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Letter

High level ab initio and density functional theory study of bond selective dissociation of CH_3SH and CH_3CH_2SH radical cations

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Abstract. Selective bond dissociation energies for CH_3SH and CH_3CH_2SH radical cations were evaluated with G1, G2, G2MP2, B3LYP, BLYP, and SVWN computational methods. It was determined that both G2 and CBSQ evaluate very accurate bond dissociation energies for thiol radical cations, while gradient-corrected BLYP computes the best energies of three employed DFT methods. For the CH_3CH_2SH radical cation, new, higher than previously estimated selective bond dissociation energies were suggested.

Key words: Ab inito – Density functional theory – Bond dissociation energies – Radical cations – Thiols

1 Introduction

There is a long standing interest in the study of chemical transformations that include bond selective dissociation processes. A bond selective dissociation process is a process that has higher probability than one would expect on the basis of statistical distribution. Most of the experimental information of these processes was gathered through UV photochemical studies and through phothoexcitation [1–5]. Recently, Ng and coworkers [6] applied collision activation to determine bond selective dissociation energies for CH_3SH^+ and $CH_3CH_2SH^+$ species. In these studies it was demonstrated that selective excitation of bonding electrons localized on a specific bond prompts dissociation of the corresponding bond. To perform the selective bond dissociation studies, Ng and coworkers [6] have estimated the bond selective dissociation energy for CH_3SH^+ and $CH_3CH_2SH^+$ from thermodynamic data available in the literature [7, 8]. Here we would like to present a high level ab initio, as well as a density functional theory evaluation of bond selective dissociation energies for these two radical cations.

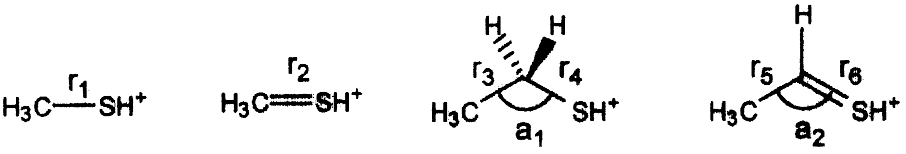
2 Computational methods

All computational studies were performed with the Gaussian 94 computational package [9]. High level ab inito calculations, including Hartree-Fock (HF) [10] and second-order Møller-Plesset (MP2) [11, 12] calculations, were performed. For the accurate computation of energies, quadratic complete basis set (CBSQ) [13, 14], Gaussian-1 (G1) [15, 16], Gaussian-2 (G2) [17], and Gaussian-2 with MP2 basis set extension correlations (G2MP2) [18] were used. Three well-known density functional methods were used: hybrid (B3LYP), gradient-corrected (BLYP), and local (SVWN) density functional methods. These methods are a combination of exchange and correlation functionals. The B3LYP method is a combination of Becke's 3 parameter exchange functional (B3) [19] and correlation functional provided by Lee-Yang-Parr (LYP) [20]. The gradient-corrected BLYP is a combination of Becke's 88 [21] exchange functional with LYP correlation functional. The local spin density approximation (LSDA or SVWN) used in these studies is a combination of exchange functional provided by Slater's expression [22] and correlation functional provided by Vasko-Wilk-Nusair's expression [23]. All computational studies are performed with 6-31G(*d*), 6-31G(*d'*), and 6-31+G(*d*) Gaussian types of basis set [24].

3 Results and discussion

To determine bond selective dissociation energies, the high level Gaussian series and complete basis set ab initio computational studies were performed. To the best of our knowledge the structural parameters of these radical cations are not available. From our experience in using both ab initio and density functional theory methods, we know that MP2, as well as hybrid DFT methods with proper basis sets, should correctly compute structural parameters for small polar molecular species [25–33]. Therefore, it is reasonable to expect that these two methods should also accurately compute the geometries of CH_3SH^+ and $CH_3CH_2SH^+$ radical cations. For instance, the CS bond distance in CH_3SH^+ and CH_2SH^+ should be 1.79 Å and 1.63 Å, respectively, indicating the double bond character of the CS bond of the latter (Table 1). It is interesting that there is no difference in the structural parameters computed with the basis set, with and without diffuse functions. The

Table 1. Structural properties of CH_3SH^+, CH_2SH^+, CH_3CHSH^+, and $CH_3CH_2SH^+$



Theory model	r_1 (Å)	r_2 (Å)	r_3 (Å)	r_4 (Å)	a_1 (°)	r_5 (Å)	r_6 (Å)	a_2 (°)
HF/6-31G(*d*)	1.813	1.616	1.525	1.840	110.6	1.478	1.638	123.0
HF/6-31G(*d′*)	1.816	1.617	1.527	1.843	110.6	1.480	1.639	122.9
MP2/6-31G(*d*)	1.786	1.619	1.520	1.803	111.1	1.469	1.636	122.5
MP2/6-31G(*d′*)	1.791	1.623	1.527	1.808	111.0	1.475	1.639	122.4
B3LYP/6-31G(*d,p*)	1.797	1.631	1.522	1.819	112.8	1.465	1.658	122.9
B3LYP/6-31 + G(*d,p*)	1.797	1.631	1.522	1.819	112.8	1.465	1.657	123.0
BLYP/6-31G(*d,p*)	1.811	1.648	1.526	1.836	114.0	1.471	1.676	122.9
BLYP/6-31 + G(*d,p*)	1.811	1.648	1.527	1.836	114.0	1.471	1.676	123.0
SVWN/6-31G(*d,p*)	1.751	1.622	1.492	1.769	114.8	1.441	1.649	122.3
SVWN/6-31 + G(*d,p*)	1.751	1.622	1.527	1.836	114.0	1.442	1.649	122.3

structural parameters computed with the B3LYP DFT method for $CH_3CH_2SH^+$ are 1.522 Å (C—C bond distance), 1.819 Å (C—S), and 112.8° (C—C—S bond angle) (Table 1). From MP2 computational studies, we have estimated that the CC (CS) bond distances in $CH_3CH_2SH^+$ and CH_2CHSH^+ should be 1.53 (1.81) Å and 1.47 (1.64) Å, respectively (Table 1).

Let us now examine selective bond dissociation energies with both ab initio and DFT methods. Total energies for molecular species necessary to determine the CH_3SH and CH_3CH_2SH radical cations selective bond dissociation energies are presented in Table 2. The computed, as well as experimentally determined, selective bond dissociation energies are presented in Table 3. There are some surprising computational results in regard to HF accuracy. Usually HF does not compute accurate energies for chemical systems owing to lack of electron correlation. In the case of the CH bond dissociation energy for the CH_3SH radical cation, the HF/6-31G(*d*) and HF/6-31G(*d′*) computed energies are virtually identical to the experimental value (Table 3). It is well documented that substantially better energies are obtained by DFT methods [34–40] but they are higher than the HF energies. Because the HF bond dissociation energy is almost identical to the experimental value, it is reasonable to expect that the DFT computed CH bond dissociation energy for the CH_3SH radical cation must be high. That was confirmed by our computational studies. All three DFT methods used (hybrid, gradient-corrected, and local) overestimate the CH bond dissociation energy. The best estimated value, 2.24 eV, is computed by the gradient-corrected BLYP/6-31+G(d) (0 K) theory level.

All four high level ab initio methods correctly estimate the CH bond dissociation energy for the CH_3SH radical cation. The best values were obtained with G2 (2.08 eV) and CBSQ (2.11 eV) when compared to the experimental value (2.09 eV). Thus it was demonstrated that these four ab initio computational approaches could even compute the correct CH bond dissociation energy for radical cations.

Let us now determine the CS bond dissociation energy for the CH_3SH radical cation. Here the HF ab initio method computes a bond dissociation energy that is substantially different (lower) than the experimental value. This is "normal" behavior for the HF ab initio method. Again, the gradient corrected BLYP computes a bond dissociation energy that is very close (in fact almost identical) to the experimental value. The hybrid B3LYP also generates an acceptable CS bond dissociation energy (Table 3). Both G2 and CBSQ ab initio computational approaches generate highly reliable CS bond dissociation energies (Table 3).

In the case of CH_3CH_2SH radical cation, selective bond dissociation energies were calculated by Ng and coworkers [6] from available thermodynamic data. Consequently, these values might not be as accurate as in the case of the CH_3SH radical cation. Because the best agreement with experimental values for the CH_3SH radical cation were obtained with G2, CBSQ, and BLYP, only computed selective bond dissociation energies for the CH_3CH_2SH radical cation, with these three computational methods, will be discussed. The G2 estimated CH bond dissociation energy is 0.12 eV higher than the projected experimental value. As demonstrated by the example of the CH_3SH radical cation, the G2 computes energies that are usually in closer agreement with the experimental rather than the obtained value in the case of CH_3CH_2SH radical cation (Table 3). On the other hand, the G2 computed values for the CC and the CS selective bond dissociation energies are exact, as estimated by Ng and coworkers (Table 3). The CBSQ computed CH bond dissociation energy for the CH_3CH_2SH radical cation is also high (1.62 eV). Contrary to the G2, the CBSQ estimates the CC and CS bond dissociation energies to be slightly higher than the Ng bond dissociation energies (Table 3). Therefore, we believe that the CH bond dissociation energy for CH_3CH_2SH should be around 1.60 eV, not 1.47 eV. Two other bond dissociation energies (CS, and CC) might be 0.02–0.05 eV higher than the Ng values.

Let us now evaluate the capability of the three most common density functional methods for computing the bond dissociation energies. As expected, computed bond dissociation energies with both gradient-corrected BLYP and hybrid B3LYP are close to the experimental values.

Table 2. Total energies (a.u.) computed with ab initio and DFT methods computed at 0 K

	CH_3SH^+	CH_2SH^+	H	CH_3^+	SH	$CH_3CH_2SH^+$	CH_3CHSH^+	CH_3	$CH_3CH_2^+$
HF/6-31G(*d*)	−437.34424	−436.76898	−0.49823	−39.19692	−398.05779	−476.35569	−475.80030	−39.52802	−78.24677
HF/6-31G(*d'*)	−437.34489	−436.76978	−0.49823	−39.19735	−398.05779	−476.35627	−475.80094	−39.52804	−78.24726
G1	−437.79747	−437.22241	−0.50000	−39.38338	−398.28547	−477.02819	−476.47126	−39.74253	−78.67080
G2	−437.80076	−437.22423	−0.50000	−39.38558	−398.28697	−477.03295	−476.47429	−39.74509	−78.67412
G2MP2	−437.79443	−437.21866	−0.50000	−39.38492	−398.27945	−477.02581	−476.46750	−39.74391	−78.67238
CBSQ	−437.80385	−437.22657	−0.49982	−39.38410	−398.28978	−477.03651	−476.47699	−39.74516	−78.67181
B3LYP/6-31G(*d,p*)	−438.31763	−437.73116	−0.50027	−39.45327	−398.73718	−477.614255	−477.04985	−39.81311	−78.80836
B3LYP/6-31+G(*d,p*)	−438.31840	−437.73193	−0.50027	−39.45331	−398.73905	−477.61574	−477.05101	−39.81750	−78.80863
BLYP/6-31G(*d,p*)	−438.27185	−437.69417	−0.49545	−39.42682	−398.71431	−477.54296	−476.98683	−39.78071	−78.75862
BLYP/6-31+G(*d,p*)	−438.27281	−437.69510	−0.49545	−39.42685	−398.71684	−477.54494	−476.98844	−39.78633	−78.75908
SVWN/6-31G(*d,p*)	−437.02182	−436.43278	−0.49394	−39.18534	−397.66477	−476.10261	−475.53667	−39.56628	−78.33764
SVWN/6-31+G(*d,p*)	−437.02281	−436.43379	−0.49394	−39.18538	−397.66675	−476.10434	−475.53811	−39.57108	−78.33792

Table 3. Heat (eV) for selected reactions computed at 0 K

Theory Level	ΔE_{I}	ΔE_{II}	ΔE_{III}	ΔE_{IV}	ΔE_{V}
HF/6-31G(*d*)	2.10	2.44	1.56	1.60	1.39
HF/6-31G(*d'*)	2.09	2.44	1.55	1.59	1.39
MP2/6-31G(*d*)[a]	1.80	3.46	1.28	1.88	1.98
G1	2.04	3.50	1.55	1.72	1.96
G2	2.08	3.49	1.59	1.73	1.96
G2MP2	2.06	3.54	1.57	1.72	2.01
CBSQ	2.11	3.54	1.62	1.76	2.04
B3LYP/6-31G(*d,p*)	2.35	3.46	1.75	1.90	1.87
B3LYP/6-31+G(*d,p*)	2.35	3.43	1.75	1.80	1.85
BLYP/6-31G(*d,p*)	2.24	3.56	1.65	1.85	1.91
BLYP/6-31+G(*d,p*)	2.24	3.51	1.66	1.73	1.88
SVWN/6-31G(*d,p*)	2.59	4.67	1.96	2.82	2.73
SVWN/6-31+G(*d,p*)	2.59	4.64	1.97	2.71	2.71
Experimental	2.09(9)	3.53(2)	1.47	1.73	1.96

[a] Calculated with the HF zero-point energy correction;
ΔE_{I} = Heat for $CH_3SH^+ \rightarrow CH_2SH^+ + H$ reaction;
ΔE_{II} = Heat for $CH_3SH^+ \rightarrow CH_3^+ + SH$ reaction;
ΔE_{III} = Heat for $CH_3CH_2SH^+ \rightarrow CH_3CHSH^+ + H$ reaction;
ΔE_{IV} = Heat for $CH_3CH_2SH^+ \rightarrow CH_2SH^+ + CH_3$ reaction;
ΔE_{V} = Heat for $CH_3CH_2SH^+ \rightarrow CH_3CH_2^+ + SH$ reaction

The bond dissociation energy for CH is also predicted to be higher than the estimated value from thermodynamic data (Table 3). On the other hand, the CC bond dissociation energy is exact, as estimated by Ng and coworkers (Table 3), while the CS bond dissociation energy is underestimated by 0.08 eV. As previously determined in the CH_3SH radical cation case, the local SVWN substantially overestimates bond dissociation energies. Similar results were obtained for the CH_3CH_2SH radical cation. All computed bond dissociation energies are around 1 eV higher than the energies obtained by the G2 and CBSQ methods (Table 3).

4 Conclusion

In conclusion, we can say that both G2 and CBSQ should produce reliable selective bond dissociation energies for thiol radical cations. Of the three studied DFT methods, gradient-corrected BLYP should produce energies that are very close to those obtained experimentally, or estimated through the G2 and CBSQ computational studies. According to our CBSQ computational study, the estimated selective bond dissociation energies for the CH_3CH_2SH radical cation from experimental thermodynamic data are too low. This is particularly true for the CH bond dissociation energy. Our best estimated value is 1.60 eV, which is 0.13 eV higher than the previously estimated value.

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