Theoretical study of cyclopropenones and cyclopropenethiones: decomposition *via* intermediates

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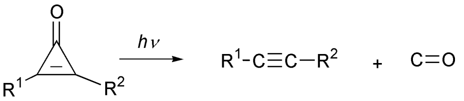
The mechanism of the decomposition of cyclopropenones and cyclopropenethiones giving acetylenes (R^1–C≡C–R^2 with $R^1 = R^2$ = H, F) plus carbon monoxide and carbon monothioxide, respectively (C=X, X = O, S) has been probed using DFT (B3LYP/6-311G(d,p)) and MO (CCSD(T)/6-31G(d)) calculations. It turns out that the decomposition is stepwise, forming first an intermediate which has the properties of a semi-carbene, semi-zwitterion, whose structure is best described in both cases as a resonance hybrid between a carbene and a zwitterion. Using the PCM model, study of the solvent effect on the reactions in three continua (water, acetonitrile and benzene) shows that solvents do not affect the shape of the potential energy surfaces but tend to stabilize all the isomers. Estimation of the first vertical excited states by CIS and TD-B3LYP methods suggests that the photochemical reactions are likely to take place in the ground state rather than in an excited state. Hardness and polarizability profiles along the reaction paths show that there is a maximum in the polarizability profile besides an inverse relationship between hardness and polarizability. Fluorine substitution tends to stabilize the intermediate making it a genuinely detectable moiety.

Introduction

Cyclopropenones are of special interest as they are known as stable compounds containing an exocyclic carbonyl group attached to a three-membered ring. The parent compound, cyclopropenone, was first synthesized in 1967,[1] isolated and subsequently characterized by Breslow *et al.*[2,3] Various properties of this compound were also later reported.[4–6] In most cases, following pyrolysis[7] or photochemical decarbonylation,[8–16] cyclopropenones (**I**) are converted into acetylenes (**II**) and carbon monoxide as illustrated in equation (1):



(1)

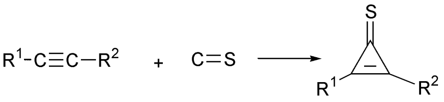
I **II**

Although this kind of reaction is of considerable interest in organic synthesis, its mechanism is not yet well understood. Kresge and co-workers[11–15] have indeed employed the reaction (1) as a method to generate *in situ* the novel class of ynols (**II**, R^2 = OH) and to study the reactivities of these compounds. A number of fundamental questions regarding the decarbonylation of cyclopropenones (**I**) to acetylenes remain, however, unanswered: (i) The main question is whether the decarbonylation of (**I**) is a concerted or stepwise process. (ii) Does this reaction take place in the electronic ground state or must it be in an excited state, as required in flash photolytic techniques?[3–6,11–16] (iii) How important is the solvent effect on this kind of reaction? (iv) Which factors (*e.g.*, substituents) favor the decarbonylation of cyclopropenones to acetylenes?

In an attempt to provide some elements of an answer to those questions posed by experimental results and in relation with our recent theoretical studies on analogous reactions of hydrogen isocyanide with acetylenes[17] and also with doubly-bonded dipolarophiles,[18–22] we have carried out quantum chemical calculations on reaction (1) for three simple cases, the parent system and two fluorinated systems ($R^1 = R^2$ = H, R^1 = H, R^2 = F and $R^1 = R^2$ = F) in order to determine the effect on various intermediates being formed in those reactions upon fluorine substitution.

Moreover, in order to be able to compare our studies with previous works[17–22] and in view of the principle of microreversibility, we have also investigated the reverse reactions of (1), namely the carbonylation of acetylenes. We set out to obtain quantitative information on various structural and energetic aspects of both types of reaction. In the simplest parent case, $R^1 = R^2$ = H, we have also constructed hardness and polarizability profiles along the intrinsic coordinate (IRC) pathways and searched for correlations between these electronic properties and the position of the transition structures as well as the calculated energy barriers. The solvent effect in three typical solvents with strongly different relative permittivities including water, acetonitrile and benzene, have also been studied.

In contrast to the widespread interest in cyclopropenones, both in theoretical and experimental studies, little is known about the higher homologues cyclopropenethiones (**III**), also a member of the substituted cyclopropenes group. To extend the scope of the study, we have also performed similar calculations for the combination of C=S and acetylenes, as illustrated in equation (2):



(2)

II **III**

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Table 1 Differences (in eV) in LUMO − HOMO energies and (IE − EA) of C=X (X = O, S) and substituted acetylenes (R)

Structure	E_{LUMO}[a] *EA*[b]	E_{HOMO}[a] *IE*[b]	E_{LUMO}(R) − E_{HOMO}(C=O)[a] *IE(C=O) − EA(R)*[b]	E_{LUMO}(C=O) − E_{HOMO}(R)[a] *IE(R) − EA(C=O)*[b]	E_{LUMO}(R) − E_{HOMO}(C=S)[a] *IE(C=S) − EA(R)*[b]	E_{LUMO}(C=S) − E_{HOMO}(R)[a] *IE(R) − EA(C=S)*[b]
C=O	**4.4**	**−14.9**				
	−2.6	*14.2*				
C=S	**1.9**	**−12.5**				
	−0.3	*11.5*				
H–C≡C–H	**5.9**	**−10.9**	**20.8**	**15.3**	**18.4**	**12.9**
	−3.3	*11.4*	*17.5*	*14.0*	*14.8*	*11.6*
H–C≡C–F	**6.6**	**−11.2**	**21.5**	**15.6**	**19.1**	**13.1**
	−3.4	*11.3*	*17.5*	*13.9*	*14.9*	*11.6*

[a] Frontier orbital energy taken from HF/6-31G(d) wavefunctions (in bold). [b] Vertical ionization energies and electron affinities obtained from B3LYP/6-311G(d,p) computations (in italic).

Methods of calculation

Structures and energies were calculated with the aid of the Gaussian 98 set of programs.[23a] All geometrical parameters were initially optimized at the HF/6-31G(d) level and then reoptimized using B3LYP/6-311G(d,p) level. Zero-point vibrational energies (ZPEs) were calculated at B3LYP/6-311G(d,p) level and were scaled down by a factor of 0.98.[23b] In the simplest case, $R^1 = R^2 = H$, geometry optimizations were also performed at CCSD(T)/6-31G(d) to verify the existence of intermediates. To follow the variations of the reactivity descriptors along the chemical processes, IRC calculations were carried out starting from the transition structure of interest at the B3LYP/6-311G(d,p) level. Atomic charges were taken from electrostatic potential driven (ESP) and natural population analysis (NPA) by using the MK and NPA options in the Gaussian program. The vertical first excitation energies were estimated by using the configuration interaction including only single-excitations CIS/6-311++G(d,p) method and time-dependent density functional theory (TD-B3LYP/6-311++G(d,p)). The solvent effect has been probed with the polarisable continuum model (PCM)[23c] using SCRF keyword in the Gaussian program. The relative permittivities were taken as equal to 78.39 for water, 36.64 for acetonitrile and 2.247 for benzene. In this paper, bond distances are given in angstroms, bond angles in degrees, total energies in hartrees, zero-point and relative energies in kilojoules per mole.

Results and discussion

As mentioned above, we have examined both directions of the equation (1). For the sake of convenience, we first present an analysis of the addition of C=X to acetylenes followed by the decomposition of the three-membered rings.

Analysis of the nature of the reaction partners

First of all, we need to classify the partners in the bimolecular reactions as electrophile or nucleophile. Table 1 lists the LUMO − HOMO energy differences, taken from HF/6-31G(d) calculations, and also the differences in vertical ionization energies (IE) and electron affinities (EA) derived from B3LYP/6-311G(d,p) computations for C=X (X = O, S) and substituted acetylenes (R).

It can be observed from Table 1 that, in all cases, the energy gaps of $\mathrm{LUMO_{C=X}} - \mathrm{HOMO_R}$ are smaller than those of $\mathrm{LUMO_R} - \mathrm{HOMO_{C=X}}$, which is also confirmed by the differences between IE and EA. Using a simple perturbation theory argument, the smaller the frontier orbital energy gap, the larger the stabilizing interaction energy between two reactants. As such, in this case, the C=X (X = O, S) species behaves as an electrophilic reagent and the substituted acetylenes as a nucleophilic reagent. This is in line with the results obtained earlier on the [2 + 1] cycloadditions of hydrogen isocyanide to acetylenes,[17] in which acetylenes also behave as a nucleophilic reagent.

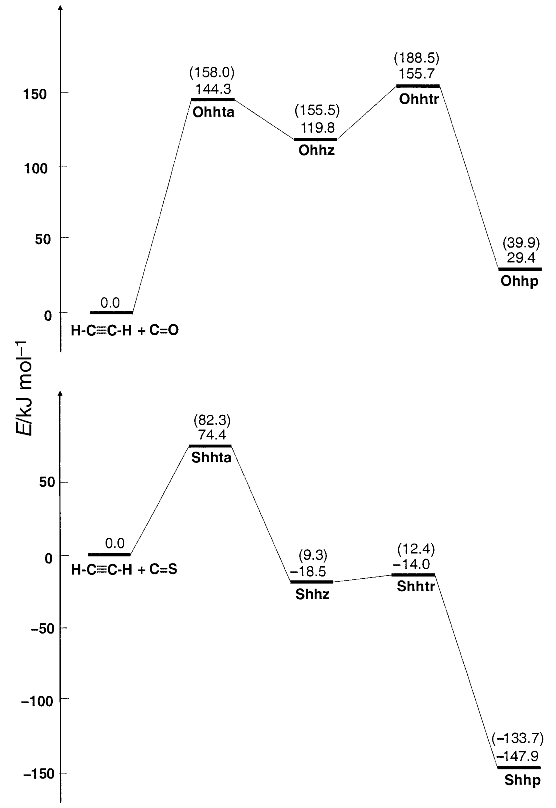


Fig. 1 Schematic potential energy profiles for the two-step addition of C=X (X = O, S) to H–C≡C–H. Relative energies obtained at B3LYP/6-311G(d,p) and CCSD(T)/6-31G(d) (values in parentheses) using B3LYP/6-311G(d,p) optimized geometries and corrected for zero-point contributions.

Reaction of unsubstituted acetylene H–C≡C–H with C=X (X = O, S)

Potential energy surfaces. Fig. 1 summarizes the relative energies for the addition of C=X (X = O, S) to H–C≡C–H computed at both B3LYP/6-311G(d,p) and CCSD(T)/6-31G(d) levels. Fig. 2 displays the main geometrical parameters of the equilibrium and transition structures, optimized at both B3LYP and CCSD(T) levels with the basis set mentioned above. The structures shown include **Xhhta**, **Xhhz**, **Xhhtr** and **Xhhp** (X = O, S). The separated systems (C=X + H–C≡C–H) are omitted for simplicity. In general, the structures are labeled by a combination of letters, in which **O** stands for X = O, **S** for X = S, **h** for $R^1 = R^2 = H$, **t** for transition structure, **a** for addition, **r** for ring closure, **z** for intermediate and **p** for the three-membered ring.

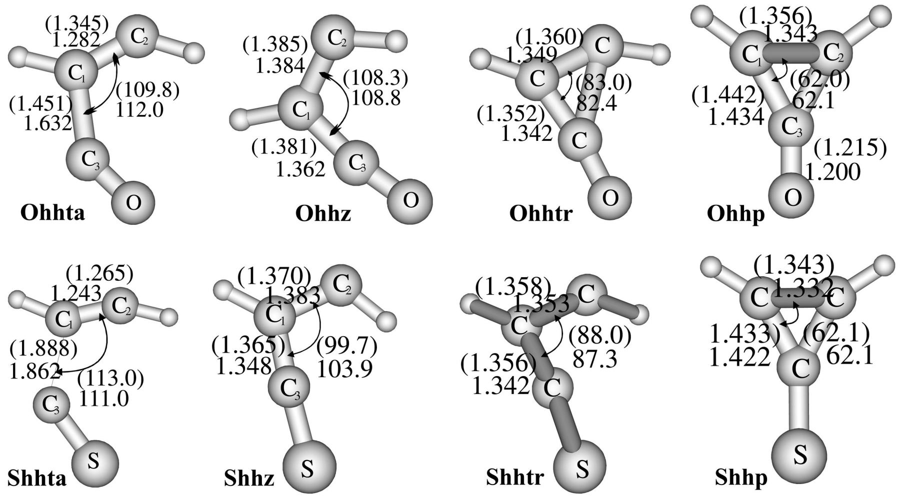


Fig. 2 Main geometrical parameters of the equilibrium and transition structures of the addition of C=X (X = O, S) to H–C≡C–H. Optimized values are from B3LYP/6-311G(d,p) and CCSD(T)/6-31G(d) (in parentheses) levels.

As can be seen in Fig. 1, the addition turns out to be a two-step process in which the rate-determining step is different in going from C=O to C=S. In the C=O case, the ring-closure step is rate-determining and the intermediate lies in a shallow potential well. In contrast, the initial addition is rate-determining in the C=S case and the transition state structure for ring-closure only lies a few kJ mol^{-1} higher in energy than the intermediate. Coupled-cluster calculations confirm those observations and the existence of intermediates. The difference between two processes arises no doubt from the relative energies between the three-membered ring and its corresponding fragments. In the oxygen case, the fact that the ring is less stable than the fragment puts the transition state for ring opening **Ohhtr** up high on the energy scale. In the sulfur case, the large exothermocity of the C=S addition markedly reduces the energy barrier for ring-closure of the intermediate **Shhz**. Proceeding in the ring decomposition direction, the C=S elimination from cyclopropenethione **Shhp** is associated with an energy barrier of 212 kJ mol^{-1}, which is by far more difficult to achieve than the decarbonylation of cyclopropenone **Ohhp** (127 kJ mol^{-1}).

Fig. 2 indicates that the C^1–C^3 intermolecular distance is 1.63 Å in **Ohhta** and 1.86 Å in **Shhta**, which is shorter than the usual distance (by about 2.0 Å) for C–C bond formation or breaking. This is presumably due to the presence of the C=X moiety.

Intrinsic reaction coordinate calculations starting from **Xhhta** show that this transition structure is actually connecting the separated reactants (C=X + H–C≡C–H) with the corresponding intermediate **Xhhz**. The latter is characterized by a short C^1–C^3 bond distance and a quite open (C^2–C^1–C^3) angle (1.36 Å and 109° in **Ohhz** and 1.35 Å and 104° in **Shhz**). The C^1–C^2 bond distance is stretched from 1.20 Å in acetylene to 1.38 Å in both intermediates. For its part, the **Xhhtr** is identified by IRC calculations as the transition structure linking the intermediate and the three-membered ring product.

The existence of the intermediates **Xhhz** is consistent with results found in previous work on the addition of HN≡C to acetylenes.[17] The C^1–C^3 bond distance in **Xhhz** is about 1.36 Å, whereas the C^1–C^2 bond distance is 1.38 Å and the angle (C^1–C^3–O) is nearly 180°. Such geometrical parameters suggest that **Xhhz** could be described as either a carbene or a zwitterion. To verify the C^1–C^3 bond nature of the intermediates **Xhhz**, we have also optimized typical structures of a ketene (CH_2=C=O) and the corresponding cation (CH_3–C≡O^+). Calculated results performed at the B3LYP/6-311G(d,p) level are recorded in Fig. 3. Accordingly, the C–C and C–O bond distances in the ketene structure are 1.31 and 1.16 Å, whereas those parameters in the ion moiety are 1.43 and 1.11 Å. In the intermediate **Ohhz**, the values are 1.36 and 1.15 Å, respectively. It is of interest to note that the C^1–C^3 bond distance in **Ohhz** lies between a single and a double bond C–C distance, so it is suggested that this intermediate has the nature of a semi-carbene, semi-zwitterion and its structure is a resonance hybrid of the two limiting structures shown:

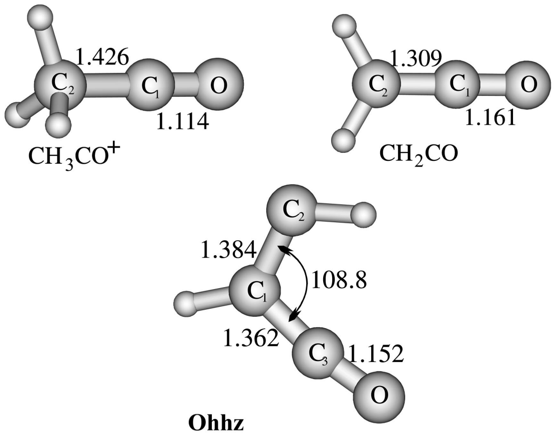


Fig. 3 B3LYP/6-311G(d,p) geometry of the intermediate **Ohhz** and two typical structures of a ketene (CH_2C=O) and the corresponding cation (CH_3C≡O^+).

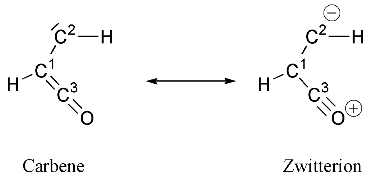


Fig. 4 plots the highest occupied molecular orbitals, HOMO, HOMO-1, HOMO-2 of the intermediates for both C=O and C=S additions. The HOMO of these singlet intermediates has an in-plane σ orbital at C^2 whereas in the HOMO-1, it is a π orbital. In this case, the π orbital is more stabilized, presumably due to the effect of conjugation, in which the electrons flow from C=O to the C^2 atom.

Furthermore, we also computed the triplet state of the intermediate **Ohhz** to compare with its singlet counterpart. The triplet structure turns out to be higher in energy than the singlet moiety by about 70 kJ mol^{-1}. The SOMO of **Ohhz** triplet is a π orbital at C^2 and the SOMO-1 is a σ orbital (*cf.* Fig. 5). Overall, we can conclude that the intermediate **Xhhz** has the properties of a singlet carbene. It is in contrast with the case of methylene (CH_2)[24] and methylcarbene (CH_3CH)[25] in which the ground state is a triplet one.

Table 2 ESP and NPA (in parentheses) charges (in atomic units) of $CH_3–C≡O^+$ and **Xhhz** (X = O, S) calculated at B3LYP/6-311G(d,p)

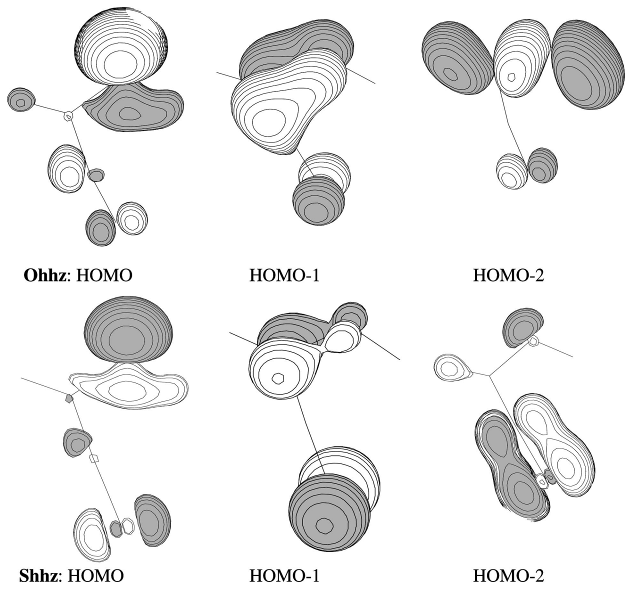
Position[a]	$CH_3–C≡O^+$	**Ohhz**	**Shhz**
C^1	0.702 (0.972)	0.210 (−0.546)	0.414 (−0.449)
C^2	−0.532 (−0.763)	−0.623 (−0.136)	−0.590 (−0.084)
C^3		0.324 (0.743)	−0.146 (−0.039)
X (O or S)	−0.030 (−0.191)	−0.219 (−0.400)	0.027 (0.211)
Sum of charges on C · · · X group	0.672 (0.781)	0.105 (0.343)	−0.119 (0.172)
Sum of charges on acetylene group		−0.413 (−0.682)	−0.176 (−0.533)

[a] Singlet state. See Fig. 3 for atoms numbering.

Table 3 Geometrical parameters and rotational constants (MHz)[a] of cyclopropenone

Source	$r(C^1C^3)$/Å	$r(C^1C^2)$/Å	$r(C^3O)$/Å	$\alpha(C^2C^1C^3)$/°	A/MHz	B/MHz	C/MHz
Microwave study[b]	1.412	1.302	1.212	62.3	32046.0	7824.9	6280.7
Microwave study[c]	1.423	1.349	1.212	61.7			
MP2/6-31G(d)[c,d,e]	1.437	1.352	1.212	61.9			
B3LYP/6-31G(d)[d]	1.435	1.344	1.204	62.1			
B3LYP/6-311G(d,p) (this work)	1.434	1.343	1.200	62.1	32310.9	7816.0	6293.6
CCSD(T)/6-31G(d) (this work)	1.442	1.356	1.215	62.0	21683.7	7694.9	6191.3

[a] See Fig. 2 for atoms numbering. [b] Ref. 4. [c] Ref. 6. [d] Ref. 16. [e] Ref. 26.


Ohhz: HOMO HOMO-1 HOMO-2

Shhz: HOMO HOMO-1 HOMO-2

Fig. 4 Highest occupied molecular orbitals of **Ohhz** and **Shhz**.

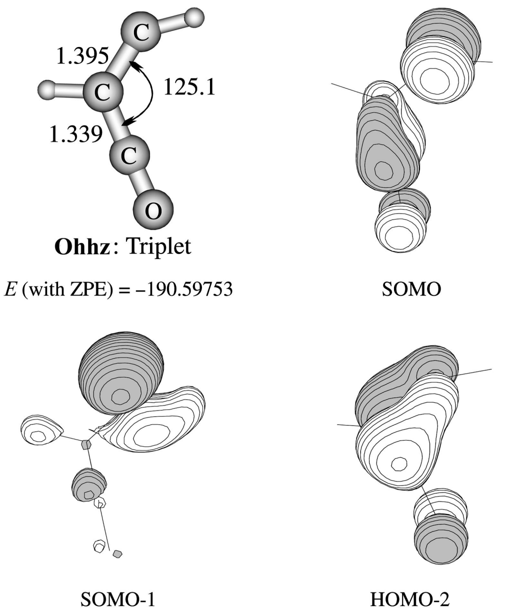


Fig. 5 Structure and SOMO, SOMO-1 and HOMO-2 of **Ohhz** triplet. Values obtained at B3LYP/6-311G(d,p). The total energy of the singlet is E (with ZPE) = −190.62421 hartree.

Table 2 emphasizes a larger concentration of negative charge on the acetylene group, whereas the C=X group is positively charged. As such, the intermediates **Xhhz** show a certain zwittterion character, rather than a biradicalar structure. In conclusion, **Xhhz** has both the properties of a singlet carbene and a zwitterion. Therefore, we can propose that it is a semi-carbene, semi-zwitterion and its structure is likely to be switched between that of a carbene and a zwitterion.

It is also interesting to compare the geometrical parameters of cyclopropenone calculated from this work with those obtained by microwave studies[4,6] and quantum chemical calculations.[6,16,26] According to Table 3, the calculated geometrical parameters in this work corroborate well with experimental and theoretical studies in the literature. Besides, we can also observe that the rotational constants obtained from microwave study[4] are better approached by the values optimized from B3LYP methods than by those from CCSD(T) methods.

In summary, our calculations reveal the existence of an intermediate in the decomposition of cyclopropenone and its thio-analogue.

Solvent effect. As far as we aware, until now there has been no study of the solvent effect on the carbonylation of acetylenes. Chiang *et al.*[11–15] only studied the solvent effect on the stability of their products in the decarbonylation of cyclopropenones. For example, the photodecarbonylation of hydroxycyclopropenones[15] produces ynolate anions ($R–C≡C–O^-$) when the solvent is water, but it gives ynols (R–C≡C–OH) in acetonitrile and dimethylformamide solutions. In those studies, the authors did not, however, pay attention to the solvent effect on the mechanism in the transformation from cyclopropenones to acetylenes.

In this work we probe the solvent effect on the carbonylation of acetylenes in three continua, one with a high relative permittivity ε (water), one with a medium ε (acetonitrile) and one with a low ε (benzene). An SCRF method with a polarizable continuum model (PCM) has been used. Although this method has some disadvantages, it seems to be a good guide in indicating trends. Due to the lack of analytical gradients, the geometry could not be optimized in solvent; therefore, only single-point SCRF calculations were performed at the B3LYP gas phase geometries using the 6-311G(d,p) basis set. As seen in Table 4, the solvent does not affect the shape of the potential energy surface, even though in most cases solvents tend to stabilize all structures relative to the reactants, especially the product **Ohhp**, irrespective of their polarity. These observations are in agreement with recent results on 1,3-dipolar cycloadditions.[27]

Estimation of the vertical first excitation energies. Different groups[3–6,11–16] have used flash photolytic techniques in experimental studies of the decarbonylation of cyclopropenones. Thus there is a legitimate question as to whether this technique is a way to supply the energy for the reaction to take place more easily in the ground state, or to promote the studied molecules to an excited state in such a way that starting from such a state the reaction can readily happen.

To answer this question, we need to estimate the first vertical excitation energies. If this energy is small, then the reaction in this excited state is probable. Calculations have been performed by using the CIS/6-311++G(d,p) and time-dependent density functional theory (TD-B3LYP/6-311++G(d,p)) methods. The results are summarized in Table 5. It can be seen that it requires a large amount of energy to promote an electron to the first excited state relative to the activation energy and the energy of reaction. As such, it seems reasonable to conclude that all the studied reactions above take place in their ground state rather than in an excited state. The flash photolytic techniques used in experiments are merely a way of giving energy to the reacting systems.

Reaction of fluoroacetylene H–C≡C–F with C=X (X = O, S)

Although fluorine is well known as the most electronegative element, it also behaves in many cases as a π-donor group. Thus, fluorine strongly stabilizes the singlet carbene through a π-donor effect. We wanted to know whether it also stabilizes the carbene intermediate identified above. In the present case, we consider the condensation of H–C≡C–F to C=O and C=S. The structures now are labeled with **h** (for $R^1 = H$) and **f** (fluorine for $R^2 = F$). Figs. 6, 7, 8 and 9 record results from B3LYP/6-311G(d,p) calculations.

Due to the unsymmetrical nature of the acetylenic derivative, addition of C=X is now possible at two carbon centers leading to two distinct reaction paths characterized by two intermediates **Xhfz1** and **Xhfz2**. As seen in Fig. 6, the intermediate **Xhfz2** having a CF-carbene framework is not only more stable than **Xhfz1** but it also lies in a really deep potential well either for X = O or X = S. Both in C=O and C=S cases, the attack to the substituted carbon *via* **Xhfta1** is more favorable. The energy barrier to the initial attack is also reduced considerably, compared with the unsubstituted case. Note that in Fig. 9, although **Ohfz2** shows the interaction between the orbitals of fluorine and the carbene center atom (C^2) leading to the stabilization of the intermediate, it is not located in the favored reaction path. The marked difference between the addition of C=O and C=S is that while in the former, the addition to the substituted carbon of acetylene is much favored over the other (by 82 kJ mol^{-1}), the energy gap becomes much smaller (5 kJ mol^{-1}) in the latter. The reason for this is not clear to us yet. Also, fluorine turns out to stabilize the cyclic ketone form relative to the fragments.

Figs. 7 and 8 show that the C^2–C^3 bond distance in **Xhfz1** is about the same as that in **Xhhz** (1.37 Å in **Ohfz1** and 1.35 Å in **Shfz1**). So, **Xhfz1** turns out to be a semi-carbene, semi-zwitterion, as in the unsubstituted case.

Table 4 Relative energies (in kJ mol^{-1}) of related structures in the H–C≡C–H + C=O reaction, in the gas phase and in solutions, using the PCM at B3LYP/6-311G(d,p)

Structure	Gas phase	Water ($\varepsilon = 78.39$)	Acetonitrile ($\varepsilon = 36.64$)	Benzene ($\varepsilon = 2.247$)
H–C≡C–H + C=O	0.0	0.0	0.0	0.0
Ohhta	144.3	138.1	135.7	135.2
Ohhz	119.8	98.6	100.5	102.3
Ohhtr	155.7	133.3	135.0	137.8
Ohhp	29.4	−8.5	−6.8	1.1

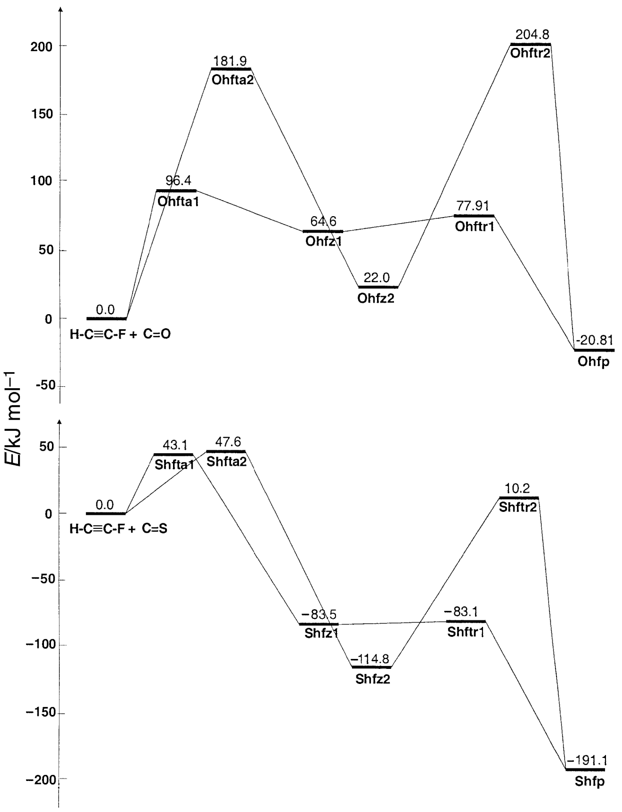


Fig. 6 Schematic potential energy profile for the two-step addition of C=X (X = O, S) to H–C≡C–F. Relative energies obtained at B3LYP/6-311G(d,p) using B3LYP/6-311G(d,p) optimized geometries and corrected for zero-point contributions.

Table 5 Vertical first excitation energies calculated from CIS/6-311++G(d,p) and TD-B3LYP/6-311++G(d,p) of related structures in the H–C≡C–H + C=O reaction

Structure	Ground State Rel. Energy/kJ mol^{-1}	Vertical first excitation energy TD-B3LYP/6-311++G(d,p) eV	 kJ mol^{-1}	 CIS/6-311++G(d,p) eV	 kJ mol^{-1}
C=O		8.4	812.6	9.1	876.1
H–C≡C–H		6.7	648.9	6.4	618.9
H–C≡C–H + C=O	0.0				
Ohhta	144.3	3.0	286.3	3.2	311.0
Ohhz	119.8	2.4	231.5	2.6	249.0
Ohhtr	155.7	2.6	249.6	2.7	258.6
Ohhp	29.4	4.0	390.2	5.9	570.1

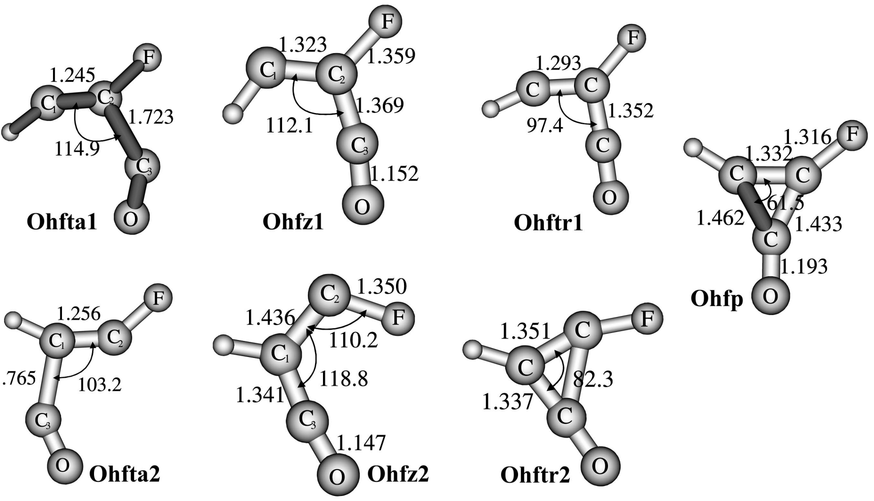


Fig. 7 Geometries along the reaction path in the reaction of H–C≡C–F + C=O. Optimized values obtained at B3LYP/6-311G(d,p).

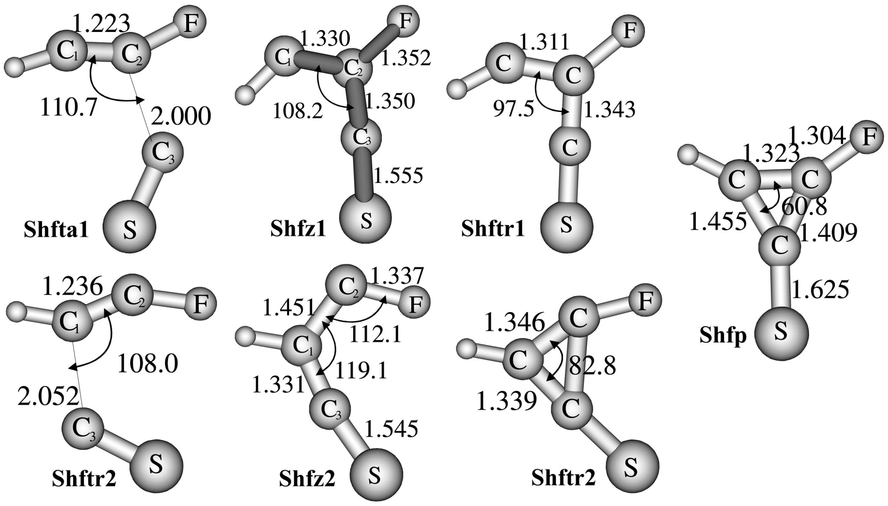


Fig. 8 Geometries along the reaction path in the reaction of H–C≡C–F + C=S. Optimized values obtained at B3LYP/6-311G(d,p).

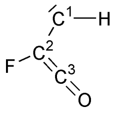
Reaction of difluoroacetylene F–C≡C–F with C=X (X = O, S)

In an attempt to gain more insight into the evolution of the attack of C=O when passing from acetylene to monofluoroacetylene, we also compute the difluoroacetylene case (F–C≡C–F) at the same B3LYP level. Calculated results are shown in Figs. 10 and 11.

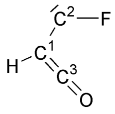
It is interesting to compare Fig. 10 (C=O + F–C≡C–F) with Fig. 1 (C=O + H–C≡C–H) and Fig. 6 (C=O + H–C≡C–F). It is clear that following successive substitution of hydrogen by fluorine atom in acetylene, the reduction of the energy barrier and the stabilization of the intermediates become remarkably high.

The activation energy for the favored reaction path is reduced from 144.3 kJ mol^{-1} in **Ohhta** (the **TS** for the attack of C=O on H–C≡C–H), *via* 96.4 kJ mol^{-1} in **Ohfta1** (the **TS** for the attack of C=O on substituted carbon of H–C≡C–F) to 67.6 kJ mol^{-1} in **Offta** (the **TS** for the attack of C=O on F–C≡C–F). This is presumably due to the interaction of the 2p(π) orbital of the carbon center with the fluorine lone pairs resulting in a more negative charge on this carbon of the acetylene. As a consequence, the attack of C=O (electrophilic reagent) to this site becomes more favorable. Note that the activation energy in **Ohfta2** (the **TS** for the attack of C=O on the unsubstituted carbon of H–C≡C–F) is much higher than in **Ohfta1**.

However, when the intermediates are already formed, those having the fluorine attached to the carbene center atom (carbon C^2 in the intermediate **Ohfz2**) will be more stabilized. As can be seen from Fig. 6, the intermediate **Ohfz2** is lower in energy than **Ohfz1**. This is no doubt due to the fact mentioned above, that the π-electron donation of fluorine reduces the π-electron deficiency of the carbene center.



Ohfz1



Ohfz2

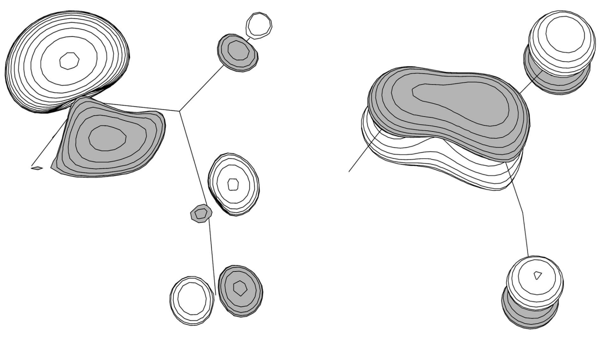
Note that the C–F bond distance of 1.307 Å and F–C–F angle of 104.5° in CF_2 (at the same level of theory) are smaller than the corresponding values in **Ohfz2** (Fig. 7) and **Offz** (Fig. 11). This can be explained by the electron-withdrawing effect of the O=C=CH- or O=C=CF- moieties resulting in a reduction of the concentration of electrons in the center atom of this carbene.

In summary, it can be concluded that, in this case, fluorine also acts as a strong π-donor group whose presence in the acetylene moiety tends to reduce the energy barrier for the initial attack and to stabilize the intermediates.

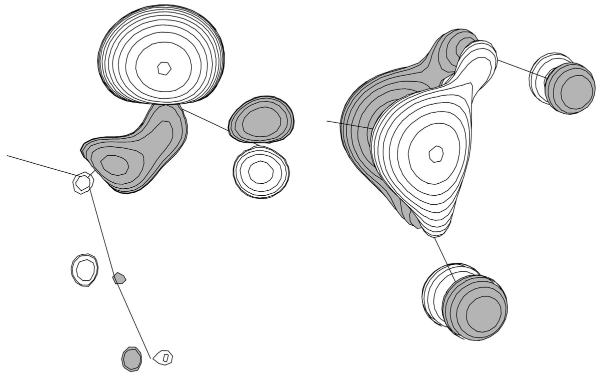
Profiles of hardness, polarizability and activation energy along an IRC path

From the principle of maximum hardness (PMH)[28,29] which states that, "there seems to be a rule of nature that molecules arrange themselves so as to be hard as possible", it has been shown[30–33] that the hardness profile along a reaction path passes through a minimum at or near the transition state for various types of reaction, such as inversion, exchange, deformation and isomerization. Recently, based on the inverse relationship between hardness and polarizability, a similar formulation on the polarizability has been proposed,[34] which states that "the natural direction of evolution of any system is toward a state of minimum polarizability", so it implies that the polarizability profile along a reaction path should pass through a maximum near or at the transition state. A lot of work[17,35] has been done to verify the validity of the above two statements. It was stated that the PMH holds under constant chemical potential (μ) and external potential ($v[r]$), but for a chemical reaction, neither μ nor $v[r]$ can be kept constant. On the other hand, in some cases, the PMH seems to be valid even though μ varies along the reaction coordinate,[35f] but in other cases[17,35a] there is no clear-cut relationship between hardness and activation energy. Therefore, the conditions for a practical application of such principles remain not well-understood.

In an attempt to verify them again, we constructed the hardness, polarizability and activation energy profiles along the intrinsic reaction coordinate (IRC) pathway only for the case of H–C≡C–H with C=X (X = O, S). The results are displayed in Fig. 12. There appears an extremum in the polarizability profile



Ohfz1: HOMO HOMO-1



Ohfz2: HOMO HOMO-1

Fig. 9 Highest occupied molecular orbitals of **Ohfz1** and **Ohfz2**.

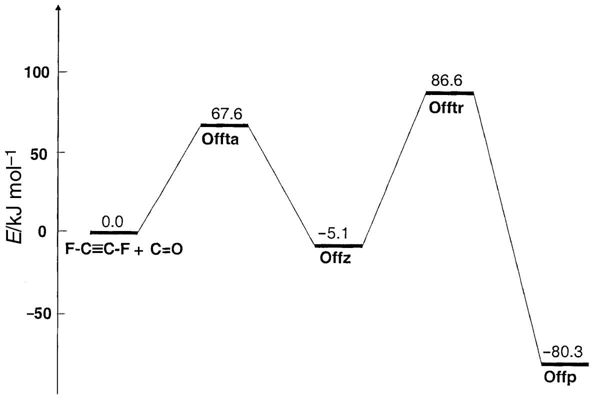


Fig. 10 Schematic potential energy profile for the two-step addition of C=O to F–C≡C–F. Relative energy obtained at B3LYP/6-311G(d,p) and corrected for zero-point contributions.

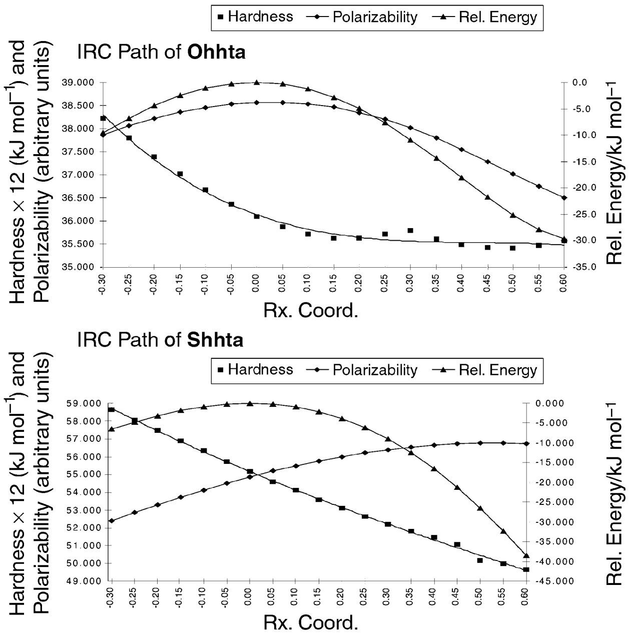


Fig. 12 Profiles of hardness (in kJ mol−1) and polarizability (in au) along the IRC pathways of the H–C≡C–H + C=X (X = O, S) reactions.

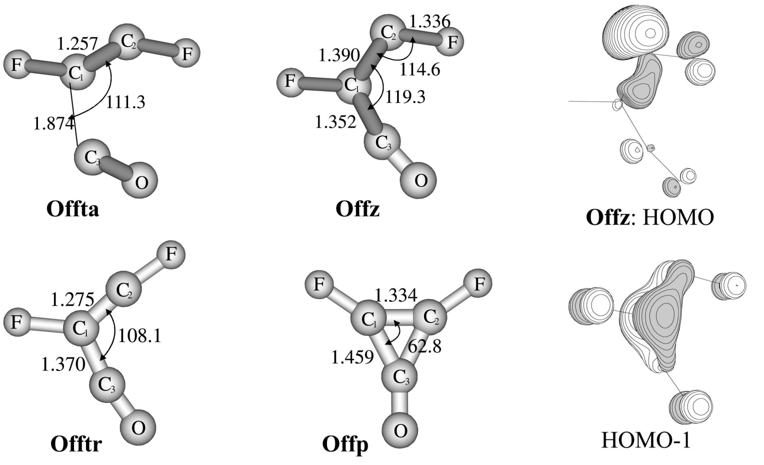


Fig. 11 Geometrical parameters of the points on the F–C≡C–F + C=O reaction and highest occupied molecular orbitals of **Offz**. All values are obtained at B3LYP/6-311G(d,p).

in the case of the reaction with C=O near the transition state, though there is no extremum at all in the sulfur case. A reverse relationship between hardness and polarizability profile emerges from both figures. Those observations are in the same vein as the previous work.[17]

Conclusions

In summary, the following conclusions can be drawn:

a) In the studied reactions, C=X (X = O, S) acts as an electrophile and substituted acetylenes as a nucleophile.

b) The addition of C=X to a substituted acetylene happens in two steps: first, an asynchronous initial attack of C=X to one of the carbons of the acetylene moiety, forming an intermediate, and second, a ring-closure step leading to a cyclopropenone or cyclopropenethione product. The rate-determining step depends on either the substituents or the nature of X (X = O, S). In some cases, it is the initial addition, whereas in the others it is the ring-closure step.

c) The intermediate has the properties of a semi-carbene, semi-zwitterion and its structure is switched between two structures of a carbene and a zwitterion. In the difluoro-substituted system, the intermediate is a genuinely stabilized species.

d) In the C=O case, due to the high thermodynamic stability of carbon monoxide, most intermediates and cyclopropenones lie higher in energy than the separated systems (C=O + R^1–C≡C–R^2). This is in contrast to the C=S case, where all intermediates, and especially cyclopropenethiones, lie much lower in energy than the separated systems (C=S + R^1–C≡C–R^2).

e) The solvent effect does not affect the shape of the potential energy surfaces. In other words, the solvent effect on the reaction is small, and tends to stabilize all the isomers.

f) Proceeding with the decomposition of the three-membered ring, it requires a large amount of energy to promote an electron to form the lowest-lying excited state, which lies above the highest-lying transition state. Thus all investigated reactions are likely to take place in the ground state rather than in an excited state.

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