Ab initio study of the energetics of photoinduced electron and proton transfer processes in a bio-inspired model of photochemical water splitting

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ARTICLE INFO

Article history:
Received 3 June 2009
In final form 29 July 2009
Available online 3 August 2009

ABSTRACT

The photochemical reaction mechanisms of a supramolecular model system consisting of a truncated chlorophyll, imidazole, and benzoquinone have been explored with ab initio electronic-structure methods. The calculations indicate that a photoinduced electron-driven proton-transfer process leads to the oxidation of imidazole and reduction of the quinone. The repeated photoinduced reduction of benzoquinone is a mechanism which can lead to the decomposition of water by sunlight.

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1. Introduction

Oxygenic photosynthesis in green plants provides the proof that the conversion of the unlimited energy resource of sunlight into useful and clean chemical energy is possible. Through billions of years of evolution, nature has developed a beautifully organized molecular machinery of stunning complexity, the photosystems (PS) I and II. In PS II, water serves as an electron donor to reneutralize the primary electron donor (chlorophyll) after the initial photoinduced charge separation. Oxidic photosynthesis reduces carbon dioxide to carbohydrates and releases molecular oxygen into the atmosphere.

Although the understanding of the functionality of the natural photosynthetic reaction centers at the molecular level is a topic of outstanding importance and represents a great intellectual challenge, there exists the very urgent problem of finding efficient fundamental molecular processes involved in photochemical water splitting. This may be possible to develop much simpler, more effective bio-inspired model systems. The available crystal structures of the photosynthetic reaction centers consist of a truncated chlorophyll (Chl), benzoquinone (Q) and a water wire connecting the electron donor (Chl) and the electron acceptor (Q) [9]. It has been shown that this model system can split a water molecule upon the absorption of a visible photon via an electron-driven proton-transfer process. The Q is thereby reduced to semiquinone (QH). The results of Ref. [9] highlight the relevance of the photochemistry of hydrogen bonds [10] for the photoinduced water-splitting process. Upon the consumption of four visible photons, four Qs are reduced to semiquinones and O2 is released according to the overall equation [9]

\[
\text{Chl} + 2\text{H}_2\text{O} + 4Q + 4h\nu \rightarrow \text{Chl} + O_2 + 4QH. \quad (1)
\]

The semiquinone disproportionate to Q and hydroquinone (QH2). The latter may serve as the reducing agent in a subsequent dark reaction. Alternatively, gaseous H2 may be recovered from hydroquinone with the use of a suitable catalyst. Note that the reaction scheme (1) elegantly solves the problem of the separation of the photoproducts H2 and O2: while O2 is immediately released in gaseous form, hydrogen remains chemically bonded in the liquid phase. It may be released in a spatially separated dark reaction.

In the present communication, we report the results of a computational study of the photoinduced reduction of Q in an alternative bio-inspired model system. The available crystal structures indicate that the Chl of the reaction center prefers to coordinate an axial ligand at the magnesium center, typically histidine [6,11]. This fact suggests the investigation of a hydrogen-bonded supramolecular structure consisting of a Chl molecule, imidazole (the chromophore of histidine) and benzoquinone. As in Ref. [9], the side chains of Chl are replaced by hydrogen atoms, with the exception of the methyl ester carbonyl group on the cyclopentanone ring which can be involved in hydrogen bonding, thus fixing the relative orientation of the three aromatic moieties. Thanks to its relatively rigid geometry, this system appears more amenable that the previous model to first-principles computational studies of the dynamics of the electron- and proton-transfer processes.
2. Computational methods

The equilibrium geometry of the chlorophyll–imidazole–benzoin (Chl–Im–Q) complex in the electronic ground state has been determined with density functional theory (DFT), employing the B3LYP functional. The vertical singlet excitation energies of Chl–Im–Q have been calculated with the CC2 method [12,13], which is a simplified and computationally efficient variant of coupled-cluster theory with single and double excitations. The excitation energies of the locally excited (LE) singlet states have additionally been calculated with the TDDFT method. (As is well known, TDDFT with standard exchange–correlation functionals fails for excited states with pronounced charge-transfer (CT) character.) The default split-valence double-zeta basis set of the Turbomole program package [14] with polarization functions on the heavy atoms (def-SV(P) [15]) has been employed in the DFT and CC2 calculations. In the latter, the resolution-of-the-identity (RI) approximation has been used for the evaluation of the electron-repulsion integrals [16].

The equilibrium geometry of the photoprotein, which is of biradical character, has been obtained by geometry optimization of the lowest triplet state of the biradical (the ground state) at the unrestricted DFT level, exploiting the fact that the singlet and triplet states of biradicals with non-overlapping singly-occupied molecular orbitals are degenerate to a very good approximation. This degeneracy has subsequently been confirmed by single-point CC2 calculations at the optimized geometry (see Table 1). The vertical excitation energies of the biradical have been determined with the CC2 and TDDFT methods.

The calculation of properties (dipole moments and transition-dipole moments) was too time-consuming at the CC2 level. Therefore, the oscillator strengths of the LE states of the complex have been computed with the TDDFT method. The oscillator strengths of the CT states are essentially zero.

3. Results and discussion

The ground-state equilibrium structure of the Chl–Im–Q hydrogen-bonded system is shown in Fig. 1a. The Cartesian coordinates of this structure are given in the Supplementary material. The rather short Mg–N bond length ($R_{MN} = 2.172$ Å) indicates a fairly strong coordination of the imidazole to the porphyrin structure.

One of the oxygens of Q forms a relatively strong hydrogen bond ($R_{OH} = 1.861$ Å) with the azine group of Im. The Q is additionally stabilized by a weak hydrogen bond ($R_{OH} = 2.398$ Å) between the carbonyl group of the Chl and one of the CH groups of Q. The aromatic rings of Im and Q are coplanar and are oriented perpendicular to the porphyrin plane (see Fig. 1a).

The vertical excitation energies of the lowest singlet states obtained with the CC2 method for the structure of Fig. 1a are given in Table 1 and are shown on the left-hand side of Fig. 2. The locally-excited states of Chl are denoted as $1\text{LE}_c$, and those of Q as $1\text{LE}_Q$. In agreement with previous ab initio calculations [17], we obtain four low-energy excited states of Chl. The excitations of Chl (shown in blue in Fig. 2) are the well-known weak $Q_{650}$ band at 2.14 eV and the stronger 'Soret' band at 3.22 eV [18]. Both of them correspond to two approximately degenerate electronic states. Our calculated values for the Chl–Im–Q complex are about 2.3 eV and 3.4 eV, respectively (see Table 1). Two $^\pi\pi^*$ excited states of Q (shown in green in Fig. 2) are located below the Soret band. They are related to weak bands observed in the gas-phase absorption spectrum of Q between 2.5 and 3.0 eV [19]. The two electronic energy levels shown in red in Fig. 2 do not have counterparts in the absorption spectra of the molecular components. These excited states, denoted as $1\text{CT}_{CQ}$, are charge-transfer excitations from Chl to Q. Since the molecular orbitals (MOs) of Chl and Q do not overlap, the oscillator strength of these transitions is essentially zero.

The excited states of Im are higher in energy and are not mixed with the low-lying excited states of the complex. The frontier MOs of the Chl–Im–Q complex are displayed in Fig. 3. The two highest occupied MOs of Chl are shown in (a) and (b), the two lowest unoccupied MOs are shown in (d) and (e). These are the $\pi$ and $\pi^*$ MOs involved in Gouterman’s four-orbital model of porphyrin [20]. The lowest $^\pi\pi^*$ LE state in Q involves the orbitals shown in (c) and (f), (c) being the lone-pair orbital and (f) being the $\pi^*$ orbital. The two low-lying CT states of the complex result from the transfer of an electron from one of the two $\pi$ orbitals of Chl (a, b) to the $\pi^*$ orbital of Q (f). The two singly occupied MOs of the CT state at its equilibrium geometry are shown in Fig. 4.

When the energy of the lowest CT state is optimized, the structure shown in Fig. 1b is obtained (the Cartesian coordinates of this structure are given in the Supplementary material). It is seen that a proton has been transferred from Im to Q. The proton has ‘followed’ the electron in the CT state, resulting in a stabilization of both CT states by about 1 eV (see Fig. 2). The resulting electronic structure is a biradical, possessing an unpaired electron on Chl and on Q. The energies of both biradical states are lower than the energy of the lowest closed-shell state at this geometry (see Fig. 2). The overall enthalpy of the hydrogen-atom transfer from Im to Q is 1.69 eV (1.65 eV) at the CC2 (DFT) level of theory.

The following qualitative picture emerges from the energy diagram and equilibrium structures shown in Fig. 2. Excitation of Chl–Im–Q to the Soret band by visible or near-UV light leads, via a radiationless transition, to the population of the lower-lying optically dark CT states. These states involve the transfer of an electron from one of the two $^\pi$ orbitals of the porphyrin system to the $^\pi^*$ orbital of Q. The electron transfer and the ensuing transfer of the proton reduce Q to semiquinone (QH). The energy-level structure in Fig. 2 suggests that the reduction of Q is a barrierless process from the Soret band. If the system relaxes to the lowest $^1\text{LE}$ state, a small barrier (arising from the crossing of the red and blue dotted lines in Fig. 2) presumably has to be overcome. Additional calculations are necessary to characterize the height of this barrier. It should be noted that Chl acts as the chromophore, electron donor as well as catalyst for this photoinduced reaction.

The photoinduced reduction of Q in the Chl–Im–Q complex is an example of the generic electron-driven proton-transfer (EDPT) process in intermolecularly hydrogen-bonded aromatic systems:

<table>
<thead>
<tr>
<th>State</th>
<th>$\Delta E$ (in eV)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\text{LE}_c(\pi\pi^*)$</td>
<td>2.27 (1.22)</td>
<td>(0.111)</td>
</tr>
<tr>
<td>$^1\text{LE}_c(\pi^*\pi)$</td>
<td>2.32 (1.25)</td>
<td>(0.072)</td>
</tr>
<tr>
<td>$^1\text{CT}_{CQ}(\pi\pi^*)$</td>
<td>2.66</td>
<td></td>
</tr>
<tr>
<td>$^1\text{CT}_{CQ}(\pi^*\pi)$</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>$^1\text{LE}_Q(\pi\pi^*)$</td>
<td>2.85 (2.43)</td>
<td>(2.2) $\times 10^{-3}$</td>
</tr>
<tr>
<td>$^1\text{LE}_Q(\pi^*\pi)$</td>
<td>3.24 (2.86)</td>
<td>(4.0) $\times 10^{-3}$</td>
</tr>
<tr>
<td>$^1\text{LE}_Q(\pi\pi)$</td>
<td>3.34 (2.31)</td>
<td>(0.242)</td>
</tr>
<tr>
<td>$^1\text{LE}_Q(\pi^*\pi)$</td>
<td>3.45 (3.20)</td>
<td>(0.384)</td>
</tr>
<tr>
<td>$^1\text{CT}_{CQ}(\pi^*\pi)$</td>
<td>1.690 (1.647)</td>
<td></td>
</tr>
<tr>
<td>$^1\text{CT}_{CQ}(\pi\pi^*)$</td>
<td>1.693</td>
<td></td>
</tr>
<tr>
<td>$S_0$</td>
<td>2.33</td>
<td></td>
</tr>
</tbody>
</table>
polar CT states of $^1\pi\pi^*$, $^1\pi\sigma^*$, or $^1\pi\sigma^*$ character drive the proton transfer, which leads, in most cases, to a conical intersection of the $S_0$ and $S_1$ energy surfaces [10]. The interchange of the $S_0$ and $^1\text{CT}$ energies as a function of the proton-transfer coordinate in Fig. 2 reveals the existence of such a seam of intersection. In multiply hydrogen-bonded systems, such as DNA base pairs or polypeptides, the excess energy of the EDPT process is insufficient for the fragmentation of the supramolecular system. In this case, the EDPT process provides an efficient mechanism for ultrafast radiationless deactivation of the electronic excitation via the $S_1$–$S_0$ conical intersection. This mechanism enhances the photostability of such systems [21–23]. In systems with a single hydrogen bond, like the Im–Q complex, the excess energy, which is available after the transfer of the proton, is sufficient to break the hydrogen bond of the biradical. This fragmentation process is well documented, for example, in clusters of phenol or indole with

Fig. 1. Ground-state equilibrium geometries of the educt (a) and product (b) forms of the Chl–Im–Q complex; upper panel: side view; lower panel: top view. The numbers denote bond lengths in Ångstroms.

Fig. 2. Energy diagram of the ground state and the lowest excited singlet states of the neutral and biradicalic forms of the Chl–Im–Q complex, determined with the CC2 method at the DFT equilibrium geometries. Dotted lines denote diabatic correlations of the states.
ammonia or water [24,25]. The EDPT process in Chl–Im–Q breaks the Im–QH hydrogen bond with a high probability, thus releasing the semiquinone. The remaining imidazolyl radical is a strong hydrogen acceptor. It can abstract a hydrogen atom from a protic environment. After the reduction (re-hydrogenation) of the imidazolyl radical, the Chl–Im complex is ready for the attachment and photoinduced reduction of another Q. This way, one Q molecule is reduced to one semiquinone (QH) molecule per absorbed photon. After the consumption of four photons, four Qs have been reduced and four hydrogen atoms have been abstracted from the protic environment. QH disproportionates spontaneously to Q and hydroquinone (QH2). The energy release of this reaction is 18.2 (13.8) kcal/mol at the CC2 (DFT) level.

The concept of hydrogen (or coupled electron–proton) transfer reactions has repeatedly been proposed for the dark reactions in photosynthesis [26–29]. The present results suggest that even the initial photoinduced reaction step may effectively be a hydrogen-transfer process: the electron transfer is followed immediately (that is, on a time scale of a few femtoseconds) by the transfer of a proton from imidazole to the quinone. In this mechanism, the creation of large electronic dipole moments is avoided and long-range dielectric effects are of less importance than in the case of pure electron-transfer chemistry. In this work, we have performed calculations for the isolated Chl–Im–Q complex. For a more complete description of the electron–proton–transfer process, specific hydrogen-bonding interactions with a protic environment as well as continuum solvation effects should be included. Solvation is expected to affect the relative energies of the 1LE and 1CT states and thus the location and energy of the conical intersections of the adiabatic energy surfaces.

While the previous [9] as well as the present calculations address merely the energetics of the photoinduced reactions, we plan to explore in future work the quantum dynamical kinetics of the electron- and proton-transfer processes, using recently developed computational methods which are tailored for electron transfer among hydrogen-bonded aromatic systems [30–33].

Acknowledgments

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) and the Ministry of Science and Education of Poland. ALS acknowledges partial support by a visitor grant of the DFG Cluster of Excellence ‘Munich-Centre of Advanced Photonics’ (www.munich-photonics.de).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.07.098.

References