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Complete Basis Set ab Initio Computational Exploration of the Lowest Energy, Unimolecular, Triplet Potential Energy Surface for Triplet Oxygen Atom Assisted Acetylene Rearrangement into Vinylidene

Branko S. Jursic*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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The unimolecular triplet potential energy surface was explored with the complete basis set method with the aim being to evaluate the possibility of the triplet oxygen atom assisted acetylene rearrangement into vinylidine. Various linear and cyclic oxygen−acetylene adducts and isomers are located, and their structures are optimized at the MP2/6-31G(d′) level of theory, with the energy evaluation at the CBSQ ab initio level of theory. These stationary points are connected with 17 transition state structures. Their interconversion activation barriers were evaluated together with the enthalpies of the reactions, and for some C_2H_2O isomers, the selective bond dissociation energies were also estimated. The experimental feasibility of some of the reaction channels was discussed, and from all calculations presented in this paper it is a general conclusion that the oxygen assisted acetylene−vinylidene rearrangement is not possible through the unimolecular reactions of the C_2H_2O isomers in their triplet states. The possibility of the existence of the two-molecule hydrogen reactions was indicated, for which additional potential energy surface exploration is required.

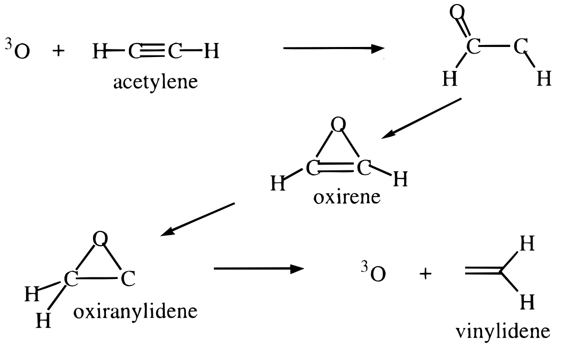
Introduction

There are many possible structural isomers that one can envision for the C_2H_2O molecular system, but only ketene has been observed experimentally.[1] Although the existence of cyclic oxyacetylene (oxirene) and oxyacetylene (formylmethylene) as the metastable intermediates was proposed for various chemical[2] reactions, there is no firm experimental evidence for their existence. There are some spectroscopic studies that indicate the possibility that some of these molecular species can exist with particular attention to oxirene[3] and oxiranylidene, which can be intermediates in the oxidation of acetylene and its transformation into the also controversial vinylidene.[4] One can imagine a scheme that can be used to transform acetylene with triplet oxygen assistance into vinylidene (Scheme 1). In this way, this reaction would be the triplet oxygen promoted acetylene rearrangement into vinylidene. Many computational studies were previously performed on various C_2H_2O molecular systems,[5] but none of them has been performed with the aim being to explore the assistance of triplet oxygen acetylene−vinylidene rearrangement through the unimolecular C_2H_2O decomposition process. If this transformation is experimentally feasible, it might become a path for generating metastable vinylidene. Here, we would like to address this problem through the complete basis set ab initio exploration of the potential energy surface for the triplet oxygen atom assisted acetylene−vinylidene rearrangement.

Computational Methods

All computational studies were performed with the Gaussian 94[6] computational package with ab initio and density functional methods according to how they are implemented in the computational package. The Complete Basis Set (CBSQ) method was developed by Petersson and co-workers.[7] The family name reflects the fundamental observation underlying these methods, namely that the largest error in the ab initio calculations results from basis set truncation. The energy of the chemical system is computed from a series of calculations. The initial calculation starts with geometry optimization and frequency calculation at the HF/6-31G(d′)[8] level of theory. The geometry is further optimized at the MP2/6-31G(d′)[9] level of theory with single-point energy calculation at QCISD(T)/6-31+(d′),[10] MP4(SDQ)/CBSB4,[11] and MP2/CBSB3.[9] The model also has empirical corrections for spin contamination and a size-consistent high-order correction. All calculations were performed with the Gaussian type of orbital.[12] For a more thorough explanation of these orbitals, see ref 13. All energies are computed for the fully optimized structures, and stationary points have all positive computed frequencies, while transition states have one imaginary frequency at the HF/6-31G(d′) level of theory. The reported geometries in this paper are computed with the MP2/6-31G(d′) theory model, and unless stated otherwise, the reported energies are computed at the CBSQ(0 K) level. In some instances, due to the MP2 convergence problem, the geometries of stationary points were optimized with the hybrid B3LYP/6-31G(d′)[14] density functional theory method. All stationary points were characterized by performing vibrational

SCHEME 1. Possible Pathway for Triplet Oxygen Assisted Acetylene Rearrangement into Vinylidene



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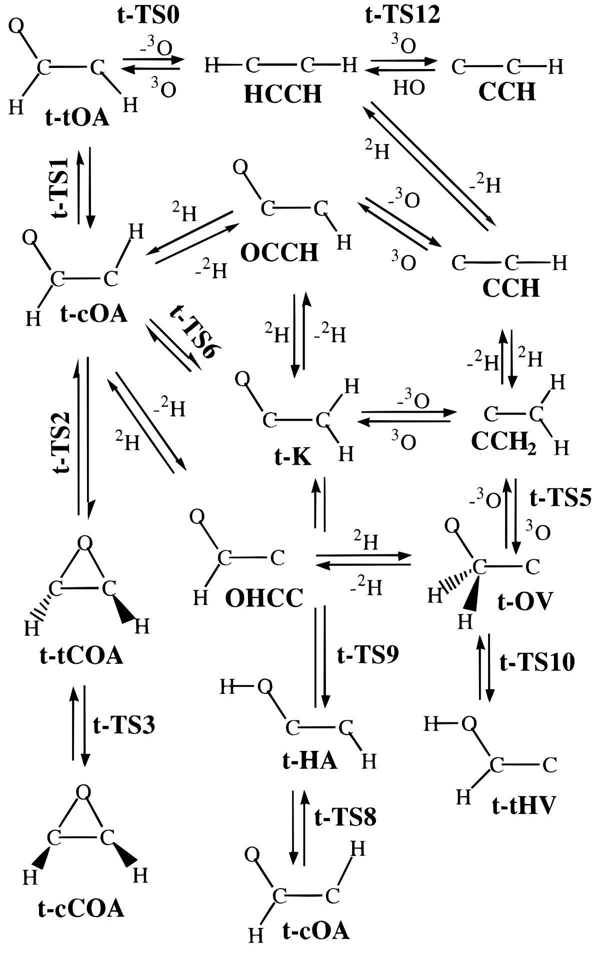
analysis and for transition state structures that have only one imaginary frequency, IRC calculations were performed to determine which of the two stationary points are connected with the transition state structure.

Results and Discussion

Although one can envision the transformation of acetylene into vinylidene through the triplet oxygen assisted rearrangement and the formation of many different C_2H_2O molecular species, only ketene in its singlet state is known experimentally. There are many computational studies that explore the structural properties and energies for various singlet C_2H_2O isomers,[5] but to the best of our knowledge, there are no extensive computational studies of this reaction in its triplet state. We have selected Petersson's complete basis set (CBSQ) ab initio method because we have demonstrated that this method is exceptionally accurate for computing thermodynamic properties of various chemical systems.[15]

SCHEME 2. Proposed Pathways for the Transformation of Acetylene into Vinylidene, Together with Some of Their Derivatives, Studied Computationally in This Work



Let us first explore the potential energy surface for the addition of triplet oxygen to singlet acetylene (Scheme 2). The transition state structures and some intermediates for these computational studies are presented in Figure 1. The first transition state structure (**t-TS0**) represents the transition state structure for the formation of a new O−C bond in the formation of triplet oxyacetylene. The structural parameters are what one would expect on the basis of transition state theory. The C−O bond distance is 1.851 Å, representing its partial formation. The HCC bond angles are between 120° and 180°, which correspond to sp^2 and sp hybridization present in an aldehyde and acetylene, respectively. It is interesting to point out that the CCH bond angle for the central carbon, which is not involved in the C−O bond formation, is closer to the sp hybridization than to the sp^2 hybridization angle. Furthermore, the OCCH dihedral angle is 0.0°, indicating that the cis triplet adduct might be more stable than the trans adduct (Figure 1). Triplet cis adduct (triplet *cis*-oxyacetylene, **t-cOA**) is actually a carbene with aldehyde functionality (Figure 1). In its triplet state, two carbon p-orbitals are each occupied with one electron. In many ways, the structural parameters should represent a classical organic molecule with two sp^2-hybridized carbons connected with a single CC bond. All computed structural parameters fully agree with this assumption. The C−O bond distance is 1.191 Å (1.204 Å in ethanal), with the OCC bond angle being 122.6° (125° in ethanal) and the HCC bond angle being 114.8° (114° in ethanal). This is only one of two isomers. The other isomer (**t-tOA**) should have quite similar structural properties to **t-cOA**, with the exception that the bond angles should change slightly. Because of the CC bond single character, the corresponding transition state for the transformation of one isomer into the other should be through simple rotation around the CC bond, while the other path through the transition state with the CCH angle inversion should have higher energy. Furthermore, if the transition state structure with the CCH angle inversion is involved in the isomerization reaction, then the CCH bond angle should be close to 180°. The lowest transition state that connects these two isomers on the potential energy surface is transition state **t-TS1**. This transition state is for rotation around the CC bond with the HCCH dihedral angle at almost 90.0° (Figure 1). As a result of this rotation, the CC bond distance is slightly longer in the transition state structure than in any of these two isomers.

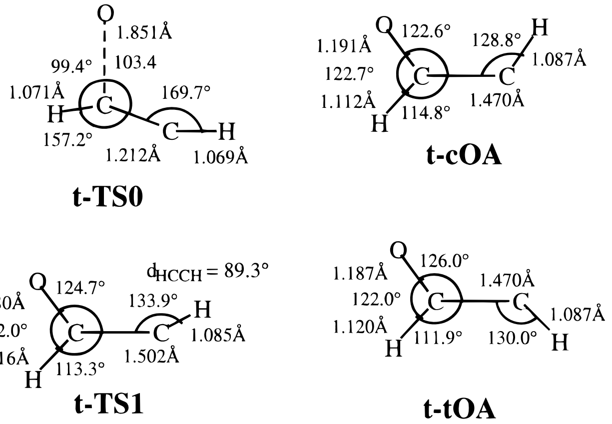


Figure 1. MP2/6-31G(d′) computed triplet structures for the transition state for triplet oxygen addition to acetylene (**t-TS0**), two isomeric triplet oxyacetylene adducts, and the transition state structure for the adducts isomerization (**t-TS1**).

Considering the facts that the transition state structure for the triplet oxygen addition to acetylene has a relatively long CO bond and that the triplet oxygen atom is a "hot" reagent, it is reasonable to expect that the activation barrier for this reaction should be very small. Furthermore, the structural differences between triplet *cis*- and *trans*-oxyacetylene are very small, indicating that they are also close in energy and that they are connected with the rotational transition state structure that is slightly higher in energy than these two isomers. Considering the fact that the triplet electron state in carbene is more stable than the one with spin located on the oxygen atom, it is also reasonable to propose that the formation of the oxygen−

TABLE 1: Total Energies (au) for Molecular Species Involved in Formation of an Oxygen−Acetylene Adduct[a]

theory	$E(^3O)$	E(HCCH)	E(**t-TS0**)	E(**t-cOA**)	E(**t-TS1**)	E(**t-tOA**)
A	−74.783471	−76.815707	−151.577494	−151.660420	−151.649221	−151.659514
B	−74.783471	−76.788581	−151.550767	−151.628634	−151.619593	−151.628066
C	−74.887677	−77.067421	−151.921663	−152.028761	−152.020209	−152.027235
D	−74.909219	−77.101402	−151.999826	−152.088929	−152.077793	−152.086474
E	−74.907382	−77.103080	−151.987463	−152.086090	−152.076360	−152.084368
F	−74.950037	−77.154128	−152.076421	−152.180255	−152.171441	−152.178690
G	−74.987068	−77.188250	−152.172772	−152.255670	−152.245660	−152.253668
H	−74.984707	−77.184161	−152.167856	−152.251325	−152.241404	−152.249288

[a] A = HF/6-31G(d′); B = HF/6-31G(d′) (0 K); C = MP2/6-31G(d′); D = QCISD(T)/6-31+G(d′); E = MP4/CBSB4; F = MP2/CBSB3; G = CBSQ (0 K); H = CBSQ. (0 K) = sum of electronic and zero-point energies.

TABLE 2: Energies (kcal/mol) for Triplet Oxygen Addition to Singlet Acetylene[a]

theory	ΔE_I	ΔH_I	ΔH_{II}	ΔE_{II}
HF/6-31G(d′)	13.6	−38.4	0.6	6.4
HF/6-31G(d′)(0 K)	13.4	−35.5	0.4	5.3
MP2/6-31G(d′)	21.0	−46.2	1.0	4.4
QCISD(T)/6-31+G(d′)	6.8	−49.1	1.5	5.4
MP4/CBSB	14.4	−47.5	1.1	5.0
MP2/CBSB	17.4	−47.7	1.0	4.5
CBSQ(0 K)	1.6	−50.4	1.3	5.0
CBSQ	0.6	−51.7	1.3	4.9

[a] (0 K) = sum of electronic and zero-point energies; ΔE_I = activation barrier for triplet oxygen addition to singlet acetylene through transition state **t-TS0**; ΔH_I = enthalpy for triplet oxygen addition to acetylene with formation of **t-cOA**; ΔH_{II} = relative energy of triplet *cis*-oxyacetylene (**t-cOA**) in regard to triplet *trans*-oxyacetylene (**t-tOA**); ΔE_{II} = activation barrier for triplet *trans*-oxyacetylene transformation into triplet *cis*-oxyacetylene.

acetylene adduct should be exothermic. To confirm our observation based on these structural properties, we have computed total energies for those molecular species (Table 1). When the relative energies are computed, a large difference between various ab initio estimates was observed. For instance, for the first reaction barrier, the MP2/6-31G(d′) estimate is 21.0 kcal/mol. If a larger basis set in combination with a higher ab initio method is applied, the activation barrier is decreasing and it is 6.8 kcal/mol at QCISD(T)/6-31+G(d′) theory level. The complete basis set ab initio method that we trust the most estimates that the reaction is practically occurring without a barrier (1.6 kcal/mol, Table 2). The differences in the computed energies will be appearing throughout the paper. As expected, the reaction with a "hot" triplet oxygen atom is predicted to be exothermic. Again, the level of the exothermicity depends on the ab initio method used. The CBSQ (0 K) computed energy is −50.4 kcal/mol (Table 2). The energies of the triplet *cis*- and *trans*-oxyacetylenes are almost identical with a slight preference, 1.3 kcal/mol, for triplet *cis*-oxyacetylene. The reaction barrier for their interconversion is in the range of the activation barrier for rotation around CC ethane single bond.

In this way, we have demonstrated that the addition of the triplet oxygen atom to acetylene should be very exothermic and should occur with a minimal or no barrier at all. There are two structural isomers, triplet *cis*- and triplet *trans*-oxyacetylene. In fact, these compounds are triplet carbenes (formylmethylidene). Considering that the interconversion of the cis−trans oxyacetylene is going through a simple C−H bond bending, it is reasonable to assume that the activation barrier should be very small. Let us now explore the transformation of triplet oxyacetylene into triplet cyclic oxyacetylene, or triplet oxirene. The transition state for this transformation is presented in Figure 2. The length of the newly formed C−O bond is 1.749 Å and is what is expected for the C−O bond distance in the transition state. In the initial molecule, the HCCH atoms are in one plane, which is no longer true for transition state **t-TS2** (Figure 2). The two hydrogens are in trans positions. There are at least three triplet oxirenes, cis (**t-cCOA**), trans (**t-tCOA**), and probably the planar (**t-pCOA**). Their structural properties and transition state structures that connect these stationary points are presented in Figure 2. There is little difference in the MP2/6-31G(d′) computed structural properties of the cis and trans triplets of cyclicoxyacetylenes. In the singlet state, there are no cis and trans isomers of cyclic oxyacetylene (oxirene), only the planar structure. On the other hand, planar oxirene (cyclic oxyacetylene, **t-pCOA**, Figure 2) is a second order transition state structure with two imaginary frequencies, while the other transition state structures have only one imaginary frequency. The CC bond distance in all the triplet oxirene isomers is somewhere between the bond distances observed in ethene (1.33 Å) and ethane (1.54 Å).[16] One can then assume that the oxirene CC bond is delocalized into the three-membered ring, making this system stable (aromatic-like). That is not exactly true because actually by exciting oxirene into its triplet state one p atomic orbital on each carbon is occupied with one electron, making it possible to have cis−trans oxirene isomers. This is, of course, not true for the singlet oxirene, which has all its atoms in one plane. In comparison of the structural properties for triplet cyclic oxyacetylenes with singlet cyclic oxyacetylene and oxyethylene (Figure 2), it is obvious that triplet state oxyacetylene has a CC bond with more single bond character, and the fact that there is no C−O double bond character in this molecule might suggest the aromatic character of triplet oxirene. Considering the bond angle problem, as well as the fact that oxyacetylene is actually a carbene that is known to be relatively stable in its triplet state, it is reasonable to assume that cyclic

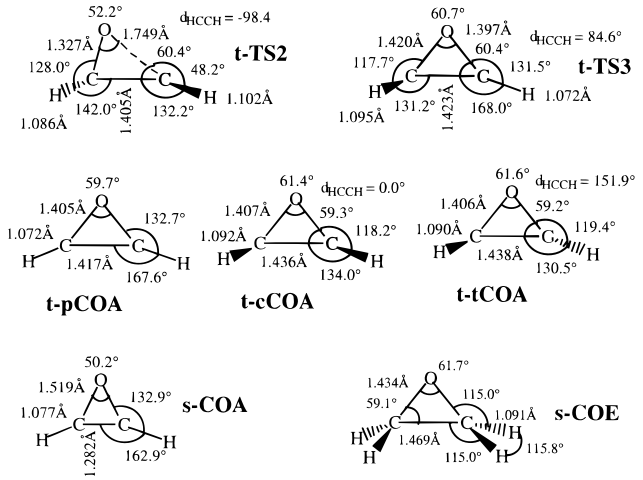


Figure 2. MP2/6-31G(d′) computed structural properties for triplet cyclic oxyacetylenes with comparison with singlet oxirene (oxyacetylene, **s-COA**) and oxyethylene (**s-COE**). The **t-TS2** is optimized with the B3LYP/6-31G(d) DFT method.

TABLE 3: Total Energies (au) for Molecular Species Involved in Transformation of Triplet Oxyacetylene into Triplet Oxirene[a]

theory	*E*(**t-TS2**)	*E*(**t-pCOA**)[b]	*E*(**t-cCOA**)	*E*(**t-TS3**)	*E*(**t-tCOA**)
HF/6-31G(d′)	−151.533022	−151.550971	−151.588607	−151.571937	−151.589337
HF/6-31G(d′) (0 K)	−151.504306	−151.521362	−151.554932	−151.540313	−151.555542
MP2/6-31G(d)	−151.906362	−151.953623	−151.988893	−151.973684	−151.989581
QCISD(T)/6-31+G(d′)	−151.993936	−152.004609	−152.036836	−152.022954	−152.037887
MP4/CBSB4	−151.970107	−152.004948	−152.037009	−152.023104	−152.038018
MP2/CBSB3	−152.062787	−152.115079	−152.143726	−152.131222	−152.144406
CBSQ (0 K)	−152.168300	−152.183245	−152.207330	−152.197196	−152.208324
CBSQ	−152.164128	−152.179296	−152.203307	−152.193217	−152.204312

[a] (0 K) = sum of electronic and zero-point energies; *E*(**t-pCOA**) =total energy for triplet planar cyclic oxyacetylene; *E*(**t-cCOA**) = total energy for triplet *cis*-oxyacetylene; *E*(**t-tCOA**) = total energy for triplet *trans*-oxyacetylene. [b] Planar structure has two imaginary frequencies as computed at the HF/6-31G(d′) theory level.

TABLE 4: Energies (kcal/mol) for Transformation of Triplet Oxyacetylene Linear Adduct into the Triplet Oxirene[a]

theory	ΔE_{III}	ΔH_{III}	ΔH_{IV}	ΔH_{V}	ΔH_{IV}
HF/6-31G(d′)	79.4	44.0	24.1	0.5	10.5
HF/6-31G(d′) (0 K)	77.7	45.5	21.4	0.4	9.2
MP2/6-31G(d′)	75.8	23.6	22.6	0.4	9.5
QCISD(T)	58.1	30.5	20.9	0.7	8.7
MP4/CBSB4	71.7	29.1	20.8	0.6	8.7
MP2/CBSB3	72.7	21.5	18.4	0.4	7.8
CBSQ (0 K)	53.6	28.5	15.7	0.6	6.4
CBSQ	53.4	28.2	15.7	0.6	6.3

[a] (0 K) = Sum of electronic and zero-point energies; ΔE_{III} = activation barrier for transformation of **t-tOA** into **t-tCOA** through transition state **t-TS2**; ΔH_{III} = enthalpy of the **t-tOA** cyclization into **t-tCOA**; ΔH_{IV} = relative energy of triplet planar **t-pCOA** in regard to triplet *trans*-**t-tCOA**; ΔH_{V} = relative energy of triplet *cis*-**t-cCOA** in regard to triplet *trans*-**t-tCOA**; ΔE_{IV} = activation barrier for transformation of triplet *cis*-**t-cOA** into triplet *trans*-**t-tCOA** through transition state **t-TS3**.

triplet oxyacetylenes are considerably less stable than the open-chain triplet oxyacetylene. Considering the negative spin interaction, it is reasonable to assume that triplet *trans*-oxirene (**t-tCOA**) with spin densities on the opposite side of the CCO plane is more stable than the triplet *cis*-oxirene (**t-cCOA**) that has two spin density maxima on the same side of the CCO plane. The activation barriers for their interconversions should be relatively small.

To confirm these relative stabilities evaluated and based on the C_2H_2O structural properties, the total energies for all species on the lowest triplet oxirene potential energy surface were computed (Table 3). The corresponding relative energies and activation barriers are presented in Table 4. The triplet cyclic oxyacetylenes (oxirenes) are less stable than their open-chain isomers. For instance, the triplet *trans*-oxyacetylene (**t-tOA**) is 28.5 kcal/mol more stable than its cyclic isomer. The activation barrier for this cyclization is estimated to be 53.6 kcal/mol (Table 4). If triplet oxirene is forced to be planar, it is 15.7 kcal/mol above the relaxed triplet cyclic *trans*-oxyacetylene (**t-tCOA**) (Table 4). On the other hand, triplet *cis*- and *trans*-oxirene are very similar in energy. Actually, the CBSQ (0 K) method estimates that the trans isomer is 0.6 kcal/mol more stable. These two stationary points on the potential energy surface are connected through the transition state **t-TS3** that lies 6.4 kcal/mol above the triplet *trans*-oxirene **t-tCOA** (Table 4). From these calculations, it is obvious that the transformation of the open-chain triplet oxyacetylene **t-cOA** or **t-tOA** into triplet oxirene is not energetically preferable, due to a very high cyclization barrier and a relatively high endothermicity of the reaction.

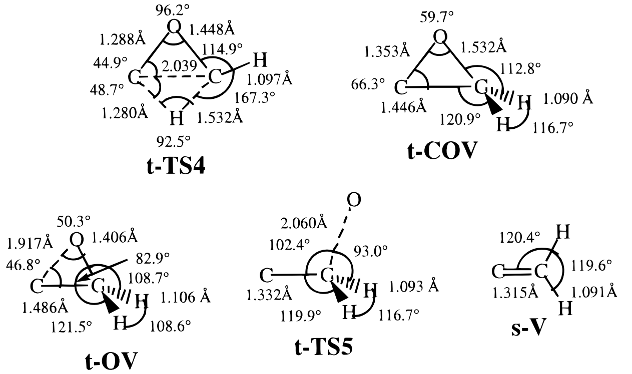


Figure 3. Some molecular species for transformation of triplet cyclic oxyacetylene into singlet vinylidene and triplet oxygen atom (the **t-TS5** is optimized at the B3LYP/6-31G(d′) theory level).

Let us assume that the transformation of the open-chain triplet oxirene into vinylidene is somehow achievable and that the triplet oxirene, due to its high energy, is a desirable source for the preparation of vinylidene. To explore this possibility, the potential energy surface was explored with the complete basis set ab initio method. The generated MP2/6-31G(d′) structures for the stationary points for this channel of the decomposition on the global C_2H_2O potential energy surface are presented in Figure 3. The backbone of this transformation is the highly reactive triplet oxiranylidene (cyclic oxyvinylidene, **t-COV**), which can be, through the elimination of a triplet oxygen atom, converted into vinylidene. The transition state structure for the triplet oxirene transformation into triplet oxiranylidene **t-TS4** represents a transfer of the hydrogen atom from one carbon atom to the other. This transition state has a peculiar structure because of the very long C−C bond distance that actually represents the partial breaking and then remaking of the CC bond with simultaneous proton transfer. The structure **t-COV** is actually a triplet carbene that can be transferred into triplet oxyvinylidene (**t-OV**). This structure has one of the longest C−O bond distances (1.917 Å). This distance is usually computed for the transition state structure for C−O bond breaking or making, but not for molecular systems at their global minima. Nevertheless, the triplet oxyvinylidene (**t-OV**) at the HF/6-31G(d′) level of theory has all positive frequencies in its computed infrared spectrum. Our attempt to generate transition state structures for the transformation of **t-COV** into **t-OV** with both ab initio and density functional theory methods was not successful. There was also a convergence problem when the optimization of the transition state structure for the oxygen atom elimination from triplet oxyvinylidene was attempted. The transition structure **t-TS5** was optimized at the B3LYP/6-31G(d′) level of theory (Figure 3). The B3LYP/6-31G(d′) geometry was used for the CBSQ evaluation of the transition state total energy. Comparing the structural properties of **t-TS5** with the two stationary points that it connects, we see that it is in structure much closer to the singlet vinylidene (**s-V**) than to the triplet oxyvinylidene (**t-**

TABLE 5: Total Energies (au) for Molecular Species Involved in the Triplet Cyclic Oxyacetylene Transformation into Triplet Oxygen and Vinylidene

theory	*E*(**t-TS4**)	*E*(**t-COV**)	*E*(**t-OV**)[a]	*E*(**t-TS5**)[a]	*E*(**s-V**)
HF/6-31G(d′)	−151.487495	−151.568341	−151.531837	−151.525854	−76.762927
HF/6-31G(d′) (0 K)	−151.462312	−151.533569	−151.501010	−151.499071	−76.737003
MP2/6-31G(d)	−151.877590	−151.964384	−151.885168	−151.847812	−76.987215
QCISD(T)/6-31+G(d′)	−151.941182	−152.014033			−77.035954
MP4/CBSB4	−151.938048	−152.013249			−77.039751
MP2/CBSB3	−152.032045	−152.119475			−77.070420
CBSQ (0 K)	−152.117975	−152.182080			−77.116669
CBSQ	−152.113591	−152.178071			−77.112583

[a] Energies at a higher theory level were not possible to obtain due to a convergence problem even when the quadratic convergence is requested; (0 K) = sum of electronic and zero-point energies.

TABLE 6: Potential Energy Profile for Triplet Cyclic Oxyacetylene (Oxirene) Transformation into Singlet Vinylidene and Triplet Oxygen Atom[a]

theory	ΔE_{V}	ΔH_{V}	ΔH_{VI}	ΔE_{VI}	ΔH_{VII}
HF/6-31G(d′)	63.9	13.2	22.9	3.8	−13.8
HF/6-31G(d′) (0 K)	58.5	13.8	20.4	1.2	−8.2
MP2/6-31G(d′)	70.3	15.8	49.7	23.4	−56.2
QCISD(T)/6-31+G(d′)	60.7	15.0			−43.2
MP4/CBSB4	62.7	15.5			−41.5
MP2/CBSB3	70.5	15.6			−62.1
CBSQ (0 K)	56.7	16.5			−49.2
CBSQ	56.9	16.5			−50.7

[a] ΔE_{V} = activation barrier (kcal/mol) for triplet oxirene (**t-tCOA**) into triplet oxiranylidene trough transition state **t-TS4**; ΔH_{V} = relative energy (kcal/mol) of triplet oxiranylidine (**t-tCOA**) in regard to triplet oxirene (**t-COV**); ΔH_{VI} = relative energy (kcal/mol) of triplet oxyvinylidene (**t-OV**) in regard to triplet oxiranylidine (**t-COV**); ΔE_{VI} = activation barrier (kcal/mol) for triplet oxygen atom elimination from triplet oxyvinylidene (**t-OV**) through transition state **t-TS5** with formation of singlet vinylidene; ΔH_{VII} = enthalpy (kcal/mol) of triplet oxygen elimination from triplet oxiranylidene (**t-COV**).

TABLE 7: Total Energies (au) for Molecular Species Involved in the Triplet Oxyacetylene Transformation into Vinylidene and Triplet Oxygen through Triplet Ketene as an Intermediate[a]

theory	*E*(**t-TS6**)	*E*(**t-K**)	*E*(**t-TS7**)
HF/6-31G(d′)	−151.552113	−151.628270	−151.661313
HF/6-31G(d′) (0 K)	−151.526495	−151.597341	−151.630564
MP2/6-31G(d)	−151.952046	−152.068130	−152.055437
QCISD(T)/6-31+G(d′)	−152.011749	−152.120923	−152.106191
MP4/CBSB4	−152.008321	−152.120432	−152.106641
MP2/CBSB3	−152.109745	−152.219887	−152.206533
CBSQ (0 K)	−152.190033	−152.288920	−152.273039
CBSQ	−152.190033	−152.284667	−152.268766

[a] (0 K) = sum of electronic and zero-point energies.

OV). If the reaction is exothermic, then the activation barrier for this reaction should be very small.

Total energies for these chemical systems are presented in Table 5. As a result of the convergence problem, it was not possible to compute the total energies for both **t-OV** and **t-TS5** at a higher theory level than MP2/6-31G(d′). The computed activation barriers and enthalpies for these transformations were presented in Table 6. Due to the fact that in **t-TS4** both C−H and C−C bond breaking and forming are involved, it comes as no surprise that the computed activation barrier is very high. The CBSQ (0 K) estimated barrier is 56.7 kcal/mol. The triplet oxiranylidene (**t-COV**) is estimated to be 16.5 kcal/mol less stable than the triplet *trans*-oxirene **t-tCOA** (Table 6). Furthermore, breaking the C−O bond in such a way that the triplet oxyvinylidene (**t-OV**) is formed from triplet oxiranylidene **t-COV** is an energetically unfavorable process. At the MP2/6-31G(d′) level of theory, it was estimated that **t-OV** is 49.7 kcal/mol less stable than triplet oxiranylidene (**t-COV**) (Table 6). If this metastable intermediate could be formed, then it should very rapidly decompose to singlet vinylidene and triplet oxygen, with the CBSQ (0 K) estimated exothermicity of the oxygen elimination −49.2 kcal/mol (Table 6).

From computed energy profiles that include triplet oxirene and its various derivatives, it is obvious that these compounds cannot be the source of vinylidene, due to their high energy demand during formation. As we have demonstrated above, formation of the triplet oxyacetylene (**t-cOA**) is energetically favorable and all reasonable oxygen assisted acetylene transformations into vinylidene must include the formation of triplet oxyacetylene. One way of coming close to the vinylidene structure is to form triplet ketene. As mentioned above, singlet ketene is the only oxyacetylene isomer that is observed experimentally. It can be obtained from oxyacetylene through a 1,2-hydrogen shift. The transition state for this rearrangement (**t-TS6**) is presented in Figure 4. It is a classical transition state structure for a 1,2-hydrogen shift. In its singlet state, the ketene CCO angle is 180°, but here, because of the singly occupied orbital on the carbon and oxygen atoms, the structure is planar with sp^2 hybridization on both carbon atoms. That is clearly demonstrated with the bond angles of **t-K** (Figure 4). Nevertheless, the C−C bond distance suggests its single bond character and rotational barrier through **t-TS7** should be relatively small. This is confirmed by computing total energies for these molecular species (Table 7).

In general, 1,2-hydrogen shifts for neutral molecular systems have high activation barriers. The triplet oxyacetylene rear-

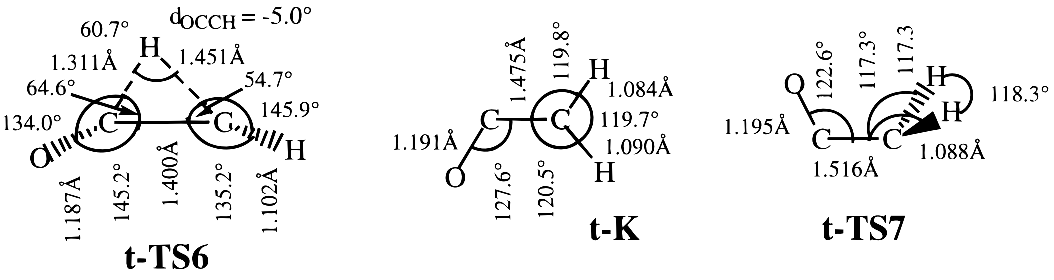


Figure 4. Molecular species for transformation of oxyacetylene into vinylidene through the ketene.

TABLE 8: Potential Energy Profile (kcal/mol) for Transformation of Triplet Oxyacetylene (t-tOA) into Triplet Ketene[a]

theory	ΔE_{VII}	ΔH_{VIII}	ΔE_{VIII}
HF/6-31G(d′)	68.0	20.2	−20.7
HF/6-31G(d′) (0 K)	64.1	19.6	−20.8
MP2/6-31G(d′)	48.1	−24.7	8.0
QCISD(T)/6-31+G(d′)	48.4	−20.0	9.2
MP4/CBSB4	48.8	−21.5	8.7
MP2/CBSB3	44.2	−24.9	8.4
CBSQ (0 K)	41.2	−20.9	10.0
CBSQ	38.5	-20.9	10.0

[a] ΔE_{VII} = activation barrier for triplet oxyacetylene (**t-cOA**) rearrangement into triplet triplet ketene (**t-K**) through transition state **tTS6**; ΔH_{VIII} = relative energy of triplet ketene (**t-K)** in regard to triplet oxyacetylene (**t-cOA**); ΔE_{VIII} = activation barrier for rotation around the CC bond for triplet ketene (**t-K)** through transition state **t-TS7**.

TABLE 9: Total Energies (au) for Molecular Species Involved in the Triplet Cyclic Oxyacetylene Transformation into Triplet Oxygen and Vinylidene[a]

theory	*E*(**t-TS8**)	*E*(**t-HA**)	*E*(**t-TS9**)
HF/6-31G(d′)	−151.505575	−151.573347	−151.513447
HF/6-31G(d′) (0 K)	−151.479493	−151.540361	−151.486689
MP2/6-31G(d)	−151.902781	−151.956813	−151.925583
QCISD(T)/6-31+G(d′)	−151.964931	−152.026580	−151.980095
MP4/CBSB4	−151.966164	−152.026559	−151.984376
MP2/CBSB3	−152.069471	−152.121342	−152.089418
CBSQ (0 K)	−152.150854	−152.199530	−152.163937
CBSQ	−152.146314	−152.195215	−152.159714

[a] (0 K) = sum of electronic and zero-point energies.

TABLE 10: Energy Profile (kcal/mol) for Hydrogen Shift Reactions for Transformation of Triplet Oxyacetylene into Triplet Ketene through Triplet Hydroxyacetylene Theory[a]

theory	ΔE_{IX}	ΔH_{IX}	ΔE_{X}	ΔH_{X}
HF/6-31G(d′)	97.2	54.6	37.6	−34.5
HF/6-31G(d′) (0 K)	93.6	55.4	33.7	−35.8
MP2/6-31G(d′)	79.1	45.1	19.6	−69.9
QCISD(T)/6-31+G(d′)	77.8	39.1	29.2	−59.2
MP4/CBSB4	75.3	37.4	26.5	−58.9
MP2/CBSB3	69.5	37.0	20.0	−61.8
CBSQ (0 K)	65.8	35.2	22.3	−56.1
CBSQ	65.9	35.2	22.3	−56.1

[a] ΔE_{IX} = activation barrier for triplet oxyacetylene (**t-cOA**) rearrangement into triplet hydroxyacetylene (**t-HA**) through transition state **t-TS8**; ΔH_{IX} = relative energy of triplet hydroxyacetylene (**t-HA**) in regard to triplet oxyacetylene (**t-cOA**); ΔE_{IX} = activation barrier for triplet hydroxyacetylene (**t-HA**) into triplet ketene (**t-K**) through transition state **tTS9**; ΔH_{X} = relative energy of triplet ketene (**t-K)** in regard to triplet hydroxyacetylene (**t-HA**).

rangement into triplet ketene is not an exception. The CBSQ computed activation barrier for this hydrogen shift is 41.2 kcal/mol. The triplet ketene (**t-K**) is actually more stable than the triplet oxyacetylene **(t-cOA)**. The CBSQ computed exothermicity of the reaction is −20.9 kcal/mol. When formed, the triplet ketene has a C−C rotational barrier around 10 kcal/mol (Table 8).

Although triplet ketene is more stable than triplet oxyacetylene, its formation from the latter is hampered by a relatively high activation barrier for the hydrogen shift from one carbon atom to the other. One possibility of avoiding this transformation is through a two-step hydrogen shift. In the first step, hydrogen is transferred to an oxygen atom from the first carbon atom with the formation of triplet hydroxyacetylene. In the second step, hydrogen is transferred from the oxygen of the triplet hydroxyacetylene to the second carbon atom with the final formation of the triplet ketene. The transition state structures and the intermediates for these rearrangements are presented in Figure 5. Again, both transition state structures **t-TS8** and **t-TS9** are classical transition state structures for hydrogen transfer. In the triplet hydroxyacetylene (**t-HA**), the CC bond distance has a double bond character with the singly occupied orbitals on each atom pointing in the more stable trans direction. Therefore, the triplet oxyacetylene has a trans configuration. The total energies for those three stationary points on the potential energy surface are presented in Table 9 with their relative energies in Table 10.

As we have anticipated, the transfer of hydrogen from oxygen to the second carbon atom through a four-membered transition state **t-TS9** occurs with a modest activation barrier. The CBSQ (0 K) estimated activation barrier is 22.3 kcal/mol (Table 10). Unfortunately, the first activation barrier that includes a three-membered transition state structure **t-TS8** for the hydrogen transfer from the first carbon to the oxygen atom is much higher than that for the hydrogen transfer from the first to the second carbon atom. The CBSQ (0 K) estimated activation barrier is 65.8 kcal/mol (Table 9). This practically eliminates the double hydrogen transfer path for the transformation of triplet oxyacetylene into triplet ketene.

It seems that the hydrogen transfer from the four-membered transition state structures is more favorable than that through the three-membered transition state structure on the triplet potential energy surface. If this is true, then the possibility exists for the transformation of triplet oxyacetylene into triplet hydroxyvinylidene through the four-membered hydrogen transfer transition state structure (**t-TS10**, Figure 6). In this scheme, the hydrogen shift is from the second carbon atom to the oxygen of triplet oxyacetylene. With this hydrogen shift the triplet *cis*-hydroxyvinylidene (**t-cHV**) should be formed. In continuation, the cis isomer can be converted into the trans isomer (**t-tHV**) through C−C bond rotation. The rotational transition state that connects **t-cHV** and **t-tHV** is **t-TS11** (Figure 6). The MP2/6-31G(d′) structural properties for the transition state structures and intermediates are presented in Figure 6. All structural properties are in agreement with the common knowledge of structural organic chemistry. For instance, the rotational **t-TS11** has a HOCC dihedral angle close to 90.0°, while the central carbon atom has all characteristics of sp^2 hybridization. The

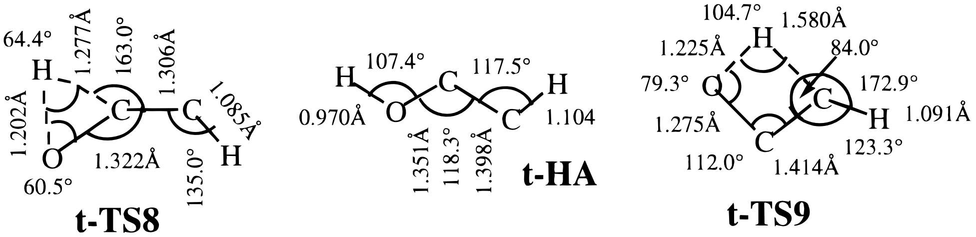
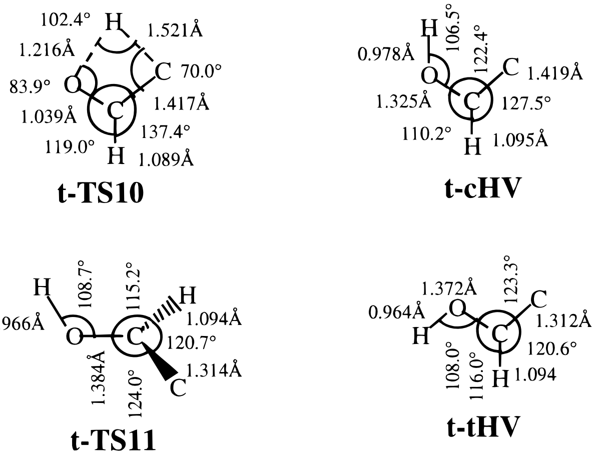


Figure 5. Some MP2/6-31G(d′) structures on the potential energy surface for transformation of triplet oxyacetylene into triplet ketene through a series of hydrogen shifts.



t-TS10 **t-cHV** **t-TS11** **t-tHV**

Figure 6. MP2/6-31G(d′) optimized structures on the triplet potential energy surface for triplet oxyacetylene transformation into triplet hydroxyvinylidene.

CC bond distance is closer to that of a double bond than to that of a single bond.

Energetic characteristics of these structures are given in Tables 11 and 12. Due to the fact that the C−H bond dissociation energy is higher than the O−H bond dissociation energy, the hydrogen transfer from carbon to oxygen is usually less favorable than that from oxygen to carbon. In our case, this is demonstrated through a relatively high activation barrier for the transformation of triplet oxyacetylene into triplet hydroxyvinylidene. The CBSQ (0 K) estimated activation barrier is 49.5 kcal/mol (Table 12). Furthermore, the triplet hydroxyvinylidene is less stable than the triplet oxyacetylene. The rotation barrier for the triplet *cis*-hydroxyvinylidene is 9.6 kcal/mol. This isomer is estimated to be 9.1 kcal/mol more stable than the triplet *trans*-hydroxyvinylidene (Table 12).

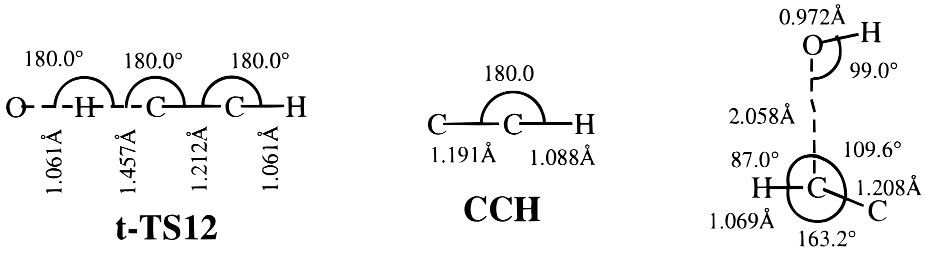
From all the calculations presented above, it is now obvious that the easily formed triplet oxyacetylene is not readily transformed to intermediates that can serve as a source of vinylidene. There are also other pathways that can result in the formation of vinylidene which initially include the hydrogen abstraction from acetylene with the triplet oxygen atom and then the recombination of hydroxyl and acetylide radicals into ketene or hydroxyvinylidene. Structural parameters for these transition state structures and radical intermediates computed with the MP2/6-31G(d′) ab initio method are presented in Figure 7. Transition state **t-TS12** is a normal transition state structure for proton transfer from one molecule to the other. Usually this occurs collinearly as in transition state structure **t-TS12**. It was not possible to optimize transition state structures for the recombination of hydroxyl and acetylide radicals into triplet hydroxyacetylene with the MP2/6-31G(d′) or B3LYP/6-31G(d′) methods. That might indicate that recombination of the radicals is occurring without a barrier. That seems to also be true for the formation of triplet hydroxyvinylidene because **t-TS13** represents a very early transition state structure that is very close to the separated radicals (Figure 7).

Energy profiles for those structural transformations are presented in Tables 13 and 14. As mentioned above, in general the activation barriers for the hydrogen abstraction with "hot" radicals are relatively low. The CBSQ (0 K) computed activation

TABLE 12: Energy Profile (kcal/mol) for Hydrogen Shift Reactions for Transformation of Triplet Oxyacetylene into Triplet Ketene through Triplet Hydroxyacetylene Theory[a]

theory	ΔE_{XI}	ΔH_{XI}	ΔE_{XII}	ΔH_{XII}
HF/6-31G(d′)	80.7	47.5	4.7	3.3
HF/6-31G(d′) (0 K)	68.9	49.0	3.5	2.6
MP2/6-31G(d′)	55.4	40.2	17.2	15.1
QCISD(T)/6-31+G(d′)	57.8	39.8	13.5	12.7
MP4/CBSB4	52.9	33.2	18.6	17.6
MP2/CBSB3	48.9	32.6	16.7	14.4
CBSQ (0 K)	49.5	36.8	9.6	9.1
CBSQ	49.4	36.8	9.4	9.4

[a] ΔE_{XI} = activation barrier for triplet *cis*-oxyacetylene (**t-cOA**) rearrangement into triplet *cis*-hydroxyvinylidene (**t-cHV**) through transition state **t-TS10**; ΔH_{XI} = relative energy of triplet *cis*-hydroxyvinylidene (**t-cHV**) in regard to triplet *cis*-oxyacetylene (**t-cOA**); ΔE_{XII} = activation barrier for triplet *cis*-hydroxyvinylidene (**t-cHV**) into triplet *trans*-hydroxyvinylidene (**t-tHV**) through triplet transition state **t-TS11**; ΔH_{XII} = relative energy of triplet *trans*-hydroxyvinylidene (**t-tHV**) in regard to triplet *cis*-hydroxyvinylidene (**t-cHV**).



t-TS12 **CCH** **t-TS13**

Figure 7. MP2/6-31G(d′) computed parameters for transformation of acetylene into hydroxyvinylidne.

TABLE 11: Total Energies (au) for Molecular Species Involved in the Triplet Cyclic Oxyacetylene Transformation into Triplet Hydroxyvinylidene[a]

theory	*E*(**t-tS10**)	*E*(**t-cHV**)	*E*(**t-TS11**)	*E*(**t-tHV**)
HF/6-31G(d′)	−151.531895	−151.584674	−151.577187	−151.579423
HF/6-31G(d′)(0 K)	−151.502890	−151.550625	−151.545015	−151.546433
MP2/6-31G(d)	−151.940510	−151.964725	−151.937269	−151.940708
QCISD(T)/6-31+G(d′)	−151.996806	−152.025505	−152.003914	−152.005195
MP4/CBSB4	−152.001723	−152.033244	−152.003534	−152.005195
MP2/CBSB3	−152.102391	−152.128384	−152.101700	−152.105447
CBSQ (0 K)	−152.176564	−152.197102	−152.181832	−152.182538
CBSQ	−152.172596	−152.192723	−152.177666	−152.177724

[a] (0 K) = sum of electronic and zero-point energies.

TABLE 13: Total Energies (au) for Molecular Species Involved in Transformation of Acetylene into Triplet Hydroxyacetylene and Triplet Hydroxyvinylidene[a]

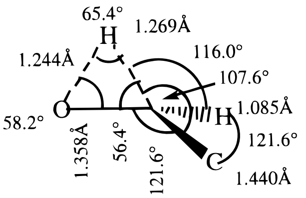
theory	E(**t-TS12**)	$E(^2OH)$	$E(^2CCH)$	E(**t-TS13**)
HF/6-31G(d′)	−151.508296	−75.379414	−76.148687	−151.522805
HF/6-31G(d′)(0 K)	−151.489486	−75.370278	−76.135048	−151.495818
MP2/6-31G(d)	−151.860318	−75.524536	−76.342787	−151.864733
QCISD(T)/6-31+G(d′)	−151.940959	−75.549519	−76.393893	−151.945842
MP4/CBSB4	−151.935501	−75.562889	−76.378317	−151.938551
MP2/CBSB3	−152.022848	−75.614485	−76.416793	−152.028907
CBSQ (0 K)	−152.134633	−75.648937	−76.478257	−152.128678
CBSQ	−152.129223	−75.645632	−76.474248	−152.123344

[a] (0 K) = sum of electronic and zero-point energies; our attempt to optimize transition state structure for hydroxyl and acetylene radical recombination into triplet hydroxyacetylene failed.

TABLE 14: Energy Profile (kcal/mol) for Hydrogen Shift Reactions for Transformation of Triplet Oxyacetylene into Triplet Ketene through Triplet Hydroxyacetylene Theory[a]

theory	ΔE^{XIII}	ΔH_{XIII}	ΔE_{XIV}	ΔH_{XIV}	ΔH_{XV}
HF/6-31G(d′)	57.0	−44.6	3.3	−35.4	−28.4
HF/6-31G(d′) (0 K)	51.8	−41.9	6.0	−28.4	−22.2
MP2/6-31G(d′)	59.5	−55.1	1.6	−61.1	−56.1
QCISD(T)/6-31+G(d′)	43.7	−42.2	−1.5	−51.5	−52.2
MP4/CBSB4	47.0	−43.5	1.7	−57.7	−53.5
MP2/CBSB3	51.0	−45.7	1.5	−60.9	−56.5
CBSQ (0 K)	25.5	−30.2	−0.9	−43.9	−45.4
CBSQ	24.9	−30.7	−2.1	−45.7	−47.3

[a] ΔE_{XI} = activation barrier for triplet oxygen hydrogen abstraction reaction from singlet acetylene through (**t-TS12**); ΔH_{XIII} = enthalpy of the hydrogen abstraction reaction; ΔE_{XIV} = activation barrier for recombination of hydroxyl radical and acetyl radical into triplet hydroxyvinylidene through **t-TS13**; ΔH_{XIV} = the enthalpy of the hydroxyl and acetylene radicals recombination into triplet hydroxyvinylidene (**t-cHV**); ΔH_{XV} = enthalpy for hydroxyl and acetylene radical recombination into triplet hydroxyacetylene.



t-TS14

Figure 8. HF/6-31G(d′) structural properties of the triplet transition state structure for triplet hydroxyvinylidene rearrangement into triplet oxyvinylidene.

TABLE 15: Total Energy (au) for t-TS14 and Activation Barrier and Enthalpy of Triplet Hydroxyvinylidene Rearrangement into Triplet Oxyvinylidene[a]

theory	E(**t-TS14**)	ΔE_{XV}	ΔH_{XVI}
HF/6-31G(d′)	−151.477653	67.2	−33.2
HF/6-31G(d′) (0 K)	−151.451428	62.2	−31.1
MP2/6-31G(d′)	−151.850791	71.5	−49.9
QCISD(T)/6-31+G(d′)	−151.924631	63.3	
MP4/CBSB4	−151.922818	69.3	
MP2/CBSB3	−152.013508	72.1	
CBSQ (0 K)	−152.104465	58.1	
CBSQ	−152.100110	58.1	

[a] ΔE_{XV} = activation barrier for triplet hydroxyvinylidene rearrangement into triplet oxyvinylidene; ΔH_{XVI} = enthalpy of the rearrangement reaction.

energy for the hydrogen abstraction from acetylene with the triplet oxygen atom is 25.5 kcal/mol (Table 14), which is not so low an activation barrier, and this reaction should not be possible at room temperature. The exothermicity of the hydrogen abstraction is estimated to be 30.2 kcal/mol. It is reasonable to expect that the two radicals, hydroxyl and acetylidene, will quickly recombine into hydroxyvinylidene and/or hydroxyacetylene. The CBSQ (0 K) calculations gave a negative activation barrier (−0.9 kcal) for the recombination with the formation of triplet hydroxyvinylidene. Of course, a negative activation barrier is a computational artifact and not reality. In the case of the CBSQ estimate, it can be explained in terms of one major obstacle of this computational approach. The energy was evaluated on the MP2/6-31G(d′) geometry, which is not necessarily also a minimum on the potential energy surface computed at a higher level of theory. Another explanation might be that the mean absolute deviation (computational error) of the CBSQ method is ±1.0 kcal/mol,[17] which makes −0.9 kcal/mol within the margin of the computational error. Therefore, it is reasonable to say that this reaction occurs without a barrier. The reaction is estimated to be very exothermic (−43.9 kcal/mol). For other radicals, we were not able to locate the transition state structure for the recombination with the formation of triplet hydroxyacetylene. This indicates that this reaction is also occurring without a barrier. The CBSQ (0 K) enthalpy of the reaction is −45.4 kcal/mol (Table 14), which is slightly lower than that for other radical recombination reactions. This also indicates that triplet hydroxyacetylene and triplet hydroxyvinylidene are almost isoenergetic.

Even if triplet hydroxyvinylidene is formed, it should first rearrange to triplet oxyvinylidene and then eliminate the triplet oxygen atom through **t-TS5** to form singlet vinylidene, as demonstrated in Figure 3. Unfortunately, as a result of convergence problems, it was not possible to estimate the activation barrier for the oxygen atom elimination at the CBSQ level of theory. If we consider that the MP2/6-31G(d′) activation barrier is about 14 kcal/mol higher than the CBSQ (0 K) computed energy for the triplet oxygen addition to acetylene (Table 6), then by some analogy the extrapolated activation barrier for the triplet oxygen atom elimination from oxyvinylidene should be below 10 kcal/mol, which is an experimentally feasible reaction. To be able to generate triplet oxyvinylidene easily, the generated triplet hydroxyacetylene should rearrange. The corresponding transition state structure for this reaction (**t-TS14**) could not be optimized with the MP2/6-31G(d′) ab initio methods, although the geometry can be optimized at the HF/6-31G(d′) level of theory. The geometry obtained in the HF/6-31G(d′) calculation (Figure 8) was used for the CBSQ energy evaluation. Computed total energies, as well as the activation barriers for this reaction are presented in Table 15. Unfortunately the estimated activation barrier for the hydrogen shift through **t-TS14** is too high. The CBSQ (0 K) estimated activation barrier for the triplet hydroxyvinylidene rearrangement is 58.1 kcal/mol. It does not help to channel this reaction through **t-TS14** because that reaction is 49.9 kcal/mol exothermic as computed with the MP2/6-31G(d′) ab initio method (Table 15). Therefore, transferring acetylene into vinylidene through the oxygen atom hydrogen abstraction reaction followed by recombination of the

TABLE 16: Total Energies (au) for Molecular Species Involved in the Triplet Cyclic Oxyacetylene Transformation into Triplet Hydroxyvinylidene[a]

theory	E(**t-TS15**)	E(OCCH)	E(**t-TS16**)	E(OHCC)	E(H)
HF/6-31G(d′)	−151.560225	−151.083422	−151.571827	−150.976029	−0.498233
HF/6-31G(d′) (0 K)	−151.536802	−151.063836	−151.549944	−150.956328	−0.498233
MP2/6-31G(d)	−151.939289	−151.490972	−151.977866	−151.337895	−0.498233
QCISD(T)/6-31+G(d′)	−151.972338	−151.536609	−152.032703	−151.408641	−0.498233
MP4/CBSB4	−151.993219	−151.525487	−152.022236	−151.393974	−0.498233
MP2/CBSB3	−152.094291	−151.636066	−152.129028		−0.499818
CBSQ (0 K)	−152.185027	−151.708685	−152.211368		−0.499818
CBSQ	-152.180429	−151.704071	−152.206264		−0.497457

[a] (0 K) = sum of electronic and zero-point energies.

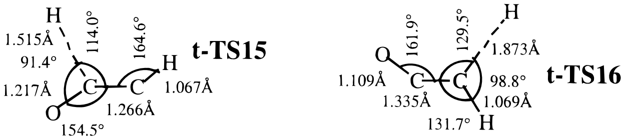


Figure 9. MP2/6-31G(d′) transition state structures **t-TS15** and **t-TS16** for hydrogen elimination and addition to triplet oxyacetylene isomers.

formed radicals into triplet hydroxyvinylidene, rearrangement of the triplet hydroxyvinylidene into triplet oxyvinylidene, and finally elimination of the triplet oxygen atom from triplet oxyvinylidene cannot be carried out experimentally because of the exceptionally high activation barrier for the rearrangement of triplet hydroxyvinylidene into triplet oxyvinylidene.

There is at least one more channel for the transformation of the readily formed triplet oxyacetylene into singlet vinylidene, reaction through a series of C−H bond-breaking and bond-making steps with an intermediate or final C−O bond-breaking step, as outlined in Scheme 2. Enthalpies for some of these reactions, such as the oxidation of acetylene, have already been computed (Table 2). The negative value for the enthalpy of the addition of the triplet oxygen to acetylene (−50.4 kcal at the CBSQ theory level with zero-point energy correction, Table 2) is also the C−O bond dissociation energy (50.4 kcal/mol) for triplet *cis*-oxyacetylene (**t-cOA**). Therefore, the C−O bond dissociation energy in **t-cOA** is 50.4 kcal/mol, which is relatively high and probably the path through which the hydrogen radical elimination from **t-cOA** is energetically more favorable. To explore the chemical transformations outlined in Scheme 2, total energies for the OCCH, OHCC, and hydrogen radicals were calculated. Direct transformations of the singlet and triplet acetylene into the corresponding vinylide were previously studied and will not be discussed here.[18]

Although determining transition state structures for the C−H as well as the C−O bond-breaking is very difficult and in many cases impossible, we have successfully optimized the transition state structure for hydrogen elimination from triplet oxyacetylene with the formation of the OCCH radical through transition state structure **t-TS15** and for the hydrogen radical addition to the OCCH radical through transition state **t-TS16,** which form triplet ketene (**t-K**) (Figure 9). The total energies for those molecular species on the triplet potential energy surface are presented in Table 16. The first transition state structure has a C−H bond distance that would be expected on the basis transition state theory, while the second transition state structure has a relatively long C−H bond distance, indicating that the transition state is very close in energy to the separated **OCCH** and **H** radicals. Therefore, the activation barrier for this reaction is expected to be relatively low. Calculated total energies for those molecular species on the potential energy surface are presented in Table 16. The activation barrier for the elimination of the hydrogen from triplet oxyacetylene is estimated to be 44.3 kcal/mol (Table 17), too high for this reaction to occur. The exothermicity of the CH bond dissociation energy for this transformation is estimated to be 29.6 kcal/mol. As expected on the basis of the structural parameters of **t-TS16**, the second transition state structure that includes the OCCH and H radical recombination occurs without barrier, although the CBSQ method gives a negative reaction barrier. The same arguments used above can be applied here for suggesting that the activation barrier is actually very close to zero. The reaction is also 50.5 kcal/mol exothermic (Table 17) or the C−H bond dissociation energy in triplet ketene is 50.56 kcal/mol. The formed triplet ketene can further decompose through **t-TS17** (Figure 10) into singlet vinylidene and the triplet oxygen atom. We were not able to optimize this transition state structure with the MP2/6-31G(d′) method; therefore, the CBSQ energy was evaluated on the HF/6-31G(d′) geometry.

TABLE 17: Activation Barriers for Hydrogen Elimination and Addition from Triplet Oxyacetylene[a]

theory	ΔE_{XVI}	ΔH_{XVII}	ΔE_{XVII}	ΔH_{XVIII}
HF/6-31G(d′)	62.9	−49.4	6.2	−29.3
HF/6-31G(d′) (0 K)	57.6	−41.8	7.6	−22.1
MP2/6-31G(d′)	56.1	−24.8	7.1	−49.5
QCISD(T)/6-31+G(d′)	73.2	−33.9	1.3	−54.0
MP4/CBSB4	58.3	−39.1	0.9	−60.7
MP2/CBSB3	53.9	−27.8	4.3	−52.7
CBSQ (0 K)	44.3	−29.6	−1.8	−50.5
CBSQ	44.5	−31.2	−2.9	−52.2

[a] ΔE_{XVI} = activation barrier for elimination hydrogen radical from triplet oxyacetylene through **t-TS15**; ΔH_{XVII} = enthalpy of the hydrogen radical elimination from triplet oxyacetylene with formation OCCH; ΔE_{XVI} =activation barrier for hydrogen radical recombination with OCCH radical with formation of triplet ketene; ΔH_{XVIII} = enthalpy of the triplet ketene formation.

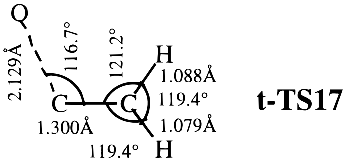


Figure 10. HF/6-31G(d′) transition state structure for oxygen elimination from triplet oxyvinylidene.

The total energy for the transition state **t-TS17** with the activation barrier and the enthalpy of the reaction for the oxygen atom elimination from triplet oxyvinylidene are presented in Table 18. The estimated activation barrier is practically the same as the C−O bond dissociation energy in triplet ketene. Both values are exceptionally high (more than 100 kcal/mol, Table 18), and the transformation of acetylene into vinylidene through triplet ketene is out of the question. The reaction is basically energetically “forbidden”, and through CBSQ ab initio computational studies we are predicting that this transformation cannot occur experimentally.

There is still at least one possibility for obtaining vinylidene from triplet oxyacetylene: the hydrogen radical elimination from

TABLE 18: Total Energy (au) for t-TS17 and Activation Barrier ($\Delta E_{\mathrm{XVIII}}$, kcal/mol) and Enthalpy of Reaction (ΔH_{XIX}, kcal/mol) for Oxygen Atom Elimination from Triplet Oxyvinylidene[a]

theory	*E*(**t-TS17**)	$\Delta E_{\mathrm{XVIII}}$	ΔH_{XIX}
HF/6-31G(d′)	−151.546307	51.4	51.4
HF/6-31G(d′) (0 K)	−151.518567	49.4	48.2
MP2/6-31G(d′)	−151.876653	120.2	121.3
QCISD(T)/6-31+G(d′)	−151.955037	104.1	110.3
MP4/CBSB4	−151.947392	108.6	108.7
MP2/CBSB3	−152.023177	123.4	125.1
CBSQ (0 K)	−152.117980	107.3	116.2
CBSQ	−152.112974	107.7	117.6

[a] (0 K) = sum of electronic and zero-point energies.

TABLE 19: Computed Bond Dissociation and Bond Association Energies (kcal/mol) in Transformation of Triplet Oxyacetylene into Vinylidene and Oxygen Atom through Oxyvinylidene as an Intermediate[a]

theory	$\mathrm{BDE_I}$	$\mathrm{BAE_I}$	$\mathrm{BDE_{II}}$
HF/6-31G(d′)	116.8	−36.1	9.1
HF/6-31G(d′) (0 K)	109.2	−29.1	12.2
MP2/6-31G(d′)	120.9	−30.8	6.4

[a] (0 K) = sum of electronic and zero-point energies; $\mathrm{BDE_I}$ = the C−H bond dissociation energy in triplet oxyacetylene with formation OCHC radical; $\mathrm{BAE_I}$ = the energy obtained by recombination of the OCHC and H radicals into oxyvinylidene; $\mathrm{BDE_{II}}$ = the C−O bond dissociation energy in triplet oxyvinylidene.

the second carbon atom of oxyacetylene, and then the radical recombination reaction with the formation of oxyvinylidene, and finally the elimination of triplet oxygen from oxyvinylidene, as its was outlined in Scheme 2. The ab initio computed bond dissociation energies for these transformations are presented in Table 19. As a result of convergence problems in computing CBSQ total energies for the OCHC radical and triplet oxyvinylidene, the highest ab initio level of theory at which the bond dissociation energies could be computed is MP2/6-31G(d′). Although the computed energies have a large computational error, it is obvious that this reaction channel is also not favorable, due to the initially very high C−H bond dissociation energy in oxyacetylene. If the OCHC radical could be formed, its transformation to vinylidene should occur very easily, as demonstrated with C−H association and C−O dissociation energies computed at the MP2/6-31G(d′) level of theory (Table 19).

Conclusion

From the very extensive CBSQ computational study of the triplet potential energy surface for the oxygen atom assisted transformation of acetylene into vinylidene, we can withdraw several very interesting conclusions. It seems that the triplet oxygen atom readily reacts with acetylene to form triplet oxyacetylene. This reaction is predicted to be exothermic (∼50.4 kcal/mol) and occurs with a negligible, or zero, reaction barrier. The other competing reaction, the triplet oxygen hydrogen abstraction from acetylene, is estimated to have a substantial activation barrier (∼25.5 kcal/mol) and is less exothermic than the simple reaction of the oxygen addition to acetylene. Thus, the oxyacetylene formed in its triplet state is actually an aldehyde carbene for which internal addition reactions into the C−O double bonds should produce a cyclic oxyacetylene, oxirene. On the triplet potential energy surface, oxirene is less (∼28.5 kcal/mol) stable than oxyacetylene. Other C_2H_2O isomers that can, by the elimination of oxygen, produce vinylidene are oxiranylidene and oxyvinylidene. Both of these species are less stable than oxirene on the triplet potential energy surface, and they are unlikely to be intermediates that lead to the triplet oxygen atom assisted transformation of acetylene into vinylidene.

The recombination of hydroxyl and acetylidene radicals might produce triplet hydroxyacetylene and triplet hydroxyvinylidene. Our computational study estimates that they are very close in energy. Through several hydrogen shifts, the molecular species can be transferred into triplet ketene and triplet oxyvinylidene, and then, through the elimination of the triplet oxygen atom, it is proposed that vinylidene can be formed. The CBSQ estimated activation barriers for the hydrogen shifts are too high, and oxygen assisted rearrangement through this channel is unlikely to be accomplished experimentally.

Bond dissociation energies in triplet oxyacetylene and triplet ketene are too high to favor the C−H bond dissociation bond association process with a final C−O bond dissociation as a channel for the oxygen assisted acetylene rearrangement into vinylidene. In general, from our exploration of the triplet oxygen−acetylene potential energy surface, we suggest that the formation of oxyacetylene will occur rapidly and that this reaction might be accomplished in low yields with hydrogen radical abstraction reaction from acetylene with triplet oxygen. The main product of this reaction, oxyacetylene (aldehyde−carbene), is unlikely to transform into vinylidene and triplet oxygen atom. Therefore, on the basis of the CBSQ calculations, the triplet oxygen atom assisted acetylene rearrangement into vinylidene is not possible if only unimolecular reactions are considered. This might be totally different if bimolecular reactions on the triplet potential energy surface are considered.[19]

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