.2 (419.8)	416.4 (422.1)	418.2 (422.6)	427.4 (422.6)	428.2 (422.9)	422.2 ±2.1
$C_4H_9^{\bullet}$	420.5 (421.6)	415.6 (421.6)	420.9 (421.6)	421.6 (421.6)	412.5 (419.1)	407.7 (419.2)	413.3 (419.3)	415.0 (419.7)	425.4 (420.8)	425.3 (420.4)	421.3
$C_5H_{11}^{\bullet}$	420.5 (421.6)	415.6 (421.6)	420.9 (421.6)	421.6 (421.6)	415.0 (421.4)	410.1 (421.7)	415.8 (421.5)	417.6 (422.1)	424.1 (419.5)	423.0 (418.4)	419.2
$C_6H_{13}^{\bullet}$	420.5	415.6	420.9	421.6	415.0	410.2	415.8	417.5	422.6	420.6	
$C_7H_{15}^{\bullet}$	420.5	415.6	420.9	421.6	415.0	410.1	415.8	417.6	421.2	418.3	
$C_8H_{17}^{\bullet}$	420.5	415.6	420.9	421.5	415.0	410.2	415.8	417.6	419.8	416.0	
$C_9H_{19}^{\bullet}$	420.5	415.6	420.9	421.6	415.0	410.1	415.8	417.6	418.4	413.6	
$C_{10}H_{21}^{\bullet}$	420.5	415.6	420.9	421.5	415.0	410.2	415.8	417.6	416.9	411.3	
$C_{11}H_2^{3}\bullet$	420.5	415.6	420.9	421.5	415.0	410.1	415.8	417.6	415.5	408.9	
$(CH_3)_2CHC^{\bullet}(CH_3)_2$	389.6 (399.7)	386.0 (399.8)	389.3 (399.8)	390.0 (399.8)	391.9 (399.7)	388.3 (400.0)	391.7 (399.7)	393.2 (400.0)	402.5 (399.8)	401.5 (399.7)	399.2 ±13
$CH_3(CH_2)_2C^{\bullet}(CH_3)_2$	386.7 (397.7)	383.0 (397.6)	386.3 (397.7)	387.0 (397.7)	390.0 (397.9)	386.2 (398.0)	389.8 (398.0)	391.3 (398.3)	399.2 (396.8)	398.0 (396.8)	399.3
$CH_3CH_2C^{\bullet}(CH_3)_2$	388.0 (398.6)	384.2 (398.5)	387.5 (398.5)	388.2 (398.5)	391.2 (399.0)	387.4 (399.1)	391.0 (399.1)	392.5 (399.4)	401.7 (399.1)	401.4 (399.7)	400.8
$(CH_3)_2C^{\bullet}CH_3$	391.6 (401.2)	387.7 (401.0)	391.2 (401.1)	391.9 (401.1)	394.0 (401.7)	389.7 (401.4)	393.6 (401.4)	395.0 (401.7)	406.0 (403.0)	406.5 (404.1)	400.4 ±2.9
$(CH_3)_3CCH^{\bullet}CH_3$	405.0 (410.6)	401.1 (410.9)	404.9 (410.5)	405.6 (410.6)	402.8 (410.0)	399.1 (410.8)	403.0 (409.9)	402.1 (408.0)	412.6 (409.1)	411.0 (408.0)	410.2
$(CH_3)_3CCH_2^{\bullet}$	423.2 (423.5)	418.8 (423.9)	423.7 (423.5)	424.3 (423.5)	418.1 (424.3)	413.4 (425.0)	418.8 (424.2)	418.1 (422.5)	427.7 (422.9)	426.7 (421.6)	419.7 ±4.2
$(CH_3)_2CHCH_2^{\bullet}$	420.5 (421.6)	415.5 (421.5)	420.7 (421.5)	421.4 (421.5)	415.8 (422.1)	410.6 (422.1)	416.2 (421.9)	417.9 (422.3)	425.9 (421.2)	425.8 (420.9)	419.2 ±4.2

not affect the terminal C—H BDE value because the induction effect takes place only over short distances and weakens with each additional bond.

To further analyze theoretical approaches, Pople 6-311++G** *split-valence* basis set was compared with Dunning's augmented versions of correlation-consistent polarized basis sets aug-cc-pVNZ. Within the B3LYP functional, uncorrelated values of aug-cc-pVDZ show the lowest BDEs. As the basis set enlarges, the values approach their limits, resulting in aug-cc-pVQZ values which are in excellent agreement with the experiment (see Tab. 1). Assessing the results within the used basis set types, 6-311++G** values are the best fit with aug-cc-pVTZ values (differences up to < 0.7 $kJ \cdot mol^{-1}$). Regarding the M06-2X functional, BDEs within Dunning's basis sets show similar trends as in B3LYP with slightly lower values. For example, BDEs of the smallest methane are 423.5 $kJ \cdot mol^{-1}$ in aug-cc-pVDZ, 430.4 $kJ \cdot mol^{-1}$ in aug-cc-pVTZ, and 432.2 $kJ \cdot mol^{-1}$ in aug-cc-pVQZ. Again, the M06-2X/6-311++G** values can be compared with the M06-2X/aug-cc-pVTZ ones (differences up to < 1.3 $kJ \cdot mol^{-1}$).

For linear hydrocarbons, the newer composite *ab initio* G4 and G4(MP2) methods exhibit different BDEs trends in comparison to the hybrid functionals. For small alkanes, i.e. methane to pentane, G4 and G4(MP2) provide higher BDE values than B3LYP and M06-2X. Furthermore, these calculated values also exceed the experimental ones ranging from 2.2 to 5.2 $kJ \cdot mol^{-1}$ (G4), and from 3.8 to 6.6 $kJ \cdot mol^{-1}$ (G4(MP2)). The G4 / G4(MP2) BDEs of higher alkanes containing 6 to 11 carbons differ in values. For both approaches, as the number of C atoms increases, BDE values of hexane to undecane decline from 422.6 $kJ \cdot mol^{-1}$ to 415.5 $kJ \cdot mol^{-1}$ for G4 and from 420.6 $kJ \cdot mol^{-1}$ to 408.9 $kJ \cdot mol^{-1}$ for G4(MP2). This decreasing trend has no explanation, as only the influence of the nearest —CH_2— groups is described by the induction effect for linear chains of sp3 carbons (McMurry, 2011). It is shown that G4 and G4(MP2) utilize an additive approach to predict thermodynamical parameters of a system. Therefore, it can be stated that DFT hybrid functionals are more reliable in homolytic cleavage of terminal C—H bonds neighboring with a longer linear hydrocarbon chain.

HAT of C—H bonds in simple branched alkanes

In the following section, theoretical C—H BDEs of the six simplest saturated hydrocarbons (see Fig. 2) was calculated by four different computational approaches (see Tab. 1). At the B3LYP/6-311++G** and M06-2X/6-311++G** levels of theory, the lowest BDE was identified for homolytic cleavage of tertiary C—H bonds in the four presented systems within the range of 386.7 $kJ \cdot mol^{-1}$ to 391.6 $kJ \cdot mol^{-1}$ for B3LYP/6-311++G**, and from 383.0 $kJ \cdot mol^{-1}$ to 387.7 $kJ \cdot mol^{-1}$ for M06-2X/6-311++G**. Differences in calculated and experimental values were up to 12.8 $kJ \cdot mol^{-1}$ (B3LYP/6-311++G**) and 9.6 $kJ \cdot mol^{-1}$ (M06-2X/6-311++G**). Slightly higher values of 405.0 $kJ \cdot mol^{-1}$ (B3LYP/6-311++G**) and 402.8 $kJ \cdot mol^{-1}$ (M06-2X/6-311++G**) were predicted for the cleavage of secondary C—H bond in the $\mathbf{(CH_3)_3CCH_2CH_3}$ molecule. Finally, HAT from primary carbon atoms in $\mathbf{(CH_3)_2CHCH_3}$ and $\mathbf{(CH_3)_3CCH_3}$ molecules is thermodynamically least favorable, which was confirmed by experimental data and all further discussed theoretical approaches.

Hybrid functionals combined with the aug-cc-pVNZ basis sets show similar trends as in the above discussed linear alkanes. BDEs approach their limits as the basis set expands. However, a deviation of the predicted and experimental values is up to ±12.6 $kJ \cdot mol^{-1}$ (B3LYP) and ±8.3 $kJ \cdot mol^{-1}$ (M06-2X) even when the largest aug-cc-pVQZ is applied. Furthermore, despite the lower computational complexity, results obtained by the 6-311++G** basis set can be ranked at the aug-cc-pVTZ and aug-cc-pVQZ levels.

In contrast to the hybrid functionals, the obtained BDE results of composite G4 and G4(MP2) show smaller deviations from the experimental data. For example, the predicted values are 427.7 $kJ \cdot mol^{-1}$ (G4) and 426.7 $kJ \cdot mol^{-1}$ (G4(MP2)) for $\mathbf{(CH_3)_3CCH_3}$ with the largest BDE deviations, which differ from the experiment by ±8.0 and ±7.0 $kJ \cdot mol^{-1}$, respectively. These methods have been proved reliable for the studied homolytic cleavage of branched alkanes. Optimization of systems with negligible additive energy contribution, showed lower error compared to that for linear molecules discussed in the previous section.

Comparison of theoretical and experimental results

A disadvantage of quantum-chemical calculations of thermodynamic quantities is that the results may vary depending on the method or the basis of atomic orbitals. Therefore, it is essential to validate the predictive accuracy of the calculations by comparing the theoretical and experimental values for the studied molecules. Tab. 2 shows the dependence parameters obtained for all theoretical treatments following the linear trend. The obtained determination coefficients R^2 are in the range of 0.953 for the M06-2X/aug-cc-pvdz to 0.973 for the G4(MP2) approach. Linear dependencies of the theoretical approaches were used to correlate the calculated BDE values of hydrocarbons.

The slopes and intercepts in Tab. 2 can be used to correct BDEs calculations based on experiment. These values can be directly compared with

Tab. 2. Linear correlation of experimental C—H BDE values of studied hydrocarbons on the calculated ones at different levels of theory.

Level of theory	Basis set	Slope	Intercept ($kJ \cdot mol^{-1}$)	R^2
B3LYP	6-311++G**	0.708	+123.93	0.960
	aug-cc-pVDZ	0.735	+116.15	0.956
	aug-cc-pVTZ	0.692	+130.48	0.960
	aug-cc-pVQZ	0.691	+130.37	0.961
M06-2X	6-311++G**	0.940	+31.31	0.959
	aug-cc-pVDZ	0.994	+14.13	0.953
	aug-cc-pVTZ	0.905	+45.39	0.962
	aug-cc-pVQZ	0.903	+44.83	0.967
G4		0.913	+32.49	0.972
G4(MP2)		0.868	+51.28	0.973

experimental values. The values are presented in parentheses in Tab. 1. As it can be seen, the correlation of linear B3LYP BDEs provided identical values for all four basis sets, varying by a maximum of 0.4 $kJ \cdot mol^{-1}$ identified for the ethane molecule. A similar trend was observed for the M06-2X functional. Unfortunately, in the most corrected BDEs, the values deviated from the experiment further, e.g. the uncorrected value of B3LYP/aug-cc-pVQZ is 439.0 $kJ \cdot mol^{-1}$ while the corrected is 433.6 $kJ \cdot mol^{-1}$. The experiment states the value of 439.3 ±0.4 $kJ \cdot mol^{-1}$. Correction of G4 and G4(MP2) BDE values also did not contribute to better agreement of the results with the experiment.

On the other hand, correction of BDE values for branched hydrocarbons provided the desired result. The hybrid functionals lessened the drifts of the experimental values to the range of –4.2 $kJ \cdot mol^{-1}$ to +2.3 $kJ \cdot mol^{-1}$. Again, these values varied minimally within the basis sets used. Correction of G4 and G4(MP2) BDE values also contributed to better agreement of the results with the experiment, reducing the highest deviations to up to ±3.2 (G4) and ±3.7 $kJ \cdot mol^{-1}$.

Conclusion

Thermodynamics of the C—H bond cleavage of simple linear and branched alkanes has been theoretically investigated. For the studied set of compounds, BDE values were calculated by DFT/B3LYP and DFT/M06-2X functionals followed by composite G4 and G4(MP2) methods. Within the DFT methods, calculations with four basis sets were performed. A comparison of BDEs showed that the reliability of the computational method depends on the type of the investigated system. For linear alkanes, B3LYP predicted values show the best fit with the experiment. Here, comparison of the results predicted by the different basis sets showed that 6-311++G** is in good agreement with the computationally more complex aug-cc-pVTZ and aug-cc-pVQZ approaches. Next, composite methods predicted BDE values of higher linear alkanes (more than five carbons) with the systematic error resulting from the theory of the method. On the other hand, the best compliance with experimental BDE in branched hydrocarbons was predicted by G4 and G4(MP2). These methods are reliable in the investigation of thermodynamic quantities of systems with no long chain of atoms and therefore the additive energy contribution included in the calculation process of the method is negligible. Finally, the predicted values were compared with available experimental data. The obtained linear dependences were used as scaling functions of the calculated BDEs for homolytic cleavage of C—H bonds. Here, correction of BDE values for linear alkanes caused them to underrun the experiment. However, correction of all results for branched alkanes caused a significant adjustment to the experimental data.

Acknowledgement

The work has been supported by the Ministry of Education, Science, Research and Sport of the Slovak Republic (No. VEGA 1/0172/25) and by the Slovak Research and Development Agency (No. APVV-23-0195, APVV-20-0213, APVV-19-0024). We are grateful to the HPC center at the Slovak University of Technology in Bratislava, which is a part of the Slovak Infrastructure of High-Performance Computing (SIVVP project, ITMS code 26230120002, funded by the European region development funds, ERDF) for the computational time and resources made available.

References

Balakrishnan A, Smith V, Stoicheff BP (1992) Phys. Rev. Lett. 68(14): 2149—2152.

Barckholtz C, Barckholtz TA, Hadad CM (1999) J. Am. Chem. Soc. 121(3): 491—500.

Becke AD (1988) Phys. Rev. A 38(6): 3098—3100.

Berkowitz J, Ellison GB, Gutman D (1994) J. Phys. Chem. 98(11): 2744—2765.

Blanksby SJ, Ellison GB (2003) Acc. Chem. Res. 36(4): 255—263.

Bordwell FG, Zhang XM, Satish AV, Cheng JP (1994) J. Am. Chem. Soc. 116(15): 6605—6610.

Curtiss LA, Jones C, Trucks GW, Raghavachari K, Pople JA (1990) J. Chem. Phys. 93(4): 2537—2545.

Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) J. Chem. Phys. 94(11): 7221—7230.

Curtiss LA, Raghavachari K, Redfern PC, Rassolov V, Pople JA (1998) J. Chem. Phys. 109(18): 7764—7776.

Curtiss LA, Redfern PC, Raghavachari K (2007) J. Chem. Phys. 126(8): 084108—084112.

De Darwent BB (1970) Bond dissociation energies in simple molecules, NBS Publication.

Dunning TH (1989) J. Chem. Phys. 90(2): 1007—1023.

Ervin KM, DeTuri VF (2002) J. Phys. Chem. A 106(42): 9947—9956.

Denisov ET, Tumanov VE (2005) Russ. Chem. Rev. 74(9): 825.

Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery JA Jr., Peralta JE, Ogliaro F, Bearpark MJ, Heyd JJ, Brothers EN, Kudin KN, Staroverov VN, Keith TA, Kobayashi R, Normand J, Raghavachari K, Rendell AP, Burant JC, Iyengar SS, Tomasi J, Cossi M, Millam JM, Klene M, Adamo C, Cammi R, Ochterski JW, Martin RL, Morokuma K, Farkas O, Foresman JB, Fox DJ (2016) Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT.

Hanwell MD, Curtis DE, Lonie DC, Vandermeersch T, Zurek E, Hutchison GR (2012) J. Cheminf. 4: 1—17.

Hariharan PC, Pople JA (1973) Theor. Chim. Acta 28: 213—222.

Klein E, Lukeš V, Cibulková Z, Polovková J (2006) J. Mol. Struct. THEOCHEM 758(2—3): 149—159.

Kováčová A (2024) Acta Chimica Slovaca 17(1): 12—21.

Lee C, Yang W, Parr RG (1988) Phys. Rev. B 37(2): 785—789.

Luo YR (2007) Comprehensive Handbook of Chemical Bond Energies, CRC Press, Boca Raton, New York.

McMurry JE (2011) Organic Chemistry, 8th Edition, Brooks Cole, Pacific Grove CA.

Mulder P, Korth HG, Pratt DA, DiLabio GA, Valgimigli L, Pedulli GF, Ingold KU (2005) J. Phys. Chem. A, 109(11): 2647—2655.

Pople JA, Headgordon M, Fox DJ, Raghavachari K, Curtiss LA (1989) J. Chem. Phys. 90(10): 5622—5629.

Raghavachari K, Trucks G, Pople J, Head-Gordon M (1989) Chem Phys. Lett. 157(6): 479—483.

Rassolov VA, Pople JA, Ratner MA, Windus TL (1998) J. Chem. Phys. 109(4): 1223—1229.

Rayne S, Forest K (2011) PEP 36(5): 410—415.

Rimarčík J, Lukeš V, Klein E, Ilcin M (2010) J. Mol. Struct. 952: 25—30.

Rimarčík J, Lukeš V, Klein E, Rottmannová L (2011) Comput. Theor. Chem. 967(2—3): 273—283.

Trotman-Dickenson AF (1965) Chem. Ind., London 379.

Zhao Y, Truhlar DG (2008) Theor. Chem. Acc. 120: 215—241.