A pathway to diphosphorus from the dissociation of photoexcited tetraphosphorus
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We report a computational study of an energetically favorable pathway for the excited-state dissociation of a tetrahedral P4 molecule into two P2 molecules via the simultaneous breaking of four chemical bonds along a highly symmetric (D2h) reaction pathway. Along this pathway, a degeneracy occurs between the first excited state of P4 and the ground state of 2P2 at a lower total energy (ca. 4.7 eV) than the initial state, indicating that the initial photoexcitation provides sufficient energy for the dissociation without significant kinetic barriers. We also found that sequential dissociation of the four P–P bonds exhibits larger activation barriers thus making this a less viable dissociation pathway. Our computational investigation uncovers complicated photochemistry in elemental phosphorus, and suggests a likely mechanism for the environmentally friendly inclusion of phosphorus atoms into organic molecules.

1. Introduction

The idea of “cracking” P4 into two P2 molecules in order to take advantage of the high reactivity of the π bonds in the latter is attractive,† but this process is not conveniently accessed thermally as very high temperatures (ca. 1100 K) are needed to break down the tetrahedral P4 molecule.2 On the other hand there have been indications since at least 1937 that UV irradiation of white phosphorus, a process that converts it into a red form, may initially bring about P2 generation.3 In one report on the P4 co-photolysis with metal carbonyl complexes, Dahl et al. mention that “P4 in solution photolyzes readily to P2 at ambient temperatures.”4 Co-photolysis of P4 with metal carbonyl complexes with formation of metal-phosphorus products has been reported in a few other cases,5 but only recently, Tofan and Cummins demonstrated the inclusion of diphosphorus moieties into organic molecules is afforded directly from the irradiation of mixtures of P4 and 1,3-dienes.6 The major organophosphorus products are cyclic compounds with a single P2 unit shared between the two fused six-membered rings. This reaction was proposed to occur through Diels–Alder additions of 1,3-diene molecules to photo-generated P2 units (Scheme 1).6

Here we report a theoretical investigation of the photolysis mechanism of P4. In this reaction, the starting point was an electronically excited state of a single P4 molecule and the endpoint was the ground state of two P2 molecules. We knew that this pathway must proceed through the dissociation of four chemical bonds and may involve a change in the electronic state. From a theoretical perspective, the problem is highly interesting in that the P4 is a small enough system to be treatable using highly accurate multi-reference quantum chemistry methods, yet the task of elucidating a low-energy pathway for photolysis involves a nontrivial exploration of the multidimensional potential energy surface (PES). In terms of experimental chemistry, an understanding of the P4 photolysis mechanism could lead to improved specificity and reaction yields for this type of photochemistry and increase the viability of this pathway as an environmentally friendly method for the incorporation of phosphorus atoms into organic molecules.7

In our explorations of the excited state PES, we found a surprising pathway for the direct dissociation of excited P4 into 2P2 that involves the simultaneous breaking of four P–P bonds. This pathway is easily visualized by placing the four phosphorus atoms on the corners of a cube such that no two atoms share a cube edge; the dissociation coordinate is equivalent to moving the top and bottom faces of the cube away from one another while contracting the P–P bonds in each diatomic subunit.

† Electronic supplementary information (ESI) available: MOLPRO input file for the CASSCF calculations and molecular geometries along both dissociation coordinates. See DOI: 10.1039/c3ra43940b
2. Theory and computational methods

Our calculations are performed on gas-phase phosphorus clusters in the absence of a solvating environment. There are a number of theoretical studies on phosphorus clusters in the literature, but most of them have focused on equilibrium configurations of the ground electronic state. For example, Häser and Ahlrichs have investigated the equilibrium geometries and energies of many phosphorus clusters sometimes containing up to thirty atoms. These studies were carried out using methods including Hartree–Fock, density functional theory (DFT), second-order Moller–Plesset perturbation theory (MP2), and CCSD. We refer to these as single-reference electronic structure methods because they are based upon the assumption that the ground-state wavefunction is mostly described by a single electron configuration or Slater determinant, which is then used as a reference state for the calculations of electron correlation effects. Single-reference methods for the calculation of excited state energies include CIS, RPA, time-dependent density functional theory (TDDFT), and EOM-CCSD.

The ground state of tetrahedral \( \text{P}_4 \) and \( \text{P}_2 \) are both closed-shell configurations with singlet spin multiplicity, and thus they are qualitatively well described by single Slater determinants. However, in general there is no reason to expect that the electronic state should stay the same throughout the entire dissociation pathway. Furthermore, the ground state of reaction intermediates may have multi-reference character (also known as static correlation); this means that the wavefunction cannot be described by a single Slater determinant. Multi-reference wavefunctions often appear in geometries where chemical bonds are broken and the system contains multiple radicals, and in these situations single-reference methods may be qualitatively incorrect. One would thus expect single-reference methods to perform well at the endpoints of the pathway but give unreasonable answers in the middle; this is indeed what we found in early exploratory calculations.

For this reason, we turn to complete active space self-consistent field (CASSCF), which is a method capable of describing static correlation; in CASSCF, the wavefunction is a linear combination of several Slater determinants, each of which represents a distinct electron configuration or orbital occupation. A CASSCF calculation is specified by choosing the number of active electrons and the number of active orbitals, and the wavefunction includes all configurations that can be constructed from placing the active electrons into the active orbitals. For example, in a CASSCF(2,2) calculation, there are two active electrons in three active orbitals, giving rise to six possible electron configurations, all of which are included in the wavefunction. The reliability of CASSCF calculations depends heavily on a good choice of the number of active electrons and the size of the active space.

In order to obtain quantitative accuracy, a calculation also needs to include dynamic correlation, which in the CASSCF picture corresponds to minuscule contributions to the energy from the electron configurations not considered in the wavefunction. Since the wavefunction does not contain sizable contributions from these
configurations, they are not treated explicitly and instead are included using perturbation theory. Therefore, we expect that methods like CASSCF with second and third order corrections from Rayleigh–Schrödinger perturbation theory (RSPT2 and RSPT3) would provide quantitative accuracy for intermediate states on the pathway.

The CASSCF calculations took the symmetry of the geometries into account; orbitals were classified into the four irreducible representations of the $D_2$ point group ($A, B_1, B_2, B_3$). Along the entire dissociation pathway, the orbital occupations corresponding to the four representations was $(9,7,7,7)$. The closed-shell orbitals were chosen to be $(7,7,7,7)$ and the active space was chosen to be $(3,2,2,2)$, because these frontier orbitals were well-separated from the occupied and virtual manifolds above and below for the entire dissociation process. The number of electronic states computed were $(3,2,2,2)$ and state-averaging was performed within each representation. This makes the level of theory CASSCF(4,9)-RSPT3.

We verified our choice of active space with a CASSCF(12,13) calculation, where the active space includes all bonding electrons but is too large for applying accurate dynamic correlation treatments; here the closed-shell orbitals was $(6,6,6,6)$ and the active space was $(4,3,3,3)$. In both the $(4,9)$ active space and the $(12,13)$ active space, the CI vector describing the ground state and the orderings of the excited states stayed the same (ESI, Fig. S1†), providing verification that the $(4,9)$ active space is a qualitatively correct description. We found that RSPT3 provided similar answers to RSPT2 but gave better agreement with the excitation energies in the tetrahedral geometry (ESI, Fig. S3†); this agreed with our intuition that RSPT3 should provide an improved treatment of dynamic correlation.

All calculations were performed with gas-phase structures using aug-cc-pVTZ basis sets and the MOLPRO software package.\textsuperscript{18}

3. Results and discussion

Sequential dissociation coordinate.

In our initial explorations, we optimized the geometry of $P_4$ in the first excited state. This caused the tetrahedral molecule to rearrange into a $C_{2v}$-symmetric structure (Scheme 2, top middle) in which one of the P–P bonds was broken. From this geometry, an electronic relaxation to the ground state leads straight back to tetrahedral $P_4$. The system is highly unlikely to follow minimum energy paths, however, since it possesses a large kinetic energy from the initial excitation; this motivated us to explore other potential pathways. We found another exothermic rearrangement leading to a $D_{2d}$-symmetric minimum (Scheme 2, top right) with a low activation barrier of $\approx 0.5$ eV in which one more P–P bond was broken. However, further bond dissociation involved much greater activation barriers of approximately $\approx 1.4$ eV; here the system proceeds through a $C_s$-symmetric transition state. Thus, a dissociation pathway passing through the molecular geometry critical points involving the \textit{sequential} breaking of P–P bonds is possible, though it may require the system to possess large amounts of kinetic energy for crossing over the large activation barriers.

Direct dissociation coordinate.

With the results of the previous exploration in mind, we reasoned that excited-state $P_4$ is likely to follow a highly ballistic trajectory without passing through the molecular geometry critical points.\textsuperscript{19} This motivated us to study a \textit{direct} dissociation coordinate in which the opposite edges of the $P_4$ tetrahedron were pulled apart linearly, involving the simultaneous breaking of four P–P bonds (Fig. 1). To our surprise we found that the energy along this coordinate was almost entirely downhill, with the exception of a very small barrier (0.1 eV) in the neighborhood of a state crossing.

Scheme 2 Molecular geometry critical points in the \textit{sequential} dissociation pathway. The bottom left is the ground state of $P_4$, and the far right is the ground state of $2P_2$. $P_4$ enters the excited state after absorbing a photon, and a geometry optimization on the excited state surface leads to the $C_{2v}$-symmetric geometry (top middle). From here, relaxation to the ground state leads back to tetrahedral $P_4$, but rearrangement into a $D_{2d}$-symmetric minimum is also possible (top right). Dissociation of the $D_{2d}$-symmetric geometry into two $2P_2$ molecules occurs with a significant activation barrier of $\approx 1.4$ eV.
To generate the direct dissociation coordinate, we first optimized both the P₄ and P₂ structures at the MP2/aug-cc-pVTZ level. The dissociated geometry was built from placing two optimized P₂ molecules 5 Å apart on the z-axis, with one P₂ molecule placed symmetrically on the x-axis and the other on the y-axis. For comparison, the distance between the two P₂ units within the optimized P₄ molecule was found to be 1.56 Å. Fifty intermediate frames were generated by linearly interpolating from P₄ to 2P₂, corresponding to a 0.070 Å increase per frame in the distance between the two units.

Calculations were carried out for each point on the dissociation trajectory. At frame 0 (the tetrahedral geometry, z-axis separation = 1.56 Å), there are two threefold-degenerate excited states between 5 eV and 6 eV corresponding to the experimental optical excitation between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). As the dissociation proceeds, the degeneracy is lifted and the excited states in the B₁ and B₂ representations increase monotonically in energy (Fig. 2 depicts the A and B₃ states, but not the B₁ and B₂ since these increase monotonically). The energy of the lowest B₃ state decreases slightly until a minimum of 4.2 eV is reached at frame 5 (dimer separation = 1.90 Å), corresponding to an excimer-like geometry.

As we proceed along this coordinate, there is a degeneracy around 4.7 eV at frame 12 (z-axis separation = 2.50 Å) where the lowest B₃ state intersects with the A(1) and A(3) states. It is unclear whether this is a true threefold degeneracy or three close intersections of twofold degeneracies. The most interesting result is that the A(3) electronic state corresponds to the ground state configuration of a P₂ dimer, and the degeneracy occurs at a lower energy with respect to the initial excitation. Thus, this provides a possible pathway for the direct dissociation of photoexcited P₄ into two P₂ molecules. We note that at this degeneracy it is also possible to cross back to the ground state surface; this is expected to lead back to the tetrahedral geometry of ground state P₄.

At the end of the trajectory, the geometry approaches that of two well-separated P₂ molecules. The A(3) state becomes the ground state at the dissociation limit and is dominated by a single determinant of coefficient 0.94. The next highest states (A(1) and A(2)) become essentially degenerate excitations of single P₂ dimers with a small exchange splitting. The excitation energy of approximately 3.8 eV is in good agreement with experimental absorption spectra of P₂.

The photochemistry along this pathway can be understood by examining the frontier orbitals (as shown in Fig. 3). At the tetrahedral P₄ geometry, the HOMO shows bonding character across four edges of the tetrahedron and antibonding character across two edges, while the LUMO has complementary character with antibonding character across four edges and bonding character across two. Our intuition is that the direct dissociation coordinate involves an electronic state where two electrons from the HOMO are promoted into the LUMO, and this electronic state would correspond to the ground state of 2P₂ at dissociation. This intuition is supported by examining the CI vector and MOs across the pathway.

Since the potential surface for P₄ dissociation is a many-dimensional hypersurface, we decided to scan the potential surface in other dimensions orthogonal to the direct dissociation coordinate. We computed two-dimensional energy profiles of the ground state and lowest two excited states along the dissociation coordinate and two orthogonal deformation coordinates and plotted the results (Fig. 4 and 5). From the plots, we can see that the excimer-like geometry found in the one-dimensional profile is really a saddle point, and the true minima involve deformations in other coordinates (this is hardly surprising because our geometry optimizations led to the...
However, the potential surface of the first excited state is smooth and mostly flat compared to the other two surfaces, lending some credence to our hypothesis that excited-state P₄ may follow a highly ballistic trajectory.

4. Conclusions

Our calculations of the excited-state potential surface of P₄ show that it may be possible to dissociate P₄ into 2P₂ by the simultaneous breaking of four P–P bonds with the energy provided by UV irradiation. While there exist many pathways that lead back to the tetrahedral geometry, this does not rule out the possibility that a small population of molecules in the excited state may proceed along or near the direct dissociation pathway to generate small amounts of P₂ in the reaction mixture. Qualitatively this is in agreement with the observations of Tofan and Cummins, in which a portion of the P₄ reactant was recovered from the reaction mixture after twelve hours of UV illumination.

While our study suggests a possible pathway for the photolysis of P₄ into 2P₂, a firmer conclusion regarding the actual dissociation mechanism would necessitate further study using non-adiabatic molecular dynamics to explore the potential energy surfaces properly. Further studies of this nature may also shed light on other aspects of the photochemistry, such as the expected quantum yield for the photolytic reaction.

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