

Correlation of the rates of solvolysis of the *N,N*-diphenylcarbamoylpyridinium ion

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ABSTRACT: Solvolyses of the *N,N*-diphenylcarbamoylpyridinium ion are subject to specific and/or general base catalysis, which can be eliminated by addition of perchloric acid or increased, especially in fluoroalcohol-containing solvents, by addition of pyridine. The uncatalyzed solvolyses in aqueous methanol and aqueous ethanol involve a weakly nucleophilically assisted ($l = 0.22$) heterolysis and the solvolyses in the pure alcohols are anomalously slow. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: *N,N*-diphenylcarbamoylpyridinium ion; solvolysis

INTRODUCTION

We have recently reported the influence of the solvent upon the specific rates of solvolysis of several *N,N*-disubstituted carbamoyl chlorides.^{1–3} Treatments in terms of the extended (two-term) Grunwald–Winstein equation^{4,5} indicate an appreciable variation in the

$$\log (k/k_0)_{\text{RX}} = lN_{\text{T}} + mY_{\text{Cl}} + c \quad (1)$$

sensitivity (l) towards changes in solvent nucleophilicity (N_{T}),⁴ including values of 0.23 for solvolyses of *N,N*-diphenylcarbamoyl chloride (**1**)¹ and 0.61 for solvolyses of *N,N*-dimethylcarbamoyl chloride (**2**).² Carbamoyl chloride solvolyses have usually been considered to be unimolecular ($S_{\text{N}}1$) in character^{6–9} and, consistent with these earlier studies, the appreciable l values were considered to involve a nucleophilic solvation of the developing acylium ion. Kim *et al.*¹⁰ have proposed, however, that **2** and other *N,N*-dialkylcarbamoyl chlorides solvolyse by an $S_{\text{N}}2$ mechanism but **1** by an $S_{\text{N}}1$ mechanism. As regards the other terms in Eqn (1), k and k_0 are the specific rates of solvolysis of RX in the solvent under consideration and in the standard solvent (80% ethanol), respectively, m is the sensitivity towards

changes in solvent ionizing power (Y_{Cl})⁵ values and c is a constant (residual) term.

For studies of solvolyses with a relatively low degree of nucleophilic participation by the solvent, it is frequently helpful to introduce an initially positively charged leaving group which leaves as a neutral molecule.^{4,11} In particular, solvolyses of the 1-adamantyl-dimethylsulfonium ion in a wide range of commonly used solvolytic solvents show specific rates of solvolysis almost independent of solvent composition and a Y^+ scale, based on the specific rate values, hardly varies from zero.¹² Accordingly, solvent nucleophilicity scales based on solvolyses of $\text{R}-\text{X}^+$ substrates can be set up according the equation

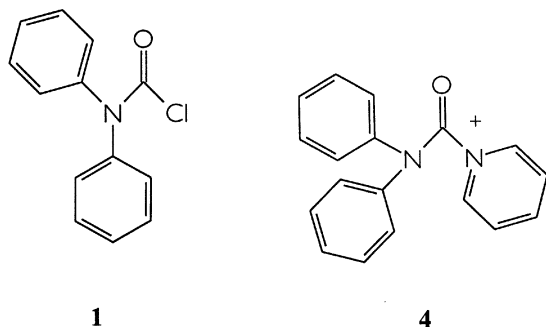
$$\log (k/k_0)_{\text{R}-\text{X}^+} = lN_{\text{T}} + c \quad (2)$$

with l set at unity and c at zero for the standard substrate.^{13,14}

Pyridinium ion substrates of this charge type, with a pyridine molecule leaving group, can be readily produced by the reaction of a carbamoyl chloride with pyridine.¹⁵ Johnson and Rumon¹⁶ have presented evidence indicating that the hydrolysis of the *N,N*-dimethylcarbamoylpyridinium ion (**3**) in pure water involves a direct nucleophilic attack by the solvent, without prior acylium ion formation. Similarly, it has been reported^{8a} that, in water, the *N,N*-diphenylcarbamoylpyridinium ion (**4**) is very sensitive to attack by nucleophiles. In view of the above observations, it is of interest to see whether the

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solvolyses of **4** show a larger sensitivity towards changes in solvent nucleophilicity than the rather low value of 0.23 associated with the solvolyses of **1**.



It has been proposed¹⁷ that a pyridine molecule leaving group is considerably more solvated at the transition state than a leaving Me_2S molecule. However, a limited amount of data for solvolyses of the 1-adamantylpyridinium ion¹⁸ give relative rates at 190 °C in acetic acid, water, and 2,2,2-trifluoroethanol (TFE) of 1:1.4:2.2, essentially identical with the ratios for the solvolyses of the 1-adamantyltrimethylsulfonium ion¹² at 70.4 °C of 1:1.7:2.6. Accordingly, we have continued to assume that the mY^+ term can be neglected⁴ and that analyses of the solvolyses of *N*-substituted pyridinium ions can be carried out in terms of Eqn (2).

RESULTS AND DISCUSSION

The specific rates of solvolysis of **4** in ethanol and methanol, in several of their mixtures with water and in 100% water are presented in Table 1. Usually the counterion is chloride but in a few instances it is trifluoromethanesulfonate. The specific rates were found to be essentially independent of the identity of the anion. For **4** in 100% water, the ratio of the second-order rate coefficient for reaction with hydroxide ion relative to the first-order rate coefficient for reaction with water molecules has been reported^{8a} as $1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1}$ (earlier, in Ref.^{8a}, a value for the second-order rate coefficient one order of magnitude lower is presented; if this value were correct, the value for the ratio is $1.7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$). Values of this magnitude lead to the possibility of a contribution involving attack by the conjugate base of a protic solvent even in neutral solution Battye *et al.*¹⁹ found, however, that in hydrolysis of the methoxycarbonylpyridinium ion, the second-order rate coefficient for OH^- attack was negligible at pH values of less than 5.4. Similarly, we find only a modest retardation of the overall specific rate on addition of $5.7 \times 10^{-3} \text{ mol dm}^{-3}$ perchloric acid to the solvolyses of **4**, also reported in Table 1. In accord with this observation, addition of 0.01 mol dm^{-3} pyridine to the solvolysis in 50% ethanol led to only an 18% increase in specific rate. Since nucleophilic substitution by pyridine would be symme-

Table 1. Specific rates of solvolysis of the *N,N*-diphenylcarbamoylpyridinium ion^a at 62.5 °C in aqueous ethanol and aqueous methanol solvents and solvent nucleophilicity values

Solvent ^b	Anion	$10^5 k(\text{s}^{-1})^c$	$10^5 k^A(\text{s}^{-1})^{c,d}$	N_T^e
100% EtOH	Cl^-	3.09 ± 0.11		+0.37
	OTf^-	3.42 ± 0.16		
90% EtOH	Cl^-	25.9 ± 0.9	23.0 ± 0.7	+0.16
80% EtOH	Cl^-	28.4 ± 0.5	25.9 ± 1.9	0.00
	OTf^-	27.5 ± 1.1		
70% EtOH	Cl^-	26.1 ± 0.8	24.3 ± 1.4	−0.20
60% EtOH	Cl^-	20.5 ± 1.1	19.8 ± 1.3	−0.39
50% EtOH	Cl^-	20.1 ± 0.9^f	19.3 ± 1.0	−0.58
	OTf^-	20.3 ± 0.5		
40% EtOH	Cl^-	17.2 ± 0.4	16.0 ± 1.2	−0.74
100% H ₂ O	Cl^-	14.5 ± 1.3	13.1 ± 0.8	−1.38
	OTf^-	13.9 ± 0.9		
100% MeOH	Cl^-	6.66 ± 0.16		+0.17
90% MeOH	Cl^-	24.0 ± 0.6	22.0 ± 1.8	−0.01
80% MeOH	Cl^-	30.0 ± 0.9	29.0 ± 1.4	−0.06
60% MeOH	Cl^-	26.9 ± 1.0	26.3 ± 1.7	−0.54
40% MeOH	Cl^-	21.2 ± 1.0	20.3 ± 1.7	−0.87
20% MeOH	Cl^-	14.9 ± 0.8	14.7 ± 0.8	−1.23

^a Substrate concentration 0.0015–0.0030 mol dm^{-3} .

^b Concentration on a v/v basis at 25.0 °C.

^c With associated standard deviation.

^d In the presence of $5.70 \times 10^{-3} \text{ M HClO}_4$.

^e From Ref.⁴.

^f In the presence of 0.0098 M pyridine, a value of $23.8 (\pm 0.7) \times 10^{-5} \text{ s}^{-1}$ was obtained.

Table 2. Specific rates of solvolysis of the *N,N*-diphenylcarbamoilpyridinium ion^a at 62.5 °C in 2,2,2-trifluoroethanol (TFE) and aqueous TFE Solvents.

Solvent ^b	Anion	10 ³ HClO ₄ ^c	10 ³ C ₅ H ₅ N ^c	10 ⁵ k(s ⁻¹) ^d
100% TFE	Cl ⁻			3.89 ± 0.27 ^e
	Cl ⁻		6.1	134 ± 12 ^e
	Cl ⁻		12.3	178 ± 11 ^{e,f}
	Cl ⁻		24.6	257 ± 9 ^e
70% TFE	Cl ⁻	5.72		20.1 ± 1.9 ^{e,g}
	Cl ⁻			1.65 ± 0.18 ^h
50% TFE	Cl ⁻	5.72		38.7 ± 1.3 ^{e,i}
	Cl ⁻			30.3 ± 0.3 ^{e,j}
	OTf ⁻			33.5 ± 1.6 ^{e,k}
	Cl ⁻		15.4	567 ± 14 ^{e,f}
	Cl ⁻		15.8	586 ± 10 ^{e,l}
	OTf ⁻		15.8	498 ± 13 ^{e,f}
	Cl ⁻		31.6	867 ± 52 ^e
	OTf ⁻		31.6	850 ± 21 ^e
	Cl ⁻			49.3 ± 5.9 ^{e,m}
	Cl ⁻			9.37 ± 0.31 ^h
	Cl ⁻			5.21 ± 0.13 ^h
	OTf ⁻			4.45 ± 0.18 ^h
	Cl ⁻			4.39 ± 0.14 ^h
	Cl ⁻			3.62 ± 0.30 ^h
	OTf ⁻			2.75 ± 0.12 ^h
	Cl ⁻			3.44 ± 0.18 ^h
	Cl ⁻			2.90 ± 0.18 ^h
	Cl ⁻			3.26 ± 0.08 ^h

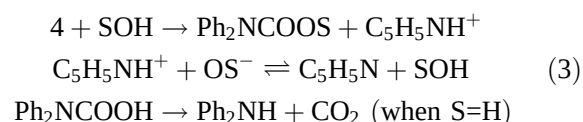
^a Substrate concentration 0.003–0.008 mol dm⁻³.^b Mixed solvents on a w/w basis; solvent nucleophilicity (*N_T*) values –3.93 for 100% TFE, –1.98 for 70% TFE and –1.73 for 50% TFE (from Ref. 4).^c In mol dm⁻³.^d Unless indicated otherwise, runs were performed in duplicate and average initial values or mean values are presented, accompanied by the standard deviation.^e Initial value.^f Single determination.^g Integrated value of 12.7 ± 0.3 at 50% reaction.^h Mean value.ⁱ Integrated value of 28.7 ± 1.1 at 50% reaction.^j Freshly prepared (and different from above) batch of substrate.^k Integrated value of 18.9 ± 0.6 at 52% reaction.^l Integrated value of 320 ± 3 at 51% reaction.^m In the presence of 0.0033 MNEt₄Cl, with integrated value of 31.6 ± 1.1 at 48% reaction.

trical, nucleophilic catalysis cannot operate and, assuming it is not a medium effect, this increase is to be expected to arise from a combination of specific and general base catalysis; it is established^{16,19,20} that pyridines can exert a moderate to weak general base catalysis in solvolyses of acylpyridinium ions.

Inspection of the data of Table 1 shows, consistent with other studies^{12,21} with little or no nucleophilic participation by the solvent, very little variation of specific rate for water and the aqueous alcohol solvents. In addition, considerably lower rates are observed in the pure alcohols, despite these being the most nucleophilic of the solvents listed. This behavior strongly suggests that **4** does not solvolyze by the direct nucleophilic attack mechanism proposed¹⁶ for **3**.

The identity of the anion was also found to be unimportant in runs carried out in trifluoroethanol (TFE) and TFE–H₂O mixtures (Table 2). An appreciable catalytic effect was presumably due to specific base

catalysis by the conjugate bases of the solvents and the addition of 5.7 × 10⁻³ mol dm⁻³ HClO₄ now led to a 10–13-fold reduction in specific rate for solvolyses in 70 and 50% TFE. In the absence of HClO₄, the specific rates decreased with extent of reaction and initial values are reported; a reduction in conjugate base concentration is expected as the pyridinium ion is produced during the solvolyses:



Addition of pyridine was found to lead to very large increases in rate for both 100 and 50% TFE solvolysis. While these observations indicate direct attack on **4** within the catalyzed pathways, it is possible that the underlying non-catalyzed solvolyses could be dominantly unimolecular (*S_N* 1) in character. Consistent with

the essentially identical rates in the presence of either chloride or trifluoromethanesulfonate as counterion and indicative of only a modest salt effect, addition to the solvolysis in 50% TFE of a concentration of tetraethylammonium chloride equal to that of the substrate led to only a 27% increase in rate.

A correlation, using Eqn (2), of the specific rates of solvolysis in water and in the nine aqueous ethanol and aqueous methanol solvents containing 20% or more water, for the runs in the presence of HClO_4 (Table 1), leads to values for l of 0.22 ± 0.04 , for the residual (constant) term c of 0.03 ± 0.05 and for the correlation coefficient of 0.887. The low value for the correlation coefficient is in part due to the limited range of N_T values (1.38 units) for these solvents. The l value is essentially identical with that observed for solvolyses of **1**, suggesting a similarity in the mechanism. The specific rate values which can then be estimated [using Eqn (2)] for ethanol and methanol are 11 and 4.5 times those actually observed (Table 1) and it is possible that the lower experimental values could be associated with the need to proceed to the solvent-separated ion–molecule pair, so as to prevent internal return. In this regard, water would be more efficient than a bulkier and less electrophilic alcohol.²² The need to consider the separation is supported by the conclusion²³ that, in the borderline solvolyses of *sec*-alkylpyridinium ions, a rate-determining $\text{S}_{\text{N}}1$ cleavage in TFE changes to a rate-determining ion–molecule pair dissociation in 1,1,1,3,3,3-hexafluoropropan-2-ol.

EXPERIMENTAL

N,N-Diphenylcarbamoylpyridinium chloride was prepared from pyridine and *N,N*-Diphenylcarbamoyl chloride (Aldrich, 98%) as described previously¹⁵; m.p. 108–109 °C (lit.^{8a} m.p. 107.5–108.5 °C). The trifluoromethanesulfonate salt of **4** was prepared as an oil by treatment of a solution of the chloride salt in acetonitrile with an equivalent amount of silver trifluoromethanesulfonate, followed by filtration and removal of the solvent under reduced pressure. The purification of the solvents and the kinetic methods were as described previously.¹ When required, initial values for the specific rates were obtained from approximately linear plots of integrated values against extent of reaction. A standardized concentrated

aqueous solution of perchloric acid was appropriately diluted for its addition to runs in aqueous alcohol solvents.

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