removing the solvent under reduced pressure, and crystallizing from 25% ethanol/75% acetone. The chloride salt did not melt below 350 °C. That used in the kinetic experiments was contaminated with about 10% of the corresponding iodide.

N,N-Dimethylpiperidinium chloride[30] was similarly prepared. Anal. Calcd for $C_7H_{16}ClN$: Cl, 23.7. Found: Cl, 23.2.

Spectral Characteristics and Changes. For **8a** in Me_2SO, λ_{max} 439 nm, ϵ 1.90×10^4 M^{-1} cm^{-1}. For **8b** in Me_2SO, λ_{max} 422 nm, ϵ 7.8×10^3 M^{-1} cm^{-1}. Upon combining **5** with pyrrolidine in Me_2SO in the absence of pyrrolidinium chloride, within 30 s a strong spectrum with λ_{max} 523 nm (ϵ 2.71×10^4 M^{-1} cm^{-1}) and 364 nm (with shoulder at 354 nm), attributed to **7a** had appeared; it slowly diminished with concomitant growing in of absorption at λ_{max} 439 nm attributed to **8a**. Upon combining **5** with purified piperidine in Me_2SO, within 1 min a strong spectrum with λ_{max} 522 nm (ϵ 2.03×10^4 M^{-1} cm^{-1}) and 367 nm (with shoulder at 357 nm) attributed to **7b** had appeared; in the absence of piperidinium chloride, this spectrum scarcely changed during 45 h, but in the presence of piperidinium chloride it slowly was superseded by a spectrum with λ_{max} 422 nm attributed to **8b**.

Kinetic procedures were the same as used by Orvik and Bunnett.[10]

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Reactions of Secondary Amines with Their *N*-(2,4-Dinitro-1-naphthyl) Derivatives To Form Jackson–Meisenheimer Adducts. Substantial Difference in Reaction Rates between Pyrrolidine and Piperidine

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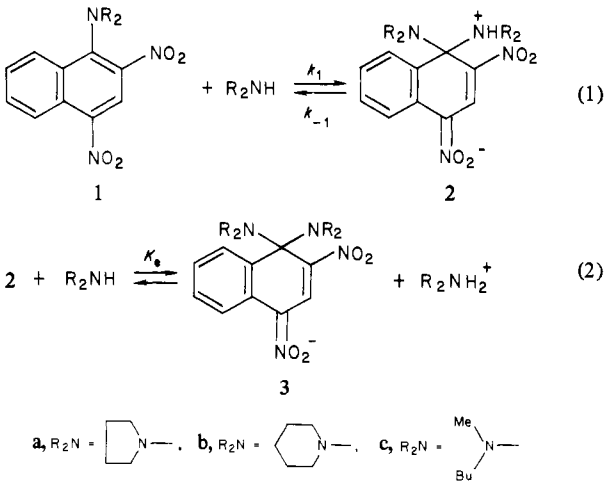
Abstract: Pyrrolidine, piperidine, and butylmethylamine react with their respective *N*-(2,4-dinitro-1-naphthyl) derivatives to form σ adducts as though the respective amide ions had attached at the 1 position. These reactions occur in dimethyl sulfoxide solution and proceed to a state of equilibrium. For the pyrrolidine and butylmethylamine reactions, equilibrium constants as well as rate constants both forward and reverse have been measured. Although two amine molecules are required to form the σ adduct, one to supply an amino moiety and the other to receive a proton, the forward reaction is only first order in amine; therefore, amine attack is not base catalyzed. Piperidine reacts so much slower than pyrrolidine, roughly $^1/_{400}$th as fast, that rate and equilibrium measurements were inconvenient. The low reactivity of the piperidine system is ascribed to stereoelectronic/conformational/steric problems in the piperidino moiety of *N*-(2,4-dinitro-1-naphthyl)piperidine as it enters the transition state.

Continuing our investigations[2,3] of pyrrolidine vis-à-vis piperidine as they take part in component steps of aromatic nucleophilic substitution by the S_NAr mechanism, we have studied the reactions of these two amines as well as that of butylmethylamine with the corresponding 2,4-dinitro-1-naphthylamines. The reactions involved are shown in Scheme I. The solvent was dimethyl sulfoxide.

The overall stoichiometry, shown in eq 3, involves two molecules of amine and forms, besides Jackson–Meisenheimer adduct **3**, a dialkylammonium ion. This stoichiometry has previously been observed for analogous processes.[4-7]

The mechanism of Scheme I involves rate-limiting step 1, not catalyzed either by base (forward) or acid (reverse), and rapid

Scheme I



proton-transfer equilibrium 2. A conceivable alternative mechanism would merge steps 1 and 2, so that eq 3 would become a

$$\mathbf{1} + 2R_2NH \rightleftarrows \mathbf{3} + R_2NH_2^+ \quad (3)$$

(1) On leave from Gunma University, Kiryu, Japan, 1970–71, under support of a fellowship from the Japanese Ministry of Education.
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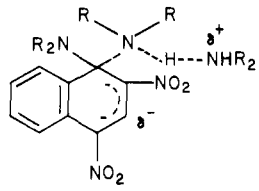
Table I. Reaction of *N*-(2,4-Dinitro-1-naphthyl)pyrrolidine with Pyrrolidine in Dimethyl Sulfoxide[a]

expt	$[C_4H_8NH]$, M	10^4k_ψ, s^{-1}	A_∞	K_3, M^{-1}
1	0.045	1.09	0.227	0.97
2	0.057	1.18	0.225	0.71
3	0.068	1.32	0.292	0.61
4	0.080	1.48	0.334	0.54
5	0.091	1.63	0.373	0.51
6	0.103	1.82	0.403	0.46
7	0.140	2.73	0.450	0.31
8	0.160	3.35	0.483	0.28
9	0.225	4.64	0.600	0.25
10	0.330	6.90	0.692	
11	0.458	9.35	0.782	
12	0.505	10.2	0.800	
13	0.582	11.8	0.810	
14	0.673	13.1	0.809	
15	0.699	13.3	0.849	

[a] Temperature: 25 °C; $[\mathbf{1a}]_0$ 3.90×10^{-5} M; pyrrolidinium chloride 0.0053 M, present in all experiments.

statement of rate-limiting steps, forward and reverse, as well as a representation of the overall equilibrium. In this alternative mechanism, forward, one amine molecule would act as a nucleophile toward carbon while the other would act as a base, removing the N–H hydrogen from the first amine as nitrogen became bonded to carbon. The transition state would be of the nature of structure **4**. In the reverse direction, this one-step



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mechanism would involve general acid catalyzed departure of a nucleofugal dialkylamino group from **3**, again via transition state **4**. Earlier studies in this laboratory[3,8] indicate that alkoxy group removal from σ adducts analogous to **3** is general acid catalyzed by substituted ammonium ions. On the other hand, no prior study provides convincing evidence that the attack of alkylamines in S_NAr-like processes is base catalyzed. Thus, considerations of analogy both encourage and discourage the concept of a one-step mechanism via transition state **4**. In such circumstances, the need for experimental evidence is especially cogent.

Results

Pyrrolidine System. The spectrum of 1-pyrrolidino-2,4-dinitronaphthalene (**1a**) in Me_2SO shows λ_{max} 439 nm (ϵ 1.7×10^4). On admixture of pyrrolidine, this spectrum is gradually supplanted by one with λ_{max} at 400 and 523 nm. The 400- and 523-nm bands are attributed to σ-adduct **3a**; other 1,1-disubstituted-2,4-dinitronaphthalene σ adducts have spectra of that type.[8,9] Moreover, recent NMR studies[10,11] indicate the presence of **3a** while giving no indication of attack of pyrrolidine at C-3 of **1a**.

The pseudo-first-order rate constant, k_ψ, for the attainment of an equilibrium is the sum of forward and reverse components. For the system of Scheme I, the kinetic expression of eq 4 should

$$k_\psi = k_1[R_2NH] + \frac{k_{-1}[R_2NH_2^+]}{K_e[R_2NH]} \quad (4)$$

prevail. Multiplying both sides by $[R_2NH]$, one obtains eq 5. On

$$k_\psi[R_2NH] = k_1[R_2NH]^2 + (k_{-1}/K_e)[R_2NH_2^+] \quad (5)$$

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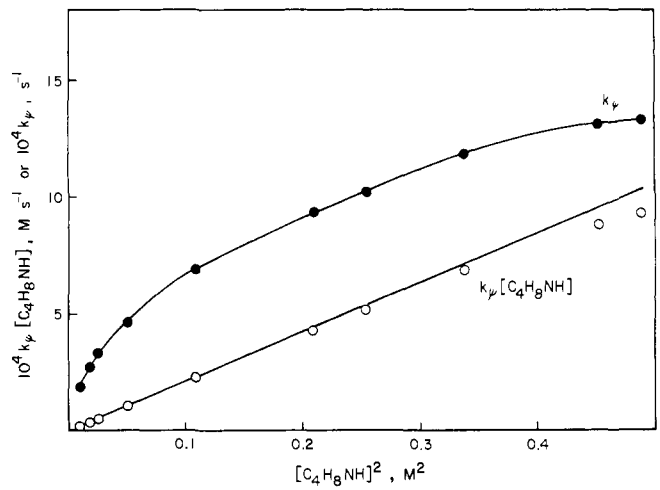


Figure 1. Reaction of **1a** with pyrrolidine. Rate data plotted according to eq 5 (open circles) and according to eq 6 (filled circles). Data from Table I.

the other hand, the one-step mechanism (cf. eq 3) would call for the kinetic expression of eq 6.

$$k_\psi = k_3[R_2NH]^2 + k_{-3}[R_2NH_2^+] \quad (6)$$

Our data (Table I) concern the rate of attainment of equilibrium at constant $[R_2NH_2^+]$ and varying $[R_2NH]$. The data afford a linear plot of $k_\psi[R_2NH]$ against $[R_2NH]^2$, as shown in Figure 1. They are in accord with eq 5 and thus consistent with the mechanistic model of Scheme I. The plot of k_ψ vs. $[R_2NH]^2$, according to eq 6, also shown in Figure 1, is strongly curved. Our data do not support the one-step mechanistic alternative.

Actually the plot of $k_\psi[R_2NH]$ vs. $[R_2NH]^2$ in Figure 1 is not perfectly straight. It curves downward slightly beyond 0.33 M pyrrolidine, probably owing to a modest change in the composition of the solvent. The highest amine concentration, 0.699 M, implies that pyrrolidine is about 4.5% of the medium.

The linear regression slope of the plot for expts 1–10, inclusive, gives the value of k_1 as $2.10 \pm 0.01 \times 10^{-3}$ M^{-1} s^{-1}. However, the intercept is just below zero and therefore cannot be used to evaluate k_{-1}/K_e, as eq 5 would suggest.

From the infinity absorbance for expt 15 (Table I), ϵ for **3** is evaluated as 2.18×10^4. This value is corroborated by other measurements of similar type at even higher pyrrolidine concentrations. However, ϵ for **3** was found to depend somewhat on the concentration of pyrrolidinium chloride; in the absence of this salt, ϵ is 1.85×10^4.

The equilibrium constant, K_3, for equilibrium reaction 3 was evaluated from ϵ for **3** and infinity absorbance measurements for runs for which at least 10% of **1** remained as such at equilibrium. The mean of the nine such K_3 values listed in Table I is 0.52 M^{-1}. Another set of seven kinetic runs at similar pyrrolidine concentrations, with similar kinetic outcome, but with no consistent trend in K_3 values, afforded an average K_3 of 0.61 M^{-1}. The mean K_3 from 16 runs is 0.56 ± 0.18 M^{-1}.

Division of k_1 by K_3 gives k_{-1}/K_e as $3.8 \pm 1.4 \times 10^{-3}$ s^{-1}.

Piperidine System. A solution of *N*-(2,4-dinitro-1-naphthyl)-piperidine (**1b**) (6.6×10^{-5} M), piperidine (1.0 M), and piperidinium chloride (1.1×10^{-2} M) in Me_2SO, maintained at 25 °C, was observed to undergo spectral changes very slowly. After 21 days a well-defined absorption spectrum with λ_{max} at 389 and 524 nm was observed. It is attributed to σ-adduct **3b**. However, only about 19% of the 21-day absorbance at 524 nm had developed in 10.6 h and only about 36% in 34.6 h. In contrast, in a similar experiment involving **1a** and pyrrolidine, equilibrium 3 was established within 45 min. From the data just mentioned, one can crudely estimate a rate constant for formation of **3b** of 5×10^{-6} M^{-1} s^{-1}.

Thus reaction rates are very much lower—by orders of magnitude—in the piperidine than in the pyrrolidine system. Because the rate constants are inconveniently low, we did not make

Table II. Reaction of *N*-Butyl-*N*-methyl-2,4-dinitro-1-naphthylamine with Butylmethylamine in Dimethyl Sulfoxide Solution[a]

expt	[BuNHMe], M	$10^4 k_\psi$, s^{-1}	A_∞	K_3, M^{-1}
16	0.153	0.62	0.380	0.38
17	0.360	1.15	0.506	0.23
18	0.459	1.60	0.533	
19	0.612	2.05	0.540	
20	0.765	2.35	0.550	

[a] Temperature: 25 °C; butylmethylammonium chloride 4.95 × 10^{-3} M, present in all experiments; $[1c]_0$ 2.47 × 10^{-5} M.

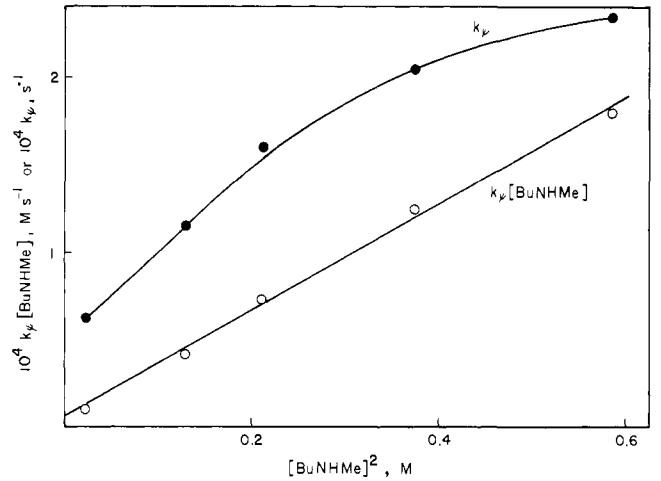


Figure 2. Reaction of **1c** with butylmethylamine. Rate data plotted according to eq 5 (open circles) and according to eq 6 (filled circles). Data from Table II.

kinetic or equilibrium measurements.

Butylmethylamine System. Upon addition of butylmethylamine, the spectrum of 2,4-dinitro-1-naphthylbutylmethylamine (**1c**) with λ_{max} at 425 nm changes gradually to a spectrum attributed to σ-complex **3c** with λ_{max} at 391 and 522 nm. With 0.875 M butylmethylamine, the latter spectrum is well defined after 4 h at 25 °C.

We determined the rates of attainment of equilibrium 3 at constant concentration of butylmethylammonium chloride and varying concentrations of the amine. Our data are displayed in Table II. They afford a linear plot of k_ψ[BuNHMe] against [BuNHMe]^2, according to eq 5, but a strongly curved plot of k_ψ against [BuNHMe]^2; see Figure 2. Thus the data are consistent with the mechanism of Scheme I but they do not conform to eq 6 and are not compatible with the one-step mechanism.

From the linear plot, after eq 5, k_1 (the slope) is evaluated as 3.1 ± 0.1 × 10^{-4} M^{-1} s^{-1}. From the intercept, k_{-1}/K_e is reckoned to be 9.5 ± 7.7 ± 10^{-4} s^{-1}. As the quotient of these two kinetic values, K_3 is calculated to be 0.33 M^{-1}, uncertain between 0.17 and 1.8.

The molar absorptivity coefficient (ϵ) for **3c** at 522 nm was evaluated as 2.38 × 10^4 from the absorbance of solutions of **1c** with excess butylmethylamine (0.6 to 1.1 M) after sufficient time to drive equilibrium 3 fully to the right. With use of this ϵ value, K_3 was calculated from the infinity absorbances from expts 16 and 17, as shown in Table II; the average K_3 so obtained is 0.30 M^{-1}.

Best Values of Constants. Assembled in Table III are the values for k_1, K_3, and the ratio k_{-1}/K_e that are in our judgement the optimum estimates of these values that can be drawn from the present work. Our data enable evaluation of these constants only for the pyrrolidine and butylmethylamine systems. For the piperidine system, we have been able to make only a crude estimate of the general magnitude of k_1.

Discussion

The most interesting result in Table III is the large difference in rate constants (k_1) for attacks by pyrrolidine and piperidine

Table III. Rate and Equilibrium Constants for the Reversible Reactions of Amines with the Corresponding *N*-(2,4-Dinitro-1-naphthylamines) in Dimethyl Sulfoxide at 25 °C

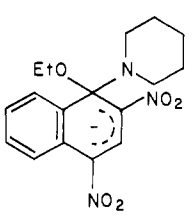
		amine		
reaction	parameter	pyrrolidine	piperidine	BuNHMe
1 → **2**	k_1, M^{-1} s^{-1}	2.1 × 10^{-3}	very low[a]	3.1 × 10^{-4}
1 ⇄ **3**	K_3, M^{-1}	0.56	*b*	0.3
3 → **1**	k_{-1}/K_e, s^{-1}	3.8 × 10^{-3}	*b*	9.5 × 10^{-4}

[a] Not determined quantitatively; crudely estimated as 5 × 10^{-6} M^{-1} s^{-1}. [b] Not determined.

at C-1 of **1a** and **1b**, respectively, to form σ-adducts **2a** and **2b**. Pyrrolidine is about 400 times more reactive. Inasmuch as these two amines demonstrate very similar rates of nucleophilic attack on numerous other aromatic sites,[2,3,6,12] the great difference in the present case is judged to arise from the influence of the amino group present in **1a** or **1b** rather than from the attacking amine molecule.

Whatever the problem is with the piperidine reaction, it does not appear to be shared by the reaction of butylmethylamine with **1c**. For this reaction, k_1 is about one-seventh as large as for the pyrrolidine reaction. That modest decrease can be attributed to steric factors in the attacking amine nucleophile. Such an assignment is precedented.[12]

The special characteristic of the piperidino group in **1b** that retards nucleophilic attack on C-1 is no doubt concerned with transition state stereoelectronic requirements which oblige conformations that can be attained only at the expense of steric compressions. Viewing conversion of **1b** to **2b** as having, in reverse, the same mechanism as the conversion of **2b** to **1b**, and the latter as akin to the expulsion of ethoxide ion from the σ-adduct intermediate (**5**) in the reaction of piperidine with 2,4-dinitro-1-



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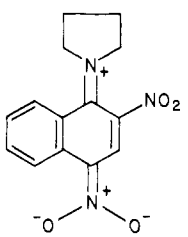

6

naphthyl ethyl ether,[3] one judges the slowness of attack of piperidine on **1b** to be due to the same factors that severely retard the general acid catalyzed conversion of **5** to **1b**. Ideas as to what those factors are are presented elsewhere.[3]

The rate constant (k_1) for attack of pyrrolidine on C-1 of **1a** is lower than on C-1 of 2,4-dinitro-1-naphthyl ethyl ether by a factor of 3 × 10^5. Probably the lesser reactivity of **1a** stems from mesomeric interaction between the amino nitrogen and the nitro groups, involving contributions from structures like **6**. Such mesomerism reduces the enthalpy of **1a** and therefore increases the enthalpy of activation to a transition state in which such interaction is much reduced.

In view of the comparative slowness even of the attack of pyrrolidine on **1a**, it is noteworthy that amine attack nevertheless occurs without catalysis by base. With respect to considerations of enthalpy, the participation of a base would no doubt help by removing a proton from the amine nitrogen as it bonded to carbon, but a severe entropic penalty would be entailed. Clearly the entropic disadvantage exceeds the enthalpic advantage.

Experimental Section

Materials. Dimethyl sulfoxide, pyrrolidine, piperidine, pyrrolidinium chloride, piperidinium chloride, **1a**, and **1b** were obtained or purified as described by Bunnett, Sekiguchi, and Smith.[3] Commercial butylmethylamine was shown by GLC (Versamide 10% on Chromosorb) to

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contain several minor impurities not easily removed by fractional distillation; it was purified by partial neutralization with HCl, removal of volatile material at reduced pressure, and recovery after basification much as described elsewhere[3] for the purification of piperidine; the distilled purified amine was shown by GLC to be of high purity. Butylmethylammonium chloride, mp 174–175 °C, was prepared by addition of 0.56 mol of HCl (as concentrated solution in water) to 0.64 mol of the amine, with stirring below 5 °C, cooling to −78 °C, collecting the crystalline salt, and recrystallizing from acetone. Anal. Calcd for $C_5H_{14}ClN$: Cl, 28.68. Found (by potentiometric titration): Cl, 28.64.

1-(Butylmethylamino)-2,4-dinitronaphthalene (**1c**) was prepared by the reaction of 1-chloro-2,4-dinitronaphthalene with a twofold excess of butylmethylamine in Me_2SO, and crystallized from ethanol; mp 69.5–70.5 °C. Anal. Calcd for $C_{15}H_{17}O_4N_3$: C, 59.40; H, 5.64; N, 13.85. Found: C, 59.60; H, 5.72; N, 13.91.

Spectral Characteristics and Changes. **1c** in Me_2SO shows a single broad absorption band with λ_{max} 425 nm, ϵ 7.80×10^3 M^{-1} cm^{-1}. Upon addition of butylmethylamine (0.875 M), the spectrum changes to one of two bands with λ_{max} 391 and 522 nm and ϵ respectively 1.45×10^4 and 2.41×10^4 M^{-1} cm^{-1}. The latter spectrum, attributed to **3c**, was essentially fully developed after 5 h at ambient temperature.

1a in Me_2SO shows a single absorption band with λ_{max} 439 nm, ϵ 1.90×10^4 M^{-1} cm^{-1}. Upon addition of pyrrolidine, the spectrum changes to one of two bands with λ_{max} 400 and 523 nm. When this spectrum due to **3a** is fully developed, ϵ at 523 nm is 1.85×10^4 M^{-1} cm^{-1} in the absence of pyrrolidinium chloride and 2.16×10^4 M^{-1} cm^{-1} in the presence of this salt (0.0104 M).

1b in Me_2SO shows a single broad absorption band with λ_{max} 422 nm, ϵ 7.8×10^3 M^{-1} cm^{-1}. Upon addition of piperidine, the spectrum slowly changes to one with two bands, λ_{max} 392 and 524 nm, attributed to **3b**, but the data were not suitable for definitive evaluation of ϵ for **3b**.

Kinetic Procedure. Reaction rates were determined by photometric observation of the absorbance at ca. 523 nm of reacting solutions. Determinations were made with use of a Gilford 2000 automated kinetics spectrophotometer with thermostated cell compartment. Good first-order behavior was observed in all cases. Rate constants were reckoned by the Guggenheim method. All kinetic runs were performed in duplicate; the rate constants reported are means of concordant values. The pseudo-first-order rate constant is symbolized k_ψ in Tables I and II.

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Acid-Catalyzed Hydrolyses of Acylpyrroles and Acylindoles. Noninvolvement of Protonated Substrates

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Abstract: The acid hydrolyses of *N*-(trifluoroacetyl)pyrrole, -indole, and -tetrahydrocarbazole and of *N*-acetylindole exhibit rate maxima in H_2SO_4 (20–40 wt %, $-H_0$ = 1–2.5) that are not due to extensive substrate protonation. The reactions have very large w and ϕ values, suggesting that there is a large difference in hydration of the initial and transition states. *N*-(Trifluoroacetyl)pyrrole is hydrated in water, and this evidence and that of hydrogen solvent isotope and salt and acid effects show that acid-catalyzed breakdown of a *gem*-diol is rate limiting. Rate maxima in acid hydrolyses of other weakly basic substrates can be explained in these terms.

Amides derived from aliphatic amines are weak bases with $pK_a \simeq -2$, and their acid hydrolyses are believed to involve a preequilibrium proton transfer followed by addition of water.[2,3]

The hydration of simple amides is energetically unfavorable[4] but should be assisted by protonation of the amide. The amino group of a first formed *gem*-diol should be readily protonated so that rapid carbon–nitrogen scission should be the preferred path of breakdown of a tetrahedral intermediate formed by addition of water to the conjugate acid of the amide. (The breakdown of amide acetals has formal similarities to the conversion of a tetrahedral intermediate into products.)[5-7] Several features of the acid hydrolysis of amides are readily understandable in these terms, for example, the rate maxima in moderately concentrated acid,[2,3] the changes in the solvent kinetic hydrogen isotope effect with increasing acid concentration,[8] and the absence of oxygen exchange between amide and water.[9] The relation between rate and acid concentration can be explained qualitatively in terms of an increasing protonation of the amide and a decreasing water activity as the acidity of the solution is increased.

N-(Trifluoroacetyl)pyrrole (**1**, **1a**) is extensively hydrated in water,[10] but its hydrolysis, although much faster than that of most other amides, can readily be followed over a wide range of pH.[11] The hydration is too fast to be followed by UV spectrophotometry, but it is slow on the NMR time scale and signals of both the amide and its hydrate are observed in aqueous acetonitrile.[10] These signals disappear as pyrrole is formed by hydrolysis. The hydrolysis is catalyzed by acids and in this paper we discuss some unusual kinetic features of this reaction.

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