

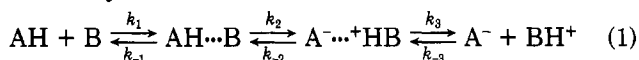
Rates of Reaction in the *p*-Nitrophenol-Triethylamine System in AcetonitrileDavid B. Marshall, Frank Strobusch,¹ and Edward M. Eyring*

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The rate constants of proton transfer between *p*-nitrophenol (AH) and triethylamine (B) in acetonitrile (ionic strength $\mu < 1.3 \times 10^{-4}$ M, 25.0 °C) were measured by the electric field jump relaxation method with spectrophotometric detection. This acid-base system sets up the following equilibria in acetonitrile: $AH + B \rightleftharpoons AH \cdots B \rightleftharpoons A^- \cdots ^+HB \rightleftharpoons A^- + BH^+$ where each of the *p*-nitrophenol species is thermodynamically stable and has a different spectral absorption maximum. The kinetic data are consistent, however, with the single equilibrium $AH + B \rightleftharpoons A^- + BH^+$ (k_f, k_b) regardless of the monitoring wavelength. Values of the rate constants are $k_f = (3.1 \pm 0.5) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = (9.0 \pm 1.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Possible reasons for the observation of this unexpectedly simple behavior are discussed.

Introduction

In a previous paper² we reported the rates of proton transfer between picric acid and the two azo indicators methyl red and dimethylaminoazobenzene in acetonitrile. Rates of ion recombination in these systems were found to be a factor of 10 slower than those expected for diffusion-controlled reactions. We postulated that solvent reorganization around the strongly solvated cation was responsible for the observed reduction in rate. In these systems, the only thermodynamically stable species are the neutral indicators and acid, and the free ions. We have now extended the study of proton transfer in dry acetonitrile at 25.0 °C using the electric field jump relaxation method to a system with neutral species, a neutral hydrogen-bonded encounter complex, an ion pair, and free ions that are all thermodynamically stable. The complete thermodynamic reaction scheme is



where AH denotes *p*-nitrophenol and B denotes triethylamine. Each of the *p*-nitrophenol species has a different absorption maximum and as such can be separately monitored. In addition hydrogen bond association between the anion and the phenol occurs:



The equilibrium constants in acetonitrile have been measured³ and are as follows: $K_1 = 4.6 \pm 0.8 \text{ M}^{-1}$, $K_2 = 0.97 \pm 0.14$, $K_3 = (8.1 \pm 0.5) \times 10^{-5} \text{ M}$, and $K_4 = 3850 \pm 850 \text{ M}^{-1}$.^{4,5} The extinction coefficients in $\text{M}^{-1} \text{ cm}^{-1}$ (with absorption maxima in nanometers subscripted) are as follows: $^3 \text{AH}$, $\epsilon_{306} = 1 \times 10^4$; $AH \cdots B$, $\epsilon_{320} = 1.2 \times 10^4$; $A^- \cdots ^+HB$, $\epsilon_{400} = 2.5 \times 10^4$; and A^- , $\epsilon_{427} = 3 \times 10^4$. The absorption of AHA^- is a superposition of the $AH \cdots B$ and $A^- \cdots ^+HB$ bands.⁶

Acetonitrile is a kinetically interesting solvent because of the simple way in which it solvates. Like other dipolar aprotic solvents, the negative end of the CH_3CN dipole is significantly less diffuse than the positive end. As a result, CH_3CN solvates cations well and anions poorly. However,

unlike dimethyl sulfoxide and dimethylformamide, two other frequently used dipolar aprotic solvents, acetonitrile has only very weakly basic properties, as has been known for a long time from spectroscopic work.⁷ In Taft's β scale of solvent basicities, the weak basicity of acetonitrile is expressed by a value even smaller ($\beta = 0.310$) than the β values of esters, aliphatic ethers, and ketones.^{8,9} Thus acetonitrile solvates not by accepting a hydrogen bond from protic donors but essentially through ion-dipole, dipole-dipole, and dispersion interactions. (These interactions are not adequately represented in Taft's π^* scale of solvent polarities; the $\pi^* = 0.713$ for acetonitrile is smaller than the π^* values of much less dissociating solvents such as chloroform, cyclopentanone, and anisole.^{8,9}) Although the mechanisms of proton transfer are fairly well understood in water¹⁰ and in nonpolar halogenated hydrocarbons,¹¹ comparison with the mechanism in acetonitrile should help in understanding the relative kinetic importance of the various types of solvent-solute interactions in these and other solvents.

Experimental Section

p-Nitrophenol (MCB practical grade) was recrystallized several times from toluene and stored in the dark (mp 114 °C, as reported in the literature). Triethylamine (MCB reagent) was purified by storing over sodium hydroxide followed by distillation and collection of the middle constant-boiling fraction from 10% phenyl isocyanate under dry conditions.

The ion pair system was formed by dissolving the *p*-nitrophenol in pure, dry acetonitrile, adding a slight excess of triethylamine, stripping off the solvent and excess reagent with 5×10^{-4} torr vacuum, followed by washing the resulting oil with hexane and storing under dry nitrogen. The assumed 1:1 *p*-nitrophenol/triethylamine stoichiometry was verified by comparing the observed (Cary 14) optical absorbances, noted in the Introduction, with those expected for a 1:1 mixture. No deviations were observed.

The acetonitrile purification and drying procedure has been previously described.² (Water concentrations are below that detectable by Karl Fischer titration and are

(1) University of Freiburg, Freiburg, Germany.

(2) F. Strobusch, D. B. Marshall, and E. M. Eyring, *J. Phys. Chem.*, **82**, 2447 (1978); D. B. Marshall, Ph.D. Thesis, University of Utah, Salt Lake City, UT, 1980.

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TABLE I: Electric Field Jump Relaxation Data for the Proton Transfer System of p-Nitrophenol (AH) and Triethylamine (B) in Acetonitrile at 25.0 °C^a

solution	[AH]	[B]	[AH...B]	[A ⁻ ...HB]	[A ⁻]	[BH ⁺]	[AHA ⁻]	10 ⁻⁵ τ ⁻¹ , s ⁻¹	
								exptl	calcd ^b
1	10.8	10.9	0.00544	0.00527	0.171	0.242	0.0713	0.794	0.620
2	116	120	0.643	0.624	0.946	5.17	4.23	5.32	5.32
3	34.5	35.1	0.0556	0.0539	0.426	0.992	0.566	1.94	1.91
4	13.7	13.8	0.00865	0.00839	0.208	0.317	0.109	0.808	0.777
5	22.2	22.5	0.0230	0.0223	0.307	0.570	0.263	1.09	1.25

^a Concentrations in units of M × 10⁵. ^b More than the correct number of significant figures to facilitate comparison.

estimated from different observations^{2,12} to be below 10⁻⁵ M.) Solution preparation and handling procedures under dry nitrogen have also been previously described.² Different solution concentrations were prepared by dilution of the stock solution made from the above-mentioned oil. The kinetic solutions were monitored at wavelengths of 450, 430, 410, 390, 370, and 350 nm. Limitations in relaxation amplitude and the optics used prohibited monitoring of shorter wavelengths. The absorbance at 370 nm or below is in any case due primarily to neutral p-nitrophenol. The absorbance of the neutral encounter complex (λ_{max} at 320 nm),³ being present at concentrations at least 20 times lower than neutral p-nitrophenol, contributes significantly less at these wavelengths.

Activity-coefficient corrections, being less than 4% in all cases, were neglected. The reported extinction coefficients³ in acetonitrile for p-nitrophenol and p-nitrophenolate (as the tetrabutylammonium salt) were verified. Concentrations of the various species in the kinetic solutions were determined by measuring the absorbance at 306 nm, neglecting the contribution of the neutral encounter complex, and calculating the concentrations of the remaining species by using an iterative program. (The error due to this neglect was calculated to be less than 1%.) These concentrations were also double-checked by adding a trace of tert-butylammonium hydroxide, measuring the absorbance of the p-nitrophenolate solution (ε₄₃₀ = 3 × 10⁴) to determine total p-nitrophenol, and then calculating concentrations of all species from the total analytical concentration with an iterative program. No deviations between the methods were observed. (The concentration of triethylamine was determined to be equal to the p-nitrophenol concentration.)

The E-jump apparatus with spectrophotometric detection has been described previously.¹³ All measurements were made at 25.0 ± 0.1 °C. Most of the curves, each an average of two to six signals, were stored in a Tektronix R7912 transient digitizer. The relaxation times were calculated with a nonlinear least-squares program using 200–400 data points per curve. Repeated calculations of at least 20 sections of the data for each curve showed no sign of a second relaxation. Each of the reported relaxation times (Table I) is the average of three to six curves. The precision between measurements for the same monitoring wavelength and the same solution was ±4%. The data for solution 5 were obtained by oscilloscope (Tektronix 7613) photographs. The precision between photographs for the

same solution was in this case ±15%, but no systematic deviations between photographs and the digitized data for the other solutions were observed.

r-Factor Analysis

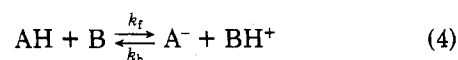
One problem of the relaxation methods is in obtaining sufficient relaxation signal amplitudes without perturbing the system so drastically that the condition for "linearization of the rate equation" no longer holds.¹⁴ Brouillard¹⁵ has recently introduced a simple method for determining the largest perturbation that can be allowed while still preserving linear conditions. The method involves calculation of the concentration change of one of the reactants that is permitted for some choice of r, which indicates the extent of equilibrium displacement. Assuming the mechanism of eq 4, the expression for the permitted change in concentration of p-nitrophenolate is

$$\Delta[A^-] \leq r(K - 1)^{-1}\{K'([A^-] + [BH^+]) + [B] + [AH]\} \quad (3)$$

where $K' = 1/(3.5 \times 10^{-4})$. If the allowed extent of displacement is taken as 1% ($r = 0.01$), then the allowed maximum changes for solutions 1 and 2 are 1.23×10^{-7} and 1.30×10^{-6} M, respectively. Experimental values of $\Delta[A^-]$, estimated from the ratio of relaxation signal amplitude (in mV) to the dc voltage output of the photomultiplier used, compared to the independently measured absorption of $[A^-]$, are 5.84×10^{-8} and 2.59×10^{-7} M. The perturbations used are therefore within the limits allowed. Results from a solution not reported here in Table I were discarded early in this work because of $\Delta[A^-]$ being ~20% over the allowed limits. Attempts to fit this solution to the equations discussed below indeed showed it falling several standard deviations away from the means calculated. This should serve to demonstrate the utility of Brouillard's method in deciding appropriate experimental concentration ranges in advance of the actual kinetic measurements.

Results and Discussion

The experimental data given in Table I agree reasonably well with the relaxation expression for the single equilibrium:



The relaxation time τ is given by¹⁶

$$1/\tau = k_f\{[AH] + [B] + (1/K)([A^-] + [BH^+])\} \quad (5)$$

where the value for K was calculated from the reported equilibrium-constant values of eq 1 as $K = K_1K_2K_3 = 3.5 \times 10^{-4}$. The rate-constant values obtained from the slope of the best straight line forced to pass through the origin

(12) In a continuation of previous work² the rates of deuteron transfer between picric acid-d and dimethylaminoazobenzene in dry acetonitrile have been measured (F. Strobusch, D. B. Marshall, and E. M. Eyring, Fast Reactions in Solution Group Meeting, Aberystwyth, Wales, 1978). No relaxation signal attributable to the transfer of a proton (from water or other protic contaminants) could be observed. From the reactant concentrations of ~10⁻⁴ M and an estimated detection limit for the signal of the protic system of 10% of the relaxation amplitude of D transfer, we conclude that less than 10⁻⁵ M of exchangeable protons (water) was present in that system.

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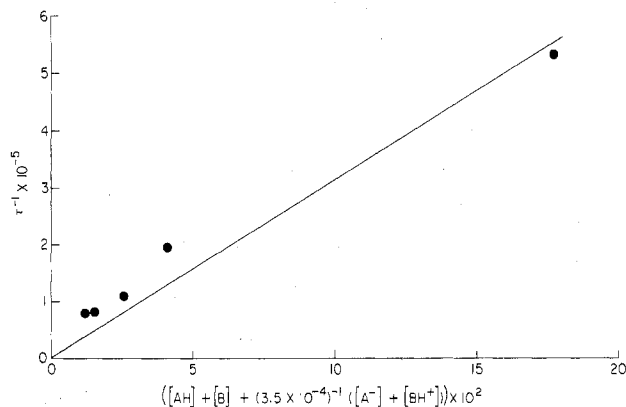


Figure 1. Plot of reciprocal relaxation times, τ^{-1} , vs. the concentration term of eq 5 for the system *p*-nitrophenol (AH) and triethylamine (B) in acetonitrile at 25.0 °C. The straight line is a linear least-squares fit of the experimental points with the line forced to pass through the origin.

(see Figure 1) and this equilibrium constant are $k_f = (3.1 \pm 0.5) \times 10^6$ and $k_b = (9.0 \pm 1.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The standard deviation between expected and experimental τ^{-1} values is $4.5 \times 10^4 \text{ s}^{-1}$ (mean deviation, $3.8 \times 10^4 \text{ s}^{-1}$). The ion recombination rate is ~ 5 times slower than the expected value for a diffusion-controlled reaction, as previously observed for ion recombination rates in acetonitrile.² No systematic differences were observed in the calculated relaxation times regardless of the monitoring wavelength. The relaxation signal amplitude differences between wavelengths corresponded to differences in total absorbance of the solutions. The relaxation signal changed sign at 350 nm, indicating that the opposite side of the equilibrium was then being monitored. This behavior indicates that only one normal mode of the reaction scheme in eq 1 is observed. In a system like that of eq 1, coupling between the individual steps eventually leads to well-separated relaxation modes and to an unexpectedly simple kinetic behavior, if one or two of the modes are not observable.¹⁷

The proton transfer between the phenol and the amine within the hydrogen-bonded complex (second step in eq 1) may be taken as extremely rapid^{6,18} because the hydrogen bond is almost symmetrical ($K_2 = 0.97$). The relaxation time for eq 1 with the simplifying assumption that the middle step equilibrates significantly faster than the outer steps is given by¹⁹

$$1/\tau = \frac{1}{2}(a_{11} + a_{22}) - \left(\frac{1}{2}(a_{11} - a_{22})\right)^2 + a_{21}a_{12}^{1/2} \quad (6)$$

with

$$a_{11} = k_1([AH] + [B]) + k_{-1}/(1 + K_2)$$

$$a_{12} = k_{-1}/(1 + K_2)$$

$$a_{21} = k_3K_2/(1 + K_2)$$

$$a_{22} = k_3K_2/(1 + K_2) + k_{-3}([A^-] + [BH^+])$$

The rate constants k_{-1} and k_{-3} calculated from the best computer fit of the data to eq 6 are $k_{-1} = (1.8 \pm 0.2) \times 10^6 \text{ s}^{-1}$ and $k_{-3} = (4.6 \pm 0.4) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, giving $k_1 = k_{-1}K_1 = (8.4 \pm 0.7) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $k_3 = k_{-3}K_3 = (3.7 \pm 0.3) \times 10^8 \text{ s}^{-1}$. The calculated τ^{-1} values are given in Table I. The standard deviation between expected and experi-

mental τ^{-1} values is $1.6 \times 10^4 \text{ s}^{-1}$, an improvement over the fit to eq 4 by a factor of 3. This improvement is expected because the number of fitting parameters has been doubled (k_f from eq 5 to k_{-1} and k_{-3} from eq 6). If it is assumed that either the first or the third step equilibrates faster than the other two, no correlation between the experimental data and the appropriate rate expressions is obtained. Combination of any one of the steps in eq 1 with eq 2 also gives no satisfactory result. Treatment of the entire system of eq 1 without any simplifying assumptions, via the normal mode formalism described by Purdie et al.,²⁰ yields essentially no new information. The relaxation time corresponding to the second normal modes is ca. 0.4–0.5 μs for all solutions, but the amplitude of this mode is equal to the third and at least 60 times smaller than the first, slowest mode, indicating that only the first mode was measured experimentally. The improvement in the fit is again not large enough to confidently discard the mechanism of eq 4. (The usefulness of the normal mode formalism is very considerable, however, and is described much more fully elsewhere.¹⁷) Treatment of the experimental data with eq 5 is equivalent to assuming that the last step of reaction 1 is equilibrating much more slowly than both of the other steps, i.e., that the condition

$$k_1([AH] + [B]), k_{-1}, k_2, k_{-2} \gg k_3, k_{-3}([A^-] + [BH^+]) \quad (7)$$

holds. The rate constant k_b of eq 4 is then to be interpreted as k_{-3} of eq 1. The conditions 7 are certainly fulfilled with rate constants $k_{-1}, k_2, k_{-2} \geq 4 \times 10^7 \text{ s}^{-1}$ and $k_1 \geq 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which are reasonable values. From eq 6 the value $k_1 = 8.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ is calculated for the rate constant of the formation of a hydrogen bond between the neutral reactants. This is very small compared to the almost diffusion-controlled values found for this type of reaction in other solvents.²¹ Thus either the rate of hydrogen-bond formation between the neutral reactants or the rate of the recombination of the ions is significantly reduced below the diffusion-controlled limit in the system considered here. We feel that our data do not warrant the detailed interpretation with eq 6. The values of the rate constants obtained with eq 5 together with the reasonable fit to this equation do support our previous assumption that the requirement of solvent reorganization around the cation causes the observed reduction in the ion recombination rate to values well below those expected for a diffusion-controlled reaction.² The assumed mechanism is analogous to the dissociative interchange (Id) mechanism²² for ligand displacement of solvent molecules in the inner solvation sphere of metal cations in solution, where removal of a solvent molecule is the rate-limiting step. As such, study of organic acid–base proton transfer reactions that involve doubly charged cations should show even more dramatic reductions in the rate of ion recombination. Kinetic studies of phenol–amine reactions in halogenated hydrocarbons¹¹ and a recent force-field calculation²³ indicate very little steric hindrance for the approach of the phenolic OH group to the nitrogen atom of triethylamine. Therefore, a large value of k_1 is expected in this system. Use of molecules with small steric factors (a small reactive site area, as compared to the total area of the molecule) should show significant reductions in the value of k_1 , since

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the cation desolvation argument does not apply to the preassociation step of the neutral molecules, but relatively insignificant reductions in the value of k_{-3} . This would not be true of more basic solvents such as dimethyl sulfoxide and dimethylformamide which are much stronger hydrogen bond acceptors than acetonitrile. In these solvents the steric factor should play a less important role in determining the magnitude of k_1 ; this magnitude should be further reduced by the need to remove hydrogen-bonded solvent molecules from the reactants.

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Kinetic Study of Protolytic Reactions in Aqueous Solutions of Triethylenediamine and Diethylenediamine by means of Ultrasonic Absorption

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The ultrasonic absorption coefficients of aqueous solutions of diethylenediamine (DEDA) and triethylenediamine (TEDA) have been measured in the frequency range 0.5–95 MHz and at concentrations ≤ 1 M. The observed excess acoustic absorption shows a frequency dependence characteristic of a single relaxation. The concentration dependence of the relaxation frequency and the pH dependence of the absorption amplitude strongly suggest the process causing the excess absorption is perturbation of a protolysis equilibrium involving the monoprotonated species. The analysis of the data is shown to be best described in terms of a two-step reaction scheme in which there is strong mutual coupling between the individual steps. Values of the rate constants and the standard volume changes for the proposed steps in the scheme are determined.

Introduction

Considerable data have been accumulated on the equilibrium properties of amines, amides, polyamines, and amino acids in H_2O . More recently, investigations of their dynamic properties in solution have increased and, despite the complex nature of the elementary steps on a molecular level, the phenomenological kinetics of proton transfer in aqueous solution is well-established. Rate constants and mechanisms have been confirmed by different chemical relaxation techniques. Ultrasonic absorption studies in particular have been useful in providing information on the dynamic properties of fast chemical processes in the liquid phase. This technique has been applied to aqueous solutions of various amines and mechanisms associated with the excess absorption have been proposed.¹⁻⁵ Many factors affecting the dynamics of proton-transfer equilibria have been discussed by Eigen and co-workers.⁶⁻⁸ It has been found⁹ in a study involving cyclic amines that k_{OH^-} shows only very little dependence on the conformational properties of the amines which could undergo ring reversal and/or nitrogen inversion. However, it was speculated that changes in k_{OH^-} found in various alkyl-substituted piperidines must be connected with the hydrogen-bonded structure of water in the vicinity of the reaction site, the magnitude of the constant increasing slightly with increasing proximity of the substituted alkyl group to the reaction site. The proposal was made⁹ that the hydrophobic alkyl groups enhance the hydrogen-bonded structure of water in the vicinity of the reaction site and the

proton transfer occurs at a faster rate because the reacting ions do not have to approach each other as closely as is normally the case.

In an attempt to probe further the effect of rigidity and hydrophobic environment in the vicinity of the reaction site on the dynamics of protolysis reactions, studies are currently being carried out on systems where variation in these characteristics occurs in a systematic manner. We report the results of studies of the dynamics of protolysis reactions involving diethylenediamine (DEDA) and triethylenediamine (TEDA) using ultrasonic absorption techniques. Together with previous results³ on ethylenediamine this work provides data which can be assessed for possible trends between the magnitude of dynamic constants and the factors mentioned above. As well, Wen et al.¹⁰ have reported recently studies of the viscosity and apparent molar volumes of aqueous TEDA solutions. They found that protonation of TEDA causes a large decrease in the partial molal volume and a considerable disruption of water structure surrounding the organic molecule. The

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