S–H bond dissociation enthalpies:
The importance of a complete basis set approach

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Abstract

The S–H homolytic bond dissociation enthalpies (BDEs) for several compounds of reference were estimated by different theoretical methods including CCSD(T), CBS-QB3, and the multi-coefficient extrapolated density functional theory multi-level approaches, MCG3-MPWB and MCG3-TS. Emphasis was placed on the importance of extrapolating theoretical BDEs to complete basis set. A very good agreement between S–H BDEs from CCSD(T) calculations and experiment is observed when a simple dual extrapolation scheme to complete basis set proposed by Truhlar is adopted. For thiophenol, our CCSD(T) estimate for the S–H BDE ($347.2 \text{ kJ mol}^{-1}$) supports a recent experimental value obtained from time-resolved photoacoustic calorimetry ($349 \pm 5 \text{ kJ mol}^{-1}$).
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1. Introduction

The thermochemistry of sulfur compounds and sulfur-centered radicals has been revisited in recent years [1,2]. Although many of the data reviewed by Benson [3] almost 30 years ago and up-dated by Griller et al. [4] remain current, the values for some key compounds have been subject to significant changes and/or their accuracy has been improved. For instance, the gas-phase S–H bond dissociation enthalpy in hydrogen sulfide (H_2S), at 298.15 K, $DH°$ (HS–H) = $381.6 \pm 0.4 \text{ kJ mol}^{-1}$ [5–7] can be compared with the value accepted in the 90s, $378 \pm 5 \text{ kJ mol}^{-1}$ [4]. Another important example is methanethiol (CH_3SH), where the presently recommended value for $DH°$ (CH_3S–H) = $365.7 \pm 2.1 \text{ kJ mol}^{-1}$ [7,8] is some 5 kJ mol^{-1} higher than the previously accepted result [4]. The slow progress towards chemical accuracy (ca. 4 kJ mol^{-1}), however, has apparently not touched the S–H bond dissociation enthalpy of thiophenol, $DH°$ (PhS–H). A reassessment of literature data by McMillen and Golden [9] led to $DH°$ (PhS–H) = $349 \pm 8 \text{ kJ mol}^{-1}$ but Griller et al. [4] have recalculated $DH°$ (PhS–H) as $338 \pm 8 \text{ kJ mol}^{-1}$ by using more recent auxiliary data. A new experimental value (331 kJ mol^{-1}), based on a thermochemical cycle involving the acidity of PhSH and the measured oxidation potential of the anion PhS$^-$ was reported by Bordwell and co-workers [10]. Finally, in our own laboratory, time-resolved photoacoustic calorimetry (TR-PAC) experiments afforded $DH°$ (PhS–H) = $349.4 \pm 4.5 \text{ kJ mol}^{-1}$ [11], a result that agrees with the recommendation by McMillen and Golden but it is some 18 kJ mol^{-1} higher than the electrochemical value. This is an unacceptable discrepancy for such a key value in organosulfur chemistry.

Although computational chemistry is a reliable tool for predicting thermochemical data [12], the accuracy of theoretical values varies considerably, depending on the theory level used and also on the reaction scheme chosen to extract the data. A recent Letter by Chandra et al. [2] predicts that $DH°$ (PhS–H) = $332.6 \pm 4.0 \text{ kJ mol}^{-1}$. This result was based on density function theory calculations (DFT) at the the (RO)B3LYP/6-311++G(2df,2p) level and the BDE corresponds to the enthalpy of the homolysis reaction

$$PhSH \rightarrow PhS^{\bullet}(g) + H^{\bullet}(g) \qquad (1)$$

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Our earlier calculations for the enthalpy of the same reaction using several DFT methods [11] clearly indicated that DFT underestimates homolytic BDEs (the results range from 312 to 319 kJ mol^{-1}). On the other hand, our G3(MP2) result (347 kJ mol^{-1}) [11] was quite close to the TR-PAC value (349.4 ± 4.5 kJ mol^{-1}). In order to find additional evidence that could support either the 'high' or the 'low' (ca. 331 kJ mol^{-1}) value of the S–H BDE, we decided to investigate the performance of different theoretical methods for predicting S–H BDEs of several sulfur compounds for which reliable experimental S–H BDEs are available.

Initially, we describe the theoretical procedures selected for this investigation. A discussion on the convergence of S–H BDEs with the basis set size for a few small molecules is then reported. This is followed by a detailed comparison between theoretical and experimental results. We conclude by emphasizing the importance of energy extrapolation schemes to complete basis set for accurate prediction of thermochemical properties.

2. Theoretical procedures

The adequacy of a given theoretical approach for predicting homolytic bond dissociation enthalpies depends on the reliable estimation of geometries, vibrational frequencies, and total energies for both closed and open-shell species. Given the slow convergence of ab initio energies with the basis set size, extrapolation procedures to infinite basis set are very important for accurate energy predictions. Therefore, the following procedure was adopted. First, geometry optimizations (with a very tight criterium) were carried out with the B3LYP hybrid functional [13,14] and correlation-consistent cc-pVTZ+d basis set. [15]. The choice of this basis set was oriented by recent investigations on molecular systems involving second row atoms. It has been pointed out that the introduction of a set of d functions in the cc-pVxZ basis set hierarchy can be relevant for extrapolating energetic properties to a complete basis set [15]. In addition, it has been shown that B3LYP/cc-pVTZ optimized structures were in very good agreement with experimental information for both closed-shell and open-shell species [16]. Such an approach yields reliable geometries, necessary for accurate energy extrapolation to complete basis set procedures. Harmonic frequencies were scaled by 0.985 as in the W1 method [17]. In a second step, single-point energy coupled cluster calculations with single and double excitations [18,19] and perturbative inclusion of triple excitations [20] (CCSD(T)) were carried out using the optimized B3LYP/cc-pVTZ+d structures. For the smallest molecules, hydrogen sulfide (H$_2$S), hydrogen disulfide (HSSH), and methanethiol (CH$_3$SH), CCSD(T) calculations with the correlation consistent basis set ($x = D, T, Q, 5$) and different extrapolation to complete basis set schemes were carried out. For the larger molecules only the dual ($x = D, T$) extrapolation scheme proposed by Truhlar [21] was used. Thermal corrections to 298.15 K of

the CCSD(T) results were taken from B3LYP/cc-pVTZ+d frequency calculations.

A recent approach to thermochemistry was recently proposed by Truhlar and collaborators [22–24]. The multi-coefficient extrapolated density functional theory for thermochemistry and thermochemical kinetics is a multi-level approach involving empirical mixing of ab initio and DFT methods. We have selected the MCG3-MPW and the MCG3-TS procedures [24]. However, instead of carrying out geometry optimizations and harmonic frequency calculations at the QCISD/MG3 level, as in Ref. [24], our reference structures and frequencies were based on B3LYP/cc-pVTZ+d optimizations. Results based on the standard CBS-QB3 method [25] are also reported.

All the calculations were performed with the GAUSSIAN-03 package of programs [26].

3. Results and discussion

Table 1 reports the CCSD(T) results for the HS–H, CH$_3$S–H, and HSS–H BDEs. Enthalpies were calculated with cc-pVxZ ($x = D, T, Q, 5$) and cc-pVxZ+d ($x = D, T, Q$) basis sets and different extrapolation schemes to complete basis set $\infty(D, T, Q)$, $\infty(T, Q, 5)$, and $\infty(D, T, Q, 5)$ were used. Exponential ($f(x) = a + \exp(-cx)$) and power-law ($f(x) = a + bx^{-3} + cx^{-5}$) behaviors were assumed to describe the convergence to infinite basis set of the Hartree–Fock and correlation energies, respectively. Results based on the simple dual $\infty(D, T)$ extrapolation scheme proposed by Truhlar [21] for CCSD(T)/cc-pVxZ ($x = D, T$) calculations, are also presented in Table 1.

Some aspects concerning the convergence of BDEs with the basis set are worth remarking. The first respects to the slow convergence of CCSD(T) energies. For H$_2$S, the S–H BDE results with $x = T$ (triple zeta) correlation-consistent basis set are ∼10 kJ mol^{-1} below the value for $x = 5$ (quintuple zeta). In general, a good agreement between different extrapolation schemes can be observed, and the present results also indicate that the inclusion of additional d functions may be not essential for estimating basis set-extrapolated S–H BDEs for the compounds presently investigated.

A second relevant aspect concerns the good agreement between the ad hoc extrapolation procedures and the simple dual $\infty(D, T)$ scheme [21]. The differences between the ad doc extrapolations and the dual scheme amount to less than 2.5 kJ mol^{-1}. Although the comparison is carried out only for the smallest molecules, it seems reasonable to assume that the dual $\infty(D, T)$ extrapolation scheme is adequate for the larger molecules of interest. The ad hoc procedures including $x = Q$ or $x = 5$ are clearly unaffordable for these systems.

Table 2 reports theoretical predictions and experimental data for the series of molecules presently investigated. Deviations (in parentheses) from selected experimental results are quite small for the different theoretical methods, CCSD(T) yielding the most accurate values. The excellent experiment-theory agreement for RS–H BDEs (R = alkyl)

Table 1
CCSD(T) results for the S–H BDE (kJ mol^{-1}) from different schemes of extrapolation to complete basis-set[a]

x	HS–H		CH$_3$S–H		HSS–H	
	cc-pVxZ	cc-pVxZ+d	cc-pVxZ	cc-pVxZ+d	cc-pVxZ	cc-pVxZ+d
D	352.1	356.1	336.0	339.8	290.4	291.1
T	371.6	373.8	354.1	356.1	303.8	304.1
Q	378.8	379.9	360.4	361.4	307.7	307.8
5	381.7	381.7			308.8	
∞(D, T, Q)[b]	384.4	385.0	365.2	365.8	310.6	310.8
∞(T, Q, 5)[b]	384.1	383.1			309.6	
∞(D, T, Q, 5)[b]	384.4	384.3			310.2	
∞(D, T)[c]	382.3 (−2.1)[d]		363.9 (−1.3)[d]		311.9 (1.3)[d]	

[a] Single-point energy calculations with B3LYP/cc-pVTZ+d geometries and frequencies.
[b] The Hartree–Fock energy was extrapolated by using the two-parameter exponential expression: $f(x) = a + \exp(-cx)$; the correlation energy was fitted to the power-law expression: $f(x) = a + bx^{-3} + cx^{-5}$.
[c] Dual extrapolation scheme of Truhlar [21].
[d] Values in parentheses are deviations from the ad hoc ∞(D, T, Q) extrapolation.

Table 2
Theoretical and experimental S–H BDEs (kJ mol^{-1}) at 298.15 K

	CCSD(T)[a,b]	CBS-QB3[b]	MCG3-MPWB[b]	MCG3-TS[b]	Exp.
HS–H	382.3 (0.7)	384.1 (2.5)	385.0 (3.4)	384.6 (3.0)	381.6 ± 0.4[c]
CH$_3$S–H	363.9 (−1.8)	364.2 (−1.5)	362.0 (−3.7)	362.7 (−3.0)	365.7 ± 2.1[d,e]
C$_2$H$_5$S–H	363.5 (−1.8)	362.2 (−3.1)	363.9 (−1.4)	363.9 (−1.4)	365.3[e]
(CH$_3$)$_2$CHS–H	368.9 (−1.0)	368.4 (−1.5)	369.5 (−0.4)	369.4 (−0.5)	369.9[e]
(CH$_3$)$_3$CS–H		369.0 (−1.7)	370.6 (−0.1)	370.3 (−0.4)	370.7[e]
C$_6$H$_5$S–H	347.2 (−1.8)	339.1 (−9.9)	339.1 (−9.9)	344.9 (−4.1)	349 ± 8;[f] 338 ± 8;[g] 331;[h] **349 ± 5**[i]
HSCH$_2$S–H	360.5	359.4	359.8	359.9	
HSCH$_2$CH$_2$S–H	361.3	360.7	361.7	361.6	
HSS–H	311.9 (−6.1)	309.4 (−8.6)	308.8 (−9.2)	308.9 (−9.1)	**318 ± 15**;[e] 295 ± 10[g]
CH$_3$SS–H	300.1 (5.1)	296.2 (1.2)	296.2 (1.2)	296.2 (1.2)	331 ± 15;[e] **295**[g]
C$_2$H$_5$SS–H	300.0	296.0	296.0	296.0	

[a] Dual ∞(D, T) extrapolation scheme [21]. Geometries and frequencies (thermal corrections to 298.15 K) are from B3LYP/cc-pVTZ+d optimizations.
[b] Values in parentheses are deviations from selected experimental data (in bold, when different values are available).
[c] Value recommended in Ref. [7]. It relies on a value at 0 K from Ref. [5] and a temperature correction from Ref. [6].
[d] Ref. [7].
[e] Value recommended in Ref. [28].
[f] Value recommended in Ref. [9].
[g] Value recommended in Ref. [4].
[h] Ref. [10].
[i] Ref. [11].

is also in keeping with the well-established fact that these BDEs are rather insensitive to the length and configuration of the alkyl chain [3]. The same pattern is suggested by the theoretical results for S–H BDEs in the dithiols HSCH$_2$SH and HSCH$_2$CH$_2$SH, although in these cases no experimental data are available.

The theoretical results for the HSS–H BDE show larger deviations from experiment, but for this system, the experimental values involve large uncertainties. The same can be said about the CH$_3$SS–H BDE. In this case, however, the calculations clearly support a value close to the one recommended by Griller et al. [4], 295 kJ mol^{-1}.

For thiophenol, CBS-QB3 and MCG3-MPWB results for S–H BDE are around 339 kJ mol^{-1}, whereas CCSD(T) and MCG3-TS lead to 347 and 345 kJ mol^{-1}, respectively. Based on the performance of CCSD(T) for the other systems in Table 2, it seems reasonable to consider that 347 kJ mol^{-1} is our best theoretical prediction, supporting the experimental value derived in our laboratory,

349 ± 5 kJ mol^{-1} [11], and the value recommended by McMillen and Golden [9], 349 ± 8 kJ mol^{-1}. Although, in the light of the present calculations we cannot discard a lower value (ca. 338 kJ mol^{-1}), the experimental value obtained by Bordwell and co-workers [10] (331 kJ mol^{-1}) is clearly too low. The same comment applies to the theoretical result reported by Chandra et al. [2] (333 kJ mol^{-1}), but, as referred above, it is well known that DFT systematically underestimates homolytic BDEs [27].

The following aspects concerning the performance of different theoretical methods for evaluating S–H BDEs, should be observed. The multi-coefficient extrapolated density functional theory multi-level procedures perform quite well for the series of molecules presently investigated. Specifically, with the exception of HSSH, for which the experimental data involve large uncertainties, deviations of MCG3-TS results from selected experimental results are less than 4 kJ mol^{-1}. This agreement seems to reflect the explicit attempt of the multi-level methods to extrapolate

to a complete basis set and full configuration interaction [24].

Finally, we should stress the importance of reliable extrapolation procedures to complete basis set for a rigorous comparison with experiment. In this sense, it appears that dual $\infty(D, T)$ scheme [21] provides a practical and reliable route to investigate energetic properties of molecules for which ad hoc extrapolation procedures are beyond computational possibilities. A similar conclusion was reported by a previous study on the O–H homolytic bond dissociation [29].

4. Conclusions

Different theoretical procedures were applied to estimate the S–H homolytic BDEs for a series of reference molecules. The multi-coefficient extrapolated density functional theory multi-level procedures perform quite well for the molecules investigated, with an accuracy almost comparable to CCSD(T) calculations based on B3LYP/cc-pVTZ+d optimized geometries and frequencies. The importance of extrapolation to complete basis set results was discussed in detail, with emphasis on the possibility of applying a simple dual $\infty(D, T)$ scheme [21] for investigating the thermochemistry of large molecules. Finally, results for the thiophenol S–H BDE based on basis set extrapolated CCSD(T) and multi-level MCG3-TS calculations (347.1 and 344.9 kJ mol^{-1}, respectively) support a recent TR-PAC value (349 ± 5 kJ mol^{-1}) [11].

Acknowledgments

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