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Quantum chemical study of hydrogen abstraction reactions of the ethynyl radical with hydrogen compounds (C_2H+HX)

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Abstract

We have theoretically investigated the hydrogen abstraction reactions of ethynyl radical with simple hydrogen compounds, C_2H+HX, using quantum chemical computations. Computations have been performed using the density functional theory with the recently proposed MPW1K functional and the 6-311++G(3df,2p) basis set. An analysis of the resulting energy barriers for hydrogen abstraction reactions has been carried out using the bond dissociation energy of the breaking X–H bond and DFT-based reactivity parameters to rationalize the reaction behavior.

Keywords: Hydrogen abstraction reactions; Ethynyl radical; Hydrogen compounds

1. Introduction

The ethynyl radical (C_2H) has been demonstrated to be an important intermediate in interstellar space [1–4] and planetary atmospheres [5]. It participates in the photochemistry of Titan's atmosphere [6]. In these cold environments, its main chemical transformation involves fast and barrier-free reactions with ions, radicals and small molecules. Therefore, its low-temperature ($T<294$ K) kinetics have received a great deal of attention [7,8].

This triatomic radical is also known to play a major role in high-temperature hydrocarbon combustion [9,10], where it is linked to the acetylene oxidation reaction. The latter process leads, via highly reactive $CH_2(a^1A_1)$ and $CH(X^2\Pi)$ to C_3H_x ($x=0$–4), and hence to C_2H and C_4H_y ($y=2$–4) [10,11]. From the C_3H_x and C_4H_y backbones, a number of routes have been proposed for formation of the first aromatic ring structures [12], the building blocks of polycyclic aromatic hydrocarbons (PAHs), that are the likely precursors of soot particles. We would refer to Ref. [13] for a recent review on reactions of the ethynyl radical.

In recent years, we have endeavored to contribute to the study of the kinetics and mechanisms of gas phase reactions of C_2H with a series of small molecules and radicals including O [10], H_2 [14,15], C_2H_2 [16,17], NO [15,18], NO_2 [19], CH_4 [20], H_2O [21], C_2H_6 [22], NH_3 [23,24] and O_2 [16,25]. For each system, we have performed kinetic experiments to measure its rate constants over a large range of temperatures, and also constructed the detailed potential energy surfaces. Using the combined approach, we have been able to determine quantitatively the molecular mechanisms. One of the common features of the ethynyl radical reactions is that when an H-atom is present in the reactant partner, the abstraction of the hydrogen atom from R–H giving rise to $HCCH+R^{\cdot}$, is either the most preferred process, or at least a competitive alternative. Nevertheless, there is no systematic study on the H-abstraction reactions of C_2H. The importance of this process and the lack of consistent and uniform information have prompted us to carry out in the present work a theoretical study on the reaction of the ethynyl radical with a number of simple hydrogen compounds, R–H, with R=H, F, Cl, Br, CH_3, NH_2, OH, SiH_3, PH_2, SH, CN, C_2H, C_2H_3, and C_2H_5. Some of these processes have been reported in the literature but the theoretical methods employed were rather disparate,

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such that they do not allow a systematic comparison to be made.

To understand the inherent electronic behavior governing the energy barrier, when it exists, we have attempted to emphasize a certain correlation between the barrier heights for hydrogen abstraction and the R–H bond dissociation energies (BDEs). We have also analyzed the reactivity of different substrates toward hydrogen abstraction reactions with C_2H radical by using different DFT-based reactivity parameters. These reactive parameters have been found to be very successful for rationalizing and understanding the reactive behavior for various types of reactions [26].

2. Methods of calculation

For each of the H-abstraction reactions considered, we computed the energy barrier using the DFT-based quantum chemical method, namely MPW1K. All calculations were performed using the GAUSSIAN 98 set of programs [27]. As the hybrid B3LYP functional is known to often underestimate the barrier heights for reactions involving hydrogen atom transfer [28], we have therefore not considered this popular functional in this study. We used density functional theory (DFT) method MPW1K to determine structures and energies. Several attempts have recently been made to improve the functionals for treating processes of hydrogen atoms [29]. In particular, the MPW1K functional [31a], which denotes a modified Perdew–Wang 1-parameter model for kinetics, has been shown to be another alternative for wide applications in kinetics [30,31]. In the latter model, the one-parameter hybrid Fock–Kohn–Sham operator is expressed as

$$F = F^{\mathrm{H}} + X\cdot F^{\mathrm{HFE}} + (1-X)(F^{\mathrm{SE}} + F^{\mathrm{GCE}}) + F^{\mathrm{C}}$$

where F^{H} is the Hartree operator, F^{HFE} is the HF exchange operator, F^{SE} is the Slater exchange operator, F^{GCE} is the gradient correction to the exchange operator, and F^{C} is the correlation operator. The parameter X is used as a control to mix different amount of HF exchange with the DFT functional in order to derive the best kinetic results. We first optimized the structures at the MPW1K/6-311++G(d,p) level and then performed a single point calculation with the larger 6-311++G(3df,2p) basis set. The barrier heights and reaction enthalpies were calculated from the large basis set results. During our calculations, we observed that the MPW1K with the larger basis set provides barrier heights comparable to the same at the CCSD(T) level with the same basis set.

The DFT-based reactive parameters have been evaluated by using B3LYP/6-311G(d,p) results. The global softness, defined as $S = 1/(\mathrm{IE}-\mathrm{EA})$, has been determined from a ΔSCF procedure, where separate SCF calculations are performed for neutral, anionic and cationic species to determine the ionization energy and electron affinity. The local reactive parameters, such as Fukui function and local softness, were also determined by using atomic charges from both the methods. However, as we could not find any meaningful correlation between them and the reaction barriers, these aspects are not discussed further in detail. Unless otherwise stated, bond lengths are given in angstroms, bond angles in degrees, and relative energies in kilojoules per mole.

3. Results and discussion

3.1. TS structures and energy barriers

The general features of the transition structures for hydrogen abstraction reactions of C_2H with a variety of substrates HX, including X = H, F, Cl, Br, CN, NC, NH_2, PH_2, CH_3, C_2H, C_2H_3, and C_2H_5, are summarized in Table 1. There are two distinct types of TSs. In most of the cases, hydrogen abstraction takes place in an almost linear fashion, i.e. the breaking X–H and the forming C-H bond are almost in a straight line. In some cases (like H_2S, HF, and PH_3), the C···H···X moiety in the TSs become significantly bent.

The bond lengths for the breaking X–H bond and the forming C–H bond can provide important indication of the nature of the TS. As indicated by heats of reaction given in Table 2, hydrogen abstraction reactions by C_2H are exothermic in nature. As a consequence, early TSs are expected from Hammond's principle. As can be seen from Table 1, in most of the cases, the forming C–Hα bond is much longer than a normal C–H bond. This bond is found to be especially long when the reaction is highly exothermic.

Table 1
The optimized bond lengths for the breaking X–H (X–Hα) and the forming C–H (C–Hα) bonds and the two bond angles ($\theta 1$ and $\theta 2$) (as shown in figure) at the transition state (TS) structures for the hydrogen abstraction reactions of C_2H radical with different substrates (HX)

	C–Hα	X–Hα	$\theta 1$	$\theta 2$
TS–H_2	1.916	0.757	179.7	179.9
TS–H_2O	1.463	1.034	174.1	142.2
TS–H_2S	1.746	1.378	153.2	115.2
TS–HF	1.244	1.130	162.8	137.2
TS–HCl	1.404	1.477	178.6	179.2
TS–HBr	1.526	1.558	178.9	179.6
TS–HCN	1.294	1.252	180.0	180.0
TS–HNC	1.317	1.231	166.6	160.1
TS–NH_3	1.598	1.066	175.1	129.5
TS–PH_3	2.072	1.419	148.9	101.1
TS–CH_4	1.889	1.108	180.0	180.0
TS–C_2H_2	1.267	1.267	179.8	179.5
TS–C_2H_4	1.776	1.113	179.3	175.7
TS–C_2H_6	2.180	1.100	177.4	172.5

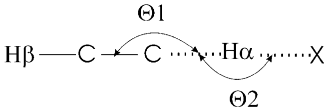

Table 2
Barrier heights [$\Delta E^{\#}$] and heats of reaction [ΔH_r] for the hydrogen abstraction reactions of different substrates with the C_2H radical as calculated from the density functional theory with MPW1K functional

Substrate	$\Delta E^{\#}$ (kJ/mol)	ΔH_r (kJ/mol)	BDE(X–H)[a] (kJ/mol)	IE (eV)[b]
H_2	4.7 (6.2)	−122.8	436.0	15.43
HF	40.5 (32.0)	−7.8	570.7	16.03
HCl	28.7 (28.9)	−143.6	431.8	12.74
HBr	19.7 (14.4)	−197.2	366.5	11.68
H_2O	16.1 (9.0)	−78.1	498.7	12.62
H_2S	−11.4 (−8.9)	−189.8	377.8	10.46
HCN	49.0 (35.1)	−27.3	527.6	13.60
HNC	48.4 (36.3)	−70.5	484.8[c]	12.18[d]
NH_3	−14.0 (−15.6)	−48.5	452.7	10.07
PH_3	−16.5 (−12.9)	−225.1	351.0	9.87
CH_4	20.6 (19.7)	−130.8	438.9	12.61
C_2H_2	50.7 (37.2)	0	556.1	11.40
C_2H_4	5.8 (2.5)	−109.5	465.3	10.51
C_2H_6	0.6 (0.4)	−150.6	423.0	11.52

Quantities within bracket correspond to the barrier heights after ZPE corrections. Experimental bond dissociation energies [BDE(X–H)] and ionization energies [IE] are also given.

[a] CRC Handbook of Chemistry and Physics, D.R. Lide (Eds.), 78th ed., CRC Press, New York, 1997–1998. The value is actually the bond dissociation enthalpy at 298 K.

[b] NIST Standard Ref. Database, Number 69, March, 2003 Release.

[c] Calculated value at the B3LYP/6-311++G(3df,2p) level.

[d] Calculated at the B3LYP/6-311G(d,p) level.

For example, in the case of PH_3, the C–Hα bond length amounts to 2.072 Å. On the other hand, hydrogen abstraction reaction with HF is the least exothermic and as a result a short C–Hα bond is observed, indicating a late TS.

The calculated energy barriers for hydrogen abstraction reactions of C_2H radical with HX [X=H, F, Cl, Br, CN, NC, NH_2, and PH_2], CH_4, C_2H_2, C_2H_4, and C_2H_6 are summarized in Table 2. We can compare the present results with those already reported in the literature. For example, the barrier heights for hydrogen abstraction from H_2, CH_4, C_2H_2, and C_2H_6 are reported to be 12.8, ∼10, 46, and 3 kJ/mol, respectively [14,20–22]. These barrier heights are found to be somewhat higher than the MPW1K results. However, we believe that, for the sake of consistency and uniformity, the MPW1K results could be used for the reactivity analysis, which is the main focus of this work.

The barrier heights cover a wide range for the present set of substrates. The hydrogen abstraction reaction between C_2H and C_2H_2 is characterized by the highest reaction barrier (37.2 kJ/mol), and that with C_2H_6 has the lowest barrier of 0.4 kJ/mol. Hydrogen abstractions from H_2S, NH_3, and PH_3 by C_2H are found to be barrier-less (negative activation barrier) processes. The barrier heights for the same process from HCN and HNC are also found to be quite large. Generally, the barrier height tends to reduce while going from the hydride of second-row element to the hydride of third-row element in the same group. It is clear from Table 2 that for H_2O, HCN, HNC, C_2H_2 and C_2H_4, the magnitude of the ZPE correction to the barrier height is substantial, amounting up to ∼25% of the classical barrier potential.

It is well known that Arrhenius pre-exponential factors per equivalent C–H bond are nearly constant, over a broad range of H-atom transfer reactions [32]. Hence, pre-exponential factors should be directly proportional to the number of equivalent abstract-able hydrogen atoms in the substrate, in accord with the reaction path degeneracy concept in transition state theory. A large pre-exponential factor coupled with a low reaction barrier will result in a greater rate constant value for hydrogen abstraction from CH_4, C_2H_4 and C_2H_6. In fact, ethane, featuring six primary hydrogens, which face a barrier to abstraction of only 0.4 kJ/mol, should have the largest rate constant value among the substrates studied here having a C–H bond.

3.2. Rationalization of the energy barriers using BDEs

Long back, Evans and Polanyi [33] suggested that for atom transfer reactions involving a given central atom, the barrier height should be proportional to the reaction enthalpy. Thus, within a series of similar reactions, the change in barrier height $\varDelta(\Delta E^{\#})$ should be related to the change in reaction enthalpy $\varDelta(\Delta H_r)$ as

$$\varDelta(\Delta E^{\#}) = \alpha \varDelta(\Delta H_r)$$

where $0 < \alpha < 1$ for exothermic reactions.

In the case of hydrogen abstraction reactions between C_2H radical and different substrates, the reaction enthalpy change $\varDelta(\Delta H_r)$ is the same as the change in the bond dissociation enthalpy of the breaking X–H bond of substrate. Thus, barrier heights for exothermic hydrogen abstraction reactions should show a linear correlation with the strength of the breaking X–H bond. This has been found to hold, in good approximation, for a great many reaction families. For example, Chandra and Uchimaru [34,35] showed recently that such correlations hold good for a series of haloalkanes and haloethers.

The covalent curve crossing model [36,37], where the main focus is on the avoided curve crossing of neutral (singlet and triplet) surfaces is also found to be useful for explaining the reactive behavior of many systems [38]. In this model, the curve crossing height (E_X) can easily be estimated from the expression

$$E_X = \frac{(D_{0R} + 0.5D_{0P})}{\left(1 + \frac{D_{0P}}{D_{0R}}\right)}$$

where D_{0R} and D_{0P} are the BDE values for the breaking and forming bonds in reactant and product, respectively. This theory essentially predicts a strong dependence of barriers on the reactant molecule bond strength, as discussed above in terms of the general principle stated by Evans–Polanyi [33].

The bond dissociation energy (BDE) values of the H–X bonds are given in Table 2. The BDE value is highest for the H–F bond (570.7 kJ/mol). This BDE value is somewhat higher than the BDE(C–H) value of 556.1 kJ/mol for C_2H_2. As a result, hydrogen abstraction from HF by C_2H is slightly endothermal and, therefore, not a favorable process. This is evidenced from the large barrier height for hydrogen abstraction from HF. For the other substrates, the BDE value of the breaking X–H bond is significantly lower than the BDE(C–H) value in C_2H_2, and the barrier height is found to be low. Fig. 1 shows the correlation between the adiabatic barrier heights (calculated here using unscaled ZPE corrections) for hydrogen abstraction and the BDE values for the breaking X–H bonds. Although this figure demonstrates a certain trend in reactivity that barrier height increases with the increase in the X–H bond strength, there are some exceptions (including HCl, HBr, HNC, and NH_3) from this correlation. In the case of HCl, HBr and HNC, the barrier heights are much higher than those expected from their X–H bond strength, whereas for NH_3, the barrier height is significantly lower than expected. In fact, our recent studies [23,24] demonstrated that the C_2H+NH_3 reaction is a barrier-free process. On the other hand, MPW1K results predict that barrier height decreases in the order HF > HCl > HBr, which is normally expected from their BDE(X–H) values, and it appears from the figure that they rather follow a separate correlation line.

An almost similar type of correlation can be observed (cf. Fig. 2) between E_X and barrier heights as well, and once again the above mentioned four molecules remain out of the correlation curve. In fact, it appears that considering a separate correlation for each type of breaking X–H bonds (such as in the cases of N–H, C–H, O–H, etc.) may be better. When we consider hydrogen abstraction for each type of bond (including the elements in the same group) separately, we always find that barrier height decreases with the weakening of the X–H bond. It may be interesting to mention here that ionization energy (IE) for NH_3 [10.8 eV], PH_3 [10.6 eV] and H_2S [10.4 eV] are significantly lower than the other substrates and incidentally hydrogen abstraction reactions from these three substrates have negative activation barrier.

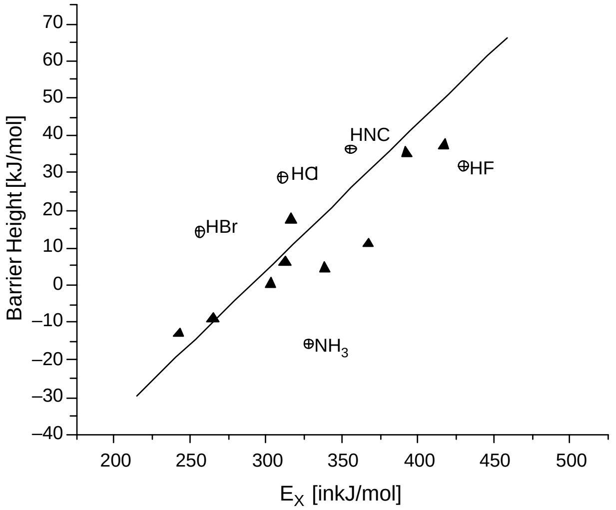

Fig. 2. Plot of barrier height for hydrogen abstraction reaction of C_2H with different substrates (given in Table 2) against the covalent curve crossing height, E_X, estimated from the equation given in the text.

Recently, Donahue and coworkers [39] put forward another approach for rationalizing radical–molecule abstraction reactions based on the crossing of reactant ground and ionic states at the transition state. In this model, the barrier height is related to the height of the ionic curve crossing. Since the initial ionic state energy is roughly equal to the (smaller) difference in ionization energy and electron affinity, IE–EA, the barrier heights should correlate with either IE or EA for a particular radical (like C_2H in our case). For the present set of substrates (S) and the given radical ($R=C_2H$), $IE_S–EA_R$ is lower than $IE_R–EA_S$. The ionization energy of the substrate should have a major role in determining the abstraction barrier height if the ionic curve crossing model holds for our systems. Nevertheless,

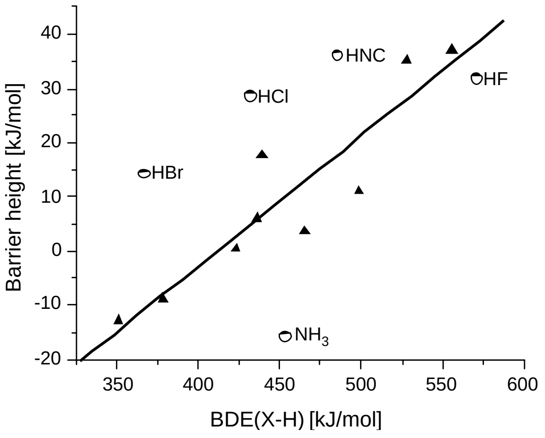

Fig. 1. Plot of MPW1K-calculated barrier height for hydrogen abstraction reaction of C_2H with different substrates (given in Table 2) against the bond dissociation energy of the breaking X–H bond.

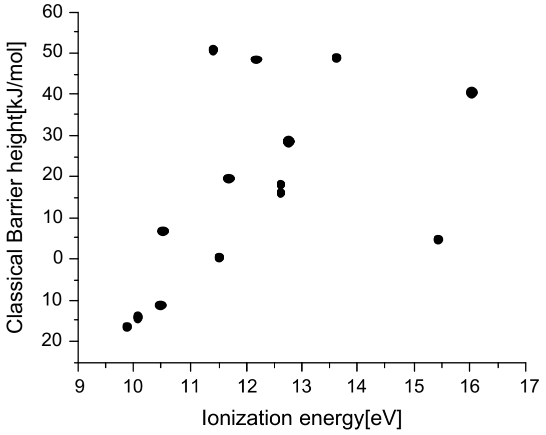

Fig. 3. Plot of barrier heights for hydrogen abstraction reaction of C_2H with different substrates (given in Table 2) against the ionization energies of substrates.

Table 3
The global softness [$S = 1/(IE - EA)$], vertical ionization energy (IE) and electron affinity (EA), and the chemical potential [$\mu = -(IE + EA)/2$] for the systems as obtained from B3LYP/6-311G(d,p)

System	S (a.u.$^{-1}$)	IE (eV)	EA (eV)	μ (eV)
C_2H	2.268	14.55	2.55	−8.55
H_2	1.340	16.53	−3.77	−6.38
HF	1.411	16.03	−3.26	−6.39
HCl	1.820	12.83	−2.12	−5.36
HBr	2.004	11.81	−1.77	−5.02
H_2O	1.741	12.50	−3.13	−4.69
H_2S	2.096	10.43	−2.55	−3.94
HCN	1.577	13.73	−3.52	−5.11
HNC	1.800	12.18	−2.94	−4.62
NH_3	1.942	10.80	−3.21	−3.80
PH_3	2.075	10.56	−2.55	−4.01
CH_4	1.553	14.17	−3.36	−5.41
C_2H_2	1.856	11.36	−3.30	−4.03
C_2H_4	2.040	10.56	−2.77	−3.90
C_2H_6	1.772	12.25	−3.10	−4.58

as seen in Fig. 3, we could not find any general correlation between barrier height and ionization energy. This clearly shows that the BDE value of the breaking X–H bond is the most important factor in determining the barrier height for hydrogen abstraction. However, the ionic curve crossing model may be important for NH_3, PH_3 and H_2S, because of their lower ionization energies.

The DFT-based reactivity parameters as obtained from the B3LYP/6-311G(d,p) results are listed in Table 3. As expected, the softness value increases while going from the hydrides of first row elements to the hydrides of second row elements, because of the larger size for the latter. But softness values do not provide any general reactivity trend toward hydrogen abstraction. In fact, if the ionic curve crossing model is important in determining the reaction barrier, a correlation should exist between chemical potential [μ] and barrier height. That is due to the fact that the chemical potential determines the ease with which an electron is transferred from one system to the other. But we could not find any such correlation. Similarly, we could not find any consistent correlation between the barrier heights and the local properties (Fukui functions and local softnesses) such as the case in other radical reactions [40].

4. Conclusions

Electronic structure calculations were used to probe the transition structure geometries and energy barriers of the hydrogen abstraction reactions of the ethynyl radical with simple hydrogen compounds. The MPW1K density functional method seems to provide reliable and consistent barrier heights for hydrogen abstraction reactions. It is confirmed that abstraction of H-atom bonded to a second-row element is more difficult to that from the third-row counterpart. For saturated hydrocarbons, the barrier decreases with increasing substitution on the carbon center (in decreasing order: CH_4, $-CH_3$, $>CH_2$,…). The BDE value of the breaking X–H bond appears to be the most important factor in determining the barrier height for hydrogen abstraction. However, the ionic curve crossing model may also be important for explaining the reactive behavior of systems like NH_3, PH_3 and H_2S, due to their low ionization energies. Hydrogen halides stay out of the reactivity correlations studied here and mechanism of their hydrogen abstraction reactions need to be studied further for better understanding.

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