C—H Bond Dissociation of Acetylene: Local Density Functional Calculations

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Abstract

The C—H bond dissociation energy of acetylene was computed by both ab initio approaches and density functional theory in a local density approximation (DFT–LDA). Structures and energies for acetylene and its dissociation products (the ethynyl and hydrogen radicals) are presented and compared. Using directly computed HCCH and HCC· energies and the exact H· value, the DFT–LDA calculations are found to yield C—H dissociation energies ranging from 129 to 131 kcal/mol, in good agreement with recent experimental and the highest level theoretical results. The DFT–LDA results show little dependence upon the computational procedure used to obtain geometries.

Introduction

There is considerable disagreement between the numerous experimental and calculated C—H bond dissociation energies of acetylene found in the literature [1–11]. Experimentally determined values range from 126.6 [4] to 132.0 [1] kcal/mol, while ab initio computed results ranging from 120.0 [5] to 133.5 [3] kcal/mol have been reported.

There is a growing interest in density functional theory (DFT) [12–25], especially using local density approximations (LDA) [18–25], as an alternative to ab initio methods for computational treatments of chemical systems and processes. It has been shown that DFT–LDA predicts a number of properties (e.g., activation energies, dipole moments, polarizabilities, structures) at a level of accuracy comparable to ab initio post-Hartree–Fock techniques [19, 20, 22, 23, 25]. A key advantage of DFT–LDA approaches is a considerable reduction in computational time and resource requirements compared to ab initio procedures [26], allowing analyses of much larger systems (as many as 100 first-row atoms).

On the other hand, DFT–LDA procedures have been found to overestimate binding energies, by as much as 50% [20, 27]. The reasons for this error are being investigated; it may, of course, be due at least in part to the use of the LDA. We have recently shown, for one specific DFT–LDA method, that atomization and dissociation energies of good accuracy can be obtained by means of empirically determined corrections to the energies of the initial molecule and the products [25].

It seems possible, however, that the energy required for the homolytic cleavage of the bond to a hydrogen, as represented by Eq. (1),

$$MH \longrightarrow M\cdot + H\cdot , \qquad (1)$$

can be calculated accurately by DFT–LDA, using the exact energy of H· and not applying any corrections to MH and M·; the latter two may be sufficiently alike that the errors in their energies will cancel. This would permit the computation of DFT–LDA dissociation energies for M—H bonds without prior determination of the correction terms for MH and M·.

Our objective in this work has been to test this possibility while simultaneously investigating DFT–LDA predictions for the controversial C—H bond dissociation energy of acetylene and to determine how these are affected by the method used for geometry optimization.

Our emphasis is on DFT–LDA calculations of the C—H bond dissociation of acetylene [Eq. (2)]. For comparison purposes, we have used an ab initio self-consistent-field molecular orbital approach (GAUSSIAN 88 [28]) to calculate optimized geometries and energies for acetylene and the ethynyl and hydrogen radicals [Eq. (2)],

$$H-C\equiv C-H \longrightarrow H-C\equiv C\cdot + H\cdot, \tag{2}$$
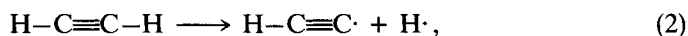
at both Hartree–Fock (HF) and post-Hartree–Fock levels (HF/STO-3G, HF/3-21G, MP2/6-311G**). These and other calculated and experimental geometries and energies are listed in Tables I and II.

We have carried out the DFT–LDA calculations with the program DMol* [26] using the DN, DNP, and DN($2d2f2g, 2p2d2f$) basis sets to optimize geometries and to compute single-point energies using HF/3-21G or HF/STO-3G optimized structures. The aforementioned DMol basis sets can be regarded as double-zeta sets of Slater orbitals, DNP and DN($2d2f2g, 2p2d2f$) being augmented by polarization functions. DMol is based on the Kohn–Sham approach [29], in which the elec-

*From Biosym Technologies, Inc.

TABLE I.   Calculated and experimental ground-state bond lengths.

| | Acetylene | | Ethynyl radical | |
Method/basis set	C—C (Å)	C—H (Å)	C—C (Å)	C—H (Å)
HF/STO-3G	1.168	1.065	1.221	1.067
HF/3-21G	1.187	1.051	1.223	1.053
MP2/6-311G**	1.214	1.064	1.178	1.063
MCSCF/DZP[a]	1.215	1.079	1.221	1.080
DMol/DN	1.213	1.077	1.222	1.074
DMol/DNP	1.213	1.077	1.213	1.080
DMol/DN($2d2f2g, 2p2d2f$)	1.199	1.082	1.202	1.085
Experimental[b]	1.203	1.061	—	—

[a]Ref. 5.
[b]Ref. 32.

TABLE II. Calculated and experimental energies.

Method[a]	Energy (Hartrees)			Dissociation energy (kcal/mol)	
	HCCH	HCC·	HCC· + H·	Without zero point correction	With zero point correction[b]
HF/STO-3G	-75.85625	-75.19611	-75.66269	121.5	115.8
HF/3-21G	-76.39596	-75.73206	-76.22826	105.2	99.6
MP2/6-311G**	-77.14839	-76.41542	-76.91523	146.3	140.7
DMol/DN	-76.62786	-75.91002	-76.41002[c]	136.7	131.1
DMol/DN//HF/3-21G	-76.62786	-75.91002	-76.41002[c]	136.7	131.1
DMol/DNP	-76.63777	-75.92179	-76.42179[c]	135.5	129.9
DMol/DNP//HF/3-21G	-76.63758	-75.92156	-76.42156[c]	135.6	129.9
DMol/DN[2d2f2g, 2p2d2f]	-76.64453	-75.92831	-76.42831[c]	135.7	130.0
DMol/DN[2d2f2g, 2p2d2f]// HF/STO-3G	-76.64207	-75.92773	-76.42773[c]	134.5	128.9
DMol/DN[2d2f2g, 2p2d2f]// HF/3-21G	-76.64302	-75.92716	-76.42716[c]	135.5	129.8

TABLE II. (Continued)

Other calculated results				
g1 (*w/o* QCI)[d]	−77.18628	−76.46026	−76.96026		141.8[e]
MP4/6-311G**[d]	−77.13994	−76.40933	−76.90933	144.7[e]	139.1[e]
g1[d]	−77.18610	−76.47345	−76.97345		133.5 ± 2.3
QCISD(T)−CBS[f]					131.54 ± .51
MRCI[g]					130.1 ± 1.0
GVB and CCCI/DZP[h]					129.7 ± (1–5)
MCSCF[i]				122.0	
Experimental					132.6 ± 1.2[j]
					132 ± 2[k]
					131.3 ± 0.7[l]
					131 ± 1[m]
					127 ± 1.5[n]
					126.647[o]

[a]For our calculated results, when the energy was computed by a procedure X that is different from that used to optimize the geometry, Y, the notation $X//Y$ is used.

[b]MP2/6-311G** zero-point vibrational energies of 0.02664 Hartrees for acetylene and 0.01765 Hartrees for the ethynyl radical have been used in this work to make all corrections.

[c]In all DMol calculations, the exact hydrogen atom energy of −0.5 Hartrees was used.

[d]Ref. 3.

[e]These energies were calculated using values reported in Ref. 3.

[f]Ref. 9.

[g]Ref. 8.

[h]Ref. 10.

[i]Ref. 5.

[j]Ref. 2.

[k]Ref. 1.

[l]Ref. 11.

[m]Ref. 7.

[n]Ref. 6.

[o]Ref. 4; the uncertainty for this value is 0.002.

tronic density is written as a sum of one-electron orbitals [Eq. (3)],

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} |\varphi_i|^2, \tag{3}$$

which are obtained numerically by solving the Kohn–Sham equations:

$$\left[-\frac{\nabla_i^2}{2} + \nu_{eff}(\mathbf{r}_i) \right] \varphi_i = \varepsilon_i \varphi_i \qquad i = 1, 2, \dots N. \tag{4}$$

As part of the LDA, the exchange/correlation contribution to the effective potential, ν_{eff}, is evaluated by the approach of von Barth and Hedin [30].

Calculated and experimental [31] bond lengths of acetylene and the ethynyl radical are given in Table I. The DFT–LDA results are in generally good agreement with the experimental and the post-HF ab initio values. It is interesting that the DFT–LDA and the MCSCF (but not the MP2) methods predict the bond lengths in the ethynyl radical to be very little changed from acetylene.

Our various calculated energies for acetylene and the ethynyl radical, and the resulting C—H bond dissociation energies of acetylene, are given in Table II. The same correction for the difference in zero-point energies was applied in all instances; it was taken from the MP2/6-311G** calculations.

As anticipated [32], the HF results in Table II underestimate the C—H dissociation energy, by 15–30 kcal/mol, whereas it is overestimated by the MP calculations. Our DFT–LDA results range from 129 to 131 kcal/mol and are in excellent agreement with most of the experimental and the highest level theoretical values. A striking feature of our DFT–LDA dissociation energies is their insensitivity to the nature of the computational method and basis set used for geometry optimization. This has also been observed in several recent studies of activation barriers and dissociation energies using DFT–LDA methods [20, 24].

In conclusion, we have demonstrated that the DFT–LDA approach can produce an accurate HCC—H bond dissociation energy, comparable to the best experimental and theoretical values, using the directly computed HCCH and HCC· energies and the exact H· energy. We anticipate that this finding will be applicable to other M—H bonds as well, so that the need to determine corrections for M and M· can be avoided.

Acknowledgments

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