Primary events in photoacid dissociation

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Postulated hydrogen-bond rearrangements accompanying photoacid excitation and dissociation are identified. Experimental evidence corroborating these suggestions is surveyed.

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1 INTRODUCTION

Acid dissociation is one of the more fundamental chemical reactions [1,2]. Strong gaseous acids which dissociate in clouds and at the surface of startospheric ice participate in the mechanisms producing acid rain and the ozone hole. Weaker acids function as buffers that determine the pH of the environment in which we live. Acids can catalyze a variety of important reactions. At metallic surfaces, proton concentrations determine corrosion rates. In living cells, they take part in enzyme action and in the storage and utilization of energy. Proton concentrations in vivo are carefully regulated, through varied mechanisms such as proton carriers and proton pumps. A relatively small decrease in the working pH value can make an organism much more susceptible to bacterial attacks.

In spite of its fundamental role in chemistry and biology, the molecular mechanism of acid dissociation is poorly understood, and only few bulk phase simulations have been performed [3–5]. We are particularly interested in the role of the solvent, e.g. water, in promoting acid dissociation and in the hydrogen-bond (HB) rearrangements which accompany it.

Strong acids dissociate in water much too fast. Hence mixing cannot serve as a trigger for their dissociation. However, certain organic chromophores, such as hydroxyaranes (denoted ROH), undergo significant enhancement in their acidity upon electronic excitation [6–8]. Such photoacids are widely used as fluorescence probes in homogeneous solutions and micro-heterogeneous systems [9]. For example, the pH of 2-naphthol (2OH) in water decreases from 9.5 to 2.8 following the absorption of a (blue) photon [6]. More enhanced photoacids, based on cyano derivatives of 2OH have been synthesized and characterized [10,11]. For example, 5-cyano-2-naphthol (5CN2OH) has pKₐ ≈ 8.7 which decreases to ≈ −0.5 upon excitation. Consequently, it is able to transfer its proton to a range of pure

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organic solvents during its excited-state lifetime. Such photoacids are natural candidates for studying the primary events in acid dissociation.

The present report draws on our recent studies of excited-state proton transfer to solvent [12–14], of proton mobility [15,16] and the structure of concentrated aqueous HCl solutions [17] to infer, if indirectly, on likely elementary steps in photoacid dissociation. These are divided into two parts: (a) Ultrafast events following photoexcitation but preceding the dissociation step itself, and (b) Fast events which occur simultaneously with proton dissociation. The following discussion is timely, because detailed simulations of large protonated water clusters [18–25] have progressed to an extent that makes a realistic study of this problem feasible. It is hoped that the insight gained from the following survey could be used in the interpretation of such simulations.

2 PHOTOEXCITATION

Consider first the ultrafast microscopic events triggered by photoexcitation, which occur prior to proton dissociation. These are depicted schematically in Fig. 1: It shows the 5CN2OH chromophore with two HBs to its OH moiety. Following excitation, electron density migrates from the hydroxyl oxygen to the ring. As the OH group becomes more positive,

- The ROH···OH₂ bond strengthens.
  \[ \text{H} \]
- The RO···HOH bond breaks.

The proton becomes partly shared by the two oxygens in a strong RO···H···OH₂ bond. As a result, the water molecule in the first solvation shell also becomes more positively charged, so that the second-shell HB shown in the figure may possibly break. Experimental evidence for the above suggestions is surveyed below.

![Fig. 1. Suggested hydrogen-bond rearrangements following photoexcitation of 5-cyano-2-naphthol.](image-url)
(a) Strengthening of HB to water acceptor.

Strengthening of a HB to a basic acceptor molecule has been demonstrated in gas phase naphthol-ammonia dimers [26,27]. From these studies it was concluded that, upon excitation to $S_1$, the ROH⋯NH$_3$ bond shortens by 0.2 Å.

In the liquid phase, evidence for such an effect comes from solvatochromic shifts in the steady-state fluorescence spectra of undissociated photoacids (the “ROH band”), such as 5CN2OH [12,14]. The influence of the ROH⋯S bond to solvents (S) of varying basicities is recognized by comparing 5CN2OH with its methoxy analog, 5-cyano-2-methoxynaphthalene (5CN2OMe). The latter compound has its hydroxylic hydrogen replaced by a methyl group, which excludes the formation of this HB. Assuming that other interactions with the solvent are nearly unchanged, the difference in frequency of the ROH band between the two compounds

$$\Delta \nu \equiv \nu(5\text{CN2OMe}) - \nu(5\text{CN2OH}),$$

could be attributed to this specific HB.

Figure 2 shows $\Delta \nu$ for different pure solvents, as a function of the empirical Kamlet-Taft solvatochromic parameter $\beta$, which measures the extent of HB accepting power of the solvent [28,29]. The closed and open circles show shifts in the excitation (or absorption) and emission spectra, respectively [12,14]. The first is sensitive to the solvent conformation around the ground-state chromophore, whereas emission occurs from the excited-state conformation. The two lines are fits to the equation

$$\Delta \nu_i = \Delta \nu_i^0 - b_i \beta,$$

where the subscript $i = 0,1$ denotes excitation ($S_0$) and emission ($S_1$), respectively. The coefficient $b_i$ is a measure of the HB donating power of the solute. We find $b_0 = -680$ cm$^{-1}$ and $b_1 = -1900$ cm$^{-1}$ for the two electronic states.$^\dagger$

The negative values of $b_i$ indicate that, for a given solvent conformation, the ROH⋯OH$_2$ bond is stronger in the excited-state and this produces the red-shift for solvents with increasing basicity parameter $\beta$. The red-shift could be understood from the migration of charge density in the excited state from the oxygen to the aromatic ring. The more positive character of the OH group in $S_1$ makes it more sensitive to stabilization by basic (electron donating) solvents.

Since emission occurs from the relaxed solvent conformation around the excited chromophore, the considerably larger absolute value of $b_1$ shows that, after excitation, solvent conformation relaxes in a way that makes this bond stronger, hence more sensitive to $\beta$. Thus the sign of the solvatochromic parameter indicates the relative ($S_1$-$S_0$) charge density change for fixed solvent conformation, whereas its magnitude indicates the extent of the nuclear rearrangement which occurs in response to the electron density migration.

$^\dagger \Delta \nu_i^0 = 65$ and 50 cm$^{-1}$ for $i = 0,1$. This is approximately zero within our error bars. The correlation coefficients are 0.90 and 0.97, respectively.
Fig. 2. Differential solvatochromic shifts of 5-cyano-2-naphthol in comparison with its methoxy analog, Eq. (1). Data from Refs. [12,14], which also give the solvent abbreviations.

Note that the effect is not unique to 5CN2OH: A similar trend is observed for 2OH [13], but the effect there is less dramatic, $b_0 = -500$ cm$^{-1}$ and $b_1 = -800$ cm$^{-1}$. This agrees qualitatively with the relative acidity order discussed in the introduction (but not quantitatively, because the acidity depends also on the stabilization of the anion). As far as ground-state solvation, 2OH and 5CN2OH do not differ much. But they do differ considerably in excited-state solvation.

In conclusion, our current evidence for the strengthening of the HB to the hydroxyl hydrogen following photo-excitation, comes from comparing steady-state spectral shifts in different solvents. A measurement demonstrating this effect in the time-domain for a fixed solvent (e.g., water) is still missing. Such experiments will hopefully be performed in the near future.

(b) Cleavage of HB to water donor.

Evidence for this process is less direct, since one cannot easily compare (otherwise identical) compounds with and without this interaction. Therefore we fit the ROH shifts to the full set of empirical Kamlet-Taft parameters, $\pi^*$, $\alpha$ and $\beta$,

$$\nu_i(\text{ROH}) = \nu_i^0 + p_i \pi^* + b_i \beta + a_i \alpha .$$  \hspace{1cm} (3)

$\pi^*$ measures the solvent polarity/polarizability effect (e.g., via dipole-dipole interactions) whereas $\alpha$ measures the solvent HB donating power. It is large for protic solvents, and
close to zero for non-protic solvents [28,29]. From the data in Refs. [13,14] we have $a_0 = 270$ cm$^{-1}$ and $a_1 = 0$ for both 2OH and 5CN2OH. The similarity of $a_0$ for the two compounds could indicate that a HB to the CN group of 5CN2OH is either very weak or of similar strength in both electronic states. Hence it does not contribute to the observed shifts.

The $a_1$ values may then be attributed predominantly to the R.O$\cdots$HS bond with different protic solvents, SH. The positive value of $a_0$ indicates that this HB is stronger in the ground state, and hence produces a blue shift in the excitation spectra. This again follows from the larger electron density on the oxygen in $S_0$, which partly shifts to the aromatic ring upon excitation to $S_1$. Thus the sign of the solvatochromic parameter is opposite when the probe molecule accepts ($a_i$) or donates ($b_i$) a HB.

The magnitude of the solvatochromic parameter indicates, again, the extent of nuclear solvent rearrangement occurring in response to the electron density change in the solute. Hence the fact that $a_0$ is small but finite and $a_1$ vanishes suggests that this bond, which exists as a weak HB in $S_0$, is absent in $S_1$. Hence it must cleave immediately after photodissociation.

A similar effect has been inferred from recent time-resolved IR measurements [30] of the CO stretch of coumarin 102 in CHCl$_3$. This band shows a strong blue shift on a sub-200 fs time scale, which indicates that the CO$\cdots$HCCl$_3$ bond breaks upon excitation. Hopefully, similar measurements on photoacids could be performed in the near future.

## 3 DISSOCIATION

Let us now consider the important question of identifying the primary steps in acid dissociation [3]. Specifically, one hopes to identify the "contact ion pair" (CIP) [2], which may be defined as the first intermediate on the dissociation pathway which possesses properties of the anionic base. It will be argued below that a hydronium in the first solvation shell of the anion, RO$^-\cdots$HO$^+$H$_2$, is is not a likely candidate for the CIP. Formation of the CIP must involve a more extended HB rearrangement. Can one establish a probable sequence of HB rearrangements that lead from the excited acid to the CIP? Any proposed structure (for the CIP) and mechanism (for its formation) should at least be consistent with available experimental observations, and these are discussed below.

(a) Anion solvation.

Since the dissociation process inevitably produces the counter anion, let us begin by considering its solvation requirements. Unlike acid solvation discussed above, the only significant HB to the anion is that donated from protic solvents, HS. The RO$^-\cdots$HS bond exhibits similar characteristics to the analogous bond with the acid, but it is considerably stronger due to the much larger negative charge on the oxygen. This is demonstrated in Fig. 3, which shows the solvatochromic shifts of 2-naphtholate, excited directly under
Fig. 3. Solvatochromic shifts of 2-naphtholate under basic conditions. Closed and open circles denote peak frequencies of the RO⁻ band in the excitation and emission spectra, respectively. The dependence on the solvent hydrogen-bond donation parameter, α, is depicted by the slopes of the two lines: \( a_0 = 3100 \text{ cm}^{-1}, \ a_1 = 1770 \text{ cm}^{-1} \). Data from Ref. [31].

basic conditions [31]. This bond induces a blue shift with increasing α which, again, may be attributed to excited-state electron density migration from the oxide to the aromatic ring. However, the \( a_i \) coefficients for RO⁻ have considerably larger values than for ROH, due to the larger negative charge on the oxide as compared with the OH moiety.

A rather striking observation is that the shifts appear to depend exclusively on the HB donation power of the solvent, as expressed by the Kamlet-Taft α parameter. There is no evidence for the role of solvent polarity (or dielectric properties) on the relative anion solvation. A single specific HB (to the oxide) is responsible for the difference in stabilization between the two electronic states.

Although this HB weakens upon excitation (\( a_1 < a_0 \)), the value of \( a_1, 1770 \text{ cm}^{-1} \), is still substantial. For 5CN2OH a similar behavior is observed [12,14], only that \( a_1 = 940 \text{ cm}^{-1} \). This smaller value is commensurate with the smaller electron density on the oxide induced by the electron-withdrawing CN group.

The large \( a_1 \) values suggest that cleavage of the HB to the oxide must cost a sizeable energetic penalty. As a consequence, the HB to the oxygen, which broke after excitation, must reform immediately after (or, perhaps, simultaneously with) the proton dissociation event.
(b) Contact hydronium is not the CIP.

A conclusion from the above discussion is that $R^\circ\stackrel{\cdots}{\text{O}}\text{H}^+\text{H}_2$ is not the correct structure for the CIP, because it may form with less extensive HB rearrangement than the (relaxed) $R^\circ\text{OH}$ which precedes it along the reaction coordinate. To form this structure, the HB to the oxygen need not break, whereas it does cleave to form the excited acid.

(c) The "slowness" of intermolecular proton transfer.

It is well established that intramolecular proton-transfer between pre-organized donor and acceptor sites may occur extremely fast, on a fs time-scale [32,33]. In comparison, proton transfer to solvent (PTTS) from even the most acidic photoacids (such as 5,8-dicyano-2-naphthol [34] and 5-cyano-1-naphthol [35]) does not seem to occur faster than several ps. Extrapolation to extreme acidity values using structure-reactivity correlations [36–40] suggests a maximal PTTS time constant of about 4 ps [35]. Thus even when the proton transfer itself is barrierless, solvent rearrangement limits the rate of acid dissociation.

(d) Proton mobility and acid dissociation.

Proton hopping between adjacent water molecules takes about 1.5 ps at room temperature [41]. It has been suggested [15] that this elementary step of proton mobility ("Grotthuss mechanism") involves cleavage of one HB (to the water molecule of destination) and formation of another (to the water molecule from which the proton originated). The suggestion that both proton mobility and exothermic proton dissociation are controlled by HB dynamics is corroborated by the (H/D) isotope effects, which are about 1.4 in both cases [35,42]. Thus, if proton migration from $R^\circ\text{OH}$ to water (in the exothermic limit of activationless transfer) takes 3–4 ps, it might involve twice the number of HB cleavage and formation events than proton mobility.

(e) The pentameric ring in concentrated HCl.

It has been suggested [17] that the X-ray [43] and neutron diffraction data [44] from concentrated aqueous HCl can be explained by the prevalence of pentameric rings bridging the anion with a protonated water dimer. If this is indeed a persistent structure in concentrated acids, it might be a transient structure in dilute acids and hence a likely candidate for the CIP, see Fig. 4(b). In comparison to having a $\text{H}_3\text{O}^+$ cation in the second solvation shell of the anion, the suggested CIP exhibits a favorable "through space" interaction between the proton and anion, whereas the hydronium alternative will have this interaction screened by intervening water molecules.

The conclusion from the above discussion is that the mechanism of ROH dissociation in water may involve the HB rearrangements shown in Fig. 4: The two HBs to oxygens 2 and 3 break (panel a), allowing them to take part in a protonated dimer stabilizing the
Fig. 4. Suggested mechanism for photoacid dissociation: (a) The sequence of hydrogen-bond rearrangements and (b) the structure of the (possible) contact ion-pair.

dissociated proton within the proposed pentameric structure. At the same time, two bonds reform: To oxygen 1 and between oxygen 4 and the ROH. The total of two HB cleavage and two HB formation events is precisely twice the number postulated for proton mobility [15], and this may account for the observation that PTTS rates in water never exceed about half the proton hopping rate between two water molecules. While this mechanism is merely a postulate, it might present a useful starting point for future simulations of acid dissociation.

References


