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Competition between excited state proton and OH^- transport via a short water wire: Solvent effects open the gate†

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We investigate the acid-base proton exchange reaction in a microsolvated bifunctional chromophore by means of quantum chemical calculations. The UV/vis spectroscopy shows that equilibrium of the keto- and enol-forms in the electronic ground state is shifted to the keto conformation in the excited state. A previously unknown mechanism involving a hydroxide ion transport along a short water wire is characterized energetically, which turns out to be competitive with the commonly assumed proton transport. Both mechanisms are shown to have a concerted character, as opposed to a step-wise mechanism. The alternative mechanism of a hydrogen atom transport is critically examined, and evidence for strong solvent dependence is presented. Specifically, we observe electrostatic destabilization of the corresponding $\pi\sigma^*$ state by the aqueous solvent. As a consequence, no conical intersections are found along the reaction pathway.

Proton transfer reactions play a crucial role in a large variety of chemical reactions, as well as in biological systems.[1–7] In aqueous solutions, where the hydrogen bond network is very extensive, these reactions can be enormously complicated due to the association of the structural reorganization of water molecules. In this context, relatively stable hydrogen bonded chains between series of water molecules have been discussed in the literature along which the proton transfer may occur.[8–14] A ”water wire” linked by hydrogen bonds may enable the transfer of protons in a concerted, where protons are transferred in a single step over the water molecules comprising the wire, or sequential von-Grotthuss hopping fashion.[12,14,15]

The mechanism of excited state proton transfer reactions in solutions may involve different pathways, depending on the reactivities of donor and acceptor sites of the compounds. In this regard, photoacid/-base molecules, known to perform proton transfer reactions after photoexcitation, have been extensively studied.[16–28] 7-Hydroxyquinoline (7HQ), a bifunctional chromophore, provides both an acidic site with proton donating functionality as well as a basic site that can accept a proton.[29–40] In aqueous solutions, 7HQ can adopt four prototropic equilibrium species, a neutral molecule (N), an enol-deprotonated anion (A), an imine protonated cation (C), and the equilibrium keto (K) form (see in Figure 1)[35–38,40]. Upon excitation to the first excited state (S_1), a proton transfer reaction is initiated, the hydroxyl group acts as a proton donor and the nitrogen atom acts as a proton acceptor. The keto form of 7HQ is found to be stable in the S_1 state, and its fluorescence is strongly Stokes shifted relative to the enol.[32,33] Hence, the occurrence of a proton transfer can be documented experimentally by the keto form.

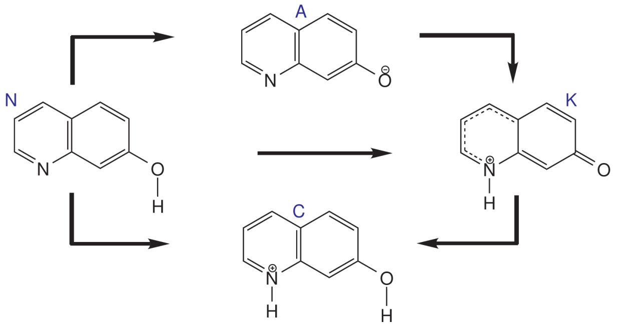

Fig. 1 Excited state enol-keto tautomerization scheme of 7HQ.

Several quantum chemical calculations can be found in the literature which have been successful in simulating particular features of the tautomerization of 7HQ starting with a pre-defined arrangement of a solvent cluster in the gas phase.[39,41–46] The photoacidity of 7HQ has been discussed by Leutwyler and co-workers based on both configuration interaction singlets (CIS) and complete active space self-consistent field (CASSCF) methods along (mixed) hydrogen bonded

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† Electronic Supplementary Information (ESI) available: Computational details, optimized geometries of the compounds in the S_1 state, their relative energies and extensive flourescence and absorption data. See DOI: 10.1039/b000000x/

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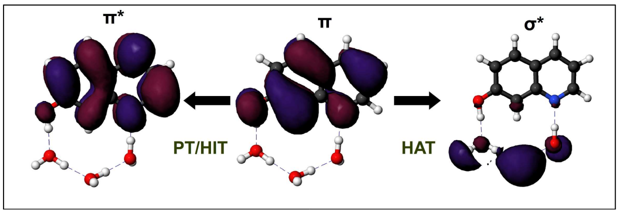

Fig. 2 Molecular orbitals of 7HQ·$(H_2O)_3$ complex in the enol geometry within implicit solvent. The ππ* electronic transition characterizes proton and hydroxide ion transfer (PT/HIT) whereas πσ* is associated with hydrogen atom transfer (HAT). The contour value was the 0.02 for π and π* states, and 0.045 for the σ* state.

wires consisting of NH_3 and/or H_2O molecules in the gas phase.[47,48] According to their results, the enol-keto tautomerization in the excited state proceeds via hydrogen atom transfer instead of proton transfer in a step-wise fashion. From their calculations, a conical intersection between excited ππ* state and a πσ* state drives the migration of an electron from the hydroxyl group to the solvent molecule (see in Figure 2). Then, a net transfer of a hydrogen atom along the hydrogen bonded wire occurs by consecutive electron and proton transfer. As a last step, a reverse crossing brings the system back into the fluorescent ππ* state of the ketonic tautomer. Sobolewski and Domcke have also reported hydrogen atom transfer reactions in the excited state dynamics of phenol in the gas phase with NH_3 and H_2O molecules.[49,50]

In this work, we investigate proton and hydroxide ion (OH^-) transfer reactions of the 7HQ·$(H_2O)_3$ complex with regards to both the release of a proton from the hydroxyl group to the water molecule and the cleaving of a proton from the water molecule to nitrogen atom in the ground (S_0), triplet (T_1), and the singlet (S_1) states in aqueous solution. Our excited state structure optimizations and transition state energetics shall clarify whether the OH^- transport process can compete with the standard photoacid picture of proton release from the donor site. Hydroxide ion transfer based mechanisms have also been reported from experimental time-resolved and steady-state fluorescence studies.[34,37]

We have performed full structure optimizations and transition state calculations of 7HQ·$(H_2O)_3$ in aqueous solution using DFT/TD-DFT[51] methods in the B3LYP/TZVP[52,53] level in the both ground and excited states with using Gaussian 09.[54] Solvation effects were captured by the conductor polarized continuum model.[55] The relative energies of the optimized geometries are reported, including the zero point energy correction (see Electronic Supplementary Information [ESI]).

We have computed two different reaction pathways for the enol-keto tautomerization of 7HQ in the S_1 state in aqueous solution. The first pathway starts with the deprotonation of

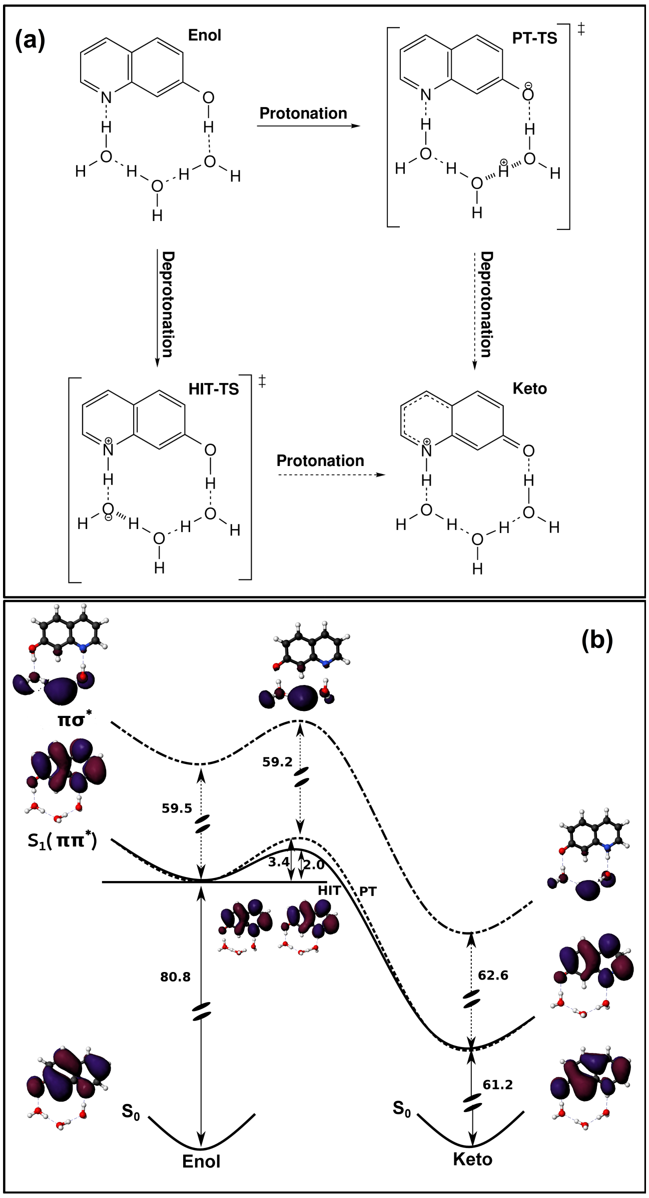

Fig. 3 (a) Scheme illustrating the excited state proton and hydroxide ion transfer (PT/HIT) mechanisms of 7HQ in presence of a water wire. The hydroxide ion transfer mechanism contains a $H_3O_2{}^-$ structure, whereas the proton transfer mechanism has a Zundel ion-type structure. (b) Schematic reaction profile of the enol-keto tautomerization reactions in the lowest ππ* and πσ* potential energy surfaces with associated molecular orbitals and relative energies in kcal mol^{-1}.

the 7HQ hydroxyl group, (see Figure 3a). Proton transport then occurs along the water wire to the nitrogen atom. In the quantum chemistry literature, only pathways starting with deprotonation of 7HQ have been considered.[41–46] An alternative mechanism starts by protonation of the nitrogen site of 7HQ. This process corresponds to the protonation of the water-exposed nitrogen, then an effective charge will be transported along the water wire. Finally the transport terminates with deprotonation of the 7HQ hydroxyl group. We denote this mechanism by hydroxide ion transfer (HIT) (see Figure 3). This mechanism has been discussed intensely in literature, where quantum chemical calculations have led to the interesting hypothesis of "magic numbers" for the length of the water wire.[56–59] At such specific numbers in the water chain, an enhanced stability of the wire has been predicted, leading to a potentially higher probability for the hydroxide ion transfer mechanism.

The transition states and reaction profiles for both mechanisms are depicted in Figure 3b. The transition state of the proton transfer pathway contains a $H_5O_2^+$ (Zundel cation), whereas the transition state of the hydroxide ion transfer occurs via $H_3O_2^-$ (Eigen-core hydrated proton). Moreover, the reaction path of hydroxide ion transfer and proton transfer were analyzed confirming that both hydroxide ion and proton transfer mechanisms happen in a concerted non-sequential way, where protons are transferred in a single step over the water wire. Compared to the study of Hassanali et al, we predict a somewhat reduced requirement of extended aqueous solvation effects for successful proton/OH^- transfer processes.[15] Nevertheless, the need for a stable arrangement of a certain number of water molecules as well as their stabilization by means of the surrounding solvent is a common finding.

Table 1 Reaction (ΔE_r) and activation (ΔE_a) energies for hydroxide ion and proton transfer (kcal mol^{-1}) in the ground (S_0), triplet (T_1), and singlet (S_1) excited states (zero point corrected).

State	ΔE_r	ΔE_a-HIT	ΔE_a-PT
S_0	2.8	10.2	15.1
T_1	-11.3	6.3	8.5
S_1	-16.7	2.0	3.4

The entire enol-keto tautomerization is exergonic by 16.7 kcal mol^{-1} and 11.3 kcal mol^{-1} in the S_1 and T_1 states, respectively (see in Table 1). In contrast to this in the ground state, the reaction is endergonic by 2.8 kcal mol^{-1} . The resulting S_1 state hydroxide ion and proton transfer pathways have similar reaction barriers of 2.0 kcal mol^{-1} and 3.4 kcal mol^{-1}, respectively. When switching to gas phase cluster conditions, the hydroxide ion transfer pathway in the lowest S_1 state exhibits a reaction barrier of 1.3 kcal mol^{-1} (see ESI). For comparison, Leutwyler and co-workers reported an activation energy of $\approx$ 20 kcal mol^{-1} for the excited state hydrogen atom transfer in the essentially same system.[47,48] We therefore believe that our hydroxide ion transfer must be considered at least as an alternative viable mechanism in the gas phase.

To investigate the possibility of excited state hydrogen atom transfer mechanisms, we analyze the first two excited electronic states and the lowest $\pi\sigma^*$ state of enol, keto, and the transition states of the hydroxide ion and proton transfer pathways (see in Table 2). The lowest $\pi\sigma^*$ state corresponds to an excited state hydrogen atom transfer mechanism, because the σ^* orbital is localized almost exclusively in the solvent region. This state is well-separated from the fluorescent S_1 state, which is in contrast with gas phase studies by Leutwyler and co-worker[47,48] where a conical intersection between $\pi\pi^*$ and $\pi\sigma^*$ was reported. Moreover, we found no $\pi\sigma^*$ state excitation of the transition state of the hydroxide ion transfer in the electronic spectra but instead a $\sigma\pi^*$ state which might correspond to an analogous electron coupled hydroxyl radical transfer mechanism.

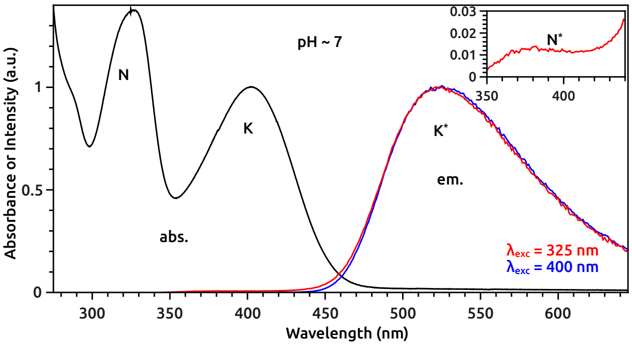

Fig. 4 Steady-state absorption and fluorescence spectra of the aqueous 7HQ. The absorption spectra at pH $\sim$ 7 is displayed to show two bands for N and K at around 325 and 410 nm, respectively. Fluorescence spectra were recorded with excitation at 325 (red) and 400 nm (blue).

The absorption and fluorescence spectra at pH $\sim$ 7 are reported in Figure 4. In neutral aqueous solution, 7HQ in the S_0 state is present both in enol and keto forms labeled N and K in the steady-state absorption and fluorescence spectra. From the excited 7HQ, only a single fluorescence band is observed, regardless of excitation wavelength, which can be assigned to the keto configuration labeled K* in the emission spectrum in Figure 4. Only a minor amount of N* emission is populated. The calculated fluorescence energies of 3.34 eV (N*) and 2.47 eV (K*) closely to the experimental values of 3.35 eV and 2.37 eV, respectively. We also identified the lowest absorption bands of the enol-deprotonated (A) and the imine protonated cation (C) labeled in Figure 1 at pH $\sim$ 13 and -1, respectively (see ESI). Photoexcitation to A* results only in an eventual fluorescent photon emission of the A* form. No emission from

Table 2 Calculated electronic vertical excitation energies (ΔE) in eV and oscillator strengths (f) of the enol, transition states of the proton and hydroxide ion transfer, and keto compound.

Enol			TS-HIT			TS-PT			Keto		
State	ΔE	f	State	ΔE	f	State	ΔE	f	State	ΔE	f
$\pi\pi^*$	3.34	0.142	$\pi\pi^*$	3.02	0.133	$\pi\pi^*$	2.85	0.135	$\pi\pi^*$	2.47	0.15
$\pi\pi^*$	4.24	0.134	$\pi\pi^*$	4.1	0.213	$\pi\pi^*$	4.15	0.07	$\pi\pi^*$	3.94	0.158
$\pi\sigma^*$	5.97	0.003	$\pi\sigma^*$	-	-	$\pi\sigma^*$	5.17	0.006	$\pi\sigma^*$	5.5	0.002

the protonated form is observed. This shows that the proton capture process from the solvent has an effective timescales for beyond the lifetime of the excited state. At low pH $\sim$ -1, the predominant C form only emits an unshifted fluorescent photon. This emission of the C* form does not exhibit any decay characteristic for a proton dissociation process into the water. Hence, the OH group of 7HQ is not acidic enough to release its proton, and the acid/base equilibrium remains basically on the acid side

In summary, quantum chemical calculations reveal a coexistence of intrinsically different tautomerization pathways in microsolvated photoacids along short water wires, which are significantly influenced by solvation effects. Besides the conventional proton (or Eigen/Zundel cation) transfer from the acidic to the basic site, we observe a novel tautomerization pathway, essentially consisting of an effective hydroxyl anion transport from base to acid. In contrast to previous reports on 7HQ, the existence of stable hydrogen atom species cannot be confirmed. Complexes involving the latter species are energetically destabilized by dielectric shielding effects due to the surrounding aqueous solvent, and may only exist in the gas phase. In particular, our calculations show that there is no conical intersection between $\pi\pi^*$ and $\pi\sigma^*$ states along the reaction path in solution.

The energy profile of the novel OH$^-$ tautomerization pathway turns out to be virtually similar to the commonly assumed proton transfer. In this context, OH$^-$ transport means the initial capture of a proton by the basic site from the solvent, followed by a corresponding proton release of the acidic site into the solvent. The presence of extended solvation, however, is not required for this pathway, so that we expect this process to be observable experimentally both in solution and in the gas phase.

The energy profile of the reaction paths show clear evidence that both transfer mechanisms happen in a concerted fashion, i.e. without stable intermediates along the water wire. While this observation does not exclude the possibility for intermediates under full solvation conditions at ambient temperatures, it illustrates that concerted proton and hydroxide ion transport mechanisms are indeed possible for short water wires.

We elucidate the coexistence of processes involving proton and hydroxide ion species. The latter is commonly partially discarded due to the unfavorable characteristics of the OH$^-$ in terms of its surprising hydrophobicity and slow diffusion properties. Our findings show that at least for short water wires, the hydroxyl anion transfer can energetically compete easily with its proton counterpart. This communication sheds new light on the molecular nature of acid-base proton exchange processes, one of the most fundamental chemical reactions in nature, and provides a novel interpretation of existing experimental observation.

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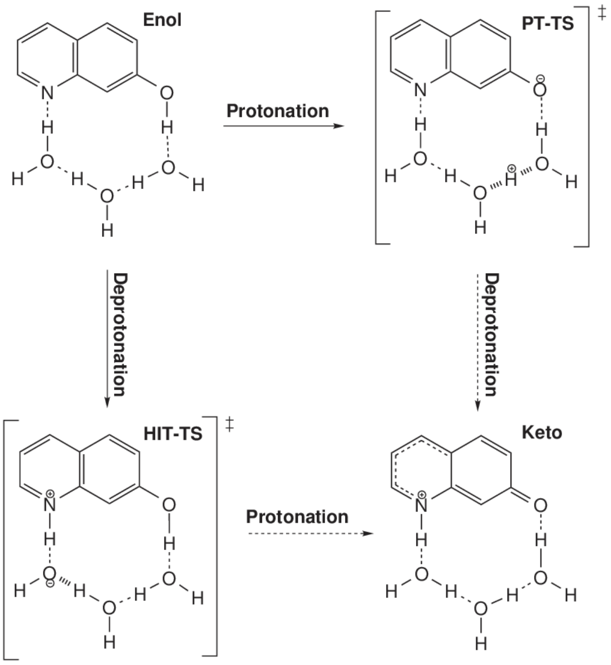
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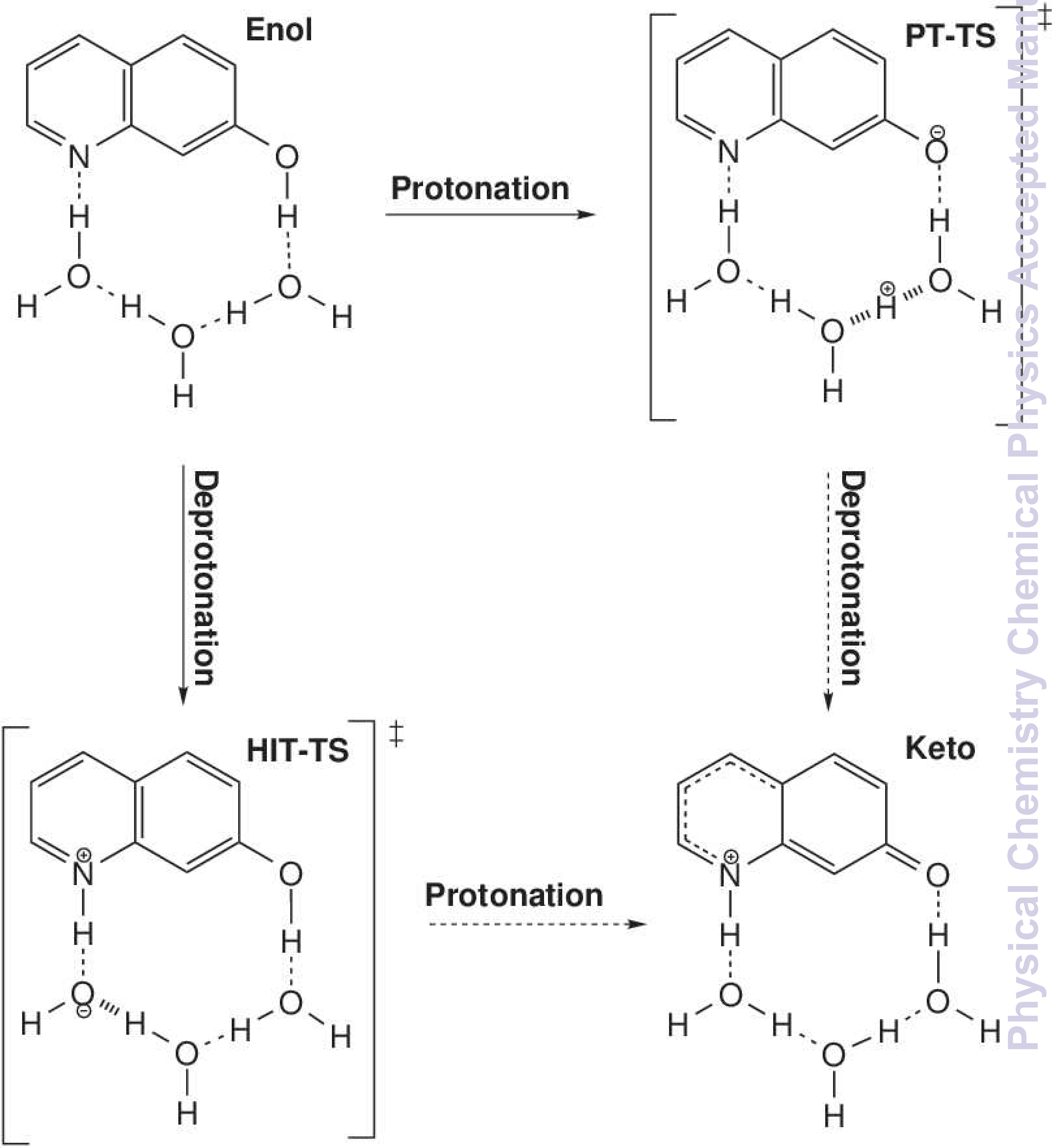
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