

Direct measurement of intrinsic proton transfer rates in diffusion-controlled reactions

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Abstract

Acid–base reactions are usually treated as diffusion-controlled. In this study we directly measure the intrinsic proton transfer rates at the reaction contact of several naphthols photoacids–carboxylic base pairs. Deviations from the diffusion-controlled limit result from the finite intrinsic proton transfer rates at contact and these rates correlate well with the total free-energy change following the reactions. The correction was made over 8 ΔpK_a units and yielded $k_r^0 = 3 \times 10^{11} \text{ s}^{-1}$ and $G_a^0 = 2.9 \text{ kcal/mol}$ for the activationless proton transfer rate and the intrinsic free-energy barrier, respectively. A similar behavior is found when the proton dissociation rates of all previously studied naphthol-like photoacids are included in the correlation. The combined correlation, over 11 ΔpK_a units, yielded $k_r^0 = 2 \times 10^{11} \text{ s}^{-1}$ and $G_a^0 = 2.5 \text{ kcal/mol}$. © 1997 Elsevier Science B.V.

1. Introduction

The rate of neutralization of acids by strong bases has always been considered to be an ultra-fast essentially instantaneous event [1]. The work of Förster [2,3], Eigen [4], Weller [5] and many others [6–9] established that these reactions proceed with diffusion-controlled efficiency. In other words, the reaction rate in solution is limited by the relatively slow mutual diffusion of the reactants. Such a process can be broken down into two fundamental aspects: the rate of mutual diffusion and the intrinsic reaction rate at contact (or more generally, the reaction dynamics which will depend on separation, orientation, etc.). In recent years attention has focused on this second aspect for fluorescence quenching reactions

which are likely to proceed via electron transfer [10,11], but little effort seems to have been made to obtain proton transfer rates in this important class of proton transfer reactions. Indeed, the experimental evidence that so many of these reactions proceed near the diffusion-controlled limit [5,6] seems to have led to the diffusion-controlled rate being used as the measure for the actual proton transfer rate.

In reality, the diffusion-controlled limit only provides a rough estimate of the actual proton transfer rates and may only give a clue to the lower limit of these rates. Consequently, the first step towards analyzing diffusion-controlled bimolecular proton transfer reactions is to establish a way of distinguishing between the diffusion part and the intrinsic chemical part of these reactions.

A good example of a previously studied reaction is that between 2-naphthol and the acetate anion. When excited, 2-naphthol becomes a moderately

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strong acid with a pK_a comparable to that of chloroacetic acid. The proton transfer to the strong acetate base is an exothermic event. This reaction was investigated by Weller [5], Laws and Brandt [7] and others [8,12]. The observed bimolecular proton transfer rate was found to be $2.9 \pm 0.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ which at 1 M base corresponds to a reaction lifetime of about 350 ps. The above reaction was usually treated as diffusion-controlled with a steric factor of 0.25 [13].

However, placing an upper limit of 350 ps on the intrinsic lifetime of the naphthol–acetate reaction at contact masks the underlying proton dynamics on time scales below this value which, in some cases of intramolecular proton transfer reactions, may be as fast as 40 fs [14].

2. Experimental

We have measured the direct proton transfer rate between a series of acid–base pairs. The photoacids were 2-naphthol and 1-naphthol, (Fluka, >99%), 8-hydroxypyrene 1,3,6-trisulfonate (HPTS; Laser grade, Kodak or Fluka >95%), 1-hydroxypyrene (Aldrich, >98%) and 5-cyano 1-naphthol (generously provided by Professor L.M. Tolbert, see Ref. [15] for details of synthesis). A full account of the photo activity of 5-cyano 1-naphthol will be published elsewhere [16]. The naphthols were twice recrystallized from 20% ethanol solutions and the HPTS, 1-hydroxypyrene and 5-cyano 1-naphthol were used as received. The bases were sodium and potassium carboxylic acid salts (Fluka, MicroSelect). The salt concentration was typically 1 and 8 M, and the solution pH was kept below the ground state pK_a of the photoacid by adding acetic or formic acid. The photoacids were excited either by 12 ps dye laser pulses or by 1 ps frequency-doubled Ti:sapphire laser pulses. Excitation wavelengths were: 295–306 nm for the 1- and 2-naphthols, 353–390 nm for HPTS and 1-hydroxypyrene and 348 nm for 5-cyano 1-naphthol. The excited-state proton transfer reaction was monitored by following the photoacid time-resolved fluorescence decay, or alternatively, by following the fluorescence rise of the generated anionic photoacid species. The time-resolved measurements were made using single-photon counting techniques. The time resolution of these experiments was typi-

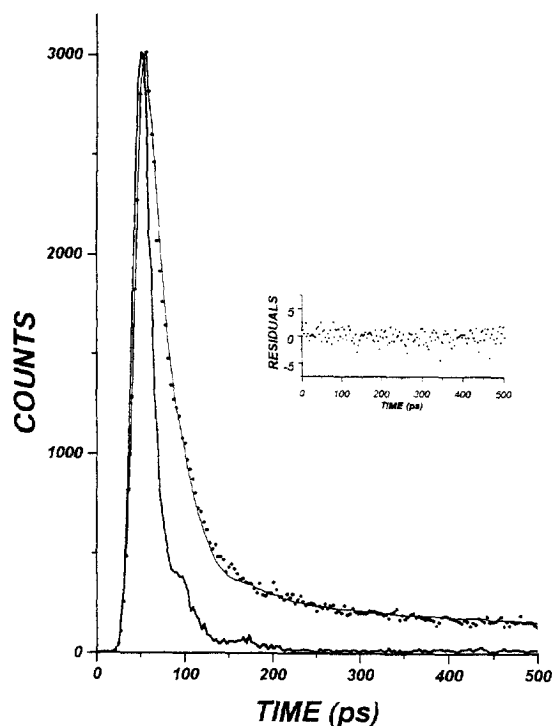


Fig. 1. The fluorescence decay of HPTS taken at 442 nm in the presence of 8 M potassium acetate. $\tau_f = 14 \pm 1$ ps. The data are fitted by 2 decaying exponents $a_1 = 98\%$, $\tau_1 = 14$ ps, $a_2 = 2\%$, $\tau_2 = 300$ ps, $\chi^2 = 1.37$. The instrument function shown is 23 ps FWHM.

cally between 5 and 2 ps. The best resolution was achieved with the Ti:sapphire based single-photon counting apparatus where the instrument function at FWHM was about 17 ps and the FWTM was about 60 ps. All measurements were carried out at $T = 22 \pm 1^\circ\text{C}$.

Fig. 1 shows the fluorescence intensity of HPTS in 8 M sodium acetate excited at 353 nm. Emission was monitored at 442 nm which is the peak emission wavelength of the acidic (ROH) form of HPTS. The kinetics are fitted by the dominant (98%) mono-exponential components of about 14 ps. The weighted residuals calculated from a fit of the data are also shown. These data are typical for all the experiments reported in this study.

3. Results

Table 1 summarizes our findings of proton transfer experiments at 8 M of salt concentration. The

Table 1
Rate of proton transfer at an 8 and 1 M base concentration

Reactive pair	ΔpK_a	Rate at 8 M (s^{-1})	8 M		1 M ^a	
			lifetime (ps)	viscosity ^b (cp)	lifetime (ps)	viscosity ^b (cp)
5-cyano-1-naphthol-acetate	-7.5	$(1.3 \pm 0.3) \times 10^{11}$	8 ± 2	9.4	—	—
1-naphthol-acetate	-5.1	$(8 \pm 1) \times 10^{10}$	12 ± 1	9.4	100 ± 20	1.15
HPTS-acetate	-4.7	$(7 \pm 1) \times 10^{10}$	14 ± 2	9.4	110 ± 10	1.15
1-naphthol-formate	-4.1	$(4 \pm 1) \times 10^{10}$	25 ± 5	4.2	—	1.01
HPTS-formate	-3.7	$(6 \pm 1) \times 10^{10}$	16 ± 2	4.2	100 ± 20	1.01
2-naphthol-acetate	-1.9	$(2.5 \pm 1) \times 10^{10}$	40 ± 10	9.4	360 ± 20	1.15
1-hydroxypyrene-acetate	-0.6	$(2 \pm 1) \times 10^9$	500 ± 100	9.4	1300 ± 100	1.15
1-hydroxypyrene-formate	0.4	$(1.6 \pm 0.4) \times 10^9$	600 ± 100	4.2	2600 ± 200	1.01

^aThe proton transfer rate to the solvent was subtracted from the measured lifetime.

^bInterpolated from Ref. [18] to 23°C.

Table 2
Comparison between the proton transfer rate of 1- and 2-naphthol to 1 M of acetate in various solvent environments

	100% water	35% (w) Methanol	90% (w) Methanol	2.6 M MgCl ₂
1-naphthol	$1 \times 10^{10} M^{-1} s^{-1}$ (estimated)	$6 \times 10^9 M^{-1} s^{-1}$	$2.710 \times 10^9 M^{-1} s^{-1}$	$7 \times 10^9 M^{-1} s^{-1}$
2-naphthol	$2.7 \times 10^9 M^{-1} s^{-1}$	$1.8 \times 10^9 M^{-1} s^{-1}$	$1 \times 10^9 M^{-1} s^{-1}$	$2.1 \times 10^9 M^{-1} s^{-1}$
1/2 ratio	3.7	3.3	2.7	3.3

direct proton transfer rate found for the 5-cyano-1-naphthol-potassium acetate ($5 ps^{-1}$) is among the fastest bimolecular proton transfer reactions measured to date.

Table 2 summarizes the bimolecular proton transfer rate between the 1- and 2-naphthol and 0.5 or 1 M solution of acetate anion. At these concentrations, the bimolecular proton transfer reaction may still be controlled by diffusion (if the activation is fast enough). Since the diffusion coefficient of the two isomers is practically identical their diffusion-controlled reaction rate should be similar. The reaction was carried out in several environments where the ultrafast proton dissociation of 1-naphthol was sup-

pressed so that the difference between the intrinsic reactivities of 1- and 2-naphthol towards the acetate anion became apparent.

Table 3 summarizes the ground state pK_a of the acids in pure water and in aqueous solution containing 8 M potassium acetate. Although the four pK_a values at 8 M acetate differ considerably from those in pure water the difference is almost identical.

4. Discussion

4.1. General consideration of the method

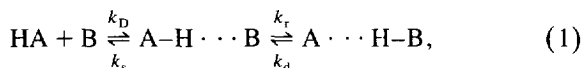
In this Letter, we report on an attempt to measure the direct intrinsic proton transfer rate in a series of acid–base reactions. First, we describe how the limitation imposed by diffusion may be circumvented in concentrated solutions. Next we show that the rates we measure are indeed the intrinsic proton transfer rates. Finally, we show the utility of our measurements to the more usual ‘low’ concentration solution chemistry. This we consider is a first step towards understanding the microscopic aspects of bimolecular proton transfer reactions.

Table 3
Salt effect on the ground pK_a of acetic acid and various photoacids

Acid	pK_a	pK_a (8 M)	pK_a (8 M) – pK_a
acetic acid	4.75	7.2	2.45
2-naphthol	9.5	12.1	2.6
1-naphthol	9.22	11.25	2.03
HPTS	6.6 ^a	9.13	2.53

^aAssuming total screening of three out of the four charges for comparison with the mono-electrolytes.

We start by considering a general two-stage bimolecular proton transfer reaction scheme



where A and B are the acid and base, respectively, and charges are omitted for generality. k_D and k_s are the diffusion-controlled reaction rates for the encounter and separation of the reaction complex and k_r and k_d are the rate constants for the intrinsic proton transfer reactions.

The overall 'on' (recombination) and 'off' (dissociation) steady-state rate constants are given by [4]

$$k_{\text{on}} = \frac{k_D k_r}{k_s + k_r}, \quad k_{\text{off}} = \frac{k_d k_s}{k_s + k_r}. \quad (2)$$

For a reaction to be near the diffusion-controlled limit $k_r \gg k_s$, i.e. diffusion is slow in comparison to the chemical transformation rate and so becomes the rate determining step,

$$k_{\text{on}} \cong k_D \quad (k_r \gg k_s). \quad (3)$$

For uncharged reactants the steady-state value of k_s is given by [17]:

$$k_s = 3D/a^2, \quad (4)$$

where D is the mutual diffusion coefficient and a is the reaction radius.

The diffusion-controlled limit is thus approached according to Eqs. (2)–(4) when $k_r \gg 3D/a^2$. The non-stationary diffusion-controlled rate constant $k_D(t)$, which is larger than its steady-state value, is given by [18]

$$k_D(t) = k_D(\infty) \left(1 + \frac{a}{(\pi Dt)^{1/2}} \right) (\text{M}^{-1} \text{s}^{-1}). \quad (5)$$

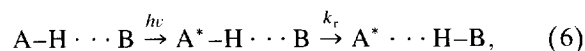
Here $k_D(\infty) = 4\pi N' D a$ is the steady-state time-independent diffusion-controlled rate constant. N' is the Avogadro number per cm^3 . For a typical acid–base reaction $a \cong 5 \text{ \AA}$, $D = 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $k_D(\infty) = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ so $k_D(t)$ is given by

$$k_D(t) = 7.5 \times 10^9 (1 + 6.3 \times 10^{-6} t^{-1/2}) (\text{M}^{-1} \text{s}^{-1}). \quad (5a)$$

Substituting for $t = 10^{-10} \text{ s}$ one obtains a rate constant after 100 ps roughly 60% larger than its steady-state value, assuming instantaneous creation

of the reacting population at time zero and an infinite recombination rate at contact ($k_r \rightarrow \infty$). In reality, the initial deviation from the steady-state rate value is much smaller than that implied by Eq. (5) due to the finite value of k_r which diminishes the effect of the sudden initiation of the reaction. Inspection of Table 4 shows that bimolecular rates at 1 M in the most exothermic region ($k_r^{-1} \leq 20 \text{ ps}$) do appear to be larger than their steady-state values. However, the time dependence of these reactions is partly masked by the parallel proton transfer reaction to the solvent (H_2O) which is still dominant in a 1 M salt concentration. This may be seen from Fig. 2 where 99.9% of the total decay amplitude is reasonably described by a single time-independent lifetime. In slower reactions when $k_r^{-1} \geq 50 \text{ ps}$ we expect the non-stationary contribution to become insignificant altogether.

We conclude that at a 1 M concentration the diffusion-controlled reaction rate may be treated as time-independent. A more refined treatment which explores the time dependence of the proton transfer rate in 1 M base solutions is now being conducted and will be reported in a following publication. At an 8 M salt concentration the average separation between the reactants is only 3.6 \AA so we assume that the reaction is initiated by the laser excitation when the reactants are already complexed in the ground-state, i.e. reaction scheme 6:



where $\text{A}^* \text{-H}$ is the excited photoacid. In this event we expect the proton transfer rate to equal the activation rate k_r . This assumption depends on all the A-H being complexed in the ground state. We checked this assumption for the 2-naphthol-acetate reaction by varying the salt concentration between 4 and 10 M. Typically, k_r was found to be almost independent of the concentration. Near the saturation limit of the salt the physical properties of the solution change rapidly as a function of the salt concentration so we expect the individual $\text{p}K_a$ values of the photoacid and the base to change significantly in this limit. For that reason the 8 M concentration was chosen as a compromise between the need to reach a 'static' reaction limit (i.e. a reaction which does not involve a preliminary diffusive step) and the neces-

Table 4

Comparison between the observed diffusion-controlled proton transfer rate constant and the calculated one assuming intrinsic rates measured at 8 M of base

Reactive pair	$k_D^0 = 4\pi N'Da^a$ ($M^{-1} s^{-1}$)	k_D (observed) ^c ($M^{-1} s^{-1}$)	$k_D = k_D^0 k_r / (k_s - k_r)^b$ ($M^{-1} s^{-1}$)
1-naph-acetate	6.7×10^9	$(10 \pm 2) \times 10^9$	$(6 \pm 1) \times 10^9$
HPTS-acetate	7.0×10^9	$(10 \pm 1) \times 10^9$	$(6 \pm 1) \times 10^9$
HPTS-formate	9.9×10^9	$(10 \pm 1) \times 10^9$	$(8 \pm 1) \times 10^9$
2-naph-acetate	6.7×10^9	$(2.8 \pm 0.1) \times 10^9$	$(3.5 \pm 0.2) \times 10^9$
1-hydroxypyrene-acetate	7.0×10^9	$(7.7 \pm 0.5) \times 10^8$	$(7.4 \pm 0.5) \times 10^8$
1-hydroxypyrene-formate	9.3×10^9	$(3.8 \pm 0.2) \times 10^8$	$(5.6 \pm 0.5) \times 10^8$

^a N' = Avogadro number per cm^3 , D = mutual diffusion coefficient, a = reaction radius.

^b k_r is the rate found at 8 M of salt and $k_s = 3D/a^2$ is the diffusion-controlled separation rate.

^cThe observed rates at 1 M salt concentration after subtraction of the proton transfer rates to the solvents.

sity to avoid salt saturation effects. Keeping this in mind no attempt was made to correlate these small changes in k_r with a kinetic model which takes into account the concentration dependence of k_r . Inspec-

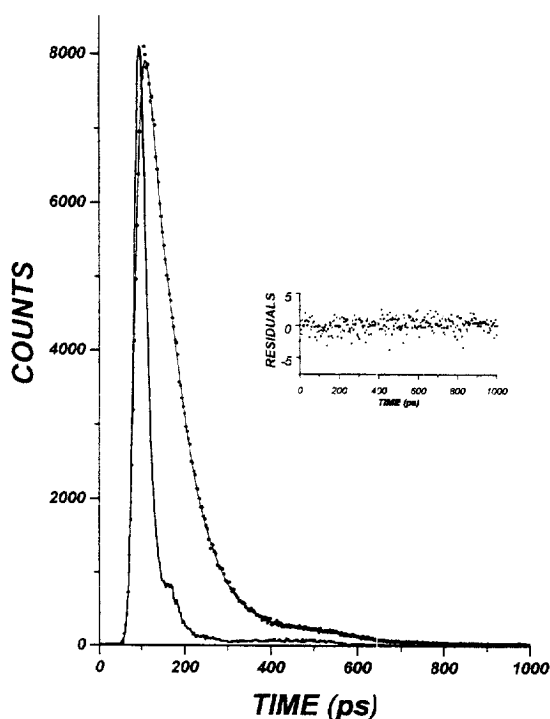


Fig. 2. The fluorescence decay of HPTS taken at 442 nm in the presence of 1 M potassium formate. The decay are fitted by 2 decaying exponents $a_1 = 99.9\%$, $\tau_1 = 50$ ps, $a_2 = 0.1\%$, $\tau_2 = 4.6$ ns. The long exponent is due to the overlap with the anion fluorescence. $\chi^2 = 1.17$ and the instrument function is 23 ps FWHM.

tion of Table 4 shows good agreement between the observed bimolecular proton transfer rates and the predicted ones assuming a two-stage reaction scheme with steady-state rate constants and substituting the proton transfer rate measured at 8 M for the intrinsic proton transfer rate k_r . In particular, the data at 8 M correctly predict more than an order of magnitude drop in the overall bimolecular proton transfer rate between 1-hydroxypyrene and the acetate and formate ions as compared with the diffusion-controlled limit. In the case of 1-hydroxypyrene and 2-naphthol, the reaction rate in 1 M salt solutions directly measure the proton transfer rate to the base and is accurate to better than 10%. However, for 1-naphthol and HPTS the proton dissociation to the solvent is still extremely rapid in 1 M salt solutions. In these cases the magnitude of the parallel proton transfer reaction to the solvent was first estimated from measurements in 1 M of strong supporting electrolytes and then subtracted from the observed dissociation rate.

The outcome of the simple kinetic analysis shown in Tables 1–4 also correctly predicts a 3:1 ratio between the low concentration reactivities of 1- and 2-naphthol. This difference in the proton transfer rate is directly observed in environments where the direct proton transfer to the base constitutes the major contribution to the total proton dissociation rate (Table 2).

The variation in the absolute value of the proton transfer rate measured at 8 M of acetate or formate (Table 1) is roughly 100 to 1 on moving from 5-cyano-1-naphthol to 1-hydroxypyrene and is much larger than any diffusion related parameter. Put to-

gether, the data of Tables 1–4 strongly suggest that the 8 M experiments do provide a method for the direct estimation of the intrinsic reactivity of bimolecular acid–base pairs and that this information is applicable in conventional low concentration reactions. We therefore have a direct way for obtaining the underlying kinetics of the proton in near diffusion-controlled reactions. In comparison with the approximate nature of previous kinetic analyses [4–6,12,19] our method allows for a direct estimation of the reaction parameters involved in the proton transfer process.

The following reaction radius values were found to best fit the kinetic data: $a_{(\text{naphthol})} = 5 \text{ \AA}$, $a_{(\text{HPTS})} = 6 \text{ \AA}$ and $a_{(\text{1-hydroxypyrene})} = 5.5 \text{ \AA}$. These values are considerably smaller than those used by Weller [13], $a = 7.5 \text{ \AA}$ for the 2-naphthol system. They are in accord with the more recent values found in the analyses of the geminate recombination reaction following the dissociation of HPTS [17] and 1-naphthol [20]. The value for the naphthols is also in close agreement with the one used in Ref. [12], i.e. $a = 5.5 \text{ \AA}$.

The mutual diffusion coefficient D was taken from the published data of Weller [13] and Lawrence et al. [12]. It was corrected assuming an η^{-1} dependence in the viscosity of the solution which was taken from Ref. [21].

4.2. Dependence of intrinsic proton transfer rate, k_r , on pK_a (acid)– pK_a (base)

We have correlated the data Table 1 according to the procedure published by Agmon and Levine [22,23]. This procedure was already utilized by Pines and Fleming [19] to correlate the dissociation rates of some photoacids with their pK_a values in water. The basic assumption in such a correlation is that within a family of similar reactions the intrinsic free-energy barrier for the reaction is modified by the total free-energy change following the reaction. In our case we have

$$\Delta G = \ln(10) (pK_{(\text{acid})} - pK_{(\text{base})}) RT \quad (7)$$

for the total free-energy change.

The free-energy barrier for the reaction G_a , is then assumed to depend on some intrinsic barrier G_a^0 and

on ΔG so the measured rates may be correlated according to an Arrhenius plot:

$$k_r = k_r^0 \exp[-G_a/RT], \quad (8)$$

where

$$G_a = \Delta G - G_a^0 \ln(n^\#) / \ln 2, \quad (9)$$

and $n^\#$ is the location of the reaction barrier along the proton coordinate, $n^\# = 0$ (reactant-like) for the endothermic limit and $n^\# = 1$ (product-like) for the exothermic one. $n^\#$ is given by

$$n^\# = \left[1 + \exp\left(\frac{-\Delta G \ln 2}{G_a^0}\right) \right]^{-1}. \quad (10)$$

Fig. 3 shows the correlation found for the proton transfer rates at 8 M of proton acceptor. The best-fit analysis yielded $k_r^0 = 3 \times 10^{11} \text{ s}^{-1}$ and $G_a^0 = 2.9 \text{ kcal/mol}$ for the activationless rate limit and the free-energy barrier for a symmetric ($\Delta pK_a = 0$) pro-

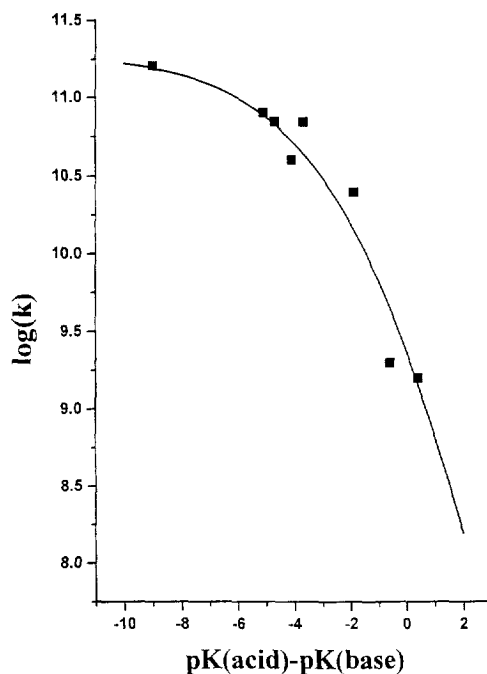


Fig. 3. The free-energy correlation of the kinetic data in Table 1. The fit is done using the Agmon–Levine correlation [22,23] with $k_r^0 = 3 \times 10^{11} \text{ s}^{-1}$ and $G_a^0 = 2.9 \text{ kcal/mol}$, for the activationless proton transfer rate and the intrinsic free-energy barrier, respectively.

ton transfer, respectively. This places the activationless limit of bimolecular proton transfer reactions somewhere between the Debye relaxation time ($\tau_D \approx 7$ ps at 25°C) and the longitudinal relaxation time $\tau_L = (\epsilon_\infty/\epsilon_0)\tau_D \approx (2 \pm 1)$ ps, found in dielectric relaxation experiments of concentrated electrolyte solutions [24] where ϵ_∞ and ϵ_0 are the dielectric constants of the solvent at ‘infinite’ and zero microwave frequencies, respectively. This limiting rate is considerably slower than some activationless intra-molecular proton transfer reactions [14], as well as slower than the major part of the solvation response of water which exceeds 100 fs in pure water [25].

4.3. Solvent-mediated proton transfer

Fig. 4 shows that to a good approximation the dissociation reaction of photoacids belongs to the same family of reactions as the direct 8 M acid–base reactions. The combined general proton transfer correlation yielded kinetic parameters which characterized the solvent coordinate rather than the proton reaction coordinate in aqueous solutions. We thus find a frequency factor of 3–5 ps⁻¹ which compares well with the expected time scale for the slow component of water reorientation time $\tau_L < \tau_r < \tau_D$, while the activation energy of ≈ 2.5 kcal/mol fits well with this model as it matches the activation energy of water dielectric relaxation at THz frequencies [26] as well as the activation energy of the proton conductivity in aqueous solutions [27]. The Arrhenius plot that we get may be written in the form

$$k_r = W_s \exp(-\Delta G^\ddagger/k_B T), \quad (11)$$

where W_s is a reaction prefactor which is determined by the solvent frequency in the reactant state, and ΔG^\ddagger is the activation free-energy along the proton coordinate which is mainly due to solvent relaxation modes along the proton transfer coordinate between the donor and acceptor potential wells. Such a form of solvent-mediated proton transfer was predicted by Ando et al. for the adiabatic limit of acid–base reactions [28]. Independently, Robinson suggested

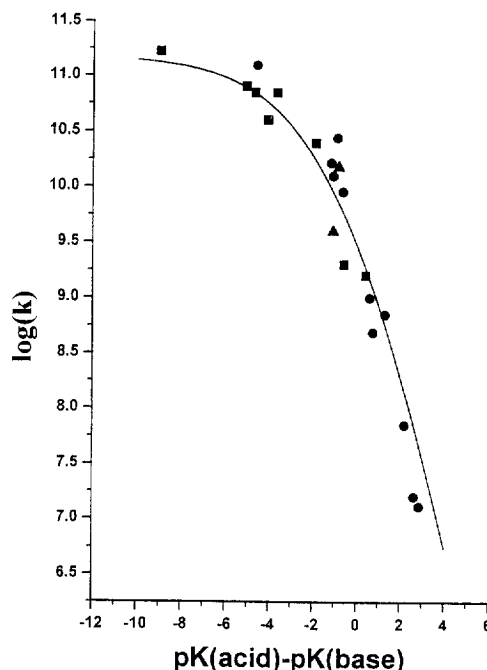


Fig. 4. The free-energy correlation of the proton dissociation rates of various photoacids (Ref. [19], ●) combined with the data of Table 1 (■). The Agmon–Levine correlation [22,23] yielded $k_r^0 = 2 \times 10^{11}$ s⁻¹ and $G_a^0 = 2.5$ kcal/mol. The figure also includes two data points of proton geminate recombination rates (▲) taken from Ref. [17] (HPTS) and [20] (1-naphthol).

that moderately strong photoacids dissociate with an Arrhenius behavior given by

$$k_d = \tau_d \exp(-\Delta G_s/k_B T), \quad (12)$$

where τ_d is the collective dipole correlation time $\tau_d \cong \tau_D$ and ΔG_s is the activation free energy of the dissociation which is mainly determined by the change in the solvent entropy following the proton solvation by water [29]. Our present work seems to confirm the general form of Eq. (12), but the explicit identification of the frequency factor with τ_d and the activation free energy with entropy changes are not supported by our findings.

5. Conclusions

We have shown that the direct proton transfer rates in nearly diffusion-limited reactions may be

directly measured in concentrated base solutions. We have further shown that these rates are also applicable for dilute base solutions.

The rate constants found at 8 M salt concentration were compared with the rate constants found at 1 M of the corresponding salt solutions. We have found that the 8 M data provided a good estimate for the intrinsic proton transfer rates within the various reaction complexes.

This important finding was checked by several self-consistent methods. We have found that by using the 8 M data one could predict the magnitude of the bimolecular diffusion-controlled rate constants found at low concentration of the salt.

A second self-consistent method was to correlate the intrinsic rate constants and the driving force of the proton transfer reaction (i.e. the pK_a difference between the proton donor and the proton acceptor).

A third method was to compare the bimolecular transfer rate of two photoacid isomers, the 1- and 2-naphthols, in several solution environments where proton transfer to the solvent (H_2O) is depressed (i.e. water–methanol mixtures and concentrated supporting electrolyte solutions). In all cases investigated the 1-naphthol molecule was roughly 3 times more reactive than the 2-isomers, as predicted from the intrinsic rates found at 8 M concentration. These observations show that the increased reactivity of 1-naphthol over 2-naphthol molecule is the result of their diverse intrinsic reactivity.

An important outcome of our approach is that we show that deviations from the diffusion-controlled rate limit in such proton transfer reactions are due to finite recombination rates on contact and not the result of 'steric factors' [5], which are the result of simple geometric constraints.

This conclusion is best realized in the case of 1- and 2-naphthols. Here the two isomers have the similar geometric structures, but their reactivities differ by about a factor of 3.

Finally, we have been able to show that although the intrinsic proton transfer process in aqueous solutions is likely to proceed along the proton coordinate, the actual process is mediated by the solvent, so the frequency factor of the reaction and the intrinsic free-energy barrier are determined by the solvent.

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