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Exploring Autoionization and Photoinduced Proton-Coupled Electron Transfer Pathways of Phenol in Aqueous Solution

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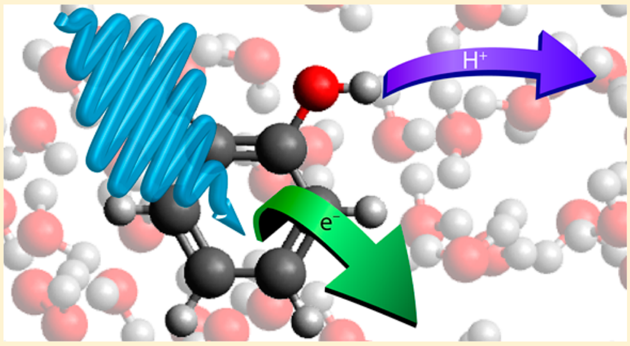
S Supporting Information

ABSTRACT: The excited state dynamics of phenol in water have been investigated using transient absorption spectroscopy. Solvated electrons and vibrationally cold phenoxyl radicals are observed upon 200 and 267 nm excitation, but with formation time scales that differ by more than 4 orders of magnitude. The impact of these findings is assessed in terms of the relative importance of autoionization versus proton-coupled electron transfer mechanisms in this computationally tractable model system.



Phenol is the chromophore of the amino-acid tyrosine, a key residue in ground- and excited-state biochemical redox reactions, such as the reaction center of Photosystem II (PSII),[1,2] and enzymatic catalysis.[3] The photophysical properties of the phenol chromophore in aqueous solution have been extensively studied on both ground[4] and excited potential energy surfaces (PESs).[5−8] Previous flash photolysis and transient absorption studies of phenol and tyrosine in aqueous solution[5,6,8−10] reveal the formation of phenoxyl (or tyrosyl) radicals and solvated electrons,[11] but the precise details of the mechanism(s) leading to these photoproducts have remained elusive. The debate as to whether the process involves excited state proton transfer (ESPT),[7] autoionization, O−H bond fission (H atom transfer), or excited-state proton-coupled electron transfer (PCET) pathways remains a matter of some controversy. A PCET pathway is understood to involve the concerted transfer of a proton and electron,[12,13] rather than a stepwise transfer, and is recognized as an important mechanism in the functioning of many biological systems.[14,15] To date, electronic structure calculations have only examined small phenol−water clusters, revealing that direct photoexcitation to the $^1\pi\sigma^*$ state leads to a net transfer of an H atom to the water cluster.[16,17]

Here we report the use of ultrafast transient absorption (TA) spectroscopy methods to investigate the excited-state dynamics of phenol-h_6 (in H_2O) and its phenol-d_1 isotopologue (in D_2O) using a femtosecond UV pump excitation, and a broadband white light supercontinuum probe that spans the electronic absorption of the phenoxyl radical and solvated electron species. The experimental apparatus has been described previously,[18] and is summarized in the Supporting Information (SI).

Figure 1a displays TA spectra for phenol-h_6 in H_2O at the displayed time delays, t, following 200 nm (6.2 eV) excitation. Two notable features are evident after t = 200 fs, the time-resolution of our transient absorption experiments at this excitation wavelength: vibrationally cold phenoxyl radicals with an electronic origin at ∼400 nm,[9,19−22] and a broad absorption attributed to solvated electrons (that peaks at ∼700 nm[23−25]). The profile of the broad solvated electron transient evolves and its band center shifts to shorter wavelength during the first 2 ps, as the electrons become fully hydrated. The assignment of the solvated electron transient was confirmed by the addition of HCl, a known electron scavenger (see SI).[26] Expanded views of early time ($t \leq 1$ ps) TA spectra in the 350−500 nm probe region are shown in Figure 1b. These data reveal an additional feature centered at 425 nm (indicated by the arrow), which we assign based on prior literature,[21,27−29] to the ground state phenol radical cation ($PhOH^{\bullet+}$), and which disappears on a subpicosecond time scale. To the best of our knowledge, this represents the first observation of the $PhOH^{\bullet+}$ species in aqueous solution near neutral pH.

The vertical ionization potential (VIP) of phenol (PhOH) in water is 7.9 eV relative to the vacuum level.[30] Excitation at 200 nm (6.2 eV) is thus unable to induce vertical ionization of phenol. The thermodynamic threshold for producing fully solvated charged products, i.e., the phenoxyl radical ($PhO^{\bullet}$), a

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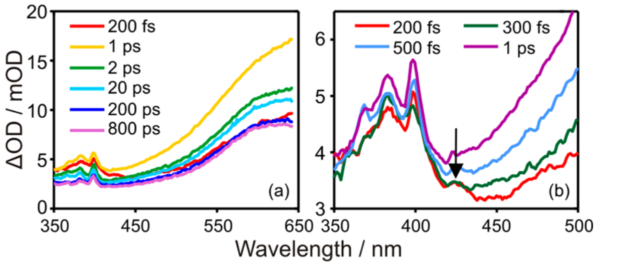

Figure 1. (a) TA spectra of 18 mM phenol-h_6/H_2O solution for displayed pump−probe time delays and 200 nm excitation. (b) Early time ($t \leq 1$ ps) TA spectra displayed on an expanded scale.

proton and a solvated electron, is estimated to be in the range 4.3−4.5 eV (see SI for the free energy landscape of PhOH and associated photoproducts). The observation of the $PhOH^{\bullet+}$ reaction intermediate (Figure 1b) thus points in favor of an autoionization mechanism, followed by rapid deprotonation. The quantum yield of solvated electron formation was extracted via calibration using the known solvated electron yield for photodetaching an electron from hydroxide at 200 nm,[31,32] yielding values of 26% (at $t = 1$ ps) and declining to ∼14% at $t = 800$ ps. We attribute this decline to geminate recombination between $PhO^\bullet$ and solvated electrons, and may involve the third geminate partner, the proton, as discussed in greater detail later. Using known molar extinction coefficients,[22,24] the ratio of phenoxyl and solvated electron products was found to be very close to 1, suggesting that few, if any, phenol molecules undergo homolytic O−H bond photodissociation at 200 nm.

These TA results are strikingly different from those reported previously for phenol-h_6 in the nonpolar solvent, cyclohexane,[33] wherein 200 nm excitation was seen to yield prompt vibrationally hot phenoxyl radicals (within 200 fs), with no evidence for solvated electrons. Such a finding is consistent with direct photodissociation on a repulsive $^1\pi\sigma^*$ PES, as found in gas phase experiments.[34−39] The solvent-dependent photochemistry of phenol, is likely dictated by the magnitude of the hydration contribution to the thermodynamics of the charged reaction products. Water is energetically able to support charged species such as protons and solvated electrons, whereas nonpolar solvents like cyclohexane are unable to do so, therefore phenoxyl radical generation in nonpolar solvents largely mirrors the gas phase reaction.[33]

Our recent transient absorption studies of *para*-methylthiophenol (*p*-MePhSH) in solution[33,40,41] illustrate that the electrostatic properties of the solvent are certainly not the sole factor dictating the photoinduced dynamics in solution. These studies showed no evidence for autoionization or PCET pathways when exciting at 267 nm or at 200 nm, even in polar ethanol solution which can support and stabilize both the electron and dipolar *p*-MePhS radical; "gas-phase"-like (i.e., S−H bond fission) dynamics[42] were seen to prevail. Two conclusions follow: First, the fact that *p*-MePhSH in ethanol has a lower VIP (7.2 eV)[41] than PhOH in water (7.9 eV)[30] shows that a lower VIP does not necessarily predicate a larger autoionization yield. Second, we conclude that the O−H bond fission process seen for PhOH in aqueous solution must be far slower, and thus a less competitive nonradiative decay pathway, than the rate of autoionization when excited at 200 nm.[43]

We now focus on the dynamics of phenol-h_6 following excitation at 267 nm, which populates the lower S_1 ($^1\pi\pi^*$) state. Spectra recorded at $t < 1$ ns are dominated by ESA from the S_1 state and a growing feature peaking at ∼600 nm that has been observed previously and assigned to ESA of phenol excimers.[33] No spectral signatures attributable to phenoxyl radicals or solvated electrons are discernible in TA spectra recorded at $t < 1$ ns (see SI). The early time kinetics of the TA signal at ∼600 nm (at the peak of the transient) are unaffected by addition of electron scavengers (see SI), implying that the quantum yield of electron ejection is negligible at $t < 1$ ns. At $t > 2$ ns, the absorption maximum shifts to longer wavelength, as the phenol excimer signal decays and the broader feature that we assign to the solvated electron rises (see Figure 2a).

The TA spectrum recorded at $t = 14$ ns clearly shows the signature of the phenoxyl radical, and electron scavenging experiments (Figure 3a) confirm the presence of solvated electrons, and the small remaining transient at ∼600 nm is due to residual phenol excimers. The phenoxyl radical yield was found to be 13% at $t = 13$ ns via calibration using the known $PhO^\bullet$ (plus solvated electron) photodetachment yield from phenolate.[22] From literature molar extinction coefficients,[22,24] we then established that for 267 nm excitation of phenol in aqueous solution, solvated electrons and phenoxyl radicals were produced in a 1:1 ratio. The yield of phenoxyl radicals increases from the earliest delay time to ∼14 ns. We, however, cannot ascertain the time in which the yield maximizes due to the limited number of discrete pump−probe time delays measured.

TA spectra recorded at selected pump−probe time delays following 267 nm excitation of phenol-d_1 in D_2O are shown in Figure 2b. These were acquired sequentially to the phenol-h_6 in H_2O data in order to minimize changes in experimental conditions. These data display the same spectral features and kinetics as for the case of phenol-h_6 in H_2O. Comparing the TA spectra from phenol-h_6/H_2O and phenol-d_1/D_2O measured at $t = 13$ ns (overlaid in Figure 3b) also shows negligible difference in the relative yields of phenoxyl radicals and solvated electrons in the two cases, implying a negligible kinetic isotope effect (i.e., KIE = 1.0 ± 0.4). Note that within the upper and lower bounds of the error (0.6−1.4), the returned KIE is very small, and does not change our discussion.

We can envision several possible mechanisms for forming phenoxyl radicals and solvated electrons on a nanosecond time scale following excitation at 267 nm; photodissociation of the O−H bond, as per the gas phase, excited state proton transfer followed by electron detachment, PCET, or autoionization. In turn, we consider the merits of each potential mechanism.

Previous experiments in nonpolar solvents[33] and in the gas phase[33,39,44,45] have shown that PhOH molecules excited to the S_1 ($^1\pi\pi^*$) state can tunnel beneath a conical intersection (CI)

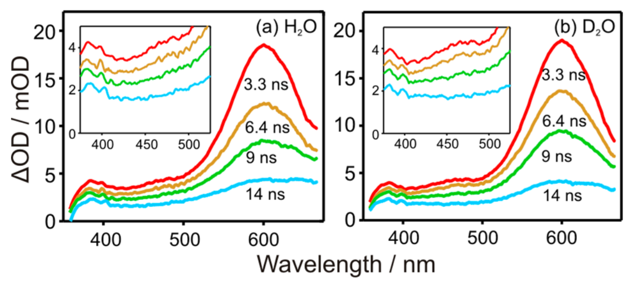

Figure 2. Comparison of (a) 90 mM phenol-h_6/H_2O and (b) phenol-d_1/D_2O TA data following 267 nm excitation, measured at selected time delays. Insets display the same time delays but focus on the 375−650 nm probe region.

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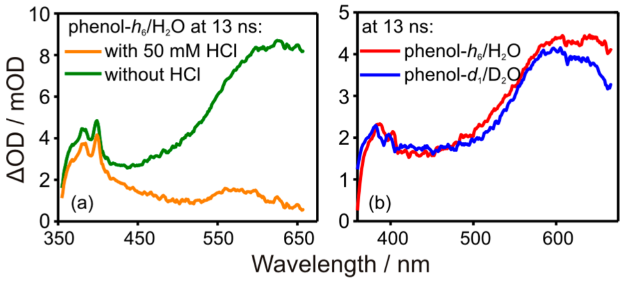

Figure 3. (a) TA spectra of phenol with and without 50 mM HCl (the electron scavenger) measured at t = 13 ns. (b) TA spectra of phenol-h_6/H_2O and phenol-d_1/D_2O measured at t = 13 ns.

associated with the S_2/S_1 ($^1\pi\sigma^*/^1\pi\pi^*$) diabatic states on a nanosecond time scale, resulting in homolytic O−H bond fission, vibrationally excited PhO$^\bullet$ radicals, and translationally excited H atoms. For this to be a viable route to forming the solvated electrons observed in the present study, which appear on a very similar nanosecond time scale, would require rapid H atom fission into $H^+_{(aq)}$ and $e^-_{(aq)}$ after the bond scission. This seems very improbable, given that the equilibrium constant for this process favors neutral H atoms rather than ionic products (by 6 orders of magnitude);[26,46] recall that reaction with H^+ is the basis for the e^- scavenging process observed in Figure 3a. The corresponding gas phase studies involving phenol-d_6 show O−D bond fission does not occur,[35] because the tunneling probability for a D atom under the S_2/S_1 CI is greatly reduced.[17,39] Therefore, such an explanation is also unable to account for the measured KIE (1.0 ± 0.4). The absence of any homolytic O−H bond fission contribution likely reflects a third effect of the polar water on the reaction: the barrier to dissociation under the S_2/S_1 CI must be larger (or significantly altered) in aqueous solution cf. in cyclohexane[33] or in the gas phase[39,47]—as predicted by previous calculations for phenol−H_2O clusters.[16]

Many prior studies have explored ESPT in phenol.[7,48−51] The pKa in the S_1 state is only 4 (cf. 9.8 in the S_0 state),[52] and potentially enables proton transfer from the UV-excited phenol to proximal water molecules and formation of an excited-state phenolate anion that can eject an electron to solvent. If the second step is rate limiting, we would expect to observe the ESA band of the phenolate(S_1) anion at ∼500 nm with a lifetime of 22 ps concomitant with electron appearance on a similar time scale.[22] Neither is consistent with the spectroscopy or kinetics evident in the present TA study. Alternatively, an ESPT process wherein the initial deprotonation step was rate limiting should be expected to have a larger associated KIE. For example, naphthol derivatives have ESPT KIEs ranging between 1.7 and 3.8.[53] Such behavior is not observed in our experiments either. Further support for excluding ESPT as the source of the observed charged photoproducts is provided by previous flash photolysis experiments which concluded that <3% of excited phenol molecules underwent ESPT within the S_1 lifetime,[47] and several other reported failures to observe any signatures of ESPT for phenol in aqueous solution.[48,49]

We now turn to consider possible PCET-based explanations. PCET on the ground state potential (i.e., following internal conversion from S_1) is considered unlikely given the observed lack of any kinetic isotope effect (KIE = 1.0 ± 0.4), cf. the KIE = 2.5 ± 0.7 value derived from electrochemical studies of PCET involving phenol(S_0) molecules by Costentin et al.[4]

Several previous studies have demonstrated PCET on an excited state PES (albeit typically occurring on picosecond time scales[54−56]). Photoinduced PCET thus merits discussion in the context of phenol. The electron and proton could be transferred into bulk solution on similar time scales in a concerted fashion, but the electron would also have to escape the first solvation shell in order to avoid fast inner-cage recombination with the phenoxyl radical and be sufficiently separated to account for the deduced ∼13% phenoxyl radical yield at t = 13 ns. Combined Monte Carlo and quantum chemical calculations show a PhOH−OH_2 hydrogen bond length of ∼1.8 Å in the PhOH(S_1) state.[57] The electrons and protons would need to be ejected distances corresponding to several solvent shells (i.e. > ∼3.6 Å) from the parent molecule, and from each other, in order to reduce loss by diffusive recombination sufficiently to achieve the observed radical and solvated electron survival probabilities. Studies by the Hammes-Schiffer group indicate that the KIE of ground state PCET reactions increases with the distance between acceptor and donor,[58] and that the rate is thus determined by the solvent reorganization time scale rather than PCET.[59] It is unclear whether such arguments will be similarly applicable to excited state PCET but, in the absence of supporting theory, we deem it unnecessarily complicated to suggest excited state PCET as the dominant route to charged products following 267 nm photoexcitation of phenol.

A simpler explanation assumes that the same mechanism identified following excitation at 200 nm applies when exciting at 267 nm also, but that it occurs on a much slower time scale. Excitation at 267 nm promotes phenol molecules to vibrationally excited levels (predominantly ring-breathing vibrations[35,60,61]) of its S_1 state, which relax to the vibrational ground state ($S_{1(v=0)}$) in several picoseconds,[62,63] thereby reducing the total energy to ∼4.5 eV. The $PhO^\bullet_{(aq)}$ + $H_3O^+_{(aq)}$ + $e^-_{(aq)}$ asymptote lies between 4.3 and 4.5 eV (see SI), i.e., only just below that of a PhOH($S_{1(v=0)}$) molecule. The deduced nanosecond reaction time scale could thus simply reflect slow autoionization from the S_1 origin to the $PhOH^+_{(aq)}$ + $e^-_{(aq)}$ asymptote, followed by rapid deprotonation. The nonobservation of phenol radical cations can be rationalized on the basis of their very short lifetime—recall the subpicosecond decay of the $PhOH^+$ transient we observe at 200 nm (see Figure 1b)—and such a photoionization mechanism would not be expected to show a significant KIE if the coupling mode involved in electron transfer does not involve O−H(D) stretching.[43,64]

The autoionization mechanism that we have proposed for photoexcited phenol has some similarities with phenolate (PhO^-) in water, which generates phenoxyl radicals and solvated electrons within the first few picoseconds.[22]The far more rapid autoionization observed for PhO^- likely reflects the 0.7 eV lower vertical ionization potential.[30] The phenol and phenolate autoionization reactions yield the same products; however, ionization of phenol also produces a third product, a proton. This complicates the geminate recombination pathways, and allows for many possible sequential reactions (see SI). The two reactions that will most probably affect the yield of phenoxyl radicals and solvated electron transients in our data include the same recombination reaction as for phenolate: phenoxyl radicals and electrons combine to form ground state phenolate molecules, which subsequently abstract a proton from an adjacent water molecule. The other mechanism involves a proton scavenging a solvated electron and then,

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upon encounter with the phenoxyl radical, reformation of the O−H bond.

The present time-resolved TA data for phenol in aqueous H_2O and D_2O solutions are therefore most plausibly understood in terms of photoinduced autoionization. Identical photoproducts are observed at short (200 nm) and long (267 nm) excitation wavelengths, but with very different formation time scales (femtosecond vs nanosecond, respectively). Electrons are ejected immediately following 200 nm excitation; the high-energy phenol radical cation intermediate is formed and rapidly deprotonates to yield $PhO^{\bullet}$ radicals. In contrast, at 267 nm the photoexcited phenol molecules initially relax to the $PhOH(S_{1(v=0)})$ level, i.e. to energies just above the minimum required to produce a $PhO^{\bullet}$ radical, a solvated electron and a proton (see energetics in the SI). The measured time scales for forming these products allied with the lack of measurable H/D KIE encourages the view that the observed products are formed via near-threshold autoionization, although the involvement of an excited state PCET mechanism cannot be wholly excluded at this stage.

Phenol in aqueous solution surely constitutes one of the simpler test beds for ab initio calculations designed to explore near-threshold autoionization or possible excited state PCET mechanisms.[65,66] Understanding the nuclear motions associated with the solute, and any coupling to specific bath modes, is now crucial in order to reveal any role for PCET at low excitation energies and to advance a detailed understanding of our favored mechanism−autoionization−in phenol, and in larger biomolecules in which phenol (and related subunits) acts as a chromophore.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01861.

> Experimental summary, transient absorption spectra at 200 nm in the presence and absence of H^+ electron scavengers, schematic free energy landscape associated with gas phase and solvated phenol, and transient absorption spectra for 267 nm irradiation of phenol with and without H^+ measured at $t < 1$ ns (PDF)

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Notes

The authors declare no competing financial interest.

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