JOC Notes

A Theoretical Study of the Formation of Phosphaacetylene by Thermolysis of Triallylphosphine

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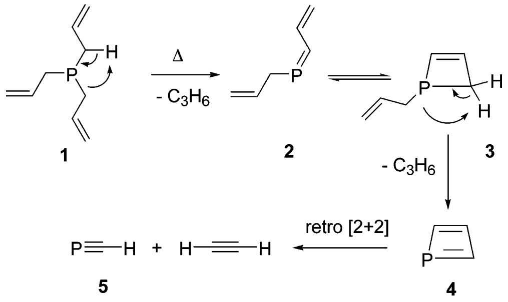
Abstract: A theoretical study of the decomposition of triallylphosphine into phosphaacetylene at the B3LYP/6-311++G(3df,2p) level has shown that the most likely mechanism involves two retroene eliminations of propene leading to vinylphosphaacetylene. Two mechanisms can account for the formation of HCP from vinylphosphaacetylene, either by a 1,2 or a 1,3 hydrogen shift. The first pathway was found to be the most favored kinetically. It is quite similar to the pathway proposed for the thermal decomposition of vinylacetylene into acetylene in the shock tube.

The discovery of phosphaacetylene by Gier[1] in 1961 was a major turning point of organophosphorus chemistry and paved the way for the development of low-coordinate phosphorus species and their carbon-like chemistry.[2] Today, the chemistry of phosphaacetylene remains poorly developed, in part because it is widely believed that this molecule is highly unstable. However, an ethereal solution of HCP can be kept for months at −20 °C. The status of HCP as a chemical curiosity might change soon as a result of two facts. First, it is now well established that HCP is one of the major forms under which phosphorus is present in planetary and stellar atmospheres.[3] Second, preliminary studies on the polymerization of unhindered phosphaalkynes are presently in progress.[4] In practice, there are only three approaches toward the synthesis of HCP. The two first ones involve the dehydrochlorination of either $MePCl_2$ at high temperature[5] or $HCCl_2PH_2$ at low temperature.[6] However, the first method is plagued by the formation of HCl as a byproduct that is highly reactive toward HCP. On the other hand, the second method requires the synthesis of a rather sophisticated primary phosphine as a prerequisite. This situation prompted us to develop a new approach which operates under neutral conditions. In 1993, we reported on the successful synthesis of HCP through flash vacuum thermolysis of the easily available triallylphosphine[7] **1** at 750 °C. Our preliminary proposal for the mechanism of formation of HCP involved as a first step a retroene reaction from **1** leading to the allylphosphabutadiene **2** with the concomitant release of propene, followed by an electrocyclization leading to the 1-allyl-1,2-dihydrophosphete **3**. Then we proposed that HCP **5** could result from the [2 + 2]-cycloreversion of the antiaromatic phosphete C_3H_3P **4** produced from **3** through a second retroene reaction (see Scheme 1).

SCHEME 1



Though the intermediacy of phosphete **4** seems unlikely, no new alternative to this mechanism has been suggested so far. The purpose of this work was to find out such an alternative mechanism and to establish its validity by a thorough theoretical study.

All our computations were realized using the Gaussian 98 and 03 packages at the B3LYP 6-311+G(d,p) level of theory for geometry optimizations, and single points were calculated at the higher B3LYP 6-311++G(3df,2p) level of energy.[8] This combination already proved to be successful for the study of the potential energy surface of the radical cation $C_4H_4^{+\bullet}$.[9] Thinking in terms of the now well-established analogy between the chemistry of low-

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‡ Ecole Polytechnique.

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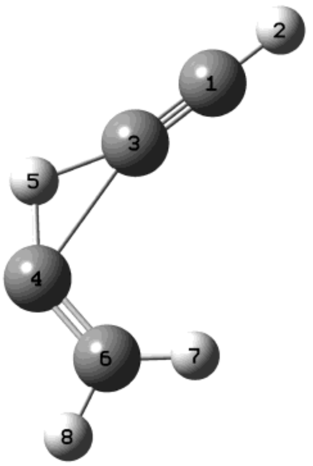
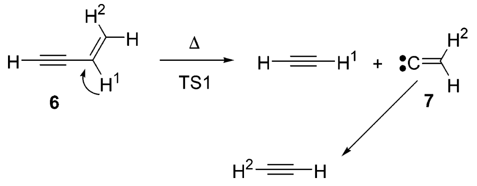


FIGURE 1. Transition state **TS1** (dissociation of vinylacetylene). Most significant distances (Å) and angles (deg): H2−C1, 1.064; C1−C3, 1.208; C3−H5, 1.326; C3−C4, 2.074; C4−H5, 1.219; C4−C6, 1.311; C6−H7, 1.080; C6−H8, 1.090; C1−C3−C5, 162.710; C1−C3−C4, 163.571; C3−H5−C4, 109.138; C3−C4−C6, 104.271; C4−C6−H7, 128.668; C4−C6−H8, 113.632.

SCHEME 2



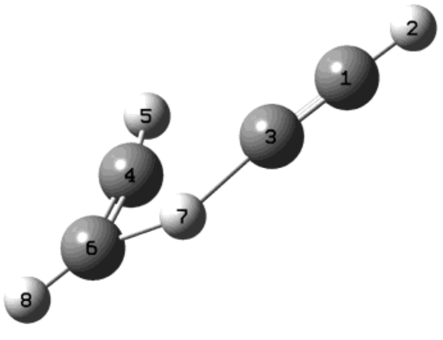
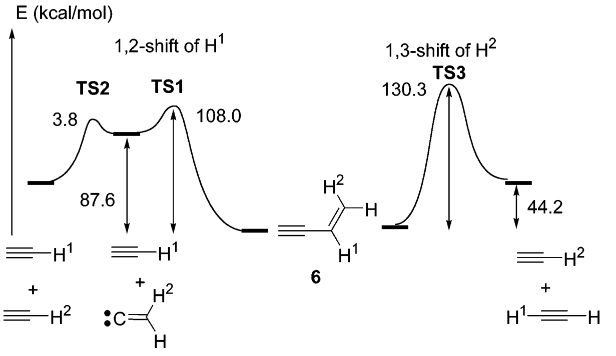


FIGURE 2. Transition state **TS3** (dissociation of vinylacetylene). Most significant distances (Å) and angles (deg): C1−H2, 1.066; C1−C3, 1.224; C3−H7, 1.547; C6−H7, 1.343; C6−H8, 1.074; C6−C4, 1.256; C4−C5, 1.073; H2−C1−C2, 178.083; C1−C3−H7, 172.881; C3−H7−C6, 142.225; H7−C6−C4, 70.453; C6−C4−C5, 166.134; H7−C6−H8, 149.597.

SCHEME 3

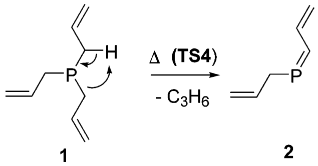


coordinate phosphorus and carbon species,[2,10] we were first interested in reexamining the unimolecular dissociation of vinylacetylene **6** in the shock tube.[11] The main decomposition pathway yields two molecules of acetylene through the proposed mechanism depicted in Scheme 2. This mechanism relies on the dissociation of vinylacetylene **6** through a 1,2-migration of the hydrogen atom H^1 and the concomitant release of one molecule of vinylidene **7**. The formation of the second molecule of acetylene was rationalized by a 1,2-hydrogen shift in **7**.[12]

Computations indicated that the system acetylene + vinylidene **7** in its singlet ground state lies around 87.6 kcal mol^{-1} higher in energy than vinylacetylene **6**. The barrier for the dissociation reaction of vinylacetylene has been evaluated by the authors as ca. 80 kcal mol^{-1}.[11] This would indicate that the transition state lies very close to the dissociation products. We felt it necessary to investigate more thoroughly this proposed dissociation pathway. The classical procedure (STQN method (QST3) followed by IRC calculation) yielded a transition state **TS1** which is depicted in Figure 1 and lies 108.0 kcal mol^{-1} above vinylacetylene **6**. The agreement with the experimental observations was therefore found to be acceptable but not perfect. On the other hand, we also investigated the nature of the transition state **TS2** (1,2-shift of hydrogen) leading to acetylene from **7**. This process was found to be highly exothermic and only requires a small activation energy of 3.8 kcal/mol (Scheme 3). This result is similar to those of earlier studies.[12]

However, another pathway can also be considered. Indeed, the formation of acetylene can imply a new mechanism that relies on the 1,3-migration of the hydrogen atom H^2 in vinylacetylene **6**. This transformation is less endothermic than the 1,2-hydrogen shift (ΔH = 44.2 kcal/mol), but calculations yielded a transition state **TS3** which is shown in Figure 2 and lies 130.3 kcal mol^{-1} above vinylacetylene **6**. Therefore, the initially proposed mechanism is the most kinetically favored (Scheme 3).

The next step of our study was to check whether a similar pathway could explain the formation of HCP **5** from triallylphosphine **1**. The first step is identical to that of the initially proposed mechanism and involves a retroene elimination of propene from **1** to yield **2**. This process was found to be endothermic (ΔH = +18.2 kcal/mol) and **TS4** lies +38.0 kcal/mol above **1** (eq 1). Note that the formation of 1-R-1-phosphabutadienes by pyrolysis of diallylphosphines R−P(allyl)$_2$ is an already known process.[13]



(1)

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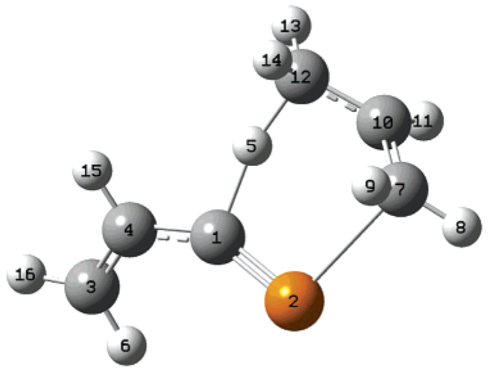
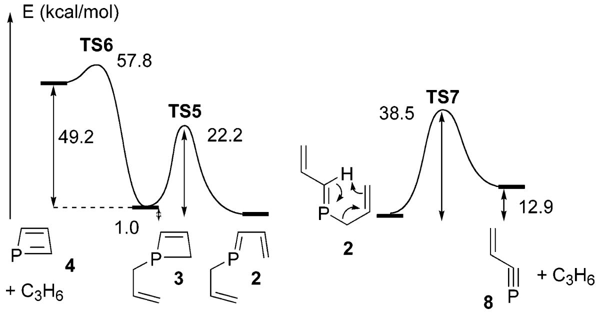


FIGURE 3. Transition state **TS7** (dissociation of 1-allyl-1-phosphabutadiene). Most significant distances (Å) and angles (deg.): P2−C1, 1.608; C1−C4, 1.441; C4−C3, 1.342; P2−C7, 2.419; C7−C10, 1.383; C10−C12, 1.417; C1−H5, 1.467; H5−C12, 1.311; P2−C1−C4, 147.690; C1−C4−C3, 125.737; P2−C1−H5, 106.929; C1−H5−C12, 161.660; H5−C12−C10, 95.533; C12−C10−C7, 121.087; C10−C7−P2, 101.268; C7−P2−C1, 99.400.

SCHEME 4



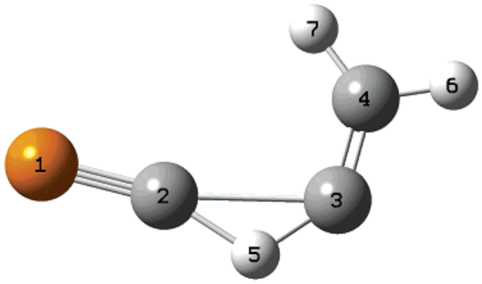


FIGURE 4. Transition state **TS8** (dissociation of vinylphosphaacetylene). Most significant distances (Å) and angles (deg): P1−C2, 1.555; C2−C3, 2.126; C2−H5, 1.337; H5−C3, 1.216; C3−C4, 1.311; C4−H6, 1.090; C4−H7, 1.081; P1−C2−C3, 166.850; C2−C3−C4, 103.755; P1−C2−H5, 161.256; C2−H5−C3, 112.597; C3−C4−H6, 113.887; C3−C4−H7, 128.638.

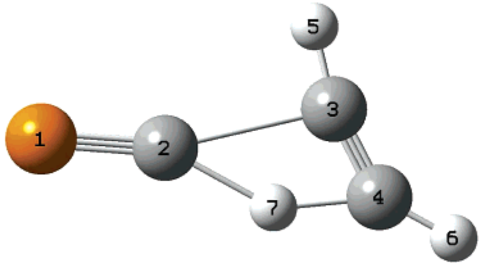


FIGURE 5. Transition state **TS9** (dissociation of vinylphosphaacetylene). Most significant distances (Å) and angles (deg): P1−C2, 1.571; C2−H7, 1.562; C2−C3, 2.191; H7−C4, 1.346; C4−H6, 1.074; C3−C4, 1.252; C3−H5, 1.072; P1−C2−H7, 155.292; P1−C2−C3, 162.950; C2−H7−C4, 145.612; H7−C4−H6, 145.657; H7−C4−C3, 68.305; H5−C3−H7, 135.065; C2−C3−H5, 89.665; H7−C2−C3, 41.758.

According to Scheme 1, the second step of our initial mechanism involves a 4π-electrocyclic reaction (leading to **3** through **TS5**) followed by a retroene elimination which finally yields **4** (through **TS6**).[14] Whereas the first step was found to be slightly endothermic ($\Delta H = +1.0$ kcal mol^{-1}) and involves a relatively weak activation barrier (**TS5** only lies +22.2 kcal mol^{-1} above **2**), the second step is highly endothermic ($\Delta H = +49.2$), **TS6** lying 57.8 kcal mol^{-1} above **3**. The structure of **TS6** was therefore found to be very similar to that of the products formed. Despite many attempts, no transition state could be localized for the [2 + 2]-cycloreversion leading to **5** + acetylene by splitting phosphete **4** (Scheme 4). This reaction being orbital-symmetry-forbidden probably proceeds via a biradical mechanism which cannot be well described by DFT.[15]

By analogy to the production of acetylene from vinylacetylene, one may propose a second pathway leading to vinylphosphaacetylene **8** from **2** (*E*-geometry) (Scheme 4). This compound has previously been made by pyrolysis of allyldichlorophosphine and its structure studied by microwave spectroscopy,[16] and a good agreement was found between our results and the reported microwave data. This transformation which can be achieved through a retroene elimination of propene was found to be slightly endothermic ($\Delta H = 12.9$ kcal mol^{-1}), and **TS7** lies +38.5 kcal mol^{-1} above **2**. Though the energetic barrier leading to **3** is smaller, the high endothermicity of the second transformation that yields **4** definitely rules out our initial mechanism (note that the system **4** + propene lies 9.7 kcal mol^{-1} above **TS7**). A view of **TS7** is presented in Figure 3, and the most significant bond lengths and bond angles are listed in the corresponding legend.

The vinylphosphacetylene route being confirmed, we then focused our study on its decomposition pathways. Like its carbon counterpart, two mechanisms can account for the formation of **5** and acetylene: a 1,2- and a 1,3-hydrogen migration. The first route yields a transition state **TS8** which is depicted in Figure 4. This transition state was found to be very similar to **TS1**, computed in the case of the decomposition of vinylacetylene. At 107.8 kcal mol^{-1}, even the magnitude of the barrier is identical (108.0 kcal mol^{-1} for **TS1**)! The study of the hydrogen 1,3-migration pathway led to a transition state **TS9** (see Figure 5) which was found higher in energy at 131.9 kcal mol^{-1}(Scheme 5). Like in the vinylacetylene rearrangement, this process was also found to be less endothermic than the 1,2-hydrogen shift. However the small activation barrier (**TS2**) needed for the rearrangement of vinylidene

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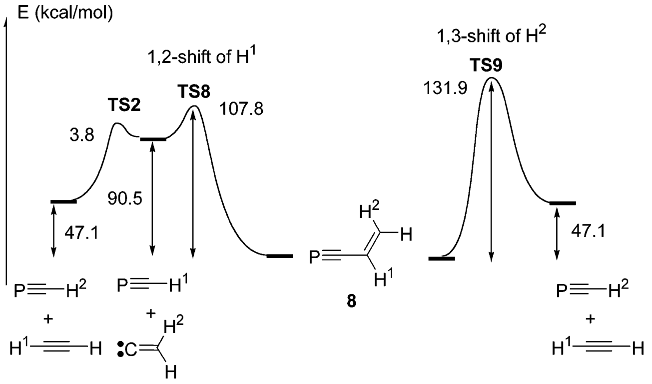
SCHEME 5



to acetylene makes the first pathway the most kinetically favored.

In conclusion, it appears that the thermal decomposition of triallylphosphine into phosphacetylene is an additional and fascinating illustration of the phosphorus–carbon analogy in their low-coordination states.

Computational Details

All computations have been performed using the Gaussian 03[8] suite of programs and gradient correct density functional theory[17] using "B3LYP" functional. "B3" is a hybrid method proposed by Becke[18] that includes a mixture of Slater functional,[19] Becke's 1988 gradient-corrected,[20] and Hartree–Fock exchange. The correlation component "LYP" is the gradient-corrected functional proposed by Lee et al.[21] All optimizations were carried out using the 6-311+G(d,p) basis set and energies were refined at the 6-311++G(3df,2p) level of theory with no imaginary frequency vibration for a minimum and one imaginary frequency vibration for a transition state. Transition states were localized using the STQN method (QST3) and their structure ascertained by IRC calculations.

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Supporting Information Available: Cartesian coordinates and energies of theoretical structures of **1**–**8** and **TS1**–**TS9** and views of **TS2, TS4, TS5,** and **TS6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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