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Prediction of methyl C–H bond dissociation energies by density functional theory calculations

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Bond dissociation energies [$E_{\mathrm{D}\,298}$(R–H) = $\Delta_{\mathrm{r}}H_{298}°$] for a series of 15 substituted methane derivatives have been determined by density functional theory (DFT) calculations using the B3LYP functionals on the 6-31G(d,p) basis set. The averages of the experimental data were satisfactorily reproduced with a mean (signed) error of −0.2 kcal mol^{-1} (1 cal = 4.184 J) and an rms deviation of 2.2 kcal mol^{-1}.

Introduction

Homolytic C–H bond dissociation energies (BDE) are fundamental data for the quantitative description of numerous chemical processes. With regard to their importance in chemistry and technology it is interesting to note that even for common, rather small methane-based compounds, such as methylamine, acetaldehyde, acetone and acetic acid *etc.*, the various experimental C–H BDE values to be found in the literature show significant deviations (compare the data of the standard data compilations listed below).[1] Moreover, for many such compounds no C–H BDEs or only rough estimates are known. This fact in part reflects the limitations of the various experimental methods, especially for cases where certain reactive groups and/or additional X–H bonds of different strengths are present in the target molecules. Hence, there is still a constant need for 'correct' BDE numbers and their experimental determination is a matter of active research. For a critical review on the state-of-the-art of three modern experimental methods see ref. 2.

The development of computer technology during the past decade increasingly renders *ab initio* quantum-chemical calculations[3] to be time- and cost-effective alternatives to the experimental approaches. However, whereas for most ground state molecules a reliable prediction of the molecular structure can be achieved on modest calculational levels, the accurate determination of thermochemical properties, particularly heats of formation, still appears to be an expensive task for molecules containing more than a few heavy atoms. Therefore, BDE values are often evaluated on lower computational levels by application of so-called 'isodesmic reactions' in order to cancel out systematic computational errors.[3b] The relative BDE data thus obtained are then calibrated against some 'standard' values. The calculation of absolute BDEs which would satisfactorily reproduce the corresponding experimental data generally requires large basis set expansions and elaborate post-Hartree–Fock (HF) calculations to account for correlational effects. Within the framework of the GAUSSIAN suite of programs GAUSSIAN-1 (G1)[4] and GAUSSIAN-2 (G2)[5] model chemistries are common protocols for such purposes. The merits of these and similar methods (CBS-4, CBS-Q) have recently been discussed.[6]

In recent years, density functional theory (DFT)[7] calculations have emerged as an attractive alternative to conventional *ab initio* procedures. The major advantage of DFT methods is the inclusion of electron correlation in the SCF procedure. Furthermore, DFT calculations are generally faster and require less computer resources than the common post-HF methods, such as the Møller–Plesset (MP) pertubational procedures. The performance of a family of DFT methods has recently been evaluated.[8]

We demonstrate here that DFT calculations using the B3LYP (= Becke3LYP) functionals[9,10] on the 6-31G(d,p) basis set are able to reproduce the C–H BDEs of a variety of methyl compounds well within the experimental error ranges without the necessity to apply isodesmic reactions. C–H bond dissociation energies were calculated for a set of 15 methane derivatives, namely methane, ethane, propane (*sec*. C–H), 2-methyl propane (*tert*. C–H), methyl fluoride, methyl chloride, methanol, methylamine, methanethiol, acetonitrile, acetaldehyde, acetone, acetic acid, dimethyl sulfone and chloroform. Besides the intention to cover a broad range of common functional groups, most of these compounds have been selected because they are the subjects of a kinetic study of hydrogen abstraction by a family of reactive oxygen-centred radicals,[11] where we correlate the rate constants for hydrogen abstraction with calculated thermodynamic and electronic properties of the reactants and transition states. As a starting point, the BDE of molecular hydrogen was also calculated. The 6-31G(d,p) basis set was selected as it represents a good compromise between computational costs and expected quality of the resulting data. The B3LYP functionals were selected because from the data presented in a number of papers it is evident that for a variety of chemical applications these functionals presently show the best overall performance among the various DFT methods. For instance, DFT procedures have been successfully applied in the determination of Si–H and C–H bond dissociation energies in silanes[12] and substituted toluenes,[13] respectively. For comparison purposes, we also present the results of the corresponding HF and MP2 calculations. The aim of this study is not to reproduce the experimental data as close as possible, but rather to show that the applied method is a practicable and reliable approach even for not-so-small molecules.

Computational procedures

Calculations were performed on a Cray Y-MP computer and a Silicon Graphics Indy workstation with the GAUSSIAN 92/DFT package of programs.[14] Geometries were fully optimized to stationary points using the split-valence 6-31G(d,p) (= 6-31G**) basis set at the restricted (for closed shell molecules) and unrestricted (for radicals) HF, MP2(FULL) and B3LYP[9] levels. For each of the UHF calculations on the radicals the expectation value of $\langle S^2\rangle$ was found to be less than 0.79 before and less than 0.751 after annihilation of the first spin contaminant by spin projection, except for $^{\bullet}$CH$_2$CN, for which more pronounced spin contamination ($\langle S^2\rangle$ 0.923 before and 0.768 after annihilation) was found. Spin contamination was lower ($\langle S^2\rangle$ 0.897 prior to, 0.763 after annihilation) for the MP2 calculations. In the DFT calculations $\langle S^2\rangle$ never exceeded 0.769 (again for $^{\bullet}$CH$_2$CN) and was always reduced to the theoretical value 0.750 by annihilation of the first (quartet) spin contaminant. However, since there is no rigorous way to

Table 1 Total electronic energies and zero point vibrational energies (ZPVE)

	(PU)HF/6-31G(d,p)		(PU)MP2/6-31G(d,p)		(PU)B3LYP/6-31G(d,p)	
Compound	E_e^0/hartrees	ZPVE/ kcal mol^{-1}	E_e^0/hartrees	ZPVE/ kcal mol^{-1}	E_e^0/hartrees	ZPVE/ kcal mol^{-1}
H_2	−1.131 333 6	6.62	−1.157 661 1	6.59	−1.178 541 3	6.39
CH_4	−40.201 704 8	29.75	−40.369 856 2	29.25	−40.524 022 3	28.25
C_2H_6	−79.238 235 0	49.71	−79.553 712 8	48.67	−79.838 737 4	46.99
C_3H_8	−118.276 159 2	68.92	−118.740 881 0	67.29	−119.155 341 1	65.10
$(CH_3)_3CH$	−157.314 556 5	87.76	−157.930 875 6	85.49	−158.472 755 4	82.70
CH_3F	−139.039 735 7	26.48	−139.367 441 9	25.56	−139.738 279 3	24.68
CH_3Cl	−499.097 899 0	25.34	−499.393 291 5	24.67	−500.112 546 1	23.82
CH_3OH	−115.046 710 1	34.60	−115.389 843 5	33.28	−115.723 953 0	32.24
CH_3NH_2	−95.213 279 5	41.65	−95.549 161 3	40.48	−95.854 964 9	39.11
CH_3SH	−437.709 027 2	30.92	−438.003 937 2	30.17	−438.705 671 1	29.03
CH_3CN	−131.932 495 9	30.50	−132.375 162 5	29.02	−132.759 156 6	28.52
CH_3CHO	−152.922 587 0	37.38	−153.391 224 4	35.89	−153.835 722 7	34.88
CH_3COCH_3	−191.972 071 7	56.08	−192.589 476 7	54.14	−193.164 220 5	52.64
CH_3COOH	−227.822 171 5	41.87	−228.469 334 4	39.88	−229.091 487 4	38.94
$CH_3SO_2CH_3$	−626.401 882 0	57.49	−627.230 476 1	55.59	−628.409 460 3	53.57
$CHCl_3$	−1 416.871 158 5	13.72	−1 417.437 443 1	13.12	−1 419.280 312 5	12.47
$^{\bullet}H$	−0.498 232 9	0	−0.498 232 9	0	−0.500 272 8	0
$^{\bullet}CH_3$	−39.564 457 1	19.35	−39.699 454 3	19.30	−39.842 884 1	18.67
$^{\bullet}C_2H_3$	−78.605 525 0	39.49	−78.885 845 7	38.80	−79.165 205 8	37.29
$^{\bullet}CH(CH_3)_2$	−117.647 491 6	58.92	−118.079 057 9	57.58	−118.488 252 3	55.49
$^{\bullet}C(CH_3)_3$	−156.689 348 0	78.05	−157.272 121 0	76.11	−157.811 010 1	73.28
$^{\bullet}CH_2F$	−138.404 314 1	15.69	−138.703 369 1	15.38	−139.067 117 9	14.86
$^{\bullet}CH_2Cl$	−498.464 510 8	14.76	−498.730 899 4	14.60	−499.441 337 1	14.02
$^{\bullet}CH_2OH$	−114.419 124 8	25.19	−114.733 453 7	24.37	−115.060 798 8	23.54
$^{\bullet}CH_2NH_2$	−94.597 943 4	33.60	−94.905 974 0	32.74	−95.205 340 1	31.60
$^{\bullet}CH_2SH$	−437.079 898 6	21.22	−437.346 042 6	20.94	−438.040 418 5	20.01
$^{\bullet}CH_2CN$	−131.310 569 3	20.18	−131.713 860 8	20.92	−132.097 773 5	19.53
$^{\bullet}CH_2CHO$	−152.305 639 3	28.15	−152.733 786 8	27.71	−153.175 915 3	26.73
$^{\bullet}CH_2COCH_3$	−191.351 708 0	46.72	−191.930 655 2	45.95	−192.502 218 9	44.11
$^{\bullet}CH_2COOH$	−227.195 096 8	32.55	−227.808 924 8	31.44	−228.425 076 5	30.40
$^{\bullet}CH_2SO_2CH_3$	−625.762 169 6	47.29	−626.559 270 5	46.04	−627.731 673 4	44.09
$^{\bullet}CCl_3$	−1 416.248 159 7	4.98	−1 416.786 633 9	4.83	−1 418.623 338 5	4.39

derive $\langle S^2 \rangle$ from a DFT calculation the significance of these values remains uncertain. Nevertheless, the DFT results can be assumed not to be significantly influenced by incorporation of higher spin states, as can be deduced from the brief discussion of this problem.[13b] The energy data for the radicals given in Table 1 refer to the spin-projected (annihilated) results.

Zero-point vibrational energy (ZPVE) corrections[15] were evaluated by vibrational analysis on the same levels of theory. In order to minimize the errors associated with the theoretical prediction of vibrational frequencies, we recalculated the scaling factors for the ZPVEs of the compounds of this study as far as experimental vibrational frequencies[16] were available, *viz*. for molecular hydrogen, methane, ethane, propane, methanol, acetonitrile, acetic acid, chloroform, methyl fluoride, methylamine, acetaldehyde, acetone, methyl chloride, methyl, ethyl, hydroxymethyl and trichloromethyl, by comparison with the calculated vibrational frequencies. ZPVE scaling factors for the (U)HF/6-31G(d,p), (U)MP2/6-31G(d,p) and (U)B3LYP/6-31G(d,p) levels amounted to 0.912 ± 0.018, 0.940 ± 0.014 and 0.975 ± 0.024, respectively. Our (U)B3LYP/6-31G(d,p) scaling factor is virtually identical to a more recent, more thoroughly evaluated one.[17] Thus, with moderately large basis sets the B3LYP DFT calculations seem to predict ZPVEs just *ca*. 3% above the experimental values.

Results and discussion

The calculated electronic energies E_e^0 and zero-point vibrational energies (ZPVE) of the substrates and derived radicals are collected in Table 1.

Bond dissociation energies $E_{D\,298}$ (R−H) (= reaction enthalpies $\Delta_r H_{298}°$ for $R-H \longrightarrow R^{\bullet} + H^{\bullet}$) at 298 K were calculated from these data with consideration of the thermal corrections $0 \longrightarrow 298$ K obtained in the frequency calculations, according to eqn. (1).[18] Calculated and experimental BDEs are listed in Table 2.

$$E_{D\,298}(R{-}H) = \Delta E_e^0 + \Delta ZPVE + \Delta(\Delta E_{vib})^{298} + \Delta E_{rot}^{298} + \Delta E_{trans}^{298} + \Delta(PV) \quad (1)$$

In the literature, the selection of experimental thermochemical data for comparison with computational results, in our view, often appears arbitrary. Authors either refer to just one common data collection or select 'most recent' experimental data (which are not necessarily of higher quality or reliability than older ones). However, with a few exceptions, namely hydrogen, methane and ethane, for those of our compounds where multiple $E_{D\,298}$ (R−H) values could be found in the literature, the data display a considerable scatter. The deviations in most cases even exceed the individual experimental error bars. This is clearly reflected by Fig. 1, where experimental BDE data† taken from the literature[1,2,19] were plotted *versus* the B3LYP/6-31G(d,p)-calculated numbers. (Only a few numbers which are commonly suspected to be in error were neglected.)

From Fig. 1 it is obvious that one might always select an experimental datum that is close to the calculated one. Since we do not feel we are in the position to judge of the quality of the various experimental data and in order to avoid the arbitrary selection of just a single number, we simply calculated by 'brute force' averaged $E_{D\,298}$ (R−H)$_{av}$ values (Table 2) from the data of Fig. 1. Thus, the standard errors of the $E_{D\,298}$ (R−H)$_{av}$ values given in Table 2 reflect the statistical scatter of the literature data rather than the uncertainties of the individual numbers

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† Not all of the experimental data displayed in Fig. 1 are entirely independent: some of the $E_{D\,298}$ values were recalculated from the same $\Delta_f H°$ (RH) or $\Delta_f H°$ ($R^{\bullet}$) by using redetermined values of either one of the two.

Table 2 Calculated (6-31G**) and experimental bond dissociation energies $E_{\mathrm{D}\,298}$ (R−H) (kcal mol^{-1})

	HF		MP2		B3LYP		Experimental BDE			
Compound	BDE	ΔBDE[a]	BDE	ΔBDE[a]	BDE	ΔBDE[a]	Average[b]	n[c]	Ref.[1b]	Ref.[2]
H_2	79.5	−24.7	95.8	−8.4	106.4	2.2	104.2 ± 0.0	(2)[d]	104.2	104.2 ± 0.0
CH_4	79.4	−25.4	100.3	−4.5	105.8	1.0	104.8 ± 0.2	(8)[e]	104.7	104.9 ± 0.4
CH_3CH_3	76.8	−23.7	98.9	−1.6	101.1	0.6	100.5 ± 0.5	(5)[f]	100.2	101.1 ± 0.4
$CH_2(CH_3)_2$	74.5	−23.1	95.3	−2.3	97.1	−0.5	97.6 ± 1.6	(8)[g]	99.4	98.6 ± 0.4
$CH(CH_3)_3$	72.7	−21.6	93.7	−0.6	94.0	−0.3	94.3 ± 1.6	(7)[h]	95.2	96.5 ± 0.4
CH_3F	77.8	−23.9	96.0	−5.7	99.1	−2.6	101.7 ± 1.3	(5)[i]	103.3	
CH_3Cl	76.6	−24.9	95.0	−6.5	99.7	−1.8	101.5 ± 0.9	(4)[j]	102.7	
CH_3OH	74.1	−22.1	92.3	−3.9	95.2	−1.0	96.2 ± 1.5	(7)[k]	94.1	96.1 ± 0.2
CH_3NH_2	67.5	−24.7	85.0	−7.2	87.7	−4.5	92.2 ± 3.0	(7)[l]	95.5	
CH_3SH	74.9	−19.2	93.1	−1.0	96.3	2.2	94.1 ± 1.9	(3)[m]		93.9 ± 2.0
CH_3CN	69.8	−23.6	96.2	2.8	93.8	0.4	93.4 ± 0.9	(5)[n]	92.6	94.8 ± 2.1
CH_3CHO	67.3	−26.9	93.5	−0.7	93.4	−0.8	94.2 ± 1.6	(6)[o]		94.3 ± 2.2
CH_3COCH_3	69.4	−25.7	94.4	−0.7	94.0	−1.1	95.1 ± 2.9	(5)[p]	98.0	
CH_3COOH	73.7	−22.3	95.2	−0.8	97.2	1.2	96.0 ± 1.9	(3)[q]	95.9[f]	
$CH_3SO_2CH_3$	80.8	−18.2	101.2	2.2	103.4	4.4	99.0 ± 2.0	(1)[s]		
$CHCl_3$	71.8	−23.8	89.4	−6.2	92.0	−3.6	95.6 ± 1.1	(6)[t]	96.1	

[a] ΔBDE = calculated $E_{\mathrm{D}\,298}$ − average experimental $E_{\mathrm{D}\,298}$. [b] Average of experimental BDE values ± standard deviation. [c] Number of individual values. [d] Refs. 1*d*,1*h*,1*k*,19*a*. [e] Refs. 1*a*,*f*,*g*; 2, 19*b*–*f*. [f] Refs. 1*a*,*b*,*e*–*g*; 19*c*,*g*. [g] Refs. 1*a*,*b*,*f*; 19*c*,*g*–*j*. [h] Refs. 1*a*,*b*,*f*; 19*c*,*g*,*i*,*k*. [i] Refs. 1*a*,*b*,*l*; 19*k*. [j] Refs. 1*a*,*b*,*l*; 19*k*. [k] Refs. 1*a*; 2; 19*l*–*n*. [l] Refs. 1*a*,*b*; 19*o*–*s*; [m] Refs. 1l; 2; 19*t*,*u*. [n] Refs. 1*a*,*b*; 19*s*,*v*–*x*. [o] Refs. 1*b*,*l*,*g*; 19*w*,*y*,*z*. [p] Refs. 1*a*,*b*,*l*; 19*z*,*aa*. [q] Refs. 19*bb*–*dd*. [r] Erroneous value of $\Delta_f H^\circ_{298}(CH_2CHOOH)$ in ref. 1*b* corrected. [s] Ref. 19*aa*; estimated value, assumed to be the same as for phenyl methyl sulfone. [t] Refs. 1*a*,*b*,*k*; 19*b*,*k*,*ee*,*ff*.

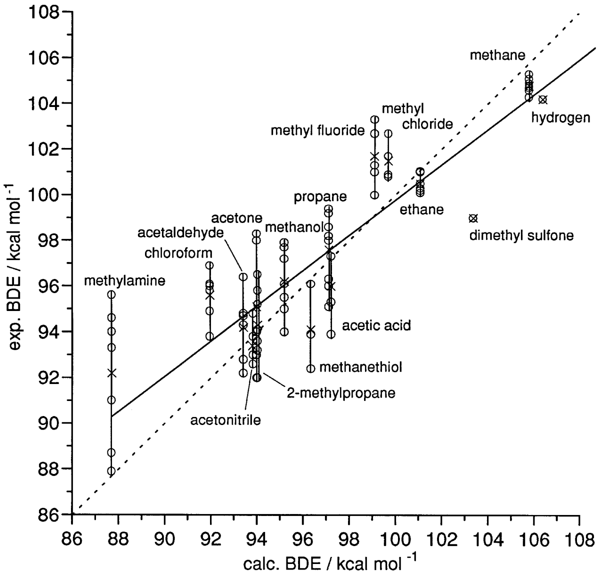

Fig. 1 Experimental *vs.* B3LYP/6-31G(d,p)-calculated bond dissociation energies. Crosses mark the averaged experimental BDEs. Solid line: regression line through all data points. Broken line: unity slope. The vertical bars do not represent error bars, they just serve as a guide to the eye.

(with the exception of dimethylsulfone, for which only a single, estimated value could be found).[19aa] This procedure, of course, may be criticized because it disregards the different quality and uncertainty of the individual data as well as the general performance of the experimental method by which the data were obtained (for such aspects see the general discussion in ref. 2). However, we think that comparison with the 'averaged' BDE numbers provides a clearer general impression on the performance of the selected DFT procedure and its predictive power. For comparison, the 'recommended' BDE values from a recent standard database[1b] and ref. 2‡ are also displayed. The standard deviations of the $E_{\mathrm{D}\,298}$ $(R{-}H)_{av}$ values of Table 2 demonstrate that the experimental BDEs of only a few of our compounds agree within an uncertainty of ±1 kcal mol^{-1}.

With regard to the size of the basis set used in the calculations and despite the fact that the foregoing analysis treats all the experimental data with equal weight, inspection of the data of Table 2 and Fig. 1 clearly reveals that the DFT method applied here reproduces the experimental BDE data for most of our compounds with very satisfying accuracy. The deviation of the calculated numbers from the experimental ones spans a range from −4.5 (methylamine) to +4.4 kcal mol^{-1} (dimethyl sulfone) with a mean (signed) error of −0.2 kcal mol^{-1} and a root mean square (rms) deviation of 2.2 kcal mol^{-1}. When compared to the values from the NIST database,[2b] the DFT results show a somewhat bigger average deviation of −0.7 kcal mol^{-1} and a rms deviation of 3.2 kcal mol^{-1}. The performance of the MP2 method is less accurate, $\Delta E_{\mathrm{D}298}$ (R−H) values ranging from −8.4 to +2.8 kcal mol^{-1}, with an average deviation of −2.3 kcal mol^{-1} and a rms deviation of 4.4 kcal mol^{-1}. It is common knowledge that without consideration of electron correlation absolute BDE values cannot be predicted by *ab initio* calculations to an acceptable degree.[3] This is clearly demonstrated by our HF results which notoriously underestimate the experimental data by more than 20 kcal mol^{-1}.

The performance of the DFT method applied here appears even more satisfying if one compares the calculated $E_{\mathrm{D}\,298}$ (R−H) values with those of the compounds, namely H_2, CH_4 and C_2H_6, for which the BDEs safely can be assumed to be 'correct', *i.e.* for which the majority of the experimental numbers are in close agreement with each other. The $E_{\mathrm{D}\,298}$ (R−H) data for CH_4 and C_2H_6 were reproduced by the DFT method with a small deviation of 1.0 and 0.6 kcal mol^{-1}, respectively (Table 2). Though the simplest system, the deviation for H_2, is somewhat bigger (+2.2 kcal mol^{-1}). This fact primarily derives from a slight overestimation of the electronic energy of the hydrogen molecule. The experimental BDE of acetonitrile also seems to be rather well defined (±0.9 kcal mol^{-1}); this value is reproduced with a deviation of +0.4 kcal mol^{-1}. Small deviations of −0.3, −0.5 and −0.8 kcal mol^{-1} were also found for 2-methylpropane, propane and acetaldehyde, respectively. However, this must be considered to be somewhat fortuitious in view of the relatively large scatter of the corresponding experimental numbers.

Generally speaking, the negative mean error of −0.2 kcal mol^{-1} (which is also indicated by the slope of the regression line in Fig. 1) implies that the B3LYP/6-31G(d,p) method tends to slightly underestimate the $E_{\mathrm{D}\,298}$ (R−H) values, or, *vice versa*, to overestimate the stabilization of the corresponding radicals.

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‡ Most of the data reevaluated by Gutman and co-workers[2] since 1988 have been revised upwards by 1–4 kcal mol^{-1}.

Though our data set is too limited by far to draw a valid general conclusion, it seems that this behaviour is particularly pronounced for halogenated compounds, since the experimental data of our three halogen compounds (CH_3F, CH_3Cl, $CHCl_3$) are all higher than the calculated numbers. On the other hand, the experimental data for methanethiol and dimethyl sulfone are probably too low by *ca.* 2 kcal mol^{-1}, in agreement with the fact that the revised value[2] for the former is indeed close to 95 kcal mol^{-1}. For dimethyl sulfone this also appears reasonable because its 'experimental' datum was assumed to be the same as for phenyl methyl sulfone,[19a] which intuitively is expected to have a slightly lower BDE than dimethyl sulfone. The experimentally least defined BDE is that of methylamine, the experimental data range from 88 to 96 kcal mol^{-1}. Our computational results predict that the 'true' value should be located in the lower half of this range (⩽90 kcal mol^{-1}).

When compared to the average accuracies reported for the sophisticated *ab initio* model chemistries G2, G2(MP2), CBS-4 and CBS-Q, it appears that the DFT procedure applied here performs comparably well. For a set of 18 compounds Ochterski *et al.*[6] obtained for these *ab inito* methods rms deviations of E_{D0} (R−H) of 1.11, 1.32, 1.41 and 0.91 kcal mol^{-1}, respectively, from the data recommended by Gutman *et al.*[2] Note, however, that in ref. 6 comparison was made only with the data at 0 K and that the selected experimental data set consisted of small, relatively well-defined compounds, *i.e.* did not contain such 'critical' cases as methylamine, methanethiol, acetaldehyde, dimethyl sulfone, *etc*.

Conclusion

The computational results presented in this paper demonstrate that density functional theory calculations on the B3LYP/6-31G(d,p) level are able to predict C−H bond dissociation energies well within the current experimental error limits. The B3LYP/6-31G(d,p) method is—in terms of computer resources and time—still a practicable procedure, but already yields results which are similar to the considerably more elaborate *ab initio* model chemistries. This view is also expressed in a recent paper,[20] in which the heats of formation of hydrocarbons and related radicals (including those of the present paper) have been calculated by various DFT procedures. The above DFT procedure thus provides a useful tool for a reliable prediction of BDE values which are otherwise difficult to access experimentally.

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