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Intermolecular photochemical proton transfer in solution: new insights and perspectives

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Abstract

Recent theoretical results on the title topic, informed by femtosecond and steady state spectroscopic studies, are reviewed. It is argued that currently employed conceptions of excited state intermolecular proton transfer of the hydroxyarene acid–base type in solution need to be extended or replaced. Among the key features involved are aspects associated with the dynamics—such as the quantum character of the proton nuclear motion and the nature of the reaction coordinate—and the electronic structure description of the reaction process. One example of the latter—the source of the greatly enhanced acidity in the excited state compared to that of the ground state—is given special attention.

Keywords: Photochemical proton transfer; Hydroxyarene; Electronic structure

1. Introduction

In this article we review and elaborate upon some of our recent work [1–3] addressed to the title topic for acid–base proton transfers. Among the various types of excited state proton transfers (ESPTs) possible, we focus on the *intermolecular* transfer of a proton in the excited electronic state of an aromatic (hydroxyarene) acid ROH in solution to a solvent molecule acting as a base. This type of ESPT reaction has been an important theme in photochemistry for many years [4,6],[1] and is one that has been strongly invigorated in recent times by modern femtochemistry experimental studies [3,7,8]. However, despite important contributions to our understanding over the years, it cannot be claimed that this type of ESPT is at all understood from a microscopic point of view; indeed, it is a central theme of this contribution that considerable revision of previous ideas is in order.

Perhaps the most striking feature of ESPT reactions is the greatly enhanced acidity—typically by a factor of 10^6 in the acidity constant, i.e. a decrease of 6 units in the pK_a value—of the excited state acid ROH* compared to its ground state form ROH [6,9–11]. This feature has long been interpreted in terms of a charge transfer (CT) picture, in which upon excitation there is a direct CT from the non-bonding orbital of the oxygen of the OH group into a π^* orbital of the aromatic ring system R, creating a partial positive charge on the O. As a result of this n–π^* CT, the coulombic repulsion of the H is then thought to explain the enhanced acidity [6b–d,f,9,10,12,13].

An alternate, rather more spectroscopic, perspective for ESPT has often been used as in e.g. Refs. [14–16]. Here the focus is on a ^1L_b–^1L_a description (in the notation of Platt [17]), invoking electronic states which are respectively polarized along the short and long axes of the acid molecule. In this view, the ESPT is considered to involve a transition between the spectroscopically accessed state (^1L_b) and a state of different symmetry (^1L_a). The latter state is thought to be more polar (although this is not immediately clear), and most importantly for our present purposes, this $^1L_b \rightarrow {}^1L_a$ dynamical transition is thought to constitute the ESPT act itself [14,15].

It is important to observe that literature discussions of the above two perspectives have been largely orthogonal; e.g., the $^1L_b/^1L_a$ scenario is silent concerning the underlying cause of the enhanced acidity. Further, as will be discussed in Section 2, neither perspective addresses very important dynamical and electronic structure issues which are already present for the *ground state* proton transfer reaction. Clearly, fundamental questions remain about ESPT and new perspectives are required both to guide and to be probed by experiments.

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[1] For reviews see [5a,b]. See also the special issues [5c–f].

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The outline of the remainder of this paper is as follows. In Section 2, we review some crucial issues for ground electronic state PT in solution, focussing on those novel aspects that will also be important for ESPT. Section 3 discusses some recent experimental results, both femtochemical and steady state, which have provided the impetus to formulate a new view of ESPT, while the initial theoretical results, focussed on electronic structure issues for ESPT, are presented in Section 4. Concluding remarks are offered in Section 5. We make no attempt here to cover the details of the research involved or to provide an exhaustive set of references; the reader is referred to the original papers [1–3] for more extensive discussion and perspective.

2. Ground electronic state proton transfer issues

As indicated in Section 1, there are a number of aspects which differ from standard descriptions that need to be considered both for ESPT and for ground state PT (GSPT). Since more detailed discussions are already available [18a–e],[2] we address here the most important of these aspects only briefly, focussing on the acid–base GSPT

$$\mathrm{AH}\cdots\mathrm{B} \rightarrow \mathrm{A}^{-}\cdots\mathrm{HB}^{+} \tag{1}$$

in a hydrogen-bonded complex surrounded by solvent molecules.

In the traditional view of GSPT in solution, the key focus is on classical motion of the proton over the proton barrier; e.g., the conventional theory of kinetic isotope effects (KIEs) [19] is based on this image. Further, to the extent that the solvent is considered, it is implied that the solvent is in equilibrium with the moving proton at each instant; one limited example of this is that for a symmetric, thermoneutral GSPT, one would consider that the equilibrium solvation free energy of the proton fixed at the transition state (the proton barrier top) and the reactant configurations should be included in the reaction activation free energy.

In a quite different perspective [18], none of these visions is appropriate. Thus, the proton nuclear motion is always quantum in character, rather than classical. (The quantum motion includes both tunneling and non-tunneling aspects.) That motion is typically faster than that of the polar solvent molecules which are strongly electrostatically coupled to the reactant pair in Eq. (1). As a consequence, the solvent molecules must rearrange first in order for the PT to proceed, the reaction coordinate is largely determined by the solvent rather than by the proton, and the reaction activation free energy is governed by this solvent rearrangement rather than being given by the height of the proton barrier. A molecular level illustration of the sort of solvent rearrangement involved in the reaction coordinate and governing the activation free energy is shown in Fig. 1 for the acid ionization of hydrochloric acid, HCl in water [18c,d], which involves a change in the coordination number of the proton-accepting water from the value appropriate for water (four) to that appropriate for the hydronium ion H_3O^+ (three).

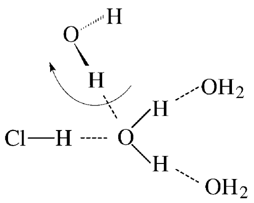

Fig. 1. Microscopic solvent motions involved in hydrochloric acid proton transfer in water.

The remarks made above apply both to the case where the proton tunnels and when it does not. In the latter situation, the proton motion remains completely quantum, having the nature of a bound, high frequency vibration. This perspective obviously strongly contrasts with the standard picture of classical motion of the proton over a barrier when tunneling does not occur. Nonetheless, it has been shown [20] that various experimental observations concerning primary kinetic isotope effects (KIEs) regarded as supporting the standard view [19]—such as the maximum KIE magnitude, the variation of the KIE with the thermodynamic reaction free energy, and the Swain–Schaad [21] relations connecting the KIE for assorted isotopes—all follow from this new perspective.

All of the GSPT features just recounted will *remain* critical for ESPT dynamics, and must be included in a realistic description. Indeed, as an early indication of this, it can be shown [22] that activation free energy–reaction free energy relations of just the sort successfully applied in ESPT ultrafast experiments [23] follow directly from the new perspective outlined above.

A final crucial aspect of GSPT reactions in solution—which actually forms an essential ingredient of the description above, but which has not yet been emphasized in our discussion—is the electronic rearrangements associated with the proton transfer act. Briefly, there is now considerable recent support [18] for the little used Mulliken [24] picture, in which there is CT from the non-bonding orbital of the base to the anti-bonding orbital of the acid. This CT, which we label n–σ*, presumably must also occur in ESPT in solution, but is not referred to in either of the CT or $^1L_b/^1L_a$ perspectives mentioned in Section 1. In the theoretical treatment of GSPT, this Mulliken n–σ* CT is described by the strong electronic resonance coupling mixing of two valence bond (VB) states, which have respectively the basic charge character of the reactants and products in Eq. (1) [18].

In summary, the dynamical and electronic features applying for GSPT in solution should also be present for ESPT in solution and although these aspects are not typically considered for ESPT, they should form an essential part of its description. In the following, we take this for granted, and focus instead on the *additional* features that could be involved for ESPT.

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[2] For a general review, see [18f].

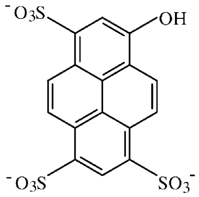

Fig. 2. Pyranine (8-hydroxy-1,3,6-pyrenetrisulfonic acid).

3. Excited state PT: experimental clues from pyranine

The present authors were convinced of the need for a complete reconsideration of both the n–π* and $^1L_b/^1L_a$ (limited) perspectives for ESPT in solution by femtosecond experimental results on the pyranine (3sPyOH) molecule (Fig. 2) in water [3]. These results are summarized briefly in Fig. 3 and are not at all consistent with previous conceptions, as now discussed.

The first major feature evident in Fig. 3 is that three times were observed in the experiment, thus suggesting three successive steps, only one of which is the actual PT step. The last of these time scales (∼87 ps) is consistent with earlier picosecond experimental results of Pines et al. [25] and is evidently associated with the PT act itself, which is also influenced by some diffusive recombination of the produced ions $3sPyO^{-*}$ and H_3O^+. The first of these times (less than ∼300 fs) can be attributed to ordinary aqueous solvation dynamics of the excited 3sPyOH* molecule produced in the initial Franck–Condon transition $S_0 \rightarrow S_1$. The intermediate step, with a time scale of ∼2.2 ps, presented something of a puzzle. Originally [3b] it was thought that some special sort of solvation dynamics involving hydrogen bonding was exclusively responsible, but the fact that some change in oscillator strength was found to be associated with it [3a]—and not for the first or last steps, see Fig. 3—suggested that it is a change in electronic state that occurs in the step (although hydrogen bonding can still be involved).[3]

These results are in clear variance with what would be expected in either of the n–π* CT or the $^1L_b/^1L_a$ scenarios. Thus, in the former perspective, a stronger Stokes shift should be observed due to the supposed pronounced change in the electronic distribution. On the other hand, in the latter perspective, there should only be one step following any initial solvation dynamics, the $^1L_b \rightarrow {}^1L_a$ transition which is supposed to be the PT act itself. In view of this situation, a tentative alternate scenario was constructed [1,27], illustrated in Fig. 4.

The scenario in Fig. 4 is presented in two different languages. In the first, which is more convenient in making the connection with the ground state reaction, we employ a VB language, in which the electronic coupling between the states providing an electronically adiabatic surface is understood but not emphasized. In this language, the three steps are respectively: (a) a first step consisting of the solvation dynamics for the locally excited (LE) state reached in absorption, a state with little CT character of any kind; (b) a second step associated with some n–π* CT from the oxygen of the OH into the ring system, producing a CT state, the second VB state; no PT is involved in this step; (c) a third step involving n–σ* CT, similar to that in the ground electronic state (see Section 1) to produce a PT electronic state, which is the final VB state; this state may involve further n–π* CT as well, an aspect related to the electronic coupling of the second and third VB states. A key point is that this last step is the PT step proper.

We pause to note that there can be a certain blurring of steps in this scheme. In particular, the time scale observed for the dynamics of the first step is roughly consonant with the shorter components of solvation dynamics of non-reactive dye molecules in water, although slower aqueous solvation dynamic components are observed as well [28]. This suggests that the first step is not necessarily completed before the second step occurs (as we noted above, hydrogen bond dynamics can certainly be involved in the electronic state changing second step).

In the alternate $^1L_b/^1L_a$ language version of the tentative scheme depicted in Fig. 4—again with the electronic coupling not emphasized, the first step is solvent relaxation in the ^1L_b state, which is equivalent to the LE state, while the second step is the $^1L_b \rightarrow {}^1L_a$ transition, but is not the PT step (as it is in the usual $^1L_b/^1L_a$ conception), since the ^1L_a state comprises two VB states, the conversion between them constituting the third step, i.e., PT.

The validity of the new ESPT image of Fig. 4 was then examined in a combined experimental/theoretical study involving a detailed analysis of the solvent dependence of both the absorption and steady state fluorescence of pyranine [1]. Here we very briefly recount only two important results of that extensive study. The first is that, under experimental pH conditions where no proton transfer is possible, the absorption and fluorescence spectra, shown in Fig. 5, are not mirror images of each other, consistent with the interconversion of an LE $= {}^1L_b$ state reached in absorption to a fluorescent ^1L_a state, *without* any PT having occurred or whose effect is readily subtracted such that only the acid form is examined. The second is that a solvatochromic analysis of the absorption and fluorescence (Fig. 6) indicates the fluorescing state has significant n–π* character and can be identified as having ^1L_a character, as distinct from the LE state reached in absorption, which instead has ^1L_b character.

This solvatochromic analysis [1] used the well-known Kamlet–Taft [29] parameters α, β and π* which describe the effect on the electronic transition of the H-bond donating ability, H-bond accepting ability and the polarisability-polarity of the solvent, respectively:

$$\nu = \nu_0 + a\alpha + b\beta + s\pi^* \qquad (2)$$

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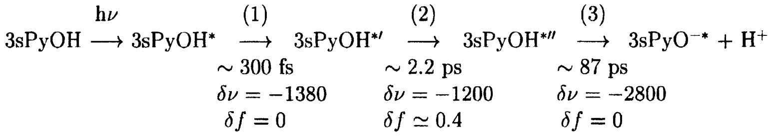
[3] For early discussion of H-bonding changes in excited states see [26a,b], see also [26c] and for some recent related developments, see [26d].



$$\mathrm{3sPyOH} \xrightarrow{h\nu} \mathrm{3sPyOH}^{*} \underset{\substack{\sim 300\ \mathrm{fs}\\ \delta\nu=-1380\\ \delta f=0}}{\xrightarrow{(1)}} \mathrm{3sPyOH}^{*\prime} \underset{\substack{\sim 2.2\ \mathrm{ps}\\ \delta\nu=-1200\\ \delta f\simeq 0.4}}{\xrightarrow{(2)}} \mathrm{3sPyOH}^{*\prime\prime} \underset{\substack{\sim 87\ \mathrm{ps}\\ \delta\nu=-2800\\ \delta f=0}}{\xrightarrow{(3)}} \mathrm{3sPyO}^{-*} + \mathrm{H}^{+}$$

Fig. 3. Summary of some results of the pyranine ESPT femtosecond experiment at pH = 4. Characteristic time scales, frequency shifts (in cm^{-1}) and oscillator strength changes are indicated for each step.

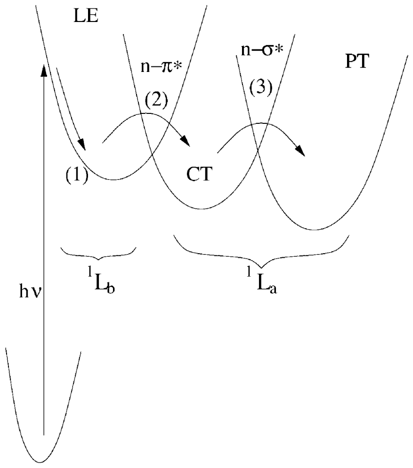


Fig. 4. Proposed scheme for the excited state dynamics of pyranine in water, both in the VB and $^1L_b/^1L_a$ perspectives. The electronic character involved in steps (2) and (3) is indicated, the first referring to the O to aromatic ring CT and the second referring to the proton-accepting base to OH bond CT. The electronic coupling between neither the VB states nor the ^1L_b and ^1L_a states is shown.

Here a, b and s are the respective weights of the corresponding Kamlet–Taft parameters, and the intercept ν_0 corresponds to the position of the maximum of absorbance or fluorescence of the isolated molecule in vacuum (generally similar to the experimental gas phase value when the latter is available). It was found that (frequencies in cm^{-1})

$$\nu^{abs} = 25460 - 270\alpha - 290\beta - 380\pi^{*};$$
$$\nu^{\mathrm{fluo}} = 27000 - 1890\alpha - 1820\beta - 1300\pi^{*} \qquad (3)$$

which display two important features. The first is that, while the stabilizing effect of the various solvent properties on the absorption band is rather small, the comparatively large and negative a, b and s values indicate a strong stabilization of the fluorescent state by the solvent involving both H-bond donating and accepting abilities as well as polarity. The conclusion is that the fluorescent state charge distribution is quite different from that of the state reached in absorption, consistent with n–π* CT in the fluorescent state much more significant than in absorption [1]. The second important feature of these results is that there is a strong contrast with the usual situation where, when the state reached in absorption and the fluorescing state are the same electronic state, the asymptotic Stokes shift $\nu_0^{abs} - \nu_0^{\mathrm{fluo}}$ is a positive value whose magnitude is indicative of geometry changes which have occurred subsequent to the absorption and prior to the fluorescence. But in the present case (Eq. (3)), this asymptotic difference $\nu_0^{abs} - \nu_0^{\mathrm{fluo}} = -1540\,\mathrm{cm}^{-1}$ is very *negative*. This observation [1] (not made in a different solvatochromic analysis of pyranine [30]) is consistent with the vacuum fluorescent state lying higher in energy than the vacuum state reached in absorption, i.e. that the former is ^1L_a and the

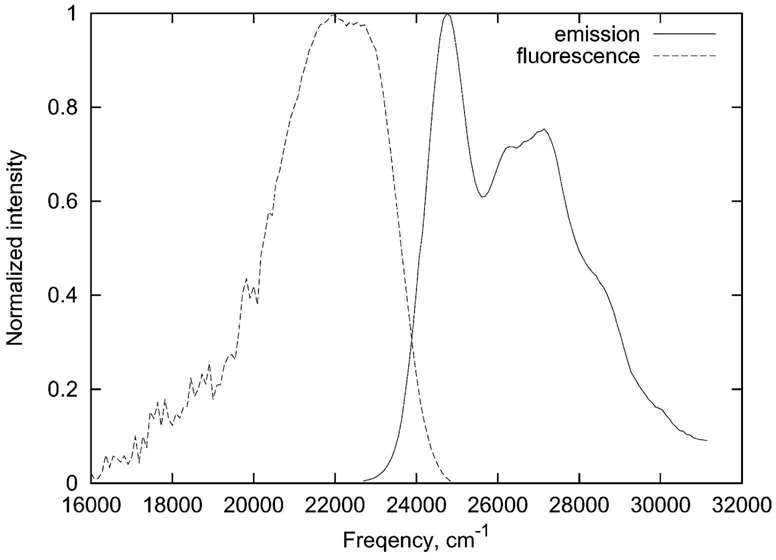


Fig. 5. Absorption and fluorescence spectra of pyranine in H_2O at pH = 2. The small contribution of the anion has been subtracted out [1]. Similar lack of mirror symmetry is observed for other solvents [1].

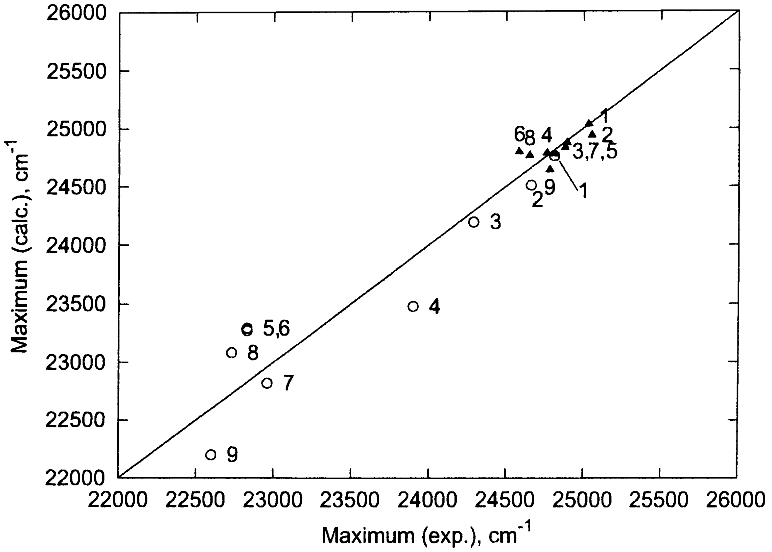


Fig. 6. Calculated maxima of absorption (filled triangles) and fluorescence (open circles) of pyranine as a function of the corresponding experimental values recorded for various solvents. The calculated maxima are obtained using the Kamlet–Taft relation 2. The weights of the solvatochromic parameters α, β and π* for absorption and fluorescence are given in Eq. (3). The largest deviation of the points from the line (representing the perfect agreement between experience and Eq. (2)) is ±500 cm^{-1}. The solvents are—1: acetonitrile, 2: N,N-dimethylformamide, 3: DMSO, 4: ethanol, 5: methanol, 6: formamide, 7: 2,2′,2″-trifluoroethanol, 8: ethyleneglycol, 9: water.

latter is ^1L_b. In conclusion, all these features are completely consistent with Fig. 4 scenario, but not with the previous conceptions. Further, evidence that a $^1L_b \rightarrow {}^1L_a$ transition does not correspond to proton transfer has also been given by the Pines group for 1-naphthol [16].

4. Excited state PT: electronic structure for phenol and substituted phenols and their anions

The ideas and results outlined above indicated that it was important to carry out high level electronic structure calculations on simpler systems to examine in detail the electronic character of an acid and its anion in the excited state. While a number of more limited electronic structure calculations had been carried out in the past [13,31], either the level of the calculations was sufficiently low (especially for pioneering older works) as to be unreliable, or else the enhanced acidity and $^1L_a/^1L_b$ issues were not addressed. This program was recently carried out for phenol and cyanophenols (*ortho*, *meta*, *para*) in vacuum [2]. Phenol was selected as the simplest aromatic acid, although upon excitation, electron transfer [32] and (in small clusters) hydrogen atom transfer can occur [33], while the cyanophenols are susceptible to experimental time dependent experiments in solution, the reaction medium of ultimate primary interest. It is to be stressed however, that these calculations do not include any proton-accepting base partner, and so are silent on the presumably n–σ* Mulliken CT aspect of the problem. Further, while certain solvation calculations were included in a limited context, calculations necessary to examine the role of a solvent coordinate were not performed. Despite these restrictions, the calculations were quite revealing.

To address the fairly challenging electronic structure issues, the ground and first two excited electronic states were calculated for the acids and the anions. Ab initio calculations were performed using the double-ζ cc-pVDZ basis set. To properly describe the anions, we added a set of *s* and *p* diffuse functions on three alternated carbon atoms of the cycle and on the oxygen. For the cyanophenols, diffuse functions were also added on the C and N atoms of the cyano group. Such a basis set is unsuitable to describe Rydberg states, but our major ultimate interest was focussed on the aqueous-phase behaviour, where contribution from Rydberg states is unlikely. The ground and the two first ππ* excited states were obtained with CASSCF state averaged calculations, followed by CASPT2 perturbative calculations in order to take into account the repolarization of the σ system together with the dynamical correlation. For phenol and phenolate, the active space consisted of eight electrons and eight π orbitals: the O p_π, the six ring π and one extravalence π orbital. For the cyano derivatives, the active space contained two more electrons and two more π orbitals. The ^1L_a and ^1L_b labels were unambiguously assigned by examination of the direction of the transition dipole moment, respectively parallel and perpendicular to the C–O axis. (This unambiguous assignment is only possible for phenol and *p*-cyanophenol, due to symmetry issues [2].) In the following, we focus only on the phenol results; those for the cyanophenols were qualitatively similar.

The first departure from accepted views is summarized in Table 1. The first important point to be seen there is that significant n–π* CT from the O into the ring expected in the

Table 1
Features of the first two valence excited singlets of phenol and phenolate[a]

Molecule	State	T_e (eV)	CT (e)
PhOH	S_0	0	0
	$S_1\,^1L_b$	4.6	0.02
	$S_2\,^1L_a$	6.3	0.09
PhO^-	S_0	0	0
	$S_1\,^1L_a$	3.8	0.45
	$S_2\,^1L_b$	4.1	~0

[a] T_e is the computed transition energy, CT is the charge transfer from O to the ring (with respect to the ground state), estimated from the variation of the dipole moment (for PhO^-) or from the variation of the Lowdin charges (for PhOH)

standard explanation of the enhanced excited state acidity is not present. Namely, for the acid, there is in fact *very little* n–π* CT from the O to the ring in the $S_1 = {}^1L_b$ state, with only a bit more in $S_2 = {}^1L_a$. On the other hand, for the anion, significant CT was found in $S_1 = {}^1L_a$ and much less in $S_2 = {}^1L_b$, an inverted pattern compared to the acid.

This inversion and significant CT in S_1 of the anion was pursued in a calculation of the state energies of the anion as a point proton was approached to the O along two geometries, shown in Fig. 7, both for the absolute energies and the excitation energy from the ground state. The upper, absolute energy, panel displays the endothermic character of acid ionization for isolated phenol, while the trends we wish to stress are more clearly shown in the bottom, transition energy panel.

As the proton approaches the PhO^- anion along the CO axis, Fig. 7 shows that there is a crossing of the ^1L_a and ^1L_b curves. Since there is less negative charge on the O in the anion ^1L_a state compared to that in the ground state, that curve rises more sharply than does the ^1L_b curve, where the charge on the anionic O is very similar to the ground state value. In the more physically relevant approach of the proton towards the anionic O along a lone pair axis, electronic coupling produces an avoided crossing between the ^1L_a and ^1L_b curves. Thus, there is a conical intersection in the problem, as a function of the OH angle. This could prove to be important in the excited state dynamics, although it does not seem likely that the conical intersection point itself would be easily reached, although this issue deserves further investigation. Finally, one needs to bear in mind, especially in connection with a comparison to Fig. 4, that the calculations shown in Fig. 7 deal only with a bare proton rather than with an H_3O^+ species, and further, do not allow for any electron flow to the bare proton.

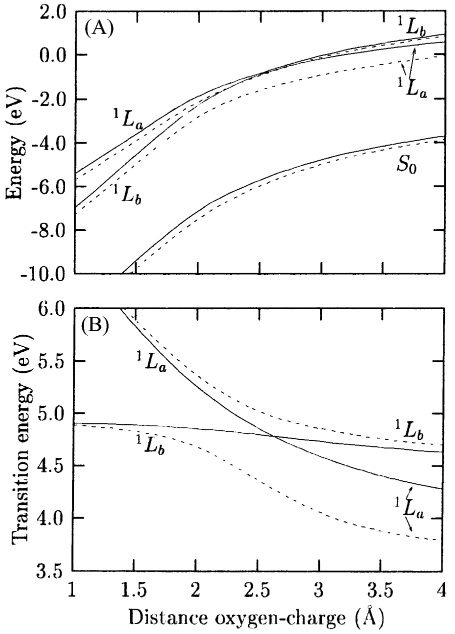


Fig. 7. Interaction between the phenolate anion and the proton, modelled as a unit positive charge. Full lines: the charge is approached on the C–O axis. Dashed lines: the charge is approached following the O–H direction in phenol. (A) S_0, ^1L_a and ^1L_b energies with respect to the ground state of phenolate alone; (B) ^1L_a and ^1L_b transition energies.

We have already noted that significant n–π* CT—expected in the S_1 state of phenol according to the standard explanation of enhanced acidity—was not observed. The question then is: What it the source of the enhanced excited state acidity? In fact, the answer is already contained in the results and the discussion presented above: it is primarily due to an effect on the *anionic* side of the ESPT reaction and not on the acid side of the reaction, as in the standard view. In the latter view, the acid is destabilized in the OH bond—the acid molecule is made a better acid, i.e. a better proton donor in the excited state. In the present view, the major effect is instead that the anion is stabilized, i.e., made a worse base in the excited state. Since negative charge has been significantly reduced on the anionic O by the n–π* CT, it is a worse proton-acceptor in the excited state.

The novel perspective just recounted was further supported by calculations of the electrical potential in the neighborhood of the O [2,34], which can be connected to the acidity, for the acid and anion in the ground and first excited states. Further, it was pointed out [2] that there will be spectroscopic signatures of this much more important n–π* CT on the anionic side compared to the acid side. For the latter, there should not be important solvatochromic shifts of the absorption with increasing solvent polarity, since the LE state does not have a charge distribution significantly different from that of the ground state. Conversely, for the former, there should be a very significant solvatochromic blue shift with increasing solvent polarity: due to the reduced charge on the O moiety in S_1 compared to S_0 resulting from the pronounced CT to the ring, there is less solvent stabilization of S_1 than of S_0. This is consistent with observations, and with our solution-phase calculations [2], carried out with the PCM method [35].

In retrospect, i.e., with the benefit of hindsight, the fundamental origin of the enhanced excited state acidity on the anion side rather than the traditionally assumed acid side [6b–d,f,9,10,12,13] is perhaps not so surprising. Certainly, as argued above, CT away from a highly negatively charged oxygen in the anion is much more plausible than from an O in a neutral OH group, and, as was noted in Ref. [2], related observations have been previously made for ground state acids [36]. For ESPT, a remark about greater CT in the anion was made in a little known paper by Schulman [37] although the implication of this for the origin of the enhanced acidity was clearly missed. Along similar lines, occasional observations of e.g. stronger polarity dependence on the anion side of the ESPT reaction have been made [38], without any conclusion that the anion side of the reaction is dominant [39]. There is, however, a brief footnote remark by Weller [36c] (footnote 3) definitely implying the dominance of the anion for ESPT acidity. But in view of the subsequent widespread and uniform opposite view [6b–d,f,9,10,12,13], it seems fair to us to say that the latter traditional view was first challenged in Ref. [2] by the demonstration that the n–π^* CT on the anion side of the reaction, and not the acid side is the fundamental origin of the enhanced excited state acidity. The above remarks should be borne in mind in considering recent statements concerning the source of enhanced excited state acidity [40,41].

Of course, the identification in Ref. [2] of the fundamental origin of the enhanced acidity being on the anionic side due to larger n–π^* CT does not directly address the issue of the *variation* of this enhancement from one acid to another. However, this variation has recently been correlated [40], via semiempirical AM1 calculations, with ring aromaticity issues, with CT on the anion side being dominant, as in Ref. [2]; again, there is a basic similarity with discussions on ground state acidity emphasizing the anion side of the reaction [36] (see especially Ref. [36c]).

The major conclusion of Ref. [2] concerning the anion side of the acid–base reaction for the excited acid ROH*, i.e., more significant n–π^* CT for the anion than for the acid, thus making the conjugate base RO^{-*} a weaker base than in the ground state, has of course consequences for general issues of excited state basicity. Here we limit our discussion to the case of excited aromatic amines RNH_2^*, which share with the hydroxyarene acids the feature that the active moiety is external to the aromatic ring. While we have performed no calculations for such amines, the implication would be that, e.g. the ESPT reaction $RNH_2^* + H_2O \rightarrow RNH_3^{+*} + OH^-$, CT into the aromatic ring of the base RNH_2^* would be much more important than for the conjugate acid RNH_3^{+*}, for which the electrons of N, which were formerly non-bonding (n) in the base, are tied up by the proton. This CT reduces the availability of the n electrons (and in the limit creating a positive charge on the NH_2 group), making RNH_2^* a weaker base in the excited state. Indeed, this coincides with the standard argument for excited bases (see e.g. Ref. [9a]). A more direct connection with the arguments of Ref. [2] would be for excited state bases (that is to say molecules which are normally bases in the ground state) acting as acids in the excited state: $RNH_2^* + H_2O \rightarrow RNH^{-*} + H_3O^+$ [42]. Here the increased acidity of RNH_2^* would originate from the greater CT in the base RNH^{-*} (whose base strength is weakened compared to the ground state RNH^-).

In concluding this section, we comment on the relationship of our increased acidity picture with the well-known fact that hydroxyarene increased excited state acidity is less pronounced for the triplet (T_1) acid than for the singlet (S_1) acid [9a]. This has been rationalized in terms of differential singlet/triplet considerations on the acid side of the reaction [6b,9b,13b,c] (although alternate arguments on the acid side have been put forward [6d,9a,13d]). We now consider how this S_1/T_1 differential excited state acidity arises in the view that it is the n–π^* CT on the anion side that is most important [2]. In the following, we assume that for the anion S_1 and T_1 are both mainly represented by the same configurations (n–π^*, CT).

To address the S_1/T_1 issue, we can propose a variant of an argument of Ref. [43]. The argument focusses on the exchange integral K_{n,π^*} related to the CT, and the relative lowering of the energy of T_1 compared to that of S_1 in the anion and in the acid. Roughly speaking, $E(T_1 - S_0)$ does not depend on the exchange integral K_{n,π^*} in contrast to the energy difference $E(S_1 - S_0)$, and thus the key energy difference $E(S_1 - T_1)$, which do. In particular, the larger is K_{n,π^*} the lower T_1 will be with respect to S_1. Now, K_{n,π^*} is expected to be smaller, the greater the degree of CT. Since the extent of CT is *smaller* in the acid form, K_{n,π^*} is larger in that form; thus T_1 is lower (compared to S_1) in the acid than T_1 (compared to S_1) in the anion. Thus, as a result of the smaller CT in the acid than in the anion, the enhanced acidity is reduced in T_1 compared to S_1. It should be noted however that this type of argument does not address the possibility that the CT is so small in the anion that one might have to consider other sorts of electronic configurations to properly describe the triplet system (see e.g. Ref. [9a]).

5. Concluding remarks

In this paper, we hope to have made clear that non-traditional concepts are necessary to account for several key features of ESPT reactions in solution, and a number of them have been proposed and supported. These new concepts should be probed by future experiments and should prove useful in interpreting those experiments. It is also the case that much theoretical work remains to be done. No full calculation following the dynamics and including the solvent has yet been done for the overall photochemical ESPT process.

Among the specific aspects which especially require clarification by such full calculations is the second step Fig. 4, involving the conversion from ^1L_b to ^1L_a (or the corresponding transition when these labels are inappropriate due to symmetry issues). Issues here include the role of the solvent rearrangement (presumably quite important since a charge redistribution is involved), the importance of internal coordinates in the acid, and the magnitude of the electronic coupling between the states involved. Some interesting initial hints are provided in the simulation study in Ref. [15a] for 1-naphthol in water (which however views the transition as determinant for ESPT, although no PT is involved in the simulation).

We also need to stress that the basic scenario Fig. 4 provides, in our view, an important and useful framework for thinking about ESPT; for example, beyond the features we have previously emphasized, Fig. 4 suggests that initial excitation to the *second* excited state could provide interesting information on the character of the dynamics associated with the $^1L_b/^1L_a$ crossing. However, one can certainly anticipate that there can be important variations in this Fig. 4 scheme. For example, the second VB state, of (^1L_a) character and with significant n–π* character could, depending on the acid involved (as well as the solvent) be sufficiently lowered in energy that a $^1L_b \rightarrow {}^1L_a$ transition could lead without significant barrier to PT, provided that the barrier arising from the crossing of that VB state with the final proton transfer VB state were sufficiently low. Alternately, again in the scenario that the barrier for the actual PT step was sufficiently low, the barrier associated with the $^1L_b \rightarrow {}^1L_a$ transition could be rate-limiting for PT. Finally, there could be $^1L_b \rightarrow {}^1L_a$ conversion without any ESPT (during the excited state lifetime) if the barrier for the PT step were sufficiently high (above and beyond the situation described above in connection with Figs. 5 and 6, where thermodynamic issues per se, due to pH conditions, prevent ESPT). Further, the entire discussion has been restricted to intermolecular single proton transfers of the acid–base variety for hydroxyarene acids. Intramolecular ESPT, for example, has yet to be treated, and in addition, the electronic scenario discussed within cannot be expected to apply to every type of photoacid. Beyond this, enhanced acidity in triplet states requires further investigation, as does the detailed applicability of the ideas presented here for excited state bases.

We have not much discussed here the rate constant for the ESPT step proper. Within either the $^1L_b/^1L_a$ perspective in Fig. 4, but within the (^1L_a) state, or within the VB perspective in Fig. 4, focussed on the final two VB states involving the n–σ* Mulliken CT picture (see Section 2), there already exist analytic expressions for the PT rate constant taking into account the solvent rearrangement, the quantum character of the proton, and the intermolecular hydrogen bond coordinate (e.g., the O–O distance between the O of the acid OH and a hydrogen-bonded O of a proton-accepting water), in the two distinct limits where the proton motion at the transition state in the solvent coordinate (see Section 2) is a bound quantum vibration [18b,22,44] and where the proton motion is instead quantum tunneling [18f,20,44,45]. Further, these expressions can include possible contributions from solvent *dynamics*, over and above the static solvent contributions to the reaction barrier [18b,45b]. These should prove useful in the analysis of experimental data (see e.g. Ref. [23]). All these expressions will only hold when the PT step is truly activated, i.e. the free energy barrier is at least a few thermal energy units. In those ESPT cases where this condition is not satisfied—and a GSPT example is provided by HCl acid dissociation in water [18c,d]—the kinetics will be non-exponential in time, and a different analysis, involving a sort of diffusion in the solvent coordinate, will be required [18d]. A possible example of such a case has been recently reported in Ref. [41].

Clearly much remains to be done on both the experimental and theoretical sides. In the former category for hydroxyarene photoacids, experiments on cyanophenol ESPT in solution are underway. For the latter, calculations for ESPT in solution aimed at clarifying, e.g., the character of the $^1L_b \rightarrow {}^1L_a$ transition as well as the PT act itself are underway.

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