

# Relaxation to equilibrium following photoacid dissociation in mineral acids and buffer solutions

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## Abstract

The relaxation to the dissociation equilibrium of a weak acid undergoing a transient  $pK_a$  change in the presence of a strong mineral acid has been the subject of considerable interest both experimentally and theoretically. Here we compare this process with the analogue event taking place in a buffer solution of a weak carboxylic acid. The comparison has been performed in identical pH and ionic strength conditions and at a sufficiently short timescale where the buffer can only affect the weak acid relaxation by proton scavenging. Although the two relaxation processes have been found to differ in their temporal behaviour, they have both resulted in identical equilibrium amplitudes of the photoacid. This observation reassures the well-known chemical wisdom that  $pK_a$  values measured in buffer solutions do not depend on the specific chemical reactivity of the buffer. We analyse the essentially many-body relaxation problem in terms of a re-normalized geminate recombination reaction which persists over longer times than the exponential relaxation to equilibrium of homogeneously distributed populations of the reactants.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Chemical kinetics in solution is governed by both chemical reactivity and diffusion (Eigen 1967). This makes chemical kinetics in solution much more complex than what the conventional rate approach to chemical kinetics implies (Weller 1961, Förster and Völker 1975, Eigen 1967).

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In the past 15 years experiments and theory have vastly expanded on the realization that the overall progress of reactions in solutions is fundamentally non-exponential. This non-exponential temporal behaviour is the result of the non-stationary concentration gradients of the reactants when the reaction proceeds (Zeldovich and Ovchinnikov 1977, Kang and Redner 1984a, 1984b, 1985, Redner and Kang 1984, Voituriiez *et al* 2005, Burlatsky and Oshanin 1991, Burlatskii *et al* 1989, Oshanin 1990, Burlatsky *et al* 1991, Oshanin and Burlatsky 1989, Naumann *et al* 1997, Naumann 1994, 1993, 1991, Pines and Fleming 1994, Agmon *et al* 1988, Pines and Huppert 1986a, 1986b, Huppert *et al* 1990, Pines *et al* 1998a, 2001, Pines and Pines 2001, Huppert *et al* 1992, Solntsev *et al* 2001b, 2001a, Szabo 1991, Agmon and Szabo 1990, Sung *et al* 1997, Yang *et al* 1997, Sung *et al* 1998, Sung and Lee 2000, 1999, Pines and Huppert 1989, Gopich and Szabo 2002, Gopich *et al* 2001, Edelshtein and Agmon 1995, Kim *et al* 1999, Popov and Agmon 2002, 2001a, 2001b, Pines *et al* 1988, 1991, Gopich and Agmon 2000, Agmon and Gopich 2000). A pure exponential decay of the concentration profiles is expected when the chemical reaction occurs without diffusion, in the so-called static limit, and in cases when stationary concentration gradients have been established after the initiation of the reaction. Recently, we have observed the static limit in the bimolecular proton-transfer reaction in hydrogen-bonding complexes of photoacids and carboxylic bases. In this case, the inner sphere of the reaction was partially made of tightly or loosely bound hydrogen-bonded complexes, where the photoacid and carboxylic bases are connected with few or even no water molecules in between, which react first upon photoexcitation (Mohammed *et al* 2005, Rini *et al* 2003). This method of preparing tightly or loosely bound hydrogen-bonded complexes as precursors for proton-transfer has the advantage of directly monitoring the on-contact reaction rates between acid and bases, reactions which proceed along hydrogen-bond links. Modern-day interest in non-stationary kinetics also stems from the realization that the dissociation reaction of any bound state, which dissociates reversibly, making it part of an equilibrating system, is inherently non-exponential (Pines and Huppert 1986a, 1986b, 1989, Pines *et al* 1988, 1991) (see equation (1)):



In a reversible dissociation reaction, one is usually interested in calculating the overall dissociation rate of AB to infinite separation of the products, A and B. This is because the standard thermodynamic state of A and B is infinite dilution, which means mutual separation of the reactants approaching infinite distance. When keeping the same standard state for both the kinetics and the thermodynamics of a reaction, one may use the general relation between the overall  $k_f$  and  $k_r$  reaction rate constants and the equilibrium constant of the reaction:

$$K_{\text{eq}} = \frac{k_f}{k_r}. \quad (2)$$

In general, the conventional rate approach to chemical kinetics deals with averaged reaction probabilities between two or more chemical states and not with the actual dynamics of the reactions, which are generally time-dependent if the reactions are diffusion assisted.

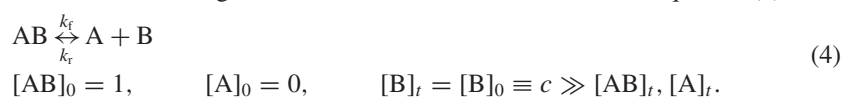
Another way to approach this problem is by realizing that the dissociation reaction of a reactive pair to infinite separation is inherently a multi-stage process (Pines and Huppert 1986a, 1986b, 1989, Pines *et al* 1988, 1991). Upon dissociation, a reactive pair will have, by definition, a non-vanishing probability of recombining upon a diffusional encounter. The fraction of the bound state which thus reforms will re-dissociate and the cycle of dissociation–recombination will continue until the pair ultimately escapes from each other. The standard reactant state following a dissociation reaction is usually defined as the state of the reactants having a vanishing back-recombination probability, and the probability of the reactants to

actually reach this state is defined as ‘the ultimate escape probability’ of the reactants. For an infinite open space without additional traps, this is the state where the reactants have reached infinite separation. It follows that, during a dissociation reaction, the relative probabilities of a reactive system of being either in the bound (product) state or in the separated (reactant) state should, among other factors, depend on the properties of the diffusive space. The asymptotic solution for the time behaviour of the geminate case when the reactive system initially consists of isolated bound pairs was found by several theoretical methods (Tachiya 1980, Pines and Huppert 1986a, 1986b, Agmon *et al* 1988, Pines *et al* 1988, Huppert *et al* 1990) and is given by equation (3) for the spherical symmetric 3d case:

$$P_t^{\text{gem}} = K_{\text{eq}}/(4\pi Dt)^{3/2} \quad (3)$$

where  $D$  is the effective diffusion coefficient separating the reactants away from the bound origin of AB.

A generalization of the geminate dissociation/recombination case is the so-called ‘target problem’, which involves relaxation to chemical equilibrium when one of the products is static and the other is diffusive and in large excess over the static one, as shown in equation (3):



The asymptotic (long-time) relaxation to equilibrium of the bound AB state has been derived analytically in 3d by several theories of various approximate nature and sophistication (Sung and Lee 2000, 1999, Agmon and Szabo 1990, Szabo 1991, Naumann *et al* 1997, Naumann 1994, 1993, 1991, Sung *et al* 1997, Yang *et al* 1997, Sung *et al* 1998, Gopich and Szabo 2002, Gopich *et al* 2001, Gopich and Doktorov 1995, Gopich and Agmon 2000, Agmon and Gopich 2000, Edelshtein and Agmon 1995, Kim *et al* 1999, Popov and Agmon 2002, 2001a, 2001b):

$$P_t^{\text{target}} = K_{\text{eq}}(4\pi Dt)^{-3/2}/(1 + cK_{\text{eq}})^3. \quad (5)$$

The similarity between the geminate case, equation (3), and the target case, equation (5), is apparent, the two equations only differing by their pre-factor. The general adequacy of equation (5) was verified experimentally using high-sensitivity single-photon counting measurements of photoacid dissociation in strong acid solutions of various concentrations (Pines and Pines 2001, Solntsev *et al* 2001a, 2001b).

There is very little reason to doubt that the equations (2) and (5) can be applied as long as one accepts the general validity of the diffusion equation and realizes the various underlying assumptions leading to equations (2)–(5). These assumptions are: an infinitely open diffusive space which is assumed to have spherical symmetry; time-independent diffusion coefficients; total lack of competing reactions; time- and space-independent chemical reactivity; and time-independent interaction potentials which are usually assumed to be Columbic with Debye–Hückel screening.

In this study we consider the target problem as a renormalized geminate-pair problem. In this approach the long-time relaxation to equilibrium in the target problem stems from the power-law decay of the geminate-pair distribution, which persists over longer times than the homogeneous recombination reaction of the reactants until they ultimately reach their equilibrium concentrations. In other words, due to the slow (power-law) decay of the initial geminate-pair distribution, it takes longer for the concentration gradient of A around B to equilibrate than the time it takes for the concentrations of A and B to equilibrate. We will not attempt to prove this suggestion analytically. Instead, we argue that this idea is very useful in predicting the behaviour of complex reactive systems which are easily accessed experimentally but may prove to be exceedingly difficult to analyse analytically using exact many-body approaches.

### 1.1. Theoretical justification for treating the target problem as a relaxation kinetics problem

Below we closely follow the paper of Gopich and Szabo (2002), which contains a general derivation of equation (5) using a relaxation kinetics approach.

The formalism is based on an approximate set of reaction–diffusion equations for the pair distribution functions which incorporate the influence of the chemical reaction by using effective rate constants that are determined self-consistently. The derivation is exact both at short and long times.

Considering reaction equation (4), AB molecules can dissociate with an effective rate constant  $k_f$  to form an unbound A–B contact pair. The particles diffuse with diffusion constants  $D_A$ ,  $D_B$  and  $D_{AB}$ . The equilibrium constant for the reaction is  $K_{\text{eq}} = \frac{k_f}{k_r} = \frac{[AB]_{\text{eq}}}{[A]_{\text{eq}}[B]_{\text{eq}}}$ , where  $[A]_{\text{eq}}$ ,  $[B]_{\text{eq}}$ , and  $[AB]_{\text{eq}}$  are equilibrium concentrations. For the pseudo-first order limit ( $[A]_t$ ,  $[AB]_t \ll [B]_t$ , so that  $[B]_t = [B]_0 = c$ ). Following the rate equation description of ordinary chemical kinetics, one has:

$$\frac{d[A]_t}{dt} = -\frac{d[AB]_t}{dt} = -k_f[A]_t[B]_0 + k_r[AB]_t. \quad (6)$$

Let  $R_t$  be the relaxation function defined as the normalized deviation from equilibrium:

$$R_t \equiv \frac{[A]_t - A_{\text{eq}}}{[A]_0 - A_{\text{eq}}} = \frac{[AB]_t - [AB]_{\text{eq}}}{[AB]_0 - [AB]_{\text{eq}}}. \quad (7)$$

To incorporate the influence of the diffusion on the kinetics, the rate equations should be modified by:

$$\frac{d[A]_t}{dt} = -\frac{d[AB]_t}{dt} = -k_f \rho_{AB}(r, t) + k_r[AB]_t \quad (8)$$

where  $\rho_{AB}(r, t)$  is the distribution function of A–B pairs separated by distance  $r$ . Introducing the deviation of the pair distribution function from its chemical kinetics value,  $p_{AB}(r, t) = \rho_{AB}(r, t) - [A(t)][B]$ , the above equation becomes:

$$\frac{d[A]_t}{dt} = -\frac{d[AB]_t}{dt} = -k_f[A]_t[B] + k_r[AB]_t - k_f p_{AB}(r, t). \quad (9)$$

An A particle from an A–B pair can react with some other B particle to generate an AB–B pair. The latter may disappear due to dissociation of AB, producing an A–B pair. Thus  $p_{AB}(r, t)$  and  $p_{ABB}(r, t)$  satisfy the coupled reaction–diffusion equations:

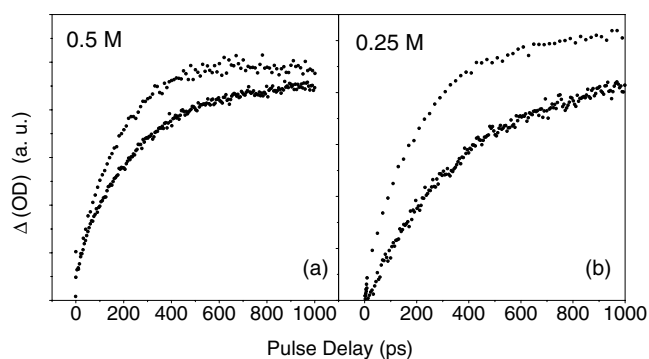
$$\begin{aligned} \frac{\partial}{\partial t} p_{AB}(r, t) &= D_{AB} \nabla^2 p_{AB} - k_f[B] p_{AB} + k_r p_{ABB}, \\ \frac{\partial}{\partial t} p_{ABB}(r, t) &= D_{CB} \nabla^2 p_{ABB} + k_f[B] p_{AB} - k_r p_{ABB}. \end{aligned} \quad (10)$$

The solution of the coupled reaction–diffusion equations at long time was given by Gopich and Szabo as:

$$R_t^{\text{target}} = K_{\text{eq}} (4\pi D t)^{-3/2} / (1 + c K_{\text{eq}})^2 \quad (11)$$

which, using the definition of  $R_t$  given in equation (7), results when solving for  $P^{\text{target}}$  with equation (5).

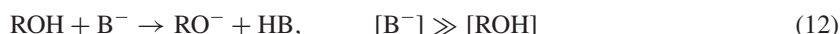
The analysis of Gopich and Szabo has compared very favourably with the simulations in 3d of Popov and Agmon (2001a, 2001b).



**Figure 1.** Comparison between the rise of the HPTS photobase measured by following the absorption change in the  $1503\text{ cm}^{-1}$  band of the HPTS photobase (upper curves) and the rise of acetic acid population as evidenced by the absorption change in the carbonyl stretching band of acetic acid at  $1740\text{ cm}^{-1}$  (lower curves). Data shown for 0.5 M (a) and 0.25 M (b) solutions of acetate base in  $\text{D}_2\text{O}$  after femtosecond laser excitation of the photoacid at 395 nm. Notice the increased time delay between the dissociation and scavenging reactions with the decrease in the acetate base concentration.

### 1.2. Photoacid dissociation in presence of proton bases

Direct proton transfer between a photoacid and a suitable base may be either unidirectional or reversible, depending on the relative  $\text{p}K_{\text{a}}$ -values of the acid–base pair. This reaction is only important at relatively high base concentrations. Recently, the acid–base reaction (equation (12)):



has been studied extensively (Pines *et al* 1997, Genosar *et al* 2000, Cohen *et al* 2001). Pines and Nibbering used time-resolved mid-IR spectroscopy to study this reaction between 8-hydroxy-1,3,6-trisulfonate-pyrene (HPTS) (a photoacid similar in reactivity and structure to 2-naphthol,6,8 disulphonate (2N68S)) and carboxylic bases (Rini *et al* 2003, 2004, Mohammed *et al* 2005). At above 1 M base concentrations, the static part of the reaction consists mainly of proton transfer within hydrogen-bonding complexes of the type  $\text{ROH} \cdots \text{B}$  or  $\text{ROH} \cdots \text{H}_2\text{O} \cdots \text{B}$ . The non-static part of the reaction followed the time dependence predicted by the Collins–Kimball–Szabo (CKS) model (Collins and Kimball 1949, Szabo 1989, Eads *et al* 1990, Shannon and Eads 1995) for irreversible (diffusion assisted) recombination kinetics. The non-static part of the reaction was the dominant part of the reaction below 1 M of base. At lower than 0.5 M base concentrations, direct proton transfer between the acid and base has diminished and the proton transfer reaction mainly consists of the photoacid dissociating to the solvent followed by the proton diffusing until being picked up (scavenged) by the base. Figure 1 shows the dissociation of the photoacid and the ensuing proton scavenging reaction in the presence of 0.5 and 0.25 M of acetate base in  $\text{D}_2\text{O}$ .

Figure 1 shows that, even with moderately high base concentrations, the dissociation of the photoacid is overwhelmingly to the solvent ( $\text{D}_2\text{O}$ ) so there is a considerable time delay between proton dissociation to the solvent and the protonation of the acetate base by picking-up the proton from the solvent (proton scavenging).

We have found the proton pick-up by the base to be well approximated by the time-independent diffusion-limited rate constant of the reaction,  $k_{\text{D}'}$ :

$$k_{\text{D}'} = 4\pi D' a_{\text{eff}} N, \quad (13)$$

where  $D'$  is the relative diffusion coefficient between the base and the solvated proton,  $N$  is Avogadro's number, and the effective reaction radius  $a_{\text{eff}}$  is defined as:

$$a_{\text{eff}}^{-1} = \int_0^{\infty} e^{U(a)/k_{\text{B}}T} r^{-2} dr \quad (14)$$

with  $a$  being the contact separation length between the reactants at their 'closest' approach.

We approximate the electrostatic potential  $U(r)$  by the Debye–Hückel (DH) ionic screening law:

$$U(r)/k_{\text{B}}T = \frac{R_{\text{D}}}{r} \frac{e^{-\kappa_{\text{DH}}(r-a)}}{1 + a\kappa_{\text{DH}}} \quad (15)$$

with,

$$R_{\text{D}} = |z_1 z_2| e^2 / \epsilon k_{\text{B}}T, \quad (16)$$

and,

$$\kappa_{\text{DH}}^2 = 8\pi e^2 I / \epsilon k_{\text{B}}T \quad (17)$$

where  $k_{\text{B}}$  is Boltzmann's constant,  $a$  is the contact radius,  $\epsilon$  is the dielectric permittivity of the solution,  $e$  is the elementary charge,  $\kappa_{\text{DH}}^{-1}$  is the screening length,  $I$  is the ionic strength, which in our case is practically equal to the acetate concentration, and  $z_1 = +1$ ,  $z_2 = -1$  are the charge numbers of the proton and the acetate, respectively.

The following reaction parameters have been used for HPTS in  $\text{D}_2\text{O}$ :  $D' = (5.8 \text{ and } 6.4) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $a = 5.5 \text{ \AA}$ ,  $R_{\text{D}} = -7.1 \text{ \AA}$ , and  $a_{\text{eff}} = (6.5 \text{ and } 6.8) \text{ \AA}$  for acetate concentrations of 0.5 and 0.25 M, respectively. From equation (13),  $k_{\text{D}'}$  is  $(2.9 \text{ and } 3.3) \times 10^{10} \text{ s}^{-1}$  for 0.5 and 0.25 M of acetate, respectively.

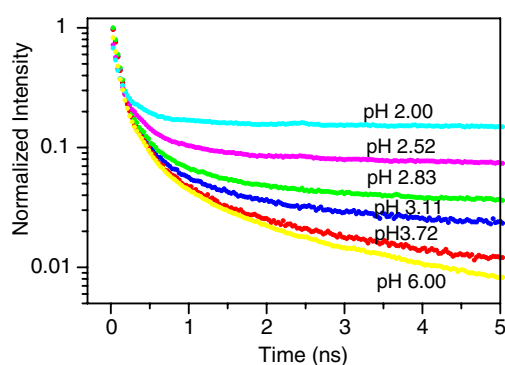
## 2. Experimental details

### 2.1. Solution preparation

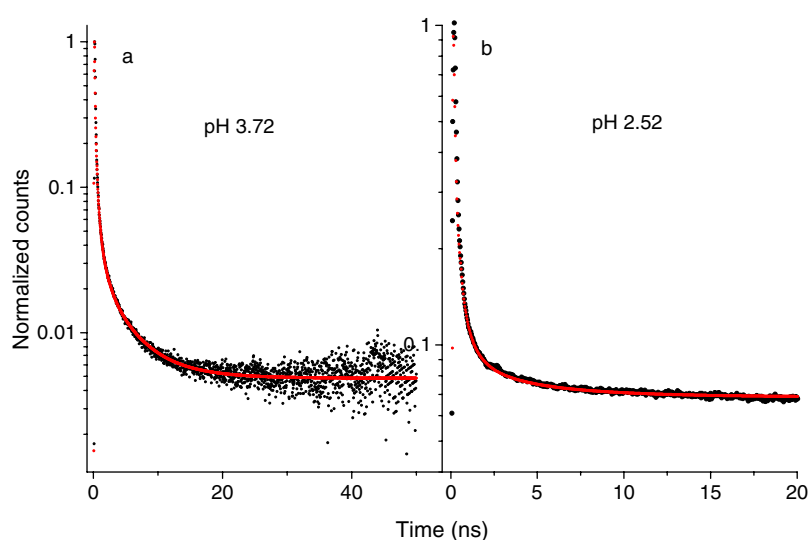
Aqueous solutions of 2-naphthol 6,8 sulfonate (2N68S) acidified by  $\text{HClO}_4$  have been prepared, as has been described before for solutions of HPTS (Pines and Pines 2001). We used 2N68S because of its longer lifetime of the excited state compared to HPTS. Buffer solutions of chloroacetic acid were prepared by adding the pure acid to the aqueous solutions of 2N68S at a neutral pH (6.5–7.5) until the desired pH was reached. Since at low pH practically all the protons have been introduced to the solution by the auto-ionization of the chloroacetic acid, we have assumed the concentration of the chloroacetate base to be equal to that of the proton. Both  $\text{HClO}_4$  and chloroacetic acid solutions were measured at  $\text{pH} = 2.000 \pm 0.003$ . We assume equal activities of the proton in the  $\text{HClO}_4$  and chloroacetic acid solutions at this pH and acid concentrations. The concentrations of the protons have thus been practically identical (10.0 mM) in both the chloroacetic acid buffer and the strong mineral acid solutions, enabling direct comparison between the two solutions.

### 2.2. Experimental setups

Time-resolved IR measurements with 150 fs time resolution were carried out at the Max Born Institute in Berlin, as described previously (Rini *et al* 2003). The single-photon counting measurements were carried out at the Ben-Gurion University of the Negev, Israel, with a set-up similar to that described elsewhere (Pines *et al* 1998a). The time resolution was about 30 ps per channel at the 50 ns scale of the apparatus. Readings at the peak channel were about 300 000, taken at a recording rate of 5 kHz and a laser excitation rate of 0.5 MHz.



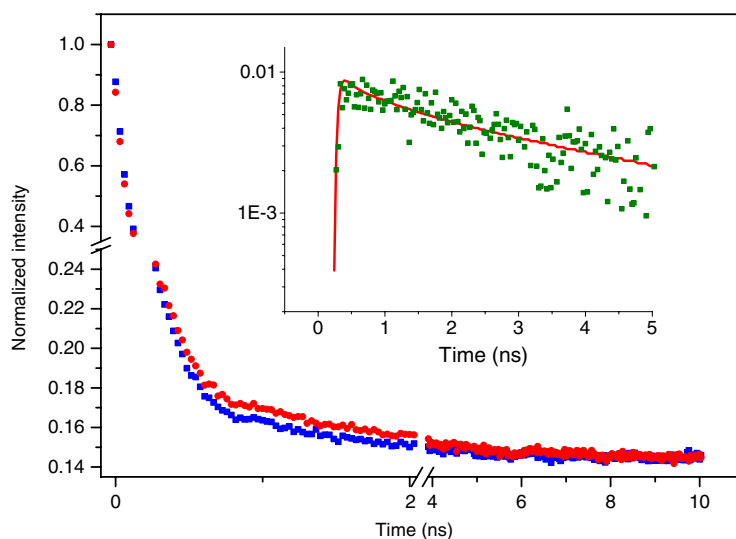
**Figure 2.** Semi-logarithmic plot of normalized fluorescence decay curves of 2N68S in water acidified by  $\text{HClO}_4$ . Data are shown after correcting for the finite fluorescence lifetime of the  $\text{RO}^-$  state by multiplying it by the factor  $\exp(t/\tau)$ ,  $\tau = 12.5$  ns.



**Figure 3.** Semi-logarithmic plot of normalized fluorescence decays of 2N68S in water acidified by  $\text{HClO}_4$  at pH 3.72 (a) and 2.52 (b). Data are shown after lifetime correction (full (black) dots). The solid (red) line is the simulated decay curve of the photoacid with pure geminate back-recombination reaction between the anion of the photoacid and  $\text{H}^+$  using the SSDP software package (Krissinel and Agmon 1996) after the addition of the normalized equilibrium population of the photoacid  $(\text{ROH})_{\text{eq}}$  as measured at very long times ( $t > 40$  ns).

### 3. Results

Figures 2 and 3 show the time evolution of the photoacid population following laser excitation at 353 nm and in the presence of increasing concentrations of  $\text{HClO}_4$ . The measured data was corrected for the excited-state lifetime (decay) of the conjugated photoacid (12.45 ns). At 5 ns full scale, the photoacid dissociation is clearly trimodal. An initial rapid photoacid dissociation independent of pH is followed by a gradual slowing down in the decay of the photoacid population as it approaches the equilibrium population. This phase of the photoacid decay appears to be pH dependent. For higher pH, the onset of the slower dissociation mode appears earlier, ultimately leading to the final stage of the reaction. This stage is a very slow approach



**Figure 4.** Decay and long-time plateau observed in dissociation of 2N68S after lifetime correction. Upper curve (dots): dissociation profile in the presence of  $10^{-2}$  M  $\text{HClO}_4$ . Lower curve (squares): same conditions as in the upper case, however now in the presence of chloroacetic acid buffer created by the self-dissociation of the carboxylic acid,  $\text{pH} = 2.00$ , having  $10^{-2}$  M of chloroacetate anion in addition to  $10^{-2}$  M of protons. Inset: the difference between the two decay curves is shown on expanded scales ((olive) squares). The solid (red) line is the calculated difference curve; see text for details.

(long-time approach) to the equilibrium concentrations of the photoacid, as determined by its  $\text{p}K_a^*$  and the  $\text{pH}$  of the solution.

The final approach to equilibrium is clearly demonstrated in figure 3. Figure 3 shows the measured dissociation curves of 2N68S on a longer timescale for two typical  $\text{pH}$  values:  $\text{pH} = 3.7$  and  $2.5$ . For both cases, the system approaches the equilibrium concentration only after 10 ns, even though the amplitude of the equilibrium concentration is about 15 times larger for the higher  $\text{pH}$ -value. This suggests that the long-time relaxation to equilibrium of the photoacid population in this  $\text{pH}$  range is largely  $\text{pH}$ -independent. Our data thus show both the short-and long-time kinetics of the proton dissociation to be insensitive to  $\text{pH}$ , while for intermediate times the observed kinetics are clearly observed to be  $\text{pH}$ -dependent.

Figure 4 compares between the photoacid dissociation profile in two solutions having practically identical  $\text{pH}$  ( $\text{pH} = 2.00$ ) but having different solution compositions. At intermediate reaction times the apparent proton release from the photoacid in the presence of  $\text{HClO}_4$  is clearly slower than in the presence of chloroacetic acid buffer, although the two decay curves ultimately approach practically identical equilibrium concentrations. The two decay curves become practically indistinguishable after about 10 ns.

The inset in figure 4 shows the difference between the two decay curves of figure 4 on expanded time and intensity scales. The difference in intensity between the two decay curves has a maximum and exhibits the following behaviour as a function of time: zero at time zero (the onset of the dissociation reaction), growing rapidly to a maximum value at about 0.5 ns, and then slowly decaying to zero at very long times when the two reactions relax to apparently an identical equilibrium amplitude. The decay curve of the bound photoacid state in the presence of the chloroacetate buffer lies below the decay curve of the photoacid in the  $\text{HClO}_4$  solution. This apparent faster decay rate of the photoacid in the buffer solution results from the additional



bimolecular scavenging reaction between the chloroacetate anion and the dissociated proton, as discussed below.

#### 4. Discussion

When a geminate pair of reactants is reversibly created in a solution that already contains an excess of one of the reactant members, the ultimate outcome of the reversible dissociation/recombination reaction is the establishment of a chemical equilibrium characterized by the finite equilibrium concentrations of the reactants. This is unlike the situation with isolated reactive pairs interacting reversibly in infinite open space. There, the ultimate fate of the reaction is the complete disappearance of the bound state. Here we argue that the first case, where the dissociation reaction ultimately results in the bound state equilibrating with the reactant state, may be approximated as a geminate-pair problem renormalized to account for the reactive pairs also taking part in the competing homogenous reaction, ultimately leading to the establishment of equilibrium populations. We do not try to generally prove this model, but rather argue that this is a reasonable qualitative as well as quantitative description of our experimental findings.

As was shown by Gopich and Szabo (2002), the decay of the reactive populations to their equilibrium values may be derived in this case using relaxation kinetics. Conventional (rate approach) descriptions of relaxation kinetics obviously fail to describe the real nature of the relaxation kinetics in question, which is not exponential but a power-law over time. Keeping this in mind, we start by writing the process in conventional relaxation-kinetic terms but do not attempt to solve the rate equations, as they obviously lead to unphysical behaviour. We rather use the kinetic model to develop a framework for elucidating the physical origins for the observed power-law relaxation to equilibrium.

For the reaction  $AB \xrightleftharpoons[k_r]{k_f} A + B$  relaxing to equilibrium, one usually writes the conventional relaxation equation:

$$[AB]_{\text{eq}} + x_{AB} \xrightleftharpoons[k_r]{k_f} ([A]_{\text{eq}} + x_A) + ([B]_{\text{eq}} + x_B). \quad (18)$$

In our case,  $x_{AB} = -x_A = -x_B = x_t$  and  $[B]_{\text{eq}} = c \gg [A]_{\text{eq}}, [AB]_{\text{eq}}$ . After cancelling the two opposing equilibrium reactions, one is left with the rate equation for the relaxation kinetics, leading to the equilibrium concentrations:

$$\frac{-dx_t}{dt} = (k_r + k_f c)x_t - k_f x_t^2. \quad (19)$$

The final stage in the development is the linearization of the differential equation (assuming a small  $x$ ) which results in the exponential decay of  $x$  over time:

$$x_t/x_0 = R_t^{\text{target}} = \exp((-k_r + k_f c)t) = \exp((-k_{\text{hom}})t). \quad (20)$$

The procedure assumes time-independent rate constants and homogeneous deviation from equilibrium concentrations. In reality, relaxations that are governed by diffusion are usually time dependent. One can rewrite equation (19) as:

$$\frac{-dx_t}{dt} = k_{\text{hom}}x_t - k_t^{\text{gem}} \quad (21)$$

where both the forward and backward processes are time dependent, so there is no simple analytic solution for the rate equation. In particular,  $k_t^{\text{gem}}$  contains the probability of the recombination of essentially geminate pairs in the presence of a competing homogeneous reaction. It has already been shown for the purely geminate recombination case that, at

relatively long times, the concentration of the bound state is proportional to the probability of the geminate-pair back-recombination reaction and that the time evolution of the bound AB state population follows that of the geminate recombination reaction. We assume a similar situation for the target problem, i.e. a relaxation function at long times which depends on the survival probability of the geminate recombination reaction. In this case, the probability of the geminate recombination reaction depends on the square of the survival probability of the geminate pair (reaction order of 2), as demonstrated by Pines *et al* in the case of the geminate quenching reaction of 1-naphtholate anin by the proton (Pines *et al* 2001). The fraction of the surviving geminate pairs at long times (we defined it as  $\Omega$ , which in this case may be identified with the ultimate survival probability of the geminate pair) when equilibrium concentrations are almost fully established is just equal to  $1 - [\text{AB}]_{\text{eq}} = [\text{A}]_{\text{eq}}$ . Realizing that  $[\text{A}]_{\text{eq}}$  is equal to  $1/(1 + K_{\text{eq}}c)$ , one arrives at equation (22):

$$R_t^{\text{target}} \approx P_t^{\text{gem}} \Omega^2 = P_t^{\text{gem}} (1 - [\text{AB}]_{\text{eq}})^2 = P_t^{\text{gem}} / (1 + K_{\text{eq}}c)^2. \quad (22)$$

The final form of  $P_t^{\text{target}} = R_t^{\text{target}} x_0$  is given by substituting  $x_0$  for its actual value,

$$x_0 = [\text{AB}]_0 - [\text{AB}]_t = [\text{A}]_{\text{eq}} = 1/(1 + K_{\text{eq}}c) \quad (23)$$

thus arriving at a pre-factor which depends on the third power of  $[\text{A}]_{\text{eq}}$  and, by doing so, recovering the analytic result, equation (5):

$$P_t^{\text{target}} = R_t^{\text{target}} x_0 \approx P_t^{\text{gem}} (1 - [\text{AB}]_{\text{eq}})^3 \approx P_t^{\text{gem}} / (1 + K_{\text{eq}}c)^3. \quad (24)$$

Based on the above reasoning, we have concluded that the long-time relaxation to equilibrium of the target problem is just a renormalized geminate recombination problem. Furthermore, the initial time progress of the dissociation reaction should also closely follow that of the geminate pair. We argue that both the early-time and the long-time behaviour of the target problem are largely determined by dynamics resembling that of a geminate pair, while the additional homogeneous reaction with the bulk protons (and the back-dissociation of the thus-formed photoacid) is mainly affecting the intermediate-time decay of the photoacid dissociation reaction. We have thus arrived at the main conclusion of this paper, namely that pair dynamics may reasonably describe the full time evolution of the photoacid dissociation reaction when it is re-normalized for the presence of the equilibrium concentrations of the photoacid/photobase system. To test this hypothesis, we have analysed our experimental data of the dissociation of the photoacid in the presence of an excess of a strong mineral acid by assuming that the full dissociation curve is represented reasonably by the function:

$$[\text{AB}]_t \approx f(t) = P_t^{\text{gem}} (1 - [\text{AB}]_{\text{eq}})^3 + [\text{AB}]_{\text{eq}} = P_t^{\text{gem}} / (1 + K_{\text{eq}}c)^3 + [\text{AB}]_{\text{eq}} \quad (25)$$

where  $[\text{AB}]_t$  is the decay over time of the photoacid population,  $[\text{AB}]_{\text{eq}}$  was taken as the observed equilibrium concentration of the photoacid measured between 40 and 50 ns following the initial dissociation, and  $P_t^{\text{gem}}$  is the numerically calculated dissociation curve of the photoacid in the pure geminate-recombination case using the SSDP software package (Krissinel and Agmon 1996). Clearly,  $f(t)$  represents a trade-off between the exact forms of the reaction at short and long times and will increasingly deviate from the actual decay at intermediate times as  $c$  increases.  $f(t)$  becomes exact when  $c$  and  $[\text{AB}]_{\text{eq}} \rightarrow 0$ .

To test  $f(t)$  against experimentally measured data, we have carried out the experiment at a low  $\text{HClO}_4$  concentration of  $\text{pH} = 3.72$ ; figure 3(a). At such a small homogeneous concentration  $c$ ,  $f(t)$  fits the full decay curve of HPTS extremely well. This implies only a minute change at this pH from a pure geminate-pair dynamics. The accuracy of the fit remains almost as good at  $\text{pH} = 2.5$ ; figure 3(b). Below this pH, the fit of our experimental data using  $f(t)$  starts to deviate noticeably at intermediate times, but remains excellent at long times (not shown).

We have also carried out the experiment with chloroacetic acid instead of perchloric acid. The weak chloroacetic acid ( $pK_a = 2.9$ ) self-dissociates and creates a buffer solution with a pH determined by the concentration of the acid and its dissociation constant. At pH 2.00 the concentrations of both the proton and the chloroacetate base ( $c_{\text{scav}}$ ) are  $10^{-2}$  M and that of the chloroacetic acid is about 70 mM. In these conditions, only the reaction of the chloroacetate base with the proton is important, because all other possible reactions of the photoacid/photobase system with the buffer are at least two orders of magnitude slower: the direct proton transfer between the photoacid and the base is not favoured because of the Coulomb repulsion between the doubly negatively charged photoacid and the negatively charged chloroacetate base (such a reaction would have resulted with a faster initial dissociating rate of the photoacid in buffer solutions than the observed dissociation rate in bulk water, an effect we have not observed even in the presence of 0.25 M of the base; see figure 1 for the analogous reaction of HPTS with acetate base). The reaction between the chloroacetic acid and the photobase is also not favoured, because the chloroacetic acid is a much weaker acid than the photoacid ( $pK_a = 2.9$  compared to  $pK_a$  0.8 of 2N68S).

The scavenging reaction of the proton by the chloroacetate base is diffusion assisted. The scavenging reaction effectively diminishes the concentration of the geminate protons and hence diminishes the probability of the geminate recombination reaction. Similar effects of proton scavenging on the geminate recombination reaction were observed for HPTS (Pines and Huppert 1989, Goldberg *et al* 1992) and 1-naphthol in the presence of acetate base. Pines and Fleming (1994) and Pines *et al* (2001, 1998b) have shown that homogeneous scavenging reactions act to reduce the effective lifetime of the geminate pair in an analogous way to the effect of the photoacid having a shorter lifetime in the excited state. Thus, the pure geminate recombination problem in the presence of homogeneously distributed proton scavengers may be treated as a pair problem, with the geminate pair having a finite lifetime that is dependent on the concentration of the scavenger and the homogeneous reaction rate of the scavenging reaction; see also Redner and Kang (1984).

The situation is more complex when the geminate recombination reaction is carried out in the presence of a low-pH buffer when both the bulk  $H^+$  and the scavenger concentrations are in excess over the initial (bound)  $H^+B$  state. In this case, we are not aware of any analytic solution or a computational simulation of the problem. As seen in figure 4, the photoacid relaxation to equilibrium is faster in the presence of the chloroacetate buffer than in the presence of  $HClO_4$ , both solutions having an identical  $H^+$  concentration. This behaviour is the expected behaviour, because the additional proton scavenging reaction with the buffer offers the relaxing chemical system an additional route for relaxation while ultimately relaxing to an identical equilibrium concentration determined by the solution pH. In the inset of figure 4 we have plotted the difference in the fluorescence intensity between the two dissociation reactions shown in figure 4. To fit the time evolution in the fluorescence intensity difference, each of the reactions were numerically fitted by the SSDP software (Krissinel and Agmon 1996), simulating for two 'pure' geminate recombination reactions, the only difference between the two geminate reactions being the reaction in chloroacetic buffer solution having a shorter (effective) lifetime:

$$P_{\text{buffer}}^{\text{gem}}(t) = P_t^{\text{gem}} \exp(-t/\tau_{\text{scav}}). \quad (26)$$

So the difference in the dissociation kinetics of the photoacid,  $H^+B$ , in the presence of  $HClO_4$   $P_{HClO_4}^{\text{gem}}(t)$  and in the presence of the chloroacetic (buffer)  $P_{\text{buffer}}^{\text{gem}}(t)$  when both solutions are at identical pH may be approximated by:

$$P_{HClO_4}^{\text{gem}}(t) - P_{\text{buffer}}^{\text{gem}}(t) = P_t^{\text{gem}}(1 - \exp(-t/\tau_{\text{scav}})). \quad (27)$$

The difference function (equation (27)) vanishes at  $t = 0$  and at  $t = \infty$ , where  $P^{\text{gem}}$  is zero and has finite positive values everywhere in between the two time limits exhibiting only one maximum point. We have calculated the difference between the two simulated dissociation curves, and convoluted the result with the instrument function. We have plotted the outcome and compared it with the difference in the dissociation curves found experimentally (inset of figure 4). We have found, within our signal-to-noise limitation, a good fit between the measured and simulated difference curves from about 0.3 ns onward after searching for an optimal  $\tau_{\text{scav}}$ . The additional decay route for the geminate-pair  $\tau_{\text{scav}}$  which best fits the experimental data was found to be 1.5 ns, which matches very well with the calculated lifetime of the scavenging reaction of the proton by the chloroacetate base, assuming diffusion limited kinetics; equation (13). Solving equation (13) for the reaction parameters between the proton and chloroacetate, we have:

$$k_{\text{scav}} = k_{\text{D}}c_{\text{scav}} = 6.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \times 10^{-2} \text{ M} = 6.3 \times 10^{-8} \text{ s}^{-1}$$

with  $D' = 10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ,  $R_{\text{D}} = -7.1 \text{ \AA}$  and an effective reaction radius  $a_{\text{eff}} = 8.4 \text{ \AA}$  for reaction between chloroacetate and the proton both present at a concentration of  $10^{-2} \text{ M}$ .

## 5. Summary

We have argued that the long-time behaviour of the so-called target problem in chemical kinetics may be viewed as a renormalized geminate recombination problem. Based on this view, we have analysed the proton dissociation reaction of an excited-state acid in the presence of an excess of a strong mineral acid as essentially undergoing a geminate back-recombination reaction, the amplitude of which is reduced by the competing homogenous reaction. The analysis of the experimental data have resulted in good fits up to a solution pH of about 2.00. Below this pH at higher homogeneous  $\text{H}^+$  concentrations we expect our fitting procedure to deteriorate. We have further explored the idea of the target problem being adequately approximated by a renormalized geminate recombination problem by carrying out the reaction in a buffer solution of a moderately weak acid, chloroacetic acid. We have shown experimentally that identical equilibrium concentrations are reached following the dissociation of the photoacid in solutions already containing either strong or weak acids. We have thus reconfirmed the well-known chemical principle that the equilibrium constant of an acid or a base is independent (apart from ionic strength effects) of the buffer solution used to measure it. We have proceeded to analyse the dissociation reaction of the photoacid in the buffer solution by assuming that it may be treated approximately as a scavenging problem of the isolated geminate pairs formed by the optically induced photoacid dissociation. We have used a numerical solution of the scavenging problem of the isolated geminate pair and, using these procedures, achieved a satisfying fit between calculated and measured reaction curves. This result points to the possibility of reducing an essentially complex many-body problem to a pair problem subject to additional constraints.

Clearly, this approach awaits further confirmation, as well as validation by analytic procedures and exact (many-body) numerical calculations.

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