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The rates of proton uptake and electron transfer at the reducing side of photosystem II in thylakoids

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Abstract

Proton and electron transfer at the reducing side of photosystem II of green plants was studied under flashing light, the former at improved time resolution by using Neutral red. The rates of electron transfer within Q_AFeQ_B were determined by pump–probe flashes through electrochromic transients. The extent of proton binding was about 1 H^+/e^-. The rates of proton transfer were proportional to the concentration of Neutral red (collisional transfer), whereas the rates of electron transfer out of Q_A^- and from $Q_AFeQ_B^-$ to the cytochrome b_6f complex were constant. The half-rise times of electron transfer (τ_e) and the apparent times of proton binding (τ_h) at 30 μM Neutral red were: $Q_A^-\Rightarrow Fe^{III}Q_B$ ($\tau_e \leq 100$ μs, $\tau_h = 230$ μs); $Q_A^-\Rightarrow Fe^{II}Q_B$ ($\tau_e = 150$ μs, $\tau_h = 760$ μs); and $Q_A^-\Rightarrow Fe^{II}Q_B^-$ ($\tau_e = 620$ μs, $\tau_h = 310$ μs).

Key words: Photosynthesis; Photosystem II; Electron transfer; Proton uptake; Quinone; Electrostatics

1. Introduction

Photosystem II (PSII) of higher plants functions as a water-plastoquinone-oxidoreductase. The vectorial electron transfer from water to bound plastoquinone across the thylakoid membrane causes proton release into the lumen and proton uptake from the stroma. When dark-adapted thylakoids are excited with a series of short flashes of light, binary oscillations as functions of the flash number of the proton uptake might occur because of the binary reduction cycle of plastoquinone according to reaction scheme 1 [1]:

$$Q_AQ_B \Rightarrow Q_A^-Q_B \xrightarrow{150\ \mu s} Q_AQ_B^- \Rightarrow Q_A^-Q_B^- \xrightarrow{500\ \mu s} Q_AQ_B^{2-}(Q_AQ_BH_2) \dashrightarrow Q_AQ_B \quad (1)$$

wherein the double arrows ($\Rightarrow$) denote the rapid reduction of the first bound quinone by pheophytin (at about 400 ps [2]), the thin arrows ($\rightarrow$) indicate forward electron transfer between the bound quinones (the transfer times are taken from [3]) and the broken arrow ($\dashrightarrow$) the replacement of the (protonated) plastoquinol by plastoquinone at position B. If the bridging non-heme iron between the two bound quinones is oxidized prior to the firing of a first flash, the reaction sequence starts according to reaction scheme 2:

$$Q_AFe^{III}Q_B \Rightarrow QA^-Fe^{III}Q_B \xrightarrow{25\ \mu s} Q_AFe^{II}Q_B \quad (2)$$

and proceeds further according to scheme 1. The half-rise time (here taken from [4]) is under debate. Depending on the pH, oscillations of proton uptake over the two-stepped reduction of the bound quinones have been observed in reaction centers [5,6] and in chromatophores [7] of purple bacteria. In thylakoids, on the other hand, the extent of proton uptake does not oscillate as a function of the flash number [8,9]. This apparent discrepancy was here re-evaluated with emphasis on the rates of proton uptake and electron transfer between Q_A and Q_B.

When thylakoid membranes are stacked, i.e. in the presence of divalent cations, the true rate of proton uptake which follows the rapid electron transfer to Q_AFeQ_B is not detectable with hydrophilic pH-indicating dyes. This is caused by multiple buffering events along the narrow partitions which separate the sites of proton uptake (in the stacked membrane domains) from the aqueous volume of the suspending medium which contains the bulk of the hydrophilic dye molecules [10]. The apparent rate can be increased by unstacking of thylakoid membranes either by mild EDTA treatment [11] or by growing seedlings under intermittent light [12]. Another way is to enhance the diffusive shuttling of protons along the partitions by added mobile buffers [34]. These measures have still resulted in rather long half-rise times of only 2.7 ms [11] and 5 ms [13], respectively. An alternative technique was used in this work. It relies on the surface adsorbed, and thereby up-concentrated, dye Neutral red [14]. As documented below, it provides much

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Dedicated to Prof. Dr. Achim Trebst, Bochum, on the occasion of his 65th birthday.

Abbreviations: BSA, bovine serum albumine; Chl, chlorophyll; Fe, non-heme iron; NR, Neutral red; P700, primary donor of photosystem I; PR, phenol red; PSI, photosystem I; PSII, photosystem II; Q_A, bound primary quinone electron acceptor of photosystem II; Q_B, secondary quinone electron acceptor of photosystem II.

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greater time resolution (some 100 μs) for proton uptake owing to a collisional proton transfer between the dye and the proton-accepting groups at the surface of the quinone binding domain. To correlate the rates of proton uptake with the rates of the redox reactions, the latter were determined by the extent of the primary electrogenic charge separation in response to closely but variably spaced pump–probe flashes. The extent of the charge separation was monitored by electrochromic absorption changes at 522 nm [15].

2. Material and methods

Thylakoids were prepared from 12-day-old pea seedlings according to [16]. Complete unstacking of the membranes was achieved by mild EDTA treatment as described previously [17]. Concentrated stock (2 mg Chl/ml) was stored frozen at −80°C, thawed and diluted at 20 μM Chl in a medium containing 10 mM NaCl and 100 μM hexacyanoferrate (III), if not otherwise indicated. The pH was adjusted to 7.0 by the addition of NaOH or HCl.

Flash spectrophotometric measurements were performed with the set-up described in [18]. Groups of saturating light flashes (wavelength >610 nm; Schott RG 610) were applied by Xenon flashlamps (10 μs FWHM). The time interval between flashes was varied between 50 μs and 250 ms, and the period of repetitive flash groups was 10 s. For signal-to-noise improvement, up to 120 transients were averaged by a Nicolet Pro30 transient recorder (30 measurements per sample under repetitive flash excitation). With material which was dark-adapted for 15 min, every transient was obtained with a fresh sample which was filled automatically into the cuvette (optical pathlength 2 cm) from a light-shielded reservoir.

Proton uptake from the suspending medium at the PSII acceptor side was measured with the hydrophilic dye Phenol red (PR) at a wavelength of 559 nm (10–40 μM) and with the amphiphilic dye Neutral red (NR) at 548 nm (2–40 μM). From traces in the presence of these dyes, traces obtained in their absence under the same conditions were subtracted (±dye).

NR responds to events at both sides of the membrane [19]. So far, this dye has been mainly used to study pH transients in the thylakoid lumen, e.g. proton release from water oxidation [16,17,20]. In this work we obtained its response to proton uptake from the stroma side as follows: (a) absorption transients which represented the sum of proton release into the lumen by water oxidation and proton uptake from the medium were recorded in the absence of buffer as the difference of transients with and without NR. (b) Absorption transients due to proton release into the lumen alone were recorded in the presence of 5.2 g/l BSA as the impermeable buffer in the medium, again as the difference with/without NR. The difference of traces a−b represented absorption transients due to proton uptake from the medium (see Fig. 1A).

Redox transients of the primary electron donor of PSI were recorded at 700 nm. Absorption transients following the first four flashes were measured with dark-adapted thylakoids in the presence of 40 μM NR (which does not absorb at 700 nm). The lag of $P700^+$ reduction following a flash was time-resolved under repetitive flash excitation (0.1 Hz) as described by Haehnel [21]. P700 was pre-oxidized during the interval between light flashes (>80%) by far-red pre-illumination which was applied through a sharp cut-off filter (Schott; RG 695) impinging perpendicularly to the measuring beam. In order to minimize the acidification of the lumen by the continous light between the flashes, 1 μM nigericin was added as uncoupler. Transients at 700 nm were recorded in the presence and absence of 80 μM NR.

Electrochromic absorption transients at 522 nm [15] served to indirectly monitor the electron transfer times from Q_A^- to Q_B (first cycle) and to Q_B^- (second cycle) in dark-adapted thylakoids. Q_A^- was generated by a pump flash and its decay monitored by a probing flash under variation of the time interval between 50 μs and 5 ms. The partial restoration of Q_A was evident from the relative extent of the transmembrane charge separation as caused by the second flash. Under the given oxidizing conditions the contribution of PSI to the charge separation upon the probing flash was negligible (see Fig. 3B for the slow recovery of $P700^+$).

3. Results

3.1. Proton uptake under excitation with repetitive flashes

We used Neutral red (NR) and Phenol red (PR) as indicator dyes and imidazole as mobile buffer. The results are documented in Fig. 1. Fig. 1A shows how the response of NR to proton uptake at the stroma side (lower trace) results from its composite response to protolytic events at both sides of the membrane (−BSA, upper trace) and its response to events at the lumen side (+BSA, middle trace). Fig. 1B compares the transient alkalinization of the medium resulting from experiments with NR (top) and with PR (bottom). The respective half-rise times were 360 μs with NR (40 μM) and much longer, namely 3.3 ms with PR (40 μM). Fig. 1C shows the reciprocal overall half-rise time of the alkalinization as seen by NR as function of the concentration of this dye. The reciprocal half-rise time was constant up to a concentration of 10 μM (400 s^{-1}) and then increased up to 40 μM (2,700 s^{-1}). In contrast to the alkalinization rate as recorded by NR, the one by PR was independent of the concentration of this dye. It was, on the other hand, increased by adding the amphiphilic and mobile buffer imidazole. At 40 μM of PR plus 40 μM of imidazole, which about halved the extent of the pH-indicating transient, the half-rise time of the alkalinization was shortened from 3.3 to 2.2 ms. It was even shorter (1.8 ms) when 15 μM of NR instead of imidazole were added. It was obvious that both imidazole and NR served as proton shuttles between the hydrophilic dye (PR) and the sites of proton uptake at the membrane surface.

3.2. Proton uptake in dark-adapted thylakoids

Proton uptake was induced by a series of four flashes of light and detected by NR (30 μM) as documented in Fig. 2A. The noisy transients were each fitted by a single exponential. The respective half-rise times were 760 μs, 310 μs, 630 μs and 390 μs when progressing from flash number one to number four. Whereas the rates of proton uptake oscillated with period two, the extents did not. Every flash induced the uptake of about one proton, in agreement with previous reports [8,9]. The experiment with NR was repeated in the presence of a much higher concentration of hexacyanoferrate (III), namely 2 mM, which slowly oxidizes the bridging non-heme iron in the dark [22]. The first flash again induced the uptake of one proton, but this time the half-time was shorter, namely 230 μs (Fig. 2B).

Proton uptake was again measured in dark-adapted thylakoids with the first and second flash spaced only

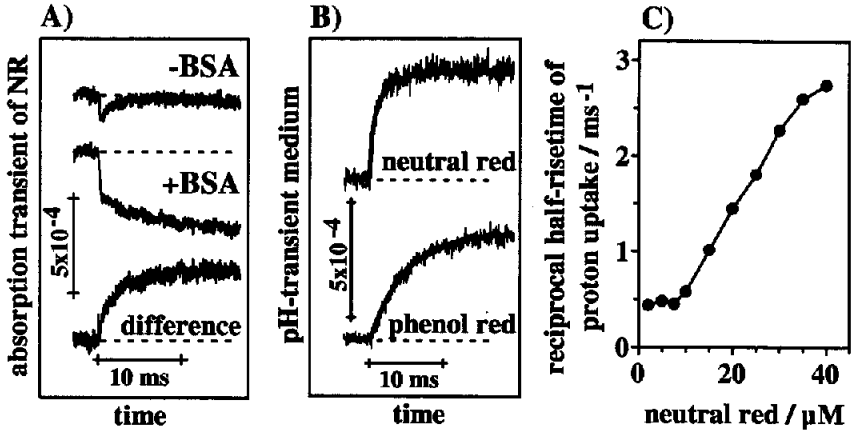

Fig. 1. Proton uptake at the reducing side of PSII under repetitive flash excitation. (A) Upper trace: absorption transient of 15 μM NR representing the sum of proton uptake from the medium and release into the lumen (+/−NR). Middle: proton release into the lumen in the presence of BSA (+/−NR). Lower trace: the difference −/+ BSA reflects proton uptake from the medium. (B) Upper trace: transient of NR (+/− 40 μM, −/+ BSA). Lower trace: transient of PR (+/− 40 μM). The half-rise times (taken from the solid lines) were 360 μs (NR) and 3.3 ms (PR). The time resolution was 17 μs per address. 60 transients were averaged. (C) Reciprocal overall rates of proton uptake (dots) as function of NR concentration.

300 μs apart from each other with 30 μM NR and 100 μM hexacyanoferrate. Proton uptake after the first flash was only about 25% completed prior to the second flash (half-rise time 760 μs) while the electron largely (~75%) resided already on Q_B (the half-rise time of the electron transfer from Q_A^- to Q_B was about 150 μs, see below). In a fraction of about 60% of the centers the second flash then induced the state $Q_A^-FeQ_B^-$ with the charge on Q_B not yet compensated by a proton. The two flashes induced the total uptake of about 1.6 protons (not shown) with biphasic kinetics. The half-rise times were similar to the ones of the transients in Fig. 2A, namely 300 μs (0.6 protons) and 1 ms (1 proton). In the presence of 30 μM DCMU, which prevents the occupation of the Q_B site, no proton uptake was detected either with 100 μM or 2 mM hexacyanoferrate (not documented).

3.3. *The extent and rates of electron transfer in dark-adapted thylakoids*

The binary oscillation of Q_AFeQ_B through the redox states was assayed by monitoring the reduction of $P700^+$ as a function of the flash number in the presence of 100 μM hexacyanoferrate and without and with 40 μM NR (not shown). Under both conditions P700 stayed oxidized (>90%) after the first flash and became reduced after the second flash and further on with damped oscillation of period two. We determined the rates of electron transfer from Q_A^- to Q_B^- and from Q_A^- to Q_B^- by monitoring the extent of electrochromic absorption changes at 522 nm with a pump–probe flash technique. Fig. 3A shows the extent of the rapid transmembrane charge separation as a function of the time spacing between the last pumping flash and the probing flash. This extent measures the

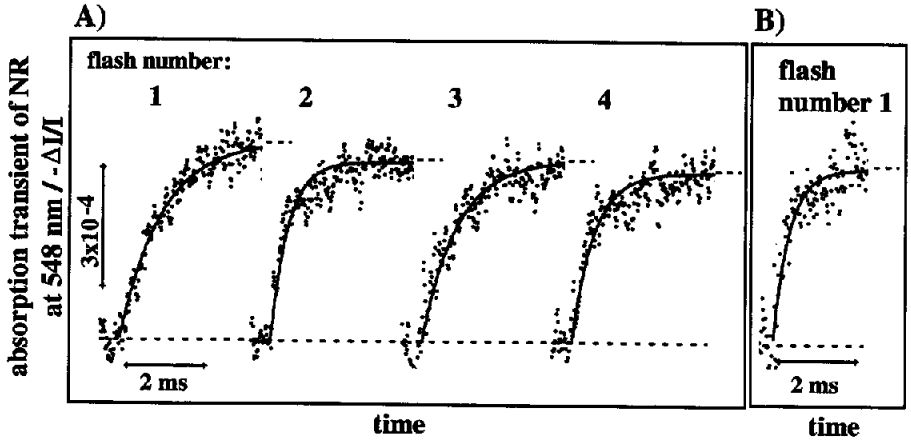

Fig. 2. Proton uptake as a function of flash number in dark-adapted thylakoids. (A) Transients of NR induced by flashes 1–4 with 100 μM hexacyanoferrate. The half-rise times were determined from single exponentials (smooth lines: for signal extents see broken lines). (B) Transient of NR induced by flash no. 1 with 2 mM hexacyanoferrate. All transients represent differences +/−NR 30 μM, −/+BSA. The time resolution was 17 μs per adress. 90 transients were averaged per flash.

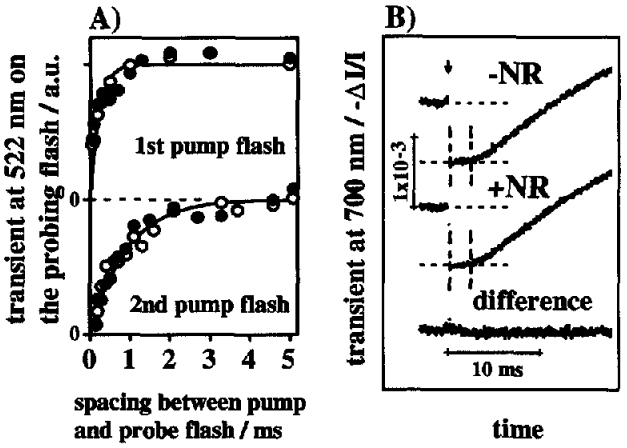

Fig. 3. (A) Extents of transients at 522 nm induced by a probing flash given at variable times after the first (upper curve) and second (lower curve) pumping flash. The broken line indicates the origin of the upper curve. (●) With 30 μM NR plus 10 mM imidazole; (○) without NR and imidazole. (B) Transients at 700 nm under repetitive flash excitation in the absence (upper trace) and in the presence (middle trace) of 80 μM NR. Lower trace: difference −/+ NR. The arrow indicates the flash. The time resolution was 20 μs per adress. 250 transients were averaged.

proportion of oxidized Q_A. The rapid charge–pair recombination in the presence of Q_A^- was not resolved here. The 'readiness' of Q_A to accept another electron is directly related to the transfer time of electrons to Q_B (first pumping flash, upper trace in Fig. 3A) and to Q_B^- (second pumping flash, lower trace in Fig. 3A). From the data points in Fig. 3A (top, filled circles) the half-rise time of the reaction $Q_A^-Q_B \rightarrow Q_AQ_B^-$ was 150 μs (smooth line). For the reaction $Q_A^-Q_B^- \rightarrow Q_AQ_B^{2-}$ it was determined as 620 μs (bottom, filled circles, smooth line). These figures were compatible with previously reported ones for spinach thylakoids [3]. We asked whether the respective rates of electron transfer from Q_A^- to Q_B or to Q_B^- were affected by the addition of NR, which, according to Fig. 1B, accelerated the rate of proton transfer. Comparison of the open circles in Fig. 3A (with 30 μM NR plus 10 mM imidazole) with the filled circles (no NR and imidazole added) revealed no effect on the rate of electron transfer.

We investigated whether the lag time of the reduction kinetics of $P700^+$, which has been attributed to proton uptake by $Q_AFeQ_B^{2-}$ [21] was shortened as well. Fig. 3B shows the lag in the absence (upper trace) and presence of 80 μM NR (middle). The lower trace represents the difference ± NR. The lag had a duration of about 2.3 ms (vertical broken lines) both in the presence and in the absence of NR.

4. Discussion

The two-electron gate formed by two bound quinone molecules, Q_A and Q_B, is a common property of the reaction centers of purple bacteria and of PSII of green plants and cyanobacteria. We investigated proton uptake by the quinone–iron system under flashing light in thylakoids of green plants. The rates of proton transfer from NR to the intrinsic uptake sites showed pronounced binary oscillations as function of the flash number, whereas the extent was about constant. The averaged rate of proton transfer was proportional to the concentration of NR, whereas the respective rates of electron transfer were independent of this parameter.

4.1. The mechanism of proton transfer to the flash-generated bases

The response of NR is faster than the one of the hydrophilic dye PR, because the former is surface adsorbed and therefore highly enriched in the reaction volume* [19]. The simplest mechanism which accounts for the observed concentration dependence of the rate of proton uptake is collisional proton transfer according to the following reaction scheme:

$$NRH^+ + X^- \underset{k^-}{\overset{k^+}{\leftrightarrow}} NR + XH \text{ with } k^+/k^- = K_X/K_N \qquad (3)$$

If the surface concentration of the dye, NR, is in large excess over the one of the proton acceptor*, X^-, the net relaxation constant k is proportional to the total concentration of the dye according to Equ. I (see [23]):

$$k = [NR]_{total} \cdot k^+ \cdot (K_X + [H^+])/(K_N + [H^+]) \qquad (I)$$

wherein K_N denotes the dissociation constant of NR, K_X the one of the accepting base, and k^+ the forward rate constant of proton transfer. An enhanced rate of proton transfer to and from NR or to other surface-bound indicator dyes has been previously reported in studies on artificial proton donors/acceptors [24], on bacteriorhodopsin [25] and on photosynthetic water oxidation [20]. One consequence of the observed concentration dependence is that the basic groups are rather slowly protonated (half-rise time about 3 ms) in the absence of NR.

4.2. The velocity of proton transfer as function of the redox state of Q_AFeQ_B

Detailed studies with reaction centers of purple bacteria have led to the conclusion that transient proton uptake is caused by amino acids in response to the electric field of Q_A^- and Q_B^-. Q_A^- is not protonated directly [5,6,26]. Our data have shown that the collisional transfer of pro-

*According to [19] more than 20% of total NR is adsorbed to the thylakoid membrane under the given salt and pH conditions. Distributing adsorbed NR equally between both surfaces, at least 10% of a total of 40 μM is expected to reside at the stromal surface, namely 4 μM (average concentration in the whole suspension). The total concentration of PSII at 20 μM Chl was less than 40 nM. If there was only one single proton-accepting group per PSII the excess of NR was about 100-fold.

tons by NR is directed to groups, X^-, which are sensitive to the redox state of Q_AFeQ_B. Thus, these groups are not just inert buffers which are remote from Q_AFeQ_B. According to rate theory, the forward rate constant (k^+ in reaction scheme 3) of proton transfer from an acid to a family of structurally related bases is the greater, the larger the pK difference between the acid and the base [23,27]. Our data would then imply that reactive basic groups have a higher pK in the presence of $Q_A^-FeQ_B^-(H^+)$ and $Q_AFe^{(III)}Q_B$ than in $Q_A^-Fe^{(II)}Q_B$.

4.3. Proton uptake in the presence of Q_A^-

It is absent in the presence of DCMU ([17] and this work). Since indirect effects of DCMU on the non-heme iron have been reported [28], it is at least conceivable that DCMU causes 'structural changes' around Q_A which abolish the ability of its environment to bind protons. In $Q_A^-Fe^{II}Q_B^-(H^+)$, on the other hand, there is proton uptake by Q_A^-. It precedes (310 μs) electron transfer to Q_B^- (620 μs). Fast proton uptake has also been observed after the reduction of $Fe^{(III)}$ (230 μs). When starting from $Q_A^-Fe^{II}Q_B$, however, proton uptake was much slower (760 μs) than electron transfer to Q_B (150 μs), even at high concentrations of NR; But no appreciable extent of proton uptake at Q_A^- was expected due to its short lifetime.

4.4. Intrinsic proton transfers which are precursors of the reactions monitored by NR

The experiment with double flashes, spaced by only 300 μs, showed that the respective velocities of the fast and the slow proton uptake by $Q_A^-FeQ_B^-$ were the same when the charge on Q_B^- was not yet compensated by proton transfer from NR, as expected for a mixture of the states $Q_AFeQ_B^-$ and $Q_A^-FeQ_B^-(H^+)$. Proton transfer was apparently directed to the same groups with the same pK values in the former and the latter case. One interpretation of this phenomenon is that the uptake of the second proton at Q_B occurs only concomittant with or after electron transfer from Q_A^-. This is in line with the situation in bacterial reaction centers where electron transfer between Q_A^- and Q_B^-, i.e. during the second reduction step, is kinetically coupled to the uptake of the second proton [29–33]. In thylakoids, internal proton transfer may be the reason why the velocity of electron transfer is independent of proton transfer from outside. If we follow the interpretation by Haehnel [21], our data imply that the flow of electrons out of Q_B^{2-} (as seen by the invariant lag of $P700^+$ reduction) is also independent of this external protonation.

Our results on thylakoids may be summarized as follows: (i) The reduction-induced uptake of protons by basic groups which cover Q_AFeQ_B is usually very slow, slower than the electron transfer between Q_A and Q_B. (ii) NR accelerates the protonation. Different velocities become apparent, which depend on the redox state of Q_AFeQ_B. (iii) The velocity of the protonation of these groups does not affect the velocity of the electron transfer between Q_A and Q_B. (iv) Under the plausible assumption that the construction of the Q_AFeQ_B pocket is similar to the one in bacteria, it is probable that there are internal proton transfers which are undetected by NR. (v) It is an apparent paradox in the light of the symmetry of Coulomb's law, that the basic groups 'feel' the redox state of Q_AFeQ_B but that the electron transfer rate is insensitive to their protonation state. Possible topological constraints, however, cannot be fully appreciated before an atomic structure is available.

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