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Coupling of electron and proton transport in photosynthetic membranes: molecular mechanism

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Abstract

Using the method of Modified Neglect of Diatomic Overlap (MNDO), the electronic structure of plastoquinol (PQH_2) and plastoquinone (PQ) in neutral, singly (PQ^{-}) and doubly (PQ^{2-}) reduced states is studied. The conformational analysis performed on these molecules shows that in the lowest energy conformation, the angle between the first link of the tail backbone and the ring plane of neutral and singly reduced PQ and plastoquinol is nearly the same and differs by 15° from that of doubly reduced PQ. Nevertheless, for all states of plastoquinone and for plastoquinol, the total energy changes by less than 0.2 eV when the studied angle is varied from 0° to 180°. As in *Rhodobacter sphaeroides*, the oxygen of the PQ ring is reported to form a hydrogen bond with a nitrogen in the ring of Histidine (His) L 190. The energy of the PQ–His complex was calculated for different redox states of PQ and for several values of the distance between the molecules (N–O distance from 0.2 to 0.5 nm). For every considered complexes, the total energy dependence on the proton position on the line connecting the N and O atoms was determined, to see if the hydrogen bond is formed. It is shown that for only singly reduced PQ this dependence has a symmetric two-well form, i.e. the hydrogen bond is formed. For neutral and doubly reduced PQ, the curve is also two-well but asymmetric, so that the proton is bound to His or to PQ, correspondingly. On the basis of these results, we propose the following scheme of electron–proton coupling. Negatively charged oxygens of PQ form H-bonds with proton donor groups of the surrounding protein and fix PQ in its pocket. While the negative charges of oxygens increase after quinone reduction, protons shift to PQ oxygens and form strong hydrogen bonds with them. Upon second PQ reduction, protons are torn away from surrounding amino acids and form covalent bonds with the quinol. Resulting PQH_2 detaches from its binding place and is replaced by a neutral PQ. The lacking protons on amino acids in the Q_B pocket are replaced by a step-by-step transfer from the stroma bulk through the proton channels. © 2002 Published by Elsevier Science B.V.

Keywords: Plastoquinone; Electron and proton transport; Photosystem 2

1. Introduction

The electron and proton transfer reactions are the central reactions of the bioenergetics of living organisms. The interesting problem in this field is the coupling mechanism of electron and proton transport. Now, it is supposed that proton transport is initiated by different reasons. As a rule, it involves both reduction and oxidation of some aromatic compounds [1]. The coupled proton transport through the membranes occurs both via special structures (proton channels or "proton wire" [2]) and the chain of water molecules or protonated amino acid residues in proteins [1]. This mechanism of proton transfer is well studied for bacteriorhodopsin [3].

However, the following question remains unanswered: what quantum-chemical properties of electron carriers and their surrounding are crucial for synchronization of electron and proton transfers? A convenient system for this consideration is the secondary plastoquinone (PQ) acceptor Q_B in the reaction centre (RC) of photosystem (PS) 2 of higher plants.

Although in some works the electronic properties of quinones were studied [4], we do not know of any work considering the electronic properties of quinones as electron and proton carriers in connection with the molecular mechanism of coupling.

This work was aimed to clarify which structural and electronic properties of plastoquinone and its environment ensure the correlation between the secondary reduction of singly reduced quinone, the proton binding to doubly reduced quinone (plastoquinol formation), plastoquinol detachment from its binding place and proton transfer across the membrane. For this purpose, we have calculated the electronic structure of the lowest energy configurations of PQ in neutral (PQ), singly (PQ^{-}) and doubly (PQ^{2-}) reduced states and of

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plastoquinol (PQH_2) and determined the total energy of the different states of the plastoquinone complex with the nearest amino acid. The nearest amino acid and its position were chosen on the basis of the reported structure of *Rhodobacter sphaeroides* reaction centre, similar to that of higher plant PS 2 [5].

2. Experimental

The electronic structure, atom charges and total energy of the molecules were calculated by the use of the MOPAC program (Copyright 1996, University of Florida) by Modified Neglect of Diatomic Overlap (MNDO) method with configuration interaction, accounting for all valence electrons. This method has been shown to give satisfactory predictions of such properties of molecules as the heat of formation, molecular dipole moments, ionization energies, electron affinity, polarization and oscillation frequencies [6]. In connection with the aim of this work, a service program has been written, permitting to fulfil the solution of several problems without interference of the user and to present the calculation results in a form convenient for analysis.

3. Results and discussion

The distributions of total charge and atom electron density along the molecule of PQ in different states of reduction are given in Table 1. Notations of atoms of PQ are presented in Fig. 1. Maximal negative charges at the reduction of PQ are localized on oxygen atoms and are twice as large as on other atoms. These charges vary from $-0.27e$ for plastoquinone to $-0.46e$ for PQ^{-} and to $-0.64e$ for PQ^{2-} (where e is the absolute value of electron charge). These values are in good accord with those calculated by Ericsson et al. [4]. At the reduction of PQ, the electrostatic potential becomes more negative and spreads to the entire molecule. As it has been found that the Q_B ring in *Rh. sphaeroides* RC rotates by 180° on Q_B reduction [7], we have performed a conformational analysis of PQ total energy depending on the torsion rotation angle between the ring plane and the first plane of the tail backbone. For conformations with minimal total energy, this dihedral angle is approximately equal for PQ, PQ^{-} and PQH_2 and differs by 15° for PQ^{2-}. Nevertheless, for each of PQ redox states, the total energy seems to be nearly independent of the above-mentioned dihedral angle, differing by less than 0.2 eV. Such "flexibility" can allow plastoquinone to change its conformation easily on reduction, as it has been shown for ubiquinone Q_B in *Rh. sphaeroides* RC [7].

To address the mechanism of proton transport, the interaction of PQ with its surrounding must be considered. Since it is known, that the reduction of PQ is coupled to the proton transfer, we have supposed that in this process a hydrogen bond is formed to the atom of PQ whose charge changes most significantly on PQ reduction, i.e. to the oxygen of PQ and that it takes part in proton transport. Stowell et al. [7] have found that in *Rh. sphaeroides* RC, one of the two

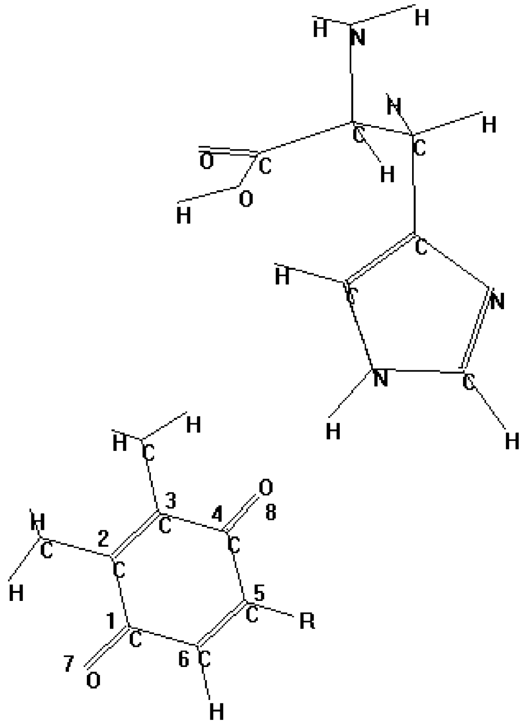

Fig. 1. Atom arrangement and numeration in plastoquinone–histidine system.

Table 1
Atom charge distributions for different plastoquinone redox states

State of plastoquinone	Atom number	Atom	Total charge	Atom electron density
PQ	1	C	0.2709	3.7291
	2	C	− 0.0775	4.0775
	3	C	− 0.1102	4.1102
	4	C	0.281	3.719
	5	C	− 0.1076	4.1076
	6	C	− 0.1074	4.1074
	7	O	− 0.2691	6.2691
	8	O	− 0.2711	6.2711
PQ^{-}	1	C	0.2362	3.7638
	2	C	− 0.1647	4.1647
	3	C	− 0.2365	4.2365
	4	C	0.2582	3.7418
	5	C	− 0.1487	4.1487
	6	C	− 0.1446	4.1446
	7	O	− 0.4594	6.4594
	8	O	− 0.4551	6.4551
PQ^{2-}	1	C	0.226	3.774
	2	C	− 0.2039	4.2039
	3	C	− 0.2992	4.2992
	4	C	0.2582	3.7418
	5	C	− 0.2658	4.2658
	6	C	− 0.2523	4.2523
	7	O	− 0.6454	6.6454
	8	O	− 0.6416	6.6416

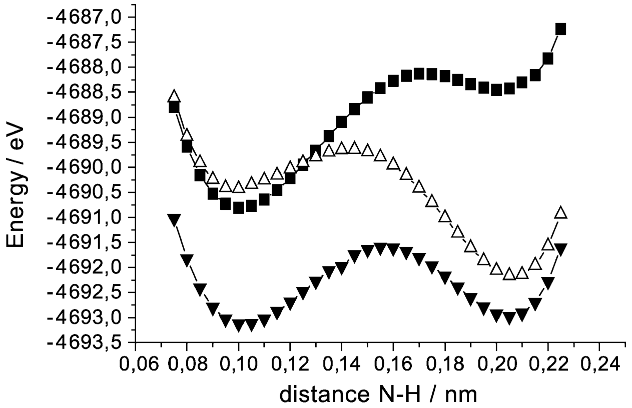

Fig. 2. Total energy of PQ–His system for different states of PQ and different N–H distance. N–H–O distance is equal to 0.3 nm. ■: charge 0; ▼: charge −1; △: charge −2.

oxygen atoms of PQ, both in neutral and singly reduced states, is within a hydrogen bond distance from a nitrogen in the ring of His L190. As this His is the only amino acid that can form a hydrogen bond with PQ in both states, we have studied the PQ–His system for different redox states of PQ. The relative position of PQ and His was chosen on the basis of the known *Rh. sphaeroides* RC structure [8] and was corrected by HyperChem program with help of data about bond length and valence angles. For this system, we estimated the total electronic energy (potential energy of nuclear moving) as a function of the proton position on the straight line connecting the nitrogen of His and the oxygen of PQ. As the quinone in *Rh. sphaeroides* RC is reported to shift on reduction [7], this calculation was repeated for different distances between the PQ and His (O–N distance from 0.2 to 0.5 nm). The resulting curves are presented in Fig. 2 and their parameters are given in Table 2. From Fig. 2, it can be seen that for fixed positions of PQ and His, the dependence of electronic energy on N–H distance bears a resemblance to a curve with two potential wells. For neutral PQ, the minimal energy corresponds to the proton position near the nitrogen of His and for PQ^{2-}, the proton is located near the oxygen atom of PQ. In the case of PQ^{-}, the curve of electronic energy is a symmetric two-well curve with minima of equal values. According to the work in Ref. [9], only for a symmetrical potential curve can proton tunnelling take place. This means that the formation of the OH bond begins in the PQ(−) state. This is in line with the results of Ref. [8] where it is supposed that the proton conjugation occurs in the PQ^{-} state. Naturally in this case, the addition of the second electron to PQ^{-} is facilitated.

The energetic characteristics of the PQ–His system in different redox states are presented in Table 2. It can be seen that in the PQ^{-} state, diminishing the distance between nitrogen of His and oxygen of PQ is followed by a decrease of electronic energy. It means that the formation of the H-bond brings about the approximation of PQ and His and consequently, a much tighter bond is formed. This result is consistent with the structural rearrangements in *Rh. sphaeroides* RC at reduction of PQ, described in Ref. [4]. As we stated above, at two-fold reduction of PQ, the proton binds to the PQ oxygen atom. From Table 2, we can observe that the total energy of the system PQ^{2-}–H–His is essentially larger than for the PQ^{-}–H–His complex. Moreover, the energy of PQ^{2-}–H–His system decreases at an increase of the distance between the oxygen of PQ and the nitrogen of His. This means that the system becomes unstable and explains the separation PQH_2 from its binding site.

On the basis of the presented data, we propose the following scheme of coupling of the electron transport to proton transfer across the membrane. Oxygen atoms, having large negative charges, form H-bonds with proton donor groups of the surrounding protein to fix the PQ position in its pocket, as is observed in bacterial reaction centres [7]. It is generally agreed that hydrogen bonds are due to electrostatic energy [10]. Consequently, when negative charges on oxygens are increased after quinone reduction, the protons that were H-bonded to them may be torn from the surrounding amino acids and form covalent bonds with the quinol. After that, resulting plastoquinol can detach from its binding place and be replaced by another quinone. Step-by-step transfer from the bulk through the proton channels replaces the lacking protons on amino acids in the QB pocket. Two such channels were shown to exist in *Rh. sphaeroides* RC [4,7]. The mechanism of the proton transfer may be similar to proton migration in bacteriorhodopsin [3]. All the more, one notes that the characteristic time of proton transfer by the bacteriorhodorpsin is equal up to an order of magnitude, the time of proton transfer across the photosynthetic membrane [11].

Table 2
Total energy of system PQ–His for different states of PQ and different N–H...–O distances

N–O distance (nm)	Charge	N–H distance (nm)	Total energy (eV)	N–H distance (nm)	Total energy (eV)
0.2	0	0.095	−4686.8852	–	–
	−1	0.095	−4689.9113	–	–
	−2	0.095	−4687.8607	–	–
0.25	0	0.1	−4689.9807	–	–
	−1	0.105	−4692.5961	–	–
	−2	0.1	−4689.9939	–	–
0.3	0	0.1	−4690.8042	0.2	−4688.45
	−1	0.1	−4693.1255	0.205	−4692.98
	−2	0.1	−4690.4293	0.205	−4692.17
0.35	0	0.1	−4691.0595	0.26501	−4688.75
	−1	0.1	−4693.2666	0.26501	−4693.06
	−2	0.1	−4691.0902	0.26501	−4692.50
0.4	0	0.1	−4691.0968	0.3201	−4688.83
	−1	0.1	−4693.2449	0.3101	−4692.99
	−2	0.1	−4691.3512	0.3101	−4692.55
0.45	0	0.1	−4691.0944	0.3601	−4688.89
	−1	0.1	−4693.1987	0.3601	−4692.93
	−2	0.1	−4691.5203	0.3601	−4692.62
0.5	0	0.1	−4691.0863	0.405	−4688.99
	−1	0.1	−4693.1612	0.405	−4692.92
	−2	0.1	−4691.631	0.405	−4692.71

The same scheme of coupling of electron transport and proton transfer across the membrane may well take place in cytb$_6$–f complex and oxygen evolving system. It should be noted that the curves similar to curves in Fig. 2 were proposed in Ref. [12] for supposed energy of H-bond at different values of donor and acceptor group pK.

The determination of the electronic structure of PQ–His system and its total energy will provide great stimulus for calculations of rate constants of electron and proton transfer near PQ$_B$ in different redox state. Such attempts were described earlier [13,14]. However, the electronic structure of carriers and its surroundings was not accounted for. Thus, this problem requires further studies.

4. Conclusions

The results of calculations show that the total energy of plastoquinone changes weakly in relation to turning of the PQ ring. This means that the conformation of PQ is determined by the surrounding species. The results of calculations of total energy of the system PQ–His can explain the relative affinity of PQ, PQ$^-$ and PQH$_2$ to the quinone binding place. The proton transfer across the membrane in RC PS 2 is triggered by increase of electron density on oxygen atoms of PQ^{2-} that gives rise to relay race proton transfer across the membrane. The same scheme of coupling of electron transport and proton transfer across the membrane may well take place in cytb$_6$–f complex and oxygen evolving system. On the basis of the proposed scheme and dependence of energy on proton position in PQ–aminoacid complex, it is possible to estimate the time of proton transfer from the stroma through the proton channel.

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