

# Kinetics and Mechanism of Proton-Transfer Reactions between *p*-Nitrophenol and Alkylamines in *N*-Methylformamide

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The kinetics of proton-transfer reactions between *p*-nitrophenol and monomethylamine and di- and triethylamines in *N*-methylformamide were studied by using the *T*-jump technique. The rate constants for direct proton transfer between the two acid-base pairs as well as for alkylammonium protolysis are reported and discussed.

## Introduction

The proton transfer between two acid-base pairs in an amphiprotic solvent is a rather complex process since it implies, besides the direct transfer, the protolysis and solvolysis of the two acid-base pairs as well as the solvent autoprotolysis. Systematic studies have mostly been carried out in aqueous solutions.<sup>1</sup> Although aqueous media continue to be of the foremost interest mainly from the practical point of view, complementary studies of proton transfer in nonaqueous media provide valuable information on solvent influence in this process, throwing a new light on its intimate mechanism.<sup>2</sup> There are, however, severe limitations in the study of the proton-transfer kinetics in nonaqueous media, not only related to solvent purification, but especially due to the lack of suitable analytical methods for pH measurements. Additional difficulties also arise in the interpretation of the experimental results when the solvent favors the formation of the ion pairs or higher aggregates leading to a more complex system.

In previous papers we have described some acid-base properties of *N*-methylformamide (NMF) which proved to be an interesting solvent for proton-transfer studies. Its rather large autoprotolysis constant,<sup>3</sup>  $(1.81 \pm 0.12) \times 10^{-11} \text{ M}^2$ , indicates that this solvent has relatively strong acidic and basic properties and may participate in the proton exchange in the presence of an acid-base pair.

The rates of protolysis and solvolysis of *p*-nitrophenol (PNP) have already been measured and reported as well as the rate of the autoprotolysis process.<sup>4</sup> Acid-base equilibria between *o*-, *m*-, and *p*-nitrophenols and different alkylamines have also been studied in NMF and the corresponding equilibrium constants reported.<sup>5</sup> The temperature dependence of these equilibria suggested that the *T*-jump method would be suitable for a kinetic study. In an amphiprotic solvent such as NMF, proton transfer between two acid-base pairs is represented by the interconnected steps given in Figure 1, where AH is PNP, A<sup>-</sup> is PNP<sup>-</sup>, B is an alkylamine, BH<sup>+</sup> is conjugate acid, and SH is NMF.

Such a system containing four states is generally characterized by three relaxation times. However, under suitable experimental conditions the concentration change of the observed species is dominantly affected by one or two relaxation times, allowing an easier analysis of the results.

In aqueous solutions the simplifying experimental conditions are achieved either at the neutrality pH when the solvent ions are in negligible concentration with respect to the other components, or when an acid-base pair is buffered, in the acidic or basic range. In NMF, however, the solvent ion concentrations near the neutrality pH are of the same order of magnitude as the PNP concentration, which must be kept below  $10^{-4}$  in order to avoid its association. When B/BH<sup>+</sup> is used as buffer in NMF (with  $c_B$  and  $c_{BH^+}$  in large excess), the relaxation times correspond to the direct transfer of protons from BH<sup>+</sup> to the three accepting moieties S<sup>-</sup>, A<sup>-</sup>, and SH. Unfortunately when the buffer components B and BH<sup>+</sup> are 2 orders of magnitude more concentrated than AH, the relaxation times become comparable to the shortest experimental heating time ( $\sim 2 \mu\text{s}$ ) and the rise time of the detector amplifier ( $\sim 1 \mu\text{s}$ ), so that the experimental determination becomes difficult and systematic errors become significant.

The simplest way to obtain kinetic information in the system given in Figure 1 was to carry out chemical relaxation experiments on PNP solutions in NMF in the presence of increasing quantities of amine within a concentration range where the equilibrium  $AH + B \rightleftharpoons A^- + BH^+$  was not too greatly one-sided, and to monitor spectrophotometrically the changes in A<sup>-</sup> concentration at a wavelength where there was no interference with other species present in the system.

In order to obtain some information concerning the role played by structural factors, the following bases were used: monomethylamine (MMA), diethylamine (DEA), and triethylamine (TEA).

## Experimental Section

NMF, PNP, and the amines were purified as previously reported.<sup>3-5</sup> PNP<sup>-</sup> concentration was measured on a SP8000 Pye Unicam spectrophotometer using the absorption maximum at 410 nm and using the molar absorptivity of PNP<sup>-</sup> at this wavelength,  $\epsilon^{410} = 2.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ . Although the presence of water traces does not influence the equilibrium between PNP and amines,<sup>3</sup> precautions were taken to exclude atmospheric moisture during the course of experiments in order to avoid the progressive hydrolysis of the solvent. The water content, determined by Karl Fisher titration, is within  $(1.6-3.9) \times 10^{-3} \text{ M}$ . The kinetic measurements were carried out within the next 10 h after solvent and amine purification. In this period there is no noticeable change in the properties of the solvent.

The *T*-jump experiments were performed with Joule heating using a 0.01  $\mu\text{F}$  capacitor charged at  $\sim 30 \text{ kV}$  and a cell with 1 cm optical path length having silica windows and platinum electrodes. The adjustment of the system to the new equilibrium conditions after *T* jump was followed spectrophotometrically by monitoring PNP<sup>-</sup> absorbance at 410 nm. To ensure a fast Joule heating, 0.15 M NaNO<sub>3</sub> was added as an inert electrolyte. Under

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TABLE I: Results of the T-Jump Experiments in Solutions of PNP and Alkylamines in NMF at 297 K

system	$c_{\text{AH}}^{\circ} \times 10^3, \text{M}$	$c_{\text{B}}^{\circ} \times 10^3, \text{M}$	$\tau^{-1} \times 10^{-4}, \text{s}^{-1}$		$\tau_{\text{II}}^{-1} \times 10^{-4}, \text{s}^{-1}$	amplitude ratio	
			one component <sup>a</sup>	two components			
PNP + MMA	4.43	4.26	1.64 (b)	2.18	15.4	2.82/-1.27	
	4.43	4.26	2.02 (b)	2.17	10.9	2.80/-0.23	
	4.43	6.38	1.81 (a)				
	4.43	6.38	1.98 (a)				
	4.43	8.51	2.60 (b)	3.41	12.7	2.91/-1.24	
	4.43	8.51	1.94 (a)				
	4.43	12.8	2.19 (a)				
	4.43	12.8	1.95 (a)				
	PNP + DEA	5.06	4.91	2.13 (a)			
		5.06	4.91	2.52 (a)			
5.06		7.36	2.39 (a)				
5.06		7.36	2.47 (a)				
5.06		9.82	1.32 (a)				
5.06		12.3	2.18 (b)	2.45	13.1	6.12/-1.50	
5.06		14.7	2.54 (b)	3.14	15.4	6.75/-3.81	
PNP + TEA		4.00	5.02	1.15 (a)			
		4.00	5.02	2.21 (a)			
		4.00	5.02	2.49 (a)			
	4.00	5.02	1.93 (a)				
	4.00	7.52	1.79 (a)				
	4.00	7.52	1.97 (a)				
	4.00	10.0	1.73 (b)	1.92	10.1	2.44/-0.25	
	4.00	10.0	2.40 (b)	3.03	15.0	2.64/-1.25	
	4.00	12.5	1.97 (a)				
	4.00	12.5	2.27 (a)				
4.00	15.0	2.19 (b)	2.87	11.6	2.66/-0.47		
4.00	15.0	2.43 (b)	3.74	16.5	3.25/-6.36		

<sup>a</sup>(a) = best solution. (b) = second best solution.

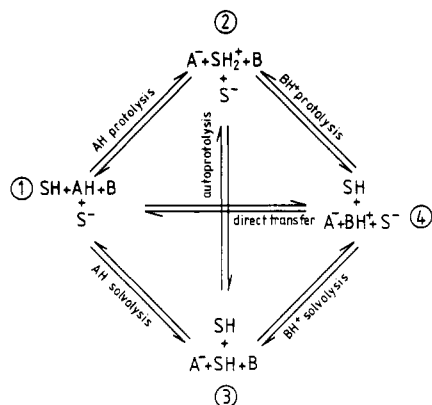


Figure 1. Proton-transfer pathways from acid AH to base B in an amphiprotic solvent SH.

these conditions the heating time was 2–3  $\mu\text{s}$  and the temperature jump 4–5 K, measured as previously reported.<sup>4</sup> Other details have already been given in that paper. The signal to noise ratio ranged between 15 and 35 with an amplifier rise time lower than 1  $\mu\text{s}$ . PNP initial (stoichiometric or weighed in) concentration was  $\sim 4 \times 10^{-5}$  M and amine concentrations ranged between  $5 \times 10^{-5}$  and  $1.5 \times 10^{-5}$  M. For the experiments in buffer solutions, PNP concentration was  $\sim 5 \times 10^{-5}$  M whereas  $c_{\text{B}}^{\circ}$  and  $c_{\text{BH}^+}^{\circ}$  were  $5 \times 10^{-3}$  and  $5 \times 10^{-2}$  M, respectively.

The relaxation transients were recorded on a Tektronix 7313 oscillograph. The semilog plots (log of signal against time) showed good linearity with correlation coefficients better than 0.994 in the case of the experiments with variable amine concentration. As Table I shows, the relaxation times for the different solutions are consistently between 25 and 90  $\mu\text{s}$ , but the reproducibility for identical samples is not sufficient for making very reliable measurements of the dependence on the amine concentration. This uncertainty is also a consequence of representing a composite relaxation process by a single relaxation time.

The relaxation times were determined by both a graphical technique and numerical analysis using DISCRETE<sup>6</sup> which, for some

of the unbuffered systems, indicated the possibility of an initial faster process of opposite, smaller amplitude. In these cases the slower relaxation time differs by less than 50% from the one representing a single relaxation process, and the faster one is within a factor 2 comparable to the heating time. Our analysis uses the results of the one-component representation. As this analysis will show, there is little reason to believe that the faster relaxation processes in the system would contribute a sizeable amplitude to the change of the monitored PNP<sup>-</sup> concentration when the concentrations of B and BH<sup>+</sup> remain low. In buffered systems the monitored A<sup>-</sup> concentration initially changes simultaneously with the temperature rise, and then continues to indicate a slower process. This behavior indicates that A<sup>-</sup> is affected by at least two normal relaxation modes, of which only the slowest relaxation time can be determined.

## Results

1. *Experiments with Variable Amine Concentration.* The results of the T-jump experiments carried out in solutions of PNP and amines (MMA, DEA, and TEA) in NMF are given in Table I which contains the stoichiometric (weighed in) concentrations of PNP and amines, and the reciprocal relaxation times obtained by using the DISCRETE program. The experimental reciprocal relaxation times are related to the following partial relaxation rates of the isolated reactions:

$$\tau_{12}^{-1} = k'_{12} + k_{21}(\bar{c}_{\text{A}^-} + \bar{c}_{\text{SH}_2^+}) \quad (1)$$

$$\tau_{13}^{-1} = k'_{31} + k_{13}(\bar{c}_{\text{AH}} + \bar{c}_{\text{S}^-}) \quad (2)$$

$$\tau_{23}^{-1} = k'_{32} + k_{23}(\bar{c}_{\text{SH}_2^+} + \bar{c}_{\text{S}^-}) \quad (3)$$

$$\tau_{14}^{-1} = k_{14}(\bar{c}_{\text{AH}} + \bar{c}_{\text{B}}) + k_{41}(\bar{c}_{\text{A}^-} + \bar{c}_{\text{BH}^+}) \quad (4)$$

$$\tau_{24}^{-1} = k'_{42} + k_{24}(\bar{c}_{\text{B}} + \bar{c}_{\text{SH}_2^+}) \quad (5)$$

$$\tau_{34}^{-1} = k'_{34} + k_{43}(\bar{c}_{\text{BH}^+} + \bar{c}_{\text{S}^-}) \quad (6)$$

where  $k'_{ij}$  are the pseudo-first-order rate constants ( $k'_{ij} = k_{ij}c_{\text{SH}}$ ) and  $\bar{c}_i$  the equilibrium concentrations.

Some of the partial relaxation rates can be obtained by calculation, using the equilibrium and rate constants reported in our previous papers,<sup>3-5</sup> summarized in Table II. The equilibrium

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**TABLE II: Equilibrium and Rate Data Used To Calculate the Partial Relaxation Times (298 K)**

system (ij) <sup>a</sup>	$K_{ij}$ , M	$k_{ij}$ , M <sup>-1</sup> s <sup>-1</sup>
PNP/SH (12)	$6.96 \times 10^{-6b}$	$4 \times 10^7d$
PNP <sup>-</sup> /SH (31)	$2.60 \times 10^{-6b}$	$2 \times 10^8d$
SH/SH (32)	$1.81 \times 10^{-11b,c}$	$4 \times 10^9d$
MMAH <sup>+</sup> /SH (42)	$2.63 \times 10^{-7e}$	
DEAH <sup>+</sup> /SH (42)	$4.57 \times 10^{-7e}$	
TEAH <sup>+</sup> /SH (42)	$6.76 \times 10^{-6e}$	

<sup>a</sup>The equilibrium constants  $K_{14}$  and  $K_{34}$  are given by  $K_{14} = K_{12}/K_{42}$  and  $K_{34} = K_{SH}/K_{BH^+}$ . <sup>b</sup>Reference 3. <sup>c</sup>In M<sup>2</sup>. <sup>d</sup>Reference 4. <sup>e</sup>Reference 5.

constants may be expressed by the above rate constants in the following equations:

$$K_{12} = K_{AH} = k'_{12}/k_{21} = \bar{c}_A(\bar{c}_{SH_2^+}/\bar{c}_{AH}) \quad (7)$$

$$K_{31} = K_{A^-} = k'_{31}/k_{13} = \bar{c}_{HA}(\bar{c}_S/\bar{c}_{A^-}) \quad (8)$$

$$K_{14} = K_c = k_{14}/k_{41} = \bar{c}_A(\bar{c}_{BH^+}/\bar{c}_{AH})\bar{c}_B \quad (9)$$

$$K_{42} = K_{BH^+} = k'_{42}/k_{24} = \bar{c}_B(\bar{c}_{SH_2^+}/\bar{c}_{BH^+}) \quad (10)$$

$$K_{34} = K_B = k'_{34}/k_{43} = \bar{c}_{BH^+}(\bar{c}_S/\bar{c}_B) \quad (11)$$

$$K_{32} = K_{SH} = k''_{32}/k_{23} = \bar{c}_{SH_2^+}\bar{c}_S \quad (12)$$

where  $k''_{32}$  is the zero-order rate constant ( $k''_{32} = k'_{32}c_{SH}$ ).

The equilibrium concentrations of the different acid or base species in NMF cannot be measured directly (except for  $\bar{c}_{A^-}$ ) but can be calculated from the stoichiometric concentrations of PNP and amine if the corresponding equilibrium constants are known. From the equations defining  $K_{SH}$ ,  $K_{AH}$ , and  $K_{BH^+}$  and from the requirements of material balance and electroneutrality of the solution, one can calculate the equilibrium concentration of lyonium ion,  $\bar{c}_{SH_2^+}$ , from the equation

$$\bar{c}_{SH_2^+}^3 + \bar{c}_{SH_2^+}^2(c^{\circ}_B - \bar{c}_{A^-} + K_{BH^+}) - \bar{c}_{SH_2^+}(K_{SH} + K_{BH^+}\bar{c}_{A^-}) - K_{SH}K_{BH^+} = 0 \quad (13)$$

If  $\bar{c}_{A^-}$  is measured experimentally,  $\bar{c}_{SH_2^+}$  can be obtained by solving numerically eq 13 which has only one positive root. With  $\bar{c}_{SH_2^+}$  and the bulk concentrations  $c^{\circ}_B$  and  $c^{\circ}_{AH}$ , all the required concentrations can be easily obtained by using the material balance and electroneutrality condition. The same concentrations can also be calculated without the direct measurement of  $\bar{c}_{A^-}$ , if  $\bar{c}_{A^-}$  is substituted into eq 13 as  $\bar{c}_{A^-} = K_{AHC^{\circ}}/(K_{AH} + \bar{c}_{SH_2^+})$

$$\bar{c}_{SH_2^+}^4 + \bar{c}_{SH_2^+}^3(K_{AH} + K_{BH^+} + c^{\circ}_B) + \bar{c}_{SH_2^+}^2(K_{AH}K_{BH^+} - K_{SH} + c^{\circ}_BK_{AH} - c^{\circ}_{AH}K_{AH}) - \bar{c}_{SH_2^+}(K_{AH}K_{SH} + K_{AH}K_{BH^+}c^{\circ}_{AH} + K_{SH}K_{BH^+}) - K_{AH}K_{SH}K_{BH^+} = 0 \quad (14)$$

Table III contains the concentrations of the different species in solution obtained by the second procedure. A direct test of the reliability of these calculations is to compare the calculated values

**TABLE III: Calculated Equilibrium Concentrations<sup>a</sup> for the System PNP + Variable Amine Concentration, in NMF, 298 K, Ionic Strength 0.2 M**

system	$c^{\circ}_{AH} \times 10^5$	$c^{\circ}_B \times 10^5$	$\bar{c}_{SH_2^+} \times 10^5$	$\bar{c}_S \times 10^5$	$\bar{c}_{A^-} \times 10^5$	$\bar{c}_{AH} \times 10^5$	$\bar{c}_B \times 10^5$	$\bar{c}_{BH^+} \times 10^5$
PNP + MMA	4.43	4.26	0.237	0.764	3.31	1.12	0.425	3.83
	4.43	6.38	0.117	1.55	3.79	0.640	1.17	5.21
	4.43	8.51	0.0766	2.39	3.99	0.440	2.20	6.31
	4.43	12.8	0.0454	3.99	4.16	0.270	4.69	8.11
	4.43	17.0	0.0337	5.37	4.22	0.210	7.45	9.55
PNP + DEA	5.06	4.91	0.254	0.712	3.71	1.35	0.749	4.16
	5.06	7.36	0.133	1.36	4.25	0.810	1.88	5.48
	5.06	9.82	0.0880	2.06	4.49	0.570	3.36	6.46
	5.06	12.3	0.0663	2.73	4.62	0.440	5.02	7.28
	5.06	14.7	0.0542	3.34	4.69	0.370	6.72	7.98
PNP + TEA	4.00	5.02	0.509	0.356	2.31	1.69	2.86	2.16
	4.00	7.52	0.377	0.480	2.59	1.41	4.83	2.69
	4.00	10.0	0.302	0.599	2.79	1.21	6.91	3.09
	4.00	12.5	0.253	0.715	2.93	1.07	9.10	3.10
	4.00	15.0	0.217	0.834	3.05	0.950	11.39	3.66

<sup>a</sup>All the concentrations are expressed in molarity, M.

of  $\bar{c}_{A^-}$  with the corresponding measured values. The data given in Table IV for the system PNP/MMA indicate a very good agreement.

Using the calculated equilibrium concentrations from Table III and the rate constants given in Table II, the partial relaxation rates  $\tau_{12}^{-1}$ ,  $\tau_{13}^{-1}$ , and  $\tau_{23}^{-1}$  can now be calculated. The results are given in Table V, together with estimated values for the partial relaxation rates  $\tau_{24}^{-1}$  and  $\tau_{34}^{-1}$ . To estimate the value for  $\tau_{34}^{-1}$ , we suppose that the proton transfer between  $BH^+$  and  $S^-$  is nearly diffusion controlled and therefore  $k_{43} \approx 4 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, which is the value obtained by using Smoluchowski's equation  $k_{diff} = 8RT/3000\eta$ . The pK difference for this reaction is large and neither of the reactants is very strongly solvated in NMF.  $\tau_{24}^{-1}$  is an estimated value for the reaction of  $SH_2^+$  with B. This reaction is not diffusion controlled, since  $SH_2^+$  is stabilized by strong solvation.<sup>4</sup> A rate constant equal to that for  $SH_2^+$  with  $A^-$  has been used for this estimate.

An analysis of the partial relaxation rates indicates that the dominant relaxation transient for the observable,  $A^-$ , results from the equilibration by three parallel pathways between state 1 and states 2, 3, and 4, which were already equilibrated by the faster steps  $2 \rightleftharpoons 3$  and  $3 \rightleftharpoons 4$ . Among the three parallel pathways, AH protolysis is less than 10% from the experimental relaxation rate and can be neglected in a first approximation, the equilibration between the states 1 and 2 being also partly accomplished via the composite pathway  $1 \rightleftharpoons 4 \rightleftharpoons 3 \rightleftharpoons 2$ . The experimentally observed relaxation rate of the change in  $A^-$  concentration is then given by

$$\tau_{\text{expt}}^{-1} = \tau_{13}^{-1} + \tau_{14}^{-1} \quad (15)$$

where  $\tau_{13}^{-1}$  can be calculated and  $\tau_{\text{expt}}^{-1}$  is obtained from the analysis of the relaxation curves. With the  $\tau_{14}^{-1}$  obtained and using the eq 4, the following linear equation results:

$$\tau_{14}^{-1}/(\bar{c}_{AH} + \bar{c}_B) = k_{14} + k_{41}(\bar{c}_{A^-} + \bar{c}_{BH^+})/(\bar{c}_{AH} + \bar{c}_B) \quad (16)$$

allowing the determination of both  $k_{41}$  and  $k_{14}$ .

On the other hand, using the eq 9,  $k_{41}$  can be calculated directly as

$$k_{41} = \tau_{14}^{-1}/[K_{14}(\bar{c}_{AH} + \bar{c}_B) + \bar{c}_{A^-} + \bar{c}_{BH^+}] \quad (17)$$

The rate constants  $k_{41}$  obtained from eq 17 and  $k_{14}$  obtained from eq 9 are given in Table VI, as averages from all measurements at different concentrations. The concentration range is too small and there is too much spread in the data points to allow the use of eq 16 to obtain both rate constants simultaneously from the concentration dependence, although this would make possible an independent (kinetic) measurement of  $K_{14}$ .

Table VI also shows values for the rate constant  $k_{43}$  for the three different amines, obtained from the assumption that the composite relaxation process can indeed be resolved into two distinguishable relaxation rates, as extracted by the numerical analysis. Attributing these relaxation processes to the simplified triangular system 1, 3, 4, where the equilibration between states 3 and 4

**TABLE IV: Experimental and Calculated Equilibrium Concentrations of Phenoxide Ion in the System PNP + MMA at 298 K in NMF**

$c_{\text{PNP}}^0 \times 10^5, \text{ M}$	$c_{\text{MMA}}^0 \times 10^5, \text{ M}$	$(\bar{c}_{\text{PNP}})_{\text{expt}} \times 10^5, \text{ M}$	$(\bar{c}_{\text{PNP}})_{\text{calcd}} \times 10^5, \text{ M}$
4.43	4.26	3.64	3.31
4.43	6.38	3.72	3.79
4.43	8.51	3.97	3.99
4.43	12.8	3.88	4.16
4.43	17.0	4.30	4.22

includes the pathway  $3 \rightleftharpoons 2 \rightleftharpoons 4$ , in which 2 is a steady state, one may show that

$$\tau_{\text{I}}^{-1} + \tau_{\text{II}}^{-1} = \tau_{14}^{-1} + \tau_{13}^{-1} + \tau_{34}^{-1} + \tau_{324}^{-1} \quad (18a)$$

where

$$\tau_{324}^{-1} = (k_{23}k_{24}/(k_{23}\bar{c}_{\text{S}^-} + k_{24}\bar{c}_{\text{B}}))(K_{\text{SH}^+}K_{42}(\bar{c}_{\text{BH}^+} + \bar{c}_{\text{S}^-})) \quad (18b)$$

is derived from the steady-state condition for  $\text{SH}_2^+$ . Even if  $k_{24}$  were diffusion controlled,  $\tau_{324}^{-1}$  would contribute less than 10% to the right-hand value of eq 18a.

The values of  $k_{43}$  in Table VI were calculated from this equation with neglect of  $\tau_{324}^{-1}$ .  $k_{34}$  is then obtained by using the equilibrium constant. Reaction  $4 \rightarrow 3$  is diffusion controlled for TEA and a few times slower for MMA and DEA. One should not give much significance to these differences, which are rather uncertain and opposite to the expected influence of steric and statistic factors. The order of magnitude shows that proton-transfer rates from acids to  $\text{S}^-$  are not reduced as much by strong solvation than those of  $\text{SH}_2^+$  to bases.

**II. Experiments in Buffer Solutions.** The advantage of buffer experiments consists of speeding up the direct proton-transfer pathway  $1 \rightleftharpoons 4$  versus the indirect AH protolysis and solvolysis pathways, due to the large excess of B and  $\text{BH}^+$  relative to AH and  $\text{A}^-$ . Based on the rate constants  $k_{14}$  and  $k_{41}$  obtained by the experiments described under subsection I, one expects that the observed concentration change of  $\text{A}^-$  follows the enforced temperature change with a delay of less than 1  $\mu\text{s}$  for concentrations B,  $\text{BH}^+$  of the order of  $10^{-3}$  M. A series of  $T$ -jump experiments was carried out under these conditions. They reveal a relaxation process in the system which is almost 10 times slower than the partial relaxation rate for the proton transfer between phenol and amine, calculated with the rate constants  $k_{14}$  and  $k_{41}$  obtained before. The relaxation rate was evaluated from plotting  $\log d$  vs time, using its linear (last) portion for which the distortion due to the fast transient (heating time) is relatively little. Five experiments were carried out for each sample and averaged over all relaxation rates obtained. The average values  $\tau_{\text{expt}}^{-1}$  and their standard deviations for all the investigated systems are given in Table VII.

For some experiments a numerical deconvolution of the data was done using the experimentally determined heating time and

rise time. The relaxation times obtained with DISCRETE after the deconvolution were in good agreement with those determined from the above plotting, indicating that it is still possible to evaluate a chemical effect, although the experimental errors become significant.

From the expression of  $K_{\text{e}}(1 \rightleftharpoons 4)$ , taking into account that  $\bar{c}_{\text{BH}^+}/\bar{c}_{\text{B}} \approx c_{\text{BH}^+}^0/c_{\text{B}}^0$  and that the autoprotolysis constant of NMF as well as the acidity constant of PNP are known, the following equilibrium concentrations result:

$$\bar{c}_{\text{A}^-} = \frac{c_{\text{B}}^0 c_{\text{AH}}^0 K_{\text{e}}}{c_{\text{B}}^0 K_{\text{e}} + c_{\text{BH}^+}^0}; \quad \bar{c}_{\text{AH}} = c_{\text{AH}}^0 - \bar{c}_{\text{A}^-} \quad (19)$$

and

$$\bar{c}_{\text{SH}_2^+} = \frac{K_{\text{a}}^{\text{AH}} c_{\text{BH}^+}^0}{K_{\text{e}} c_{\text{B}}^0}; \quad \bar{c}_{\text{S}^-} = K_{\text{SH}}/\bar{c}_{\text{SH}_2^+} \quad (20)$$

The values of these equilibrium concentrations are given in Table VIII for the three systems investigated. Using the already known rate constants for the reactions  $1 \leftrightarrow 2$ ,  $1 \leftrightarrow 3$ , and  $2 \leftrightarrow 3$ , the rate constants obtained above for  $1 \leftrightarrow 4$ , and the same estimates as before for  $2 \leftrightarrow 4$  and  $3 \leftrightarrow 4$ , a complete numerical calculation of the kinetic normal modes of relaxation can now be carried out for each set of concentrations in the buffered solutions. The results of such a calculation are shown in Table VII. Under buffered conditions the eigenvalues of the relaxation matrix (normal modes of the linearized kinetic rate equations) are mutually separated by at least 1 order of magnitude. The eigenvectors associated with each eigenvalue indicate the stoichiometry of each of the kinetically uncoupled normal reactions. They show clearly that the fastest relaxation process in the system corresponds to the equilibration of  $\text{BH}^+$  solvolysis  $\text{BH}^+ + \text{S}^- \rightleftharpoons \text{B} + \text{SH}$ , with a relaxation time of the order of nanoseconds under the buffered conditions. Proton exchange between  $\text{BH}^+$  and  $\text{A}^-$  equilibrates in the intermediate range, with a relaxation time below a microsecond. The slowest process is the equilibration of the  $\text{SH}_2^+$  concentration which occurs mainly via the reaction  $\text{BH}^+ + \text{SH}$ , and occurs within a few microseconds. This slowest step will also be visible in the optically monitored  $\text{A}^-$  concentration, which readapts itself to the changing concentration of  $\text{BH}^+$ . We conclude that the measurable (slowest) relaxation process in a B/ $\text{BH}^+$  buffered system is dominated by the partial relaxation time  $\tau_{24}$ , which is given by

$$\tau_{24}^{-1} = k_{24}(K_{42}\bar{c}_{\text{BH}^+} + \bar{c}_{\text{SH}_2^+} + \bar{c}_{\text{B}}) \approx k_{24}c_{\text{B}}^0 \quad (21)$$

From the measurements in buffered solutions one obtains an experimental value of  $k_{24}$  (cf. Table IX) which is somewhat smaller than our previous estimate, and which also reflects the difference in basicity of the different amines.

The numerical calculation of the eigenvalues and eigenvectors of the normal relaxation modes with the set of rate constants obtained so far (Table IX), and with the concentrations of the

**TABLE V: Partial Relaxation Times in the System PNP + Alkylamines in NMF**

system	$c_{\text{PNP}}^0 \times 10^5, \text{ M}$	$c_{\text{B}}^0 \times 10^5, \text{ M}$	$\tau_{12}^{-1} \times 10^{-4}, \text{ s}^{-1}$	$\tau_{13}^{-1} \times 10^{-4}, \text{ s}^{-1}$	$\tau_{23}^{-1} \times 10^{-4}, \text{ s}^{-1}$	$\tau_{24}^{-1} \times 10^{-4}, \text{ s}^{-1}$	$\tau_{34}^{-1} \times 10^{-4}, \text{ s}^{-1}$
PNP/MMA	4.43	4.26	0.178	0.471	3.90	(0.0344)	(45.9)
	4.43	6.38	0.193	0.539	6.50	(0.0657)	(54.6)
	4.43	8.51	0.200	0.680	9.62	(0.115)	(62.3)
	4.43	12.8	0.206	0.994	15.7	(0.238)	(75.9)
	4.43	17.0	0.208	1.28	21.1	(0.375)	(87.2)
PNP/DEA	5.06	4.91	0.195	0.511	3.77	(0.0524)	(35.3)
	5.06	7.36	0.213	0.534	5.82	(0.103)	(43.2)
	5.06	9.82	0.221	0.636	8.38	(0.175)	(49.9)
	5.06	12.3	0.226	0.754	10.9	(0.275)	(55.9)
	5.06	14.7	0.228	0.873	13.2	(0.341)	(61.2)
PNP/TEA	4.00	5.02	0.147	0.507	3.37	(0.202)	(11.1)
	4.00	7.52	0.154	0.473	3.34	(0.294)	(13.7)
	4.00	10.0	0.159	0.455	3.51	(0.394)	(15.8)
	4.00	12.5	0.163	0.450	3.77	(0.501)	(16.3)
	4.00	15.0	0.166	0.450	4.10	(0.614)	(19.0)

<sup>a</sup>The values quoted are for  $k_{24} \approx 5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , estimated compared to the rate constant of proton transfer between  $\text{SH}_2^+$  and  $\text{A}^-$ . <sup>b</sup>The values quoted are for diffusion-controlled  $k_{43}$ .

**TABLE VI: Rate Constants of Some Proton-Transfer Reactions in NMF, 298 K**

system		$k_{14}, \text{M}^{-1} \text{s}^{-1}$	$k_{41}, \text{M}^{-1} \text{s}^{-1}$
acid	base		
PNP	MMA	$5 \times 10^8$	$2 \times 10^7$
PNP	DEA	$4 \times 10^8$	$3 \times 10^7$
PNP	TEA	$1 \times 10^8$	$1 \times 10^8$

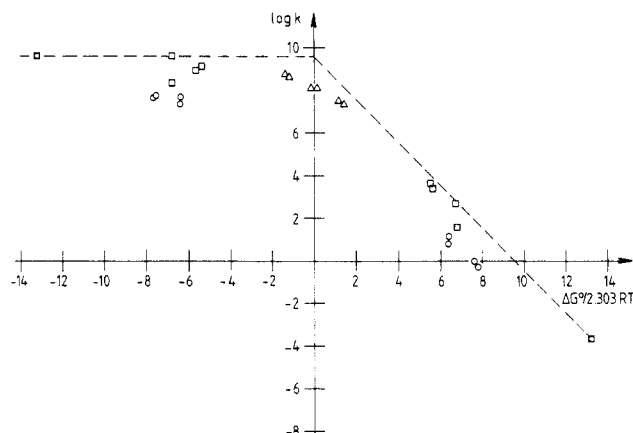
system		$k'_{34}, \text{s}^{-1}$	$k_{43}, \text{M}^{-1} \text{s}^{-1}$
acid	base		
SH	MMA	$7 \times 10^4$	$1 \times 10^9$
SH	DEA	$4 \times 10^4$	$9 \times 10^8$
SH	TEA	$8 \times 10^3$	$3 \times 10^9$

experiments with variable amine, discussed under subsection I, confirms that under these conditions reactions involving  $\text{A}^-$  contribute at most a few percent of the two faster normal modes. These modes represent almost exclusively the equilibration of the states 4, 3, 2 of the right-hand triangular subsystem in the reaction scheme (Figure 1). The slowest normal mode equilibrates the  $\text{AH}/\text{A}^-$  ratio, for about 40% via the reaction  $\text{AH} + \text{B} \rightleftharpoons \text{A}^- + \text{BH}^+$  and for 60% via the reaction  $\text{AH} + \text{S}^- \rightleftharpoons \text{A}^- + \text{SH}$ . The rate constants for proton-transfer reactions in NMF, determined in this and previous investigations, are collected in Table IX. The correlation between proton-transfer rates and  $\Delta pK$  values is shown in Figure 2.

### Discussion

Different and opposing effects cooperate to establish the observed rate constants, given in Table IX. Among them the most important are the reaction free energy as the driving force, the steric factors, the electrostatic interactions altered by the ionic atmosphere, and various structural factors including hydrogen bond formation.

(a) *The Proton Transfer from PNP to Amine B.* The calculated  $\Delta pK$  ( $pK_{\text{acceptor}} - pK_{\text{donor}}$ ) indicate that all these reactions are thermodynamically favorable (1.42, 1.18, and 0.01 for MMA, DEA, and TEA, respectively). The differences among the rate constants are determined in this case by the other factors. For



**Figure 2.** Kinetic vs thermodynamic properties of some proton-transfer equilibria in *N*-methylformamide at 298 K.  $\Delta$ , PNP-amine direct transfer;  $\square$ , transfers involving  $\text{S}^-$ ;  $\circ$ , transfers involving  $\text{SH}_2^+$ .

a molecule-molecule reaction the long-range interactions can be neglected and the steric factors should give the following sequence:  $k_{\text{MMA}} > k_{\text{DEA}} > k_{\text{TEA}}$ , which was also found experimentally. At the same time the decrease  $\Delta pK$  from 1.42 to 0.01, close to the transition to thermodynamically unfavorable transfer, acts in the same direction. It is noteworthy that these tendencies outweigh the inductive effect of the alkyl groups which are expected to act in the opposite direction. On the other hand, although these proton-transfer reactions are thermodynamically favorable, their rate constants are at least an order of magnitude below the diffusion limit ( $\sim 4 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ ). This behavior must be ascribed to the existence of an activation barrier associated with the desolvation of the phenol, which obviously forms a strong hydrogen bond ( $\Delta G^\circ \approx 10 \text{kJ mol}^{-1}$ ) to the carbonyl group of the solvent.

(b) *The Proton Transfer from Alkylammonium Ions to PNP.* Although these reactions occur between oppositely charged ions, they are slower than the corresponding forward molecule-molecule reactions, because they reflect the free energy differences that must be overcome when a proton is transferred from the pro-

**TABLE VII: Experimental Relaxation Times and Calculated Relaxation Eigenvalues in Buffer Solutions, for the System PNP/MMA, DEA, and TEA in NMF, 298 K, Ionic Strength 0.2 M**

system	$c_{\text{AH}}^0 \times 10^3, \text{M}$	$c_{\text{BH}^+}^0 \times 10^3, \text{M}$	$c_{\text{B}}^0 \times 10^3, \text{M}$	$\tau_{\text{exp}}^{-1} \times 10^{-5}, \text{s}^{-1}$	$\tau_1^{-1} \times 10^{-5}, \text{s}^{-1}$	$\tau_2^{-1} \times 10^{-5}, \text{s}^{-1}$	$\tau_3^{-1} \times 10^{-5}, \text{s}^{-1}$
PNP/MMA/MMAH <sup>+</sup>	5.39	50.0	5.2	$3.1 \pm 0.6$	551	38	2.9
	5.39	50.0	7.5	$3.4 \pm 0.7$	551	50	4.2
	5.39	50.0	11.2	$4.5 \pm 0.9$	551	69	6.2
	5.39	50.0	15.0	$6.2 \pm 1.2$	551	89	8.3
PNP/DEA/DEAH <sup>+</sup>	5.00	50.0	1.96	$3.8 \pm 0.8$	450	23	1.0
	5.00	50.0	3.44	$4.3 \pm 0.9$	450	30	1.8
	5.00	50.0	4.91	$4.8 \pm 1.0$	450	36	2.6
	5.00	50.0	7.36	$5.8 \pm 1.2$	450	47	3.9
PNP/TEA/TEAH <sup>+</sup>	5.00	5.00	2.20	$1.9 \pm 0.4$	160	9.4	1.2
	5.00	5.00	4.40	$2.0 \pm 0.4$	160	12	2.3
	5.00	5.00	6.60	$2.2 \pm 0.4$	160	15	3.4
	5.00	5.00	8.80	$3.1 \pm 0.6$	160	18	4.6

<sup>a</sup> Experimental average values and their standard deviations. <sup>b</sup> Relaxation eigenvalues from normal-mode calculations.

**TABLE VIII: Calculated Equilibrium Concentrations of the System PNP/Buffers BH<sup>+</sup>/B in NMF, 298 K, Ionic Strength 0.2 M**

system	$c_{\text{PNP}}^0 \times 10^3, \text{M}$	$c_{\text{BH}^+}^0 \times 10^3, \text{M}$	$c_{\text{B}}^0 \times 10^3, \text{M}$	$\bar{c}_{\text{A}^-} \times 10^5, \text{M}$	$\bar{c}_{\text{AH}} \times 10^5, \text{M}$	$\bar{c}_{\text{SH}_2^+} \times 10^5, \text{M}$	$\bar{c}_{\text{S}^-} \times 10^5, \text{M}$
PNP + MMA/MMAH <sup>+</sup> $K_e = 26.4$	5.39	50.0	5.20	3.95	1.44	0.253	0.714
	5.39	50.0	7.50	4.30	1.09	0.176	1.03
	5.39	50.0	11.2	4.61	0.780	0.118	1.54
	5.39	50.0	15.0	4.79	0.604	0.0880	2.06
PNP + DEA/DEAH <sup>+</sup> $K_e = 15.3$	5.00	50.0	1.96	1.87	3.12	1.16	0.156
	5.00	50.0	3.44	2.56	2.44	0.661	0.274
	5.00	50.0	4.91	3.00	2.00	0.463	0.391
	5.00	50.0	7.36	3.46	1.54	0.309	0.586
PNP + TEA/TEAH <sup>+</sup> $K_e = 1.0$	5.00	5.00	2.20	1.53	3.47	1.58	0.114
	5.00	5.00	4.40	2.34	2.66	0.791	0.230
	5.00	5.00	6.60	2.84	2.15	0.527	0.343
	5.00	5.00	8.80	3.19	1.81	0.395	0.460

TABLE IX: Kinetic vs Thermodynamic Properties of Some Proton-Transfer Equilibria in *N*-Methylformamide at 298 K

reaction	proton acceptor	proton donor	$\Delta pK^a$	$\Delta G^\circ$ , kJ mol <sup>-1</sup>	$k_{ij}$ , M <sup>-1</sup> s <sup>-1</sup>	log $k_{ij}$
1 → 4	MMA	PNP	+1.42	-8.1	$5 \times 10^8$	8.7
4 → 1	PNP <sup>-</sup>	MMAH <sup>+</sup>	-1.42	+8.1	$2 \times 10^7$	7.3
3 → 4	MMA	SH	-5.39	+30.7	$4 \times 10^3$	3.6
4 → 3	S <sup>-</sup>	MMAH <sup>+</sup>	+5.39	-30.7	$1 \times 10^9$	9.0
2 → 4	MMA	SH <sub>2</sub> <sup>+</sup>	+7.81	-44.5	$3 \times 10^7$	7.5
4 → 2	SH	MMAH <sup>+</sup>	-7.81	+44.5	0.5	-0.30
1 → 4	DEA	PNP	+1.18	-6.73	$4 \times 10^8$	8.6
4 → 1	PNP <sup>-</sup>	DEAH <sup>+</sup>	-1.18	+6.73	$3 \times 10^7$	7.5
3 → 4	DEA	SH	-5.63	+32.1	$2 \times 10^3$	3.3
4 → 3	S <sup>-</sup>	DEAH <sup>+</sup>	+5.63	-32.1	$9 \times 10^8$	8.9
2 → 4	DEA	SH <sub>2</sub> <sup>+</sup>	+7.57	-43.1	$5 \times 10^7$	7.7
4 → 2	SH	DEAH <sup>+</sup>	-7.57	+43.1	1	0.0
1 → 4	TEA	PNP	+0.01	-0.06	$1 \times 10^8$	8.0
4 → 1	PNP <sup>-</sup>	TEAH <sup>+</sup>	-0.01	+0.06	$1 \times 10^8$	8.0
3 → 4	TEA	SH	-6.80	+38.8	$5 \times 10^2$	2.7
4 → 3	S <sup>-</sup>	TEAH <sup>+</sup>	+6.80	-38.8	$3 \times 10^9$	9.5
2 → 4	TEA	SH <sub>2</sub> <sup>+</sup>	+6.40	-36.5	$2 \times 10^7$	7.3
4 → 2	SH	TEAH <sup>+</sup>	-6.40	+36.5	7	0.84
1 → 2	SH	PNP	-6.39	+36.4	17	1.2
2 → 1	PNP <sup>-</sup>	SH <sub>2</sub> <sup>+</sup>	+6.39	-36.4	$4 \times 10^7$	7.6
1 → 3	S <sup>-</sup>	PNP	+6.81	-38.8	$2 \times 10^8$	8.3
3 → 1	PNP <sup>-</sup>	SH	-6.81	+38.8	34	1.5
2 → 3	S <sup>-</sup>	SH <sub>2</sub> <sup>+</sup>	+13.2	-75.2	$4 \times 10^9$	9.6
3 → 2	SH	SH	-13.2	+75.2	$2 \times 10^{-4}$	-3.7

$$^a \Delta pK = pK_{a, \text{acceptor}} - pK_{a, \text{donor}} = (-\Delta G^\circ)/2.303RT. \quad pK_{\text{SH}_2^+} = -1.23 \\ = \log c_{\text{SH}}. \quad pK_{\text{SH}} = 11.97 = -\log K_{\text{SH}} + \log c_{\text{SH}}.$$

tonated amine to the phenolate, which is in all cases a weaker base than the amine. The stabilities of the substituted ammonium acids in NMF are MMAH<sup>+</sup> > DEAH<sup>+</sup> > TEAH<sup>+</sup>, in contrast to the gas phase, where the stability increases in the opposite sense. The effect of the solvent is explained by the increasing size of the hydrogen-bonded solvation structure over which the excess charge can be distributed.<sup>5</sup> In the gas phase, MMAH<sup>+</sup> is the smallest ion of the three, whereas in NMF solution it can bind three solvent molecules by hydrogen bonds. TEAH<sup>+</sup> is more stable in the gas phase, due to its larger polarizable volume, but it can only bind one solvent molecule by a hydrogen bond. As a consequence, the additional stabilization of the ammonium acids by a hydrogen-bonding solvent is much larger for MMAH<sup>+</sup> than for TEAH<sup>+</sup>. The same remark applies to DEAH<sup>+</sup>, the stability of which remains intermediate between the two others.

The free energy of the hydrogen-bonded complex ArOH...B in which the actual proton transfer from the amine nitrogen to the phenol oxygen occurs, is higher than the free energy of the separated molecules after the transfer. The difference between these two states is mainly determined by the different hydrogen bond energies of phenol-amine versus phenol-solvent. In the "activated complex" (or the state with the highest free energy in the reaction pathway) a phenol and an amine molecule are neighbors to each other but neither of them is hydrogen bonded.

(c) *The Proton Transfer from Alkylammonium Ions to Lyate Ion.* These reactions are thermodynamically highly favorable and

may well approach the diffusion limit. The individual differences escape the present analysis. It must be pointed out, however, that a free energy difference corresponding to  $\Delta pK \approx 6$  is in itself not sufficient to guarantee a diffusion-controlled transfer of the proton. The reaction SH<sub>2</sub><sup>+</sup> + PNP<sup>-</sup>, with a  $\Delta pK$  of +6.39, is almost 100 times slower than the reaction between RNH<sup>+</sup> and S<sup>-</sup>. We have already explained<sup>4</sup> the particular kinetic stability of the lyonium ion SH<sub>2</sub><sup>+</sup>, where the proton is solvated in a homonuclear hydrogen bond between two solvent molecules. Such a bond is much more stable than the heteronuclear hydrogen bond which stabilizes the protonated carbonyl group of NMFH<sup>+</sup> in an aqueous medium. Therefore, the autoprotolysis constant of NMF is much larger than the value derived from its  $pK$  in water.<sup>3,4</sup> In the case of the protonated amines, the hydrogen bond in NMF is formed between a nitrogen and an oxygen atom. These bonds are, in general, much weaker than hydrogen bonds between two oxygen atoms, and certainly very much weaker than the strong homonuclear bond in SH<sub>2</sub><sup>+</sup>. Protonated amines, then, can react by a diffusion-controlled mechanism with S<sup>-</sup>, if the hydrogen bonds of its solvation structure are kinetically labile. Our experiments should have shown a more complicated behavior if the bond energy exceeded more than a few kT. The acidic proton of a phenol molecule is already engaged in much stronger O-H...O hydrogen bond interactions. In this case the solvation structure is stable enough to prevent a diffusion-controlled proton transfer between PNP and S<sup>-</sup>, although the free energy difference is favorable and of the same order of magnitude as that between ammonium acids and S<sup>-</sup>.

(d) *Proton Transfer from Lyonium to Amines.* This exoenergetic reaction ( $\Delta pK \approx 6-7$ ) is responsible for the relaxation process observed under buffered conditions, where protons are transferred more rapidly from BH<sup>+</sup> to A<sup>-</sup> than from SH<sub>2</sub><sup>+</sup> to B. Direct transfer from SH<sub>2</sub><sup>+</sup> to A<sup>-</sup> or S<sup>-</sup> does not contribute to the equilibration under these conditions since  $\bar{c}_{A^-}$  or  $\bar{c}_{S^-}$  are very much smaller than  $\bar{c}_B$ . The rate constants for proton transfer from the homonuclear solvation structure between oxygen atoms in SH<sub>2</sub><sup>+</sup> to an accepting neutral nitrogen base B is found to be somewhat smaller than to the negatively charged oxygen base A<sup>-</sup>. The rate-limiting step includes an energetic activation barrier (breaking the strong solvation structure) and also a steric factor, since the rate constant decreases with increasing number of alkyl substituents on the base.

(e) *The proton transfer from solvent to amines* is thermodynamically unfavorable. The sequence  $k_{\text{MMA}} > k_{\text{DEA}} > k_{\text{TEA}}$  follows the increase of the thermodynamic barrier as explained before, the other factors remaining also of little importance. This behavior is similar to that in aqueous solutions<sup>7</sup> where, however, the sequences of the corresponding rate constants follow a different order of amine basicities, which has its origin in the stronger interference of the hydrocarbon moieties of the substituted amines with the structure of a hydrogen-bonded solvent.<sup>5</sup>

**Registry No.** PNP, 100-02-7; MMA, 74-89-5; DEA, 109-89-7; TEA, 121-44-8.

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