Reactions of *N*-Heteroaromatic Bases with Nitrous Acid. Part 9.[1] Kinetics of the Nitrosation of 1-Methyl-3- and 1-Methyl-4-methylaminopyridinium Perchlorate in Aqueous Perchloric Acid and ^{13}C Nuclear Magnetic Resonance Spectra of 1- Methyl-4-alkylamino-substituted Pyridinium Ions

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The nitrosation of 1-methyl-3-methylaminopyridinium perchlorate in 0.001—0.50M-perchloric acid and of 1-methyl-4-methylaminopyridinium perchlorate in 0.10—4.00M-perchloric acid is of first order in both the amine salt and nitrous acid. The rate coefficients increase with an increase in the concentration of perchloric acid and sodium perchlorate. At constant ionic strength the rate coefficients show a rectilinear dependence on $[H^+]$ and on the h_0 parameter of the medium. The non-equivalence of the two α- and the two β-carbons observed in the ^{13}C n.m.r. spectra of 1-methyl-4-methylamino- and 1-methyl-4-ethylamino-pyridinium perchlorate, but not in that of 1-methyl-4-dimethylaminopyridinium perchlorate, and the values of the energy barrier of rotation determined for the former amines indicate that the exocyclic carbon–nitrogen bond has substantial double-bond character. The present results are in accord with the conclusion that the nitrosation of the protonated β-aminopyridines involves an interaction between the nitrosating species and the exocyclic amino group, whilst the nitrosation of the protonated γ-aminopyridines involves an association of the nitrosating species with the π-electrons of the pyridinium nucleus.

Nitrosation of 2-, 3-, and 4-methylaminopyridine in aqueous perchloric acid was shown to proceed mainly by the interaction of the nitrous acidium ion with the monoprotonated form of these amines and was assumed to be the rate-determining stage in the diazotisation of the corresponding primary amines.[2,3] It was also concluded that the nitrosation and diazotisation of the free form of the α-, β-, and γ-aminopyridines and the protonated form of the α- and γ-aminopyridines involve an initial interaction between the nitrosating species and the heteroaromatic nucleus of the amine molecule, whilst the nitrosation and diazotisation of the protonated form of the β-aminopyridines involve direct interaction between the nitrosating species and the exocyclic amino group.[2,3] Furthermore, a study of the kinetics of the diazotisation of 1-methyl- and 1-methoxy-4-aminopyridinium perchlorate in aqueous perchloric acid provided evidence that the diazotisation of the γ-aminopyridines involves the protonated form of these amines.[1]

This paper presents a study of the kinetics of the nitrosation of 1-methyl-3- and 1-methyl-4-methylaminopyridinium perchlorate in aqueous perchloric acid and a study of the ^{13}C n.m.r. spectra of 1-methyl-4-methylamino-, 1-methyl-4-ethylamino-, and 1-methyl-4-dimethylamino-pyridinium ion. The results are in good agreement with the mechanisms proposed earlier for the nitrosation of the secondary and the diazotisation of the primary α-, β-, and γ-aminopyridines[1–3] in the protonated form and throw more light on the nature of these reactions.

Results and Discussion

The kinetics of the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate were examined in 0.001—0.50M-perchloric acid. As in the case of the nitrosation of 3-methylaminopyridine[2b] the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate is not reversible since the *N*-nitroso derivatives of these amines do not hydrolyse under the present experimental conditions. Even in 5.0M-perchloric acid solutions 3-*N*-nitroso- and 1-methyl-3-*N*-nitroso-methylaminopyridinium perchlorate are <5% hydrolysed at 2 °C in 15 days.

The present results show that the reaction follows rate expression (1). Thus the stoicheiometric second-order rate

$$\text{Rate} = \bar{k}_2[\text{1-Me-3-MeNH-pyridinium perchlorate}][\text{Nitrous acid}] \quad (1)$$

coefficients ($\bar{k}_2$) obtained by using rate expression (1) and various initial concentrations of the reactants remained constant at a given acidity for at least 80% reaction (Tables 1 and 6). Moreover, the validity of rate expression (1) was confirmed by the observation that for a number of acidities a two-fold increase in the concentration of either reactant caused a two-fold increase in the initial rate of the reaction, whilst a two-fold increase in the concentration of both reactants caused a four-fold increase.

The values of $\bar{k}_2$ for the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate increase with an increase in the acidity of the medium (Table 1) and a plot of the values of log $\bar{k}_2$ against the values of pH of the reaction mixtures is a straight line with a slope of 1.22. This result is similar to those of the nitrosation of 3-methylaminopyridine and the diazotisation of 3-aminopyridine for which the straight lines obtained have slopes of 1.24 and 1.25, respectively.[2b]

The values of $\bar{k}_2$ (Table 2) increase with an increase in the ionic strength of the medium (μ) in 0.01M-perchloric acid containing various concentrations of sodium perchlorate (up to 0.5M) and a plot of log $\bar{k}_2$ against $\sqrt{\mu}$ gave a straight line with a slope of 1.12. This result is similar to those of the nitrosation of 3-methylaminopyridine[2b] (slope 1.06) and the diazotisation of 3-aminopyridine[2b] (slope 0.91) and it shows that the reaction involves charged species.[4a]

In solutions kept at a constant ionic strength of 0.5 by the addition of sodium perchlorate the dependence of the values of $\bar{k}_2$ on the acidity of the medium is rectilinear, *i.e.* $\bar{k}_2 \propto [H^+]$, since a plot of log $\bar{k}_2$ against −pH (Table 2) is a straight line with a slope of 1.02. This rectilinear dependence of $\bar{k}_2$ on $[H^+]$ is

Table 1. Nitrosation of 1-methyl-3-methylaminopyridinium perchlorate (amine salt = A.S.) at 2.0 °C; dependence of $\bar{k}_2$ [equation (1)] on the concentration of an excess of perchloric acid and constancy at a given acidity

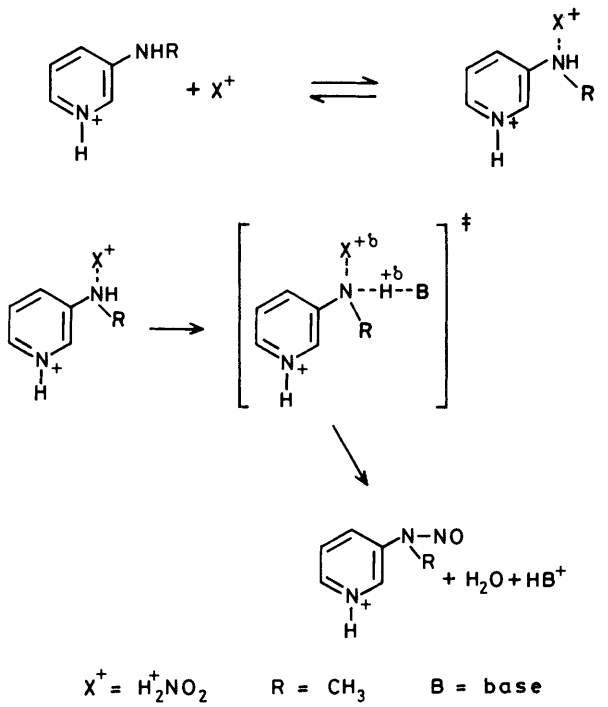
$[HClO_4]$/M	pH*	10^4 [A.S.]/M	$10^4[HNO_2]$/M	k_2/l mol^{-1} s^{-1}	Mean $\bar{k}_2$/l mol^{-1} s^{-1}
0.001	2.96				0.033 ± 0.004
0.005	2.41	5.0	5.0	0.168	0.167 ± 0.003
		5.0	10.0	0.170	
		10.0	5.0	0.167	
		10.0	10.0	0.162	
0.010	2.12				0.354 ± 0.015
0.050	1.35				2.53 ± 0.09
0.100	1.16				6.81 ± 0.27
0.250	0.60†				25.2 ± 1.8
0.500	0.20†				84.4 ± 4.5

* Values determined by pH meter. † H_0 values. *Cf.* ref. 2.

Table 2. Nitrosation of 1-methyl-3-methylaminopyridinium perchlorate at 2.0 °C; dependence of $\bar{k}_2$ [equation (1)] on the concentration of perchloric acid at constant ionic strength of 0.50 and on the concentration of sodium perchlorate in 0.01M-perchloric acid

$[HClO_4]$/M	pH*	$\bar{k}_2$/l mol^{-1} s^{-1}	$[NaClO_4]$/M	$\bar{k}_2$/l mol^{-1} s^{-1}
0.001	2.91	0.153 ± 0.008		
0.005	2.22	0.898 ± 0.081	0.01	0.440 ± 0.004
0.010	1.91	1.89 ± 0.14	0.02	0.486 ± 0.006
0.050	1.22	9.45 ± 0.35	0.05	0.591 ± 0.009
0.100	0.93	18.9 ± 0.2	0.075	0.633 ± 0.003
0.250	0.50†	54.2 ± 5.3	0.10	0.672 ± 0.010
0.500	0.20†	84.5 ± 4.5	0.15	0.808 ± 0.005
			0.20	0.944 ± 0.013
			0.49	1.89 ± 0.014

* Values determined by pH meter. † H_0 values. *Cf.* ref. 2.



Scheme 1.

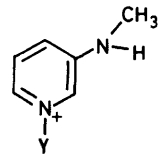
similar to that observed for the nitrosation of 3-methylaminopyridine[2b] (slope 1.0) and the diazotisation of 3-aminopyridine[2b] (slope 1.02). Thus rate expression (1) can be expanded to (2) since 1-methyl-3-methylaminopyridinium ion, like 3-amino- and 3-methylamino-pyridinium ion,[2b] must not be protonated under the present experimental conditions.

$$\text{Rate} = k_3[\text{1-Me-3-MeNH-pyridinium perchlorate}][HNO_2][H^+] \quad (2)$$

Rate expression (2) is similar to that of the nitrosation and the diazotisation of the more basic secondary and primary β-aminopyridines respectively[2b] and provides evidence that the monoprotonated form of the β-aminopyridines are involved in these reactions and that the nitrosation step is the rate-determining stage in the diazotisation of the primary β-aminopyridines.

The value of k_3 for the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate, which is 134 l^2 mol^{-2} s^{-1}, is in good agreement with the values of k_3 for the nitrosation of the protonated β-methylaminopyridines. It has been suggested[2b] that these reactions proceed by a direct attack of the nitrosating species (nitrous acidium ion) on the exocyclic amino nitrogen and migration of an amino proton to the medium, as shown in Scheme 1.

A comparison of the values of k_3 shows a decreasing order of reactivity from 3-methylaminopyridinium ion (**Ia**) (k_3 171 l^2 mol^{-2} s^{-1})[2a] to 1-hydroxy-3-methylaminopyridinium ion (**Ib**) (k_3 160 l^2 mol^{-2} s^{-1})[2a] and last to 1-methyl-3-methylaminopyridinium ion (**Ic**) (k_3 134 l^2 mol^{-2} s^{-1}). This order of reactivity



(**I**)

a; Y = H

b; Y = OH

c; Y = CH_3

may be due to a combination of a change in the solvation[5] of the substituted pyridinium ion incurred by the introduction of a group other than hydrogen on the ring nitrogen and the inductive effect of that group.

It seems, therefore, that the rate of the nitrosation of the protonated β-aminopyridines is affected by the ease of abstraction of the proton by the medium. Since the differences in the acidities of the amino hydrogen for these molecules are not

Table 3. Nitrosation of 1-methyl-4-methylaminopyridinium perchlorate (A.S.) at 2.0 °C; dependence of $\bar{k}_2$ [equation (3)] on the concentration of an excess of perchloric acid and constancy at a given acidity

$[HClO_4]$/M	H_0*	10^4[A.S.]/M	$10^4[HNO_2]$/M	$10^2\bar{k}_2$/l mol^{-1} s^{-1}	Mean $10^2\bar{k}_2$/l mol^{-1} s^{-1}
0.10	1.02				0.519 ± 0.005
0.20	0.67				1.42 ± 0.05
0.50	0.20				6.67 ± 0.06
1.00	−0.22				29.5 ± 0.8
2.00	−0.78	0.125	1.25	178	177 ± 8
		0.250	1.25	168	
		0.125	2.50	176	
		0.250	2.50	187	
3.00	−1.23				1 013 ± 25
4.00	−1.72				4 057 ± 120

* *Cf.* ref. 3.

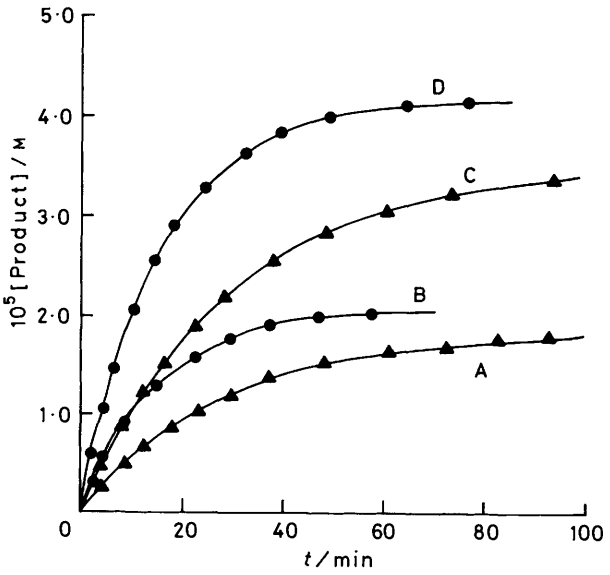
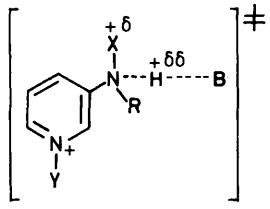


Figure. Nitrosation of 1-methyl-4-methylaminopyridinium perchlorate (amine salt) in 2.0M-perchloric acid and at 2 °C; variation of reaction rate with initial concentration of amine salt and nitrous acid; A, 2.5×10^{-5} and 2.5×10^{-4}M; B, 2.5×10^{-5} and 5.0×10^{-4}M; C, 5.0×10^{-5} and 2.5×10^{-4}M; D, 5.0×10^{-5} and 5.0×10^{-4}M. Initial rates: A, 5.5×10^{-7}; B, 10.6×10^{-7}; C, 10.6×10^{-7}; D, 23.0×10^{-7} mol l^{-1} min^{-1}



(II)

X = $H_2^+NO_2$

Y = H, OH, CH_3

expected to be substantial, the differences in the observed rates of these reactions are expected to be small. Thus the transition state could be better represented as structure (**II**). However, it is also likely that the small differences in the k_3 values could be due to the acidity dependence of the activity coefficients for the pyridinium ion substrates.

The kinetics of the nitrosation of 1-methyl-4-methylaminopyridinium perchlorate were examined in 0.10—4.00M-perchloric acid. As in the case of the nitrosation of 2- and 4-methylaminopyridine under similar conditions[2a] the nitrosation of 1-methyl-4-methylaminopyridinium perchlorate is reversible because the nitrosamine formed is denitrosated. Thus the values of the stoicheiometric second-order rate coefficients ($\bar{k}_2$) obtained by using rate expression (3) and various initial

Rate =
$\bar{k}_2$[1-Me-4-MeNH-pyridinium perchlorate][Nitrous acid] −
$\bar{k}_1$[1-Me-4-MeN(NO)-pyridinium perchlorate] (3)

concentrations of reactants were satisfactorily constant (Table 3) at a given acidity for at least 70% reaction (Table 6). Moreover, rate expression (3) was reduced to (4) when only the initial rates of the reaction were considered. Thus a two-fold

Rate = $\bar{k}_2$[1-Me-4-MeNH-pyridinium perchlorate]
[Nitrous acid] (4)

increase in the concentration of either reactant caused a two-fold increase in the initial rate of the reaction, whilst a two-fold increase in the concentration of both reactants caused a four-fold increase (Figure).

A plot of the values of log $\bar{k}_2$ against the values of H_0 of the acid solutions (Table 3) is a straight line with a slope of 1.45. This result is similar to those of the nitrosation of 2- and 4-methylaminopyridine[2a] (slopes 1.18 and 1.37, respectively). Moreover the values of $\bar{k}_2$ (Table 4) increase with an increase in the ionic strength of the medium (μ) in 1.0M-perchloric acid containing various concentrations of sodium perchlorate (up to 3.0M). Thus a plot of log $\bar{k}_2$ against μ is a straight line with a slope of 0.48, which is reduced to 0.26 when the $\bar{k}_2$ values are corrected to refer to a common value of h_0 corresponding to 1.0M-perchloric acid. These results are similar to those of the nitrosation of 2- and 4-methylaminopyridine[2a] and they show that the reaction involves charged species.[4a]

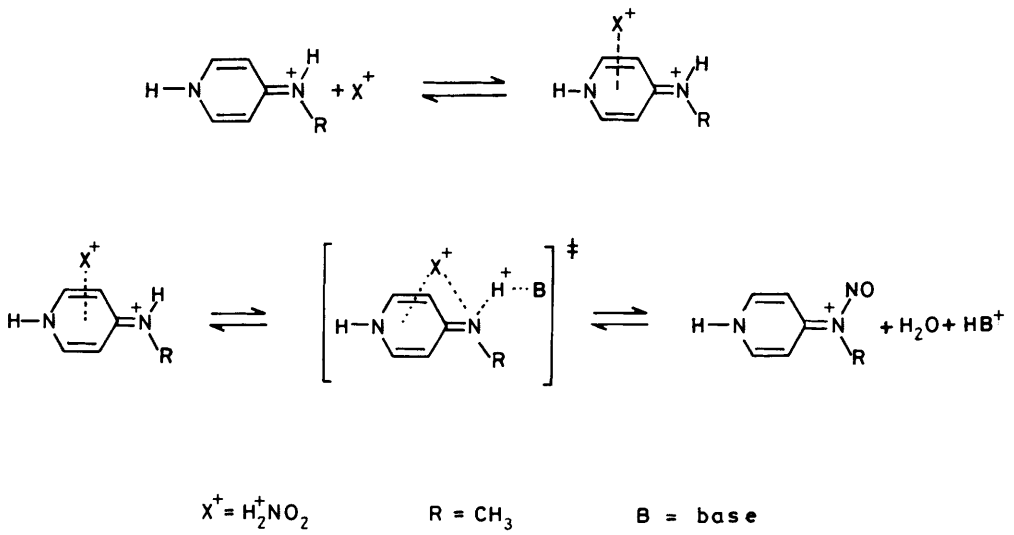
In solutions kept at constant ionic strength of 3.0 by the addition of sodium perchlorate the values of $\bar{k}_2$ (Table 4) increase with an increase in the acidity of the medium and a plot of log $\bar{k}_2$ against H_0 is a straight line with a slope of 0.93 thus indicating that this dependence is rectilinear, *i.e.* $\bar{k}_2 \propto h_0$. This result is similar to those found for the nitrosation of 2- and 4-methylaminopyridine for which the slopes of the straight lines were found to be 0.90 and 0.93, respectively.[2a] Moreover, this rectilinear dependence on the acidity of the medium justifies the corrections that are made on the values of $\bar{k}_2$, when examining the medium effect of perchloric acid, so that they refer to a common value of H_0 of the acid solutions.

The above results indicate that rate expression (4) can be

Table 4. Nitrosation of 1-methyl-4-methylaminopyridinium perchlorate at 2.0 °C; dependence of $\bar{k}_2$ [equation (3)] on the concentration of perchloric acid at constant ionic strength of 3.0 and on the concentration of sodium perchlorate in 1.00M-perchloric acid

$[HClO_4]$/M	H_0^*	$\bar{k}_2$/l mol^{-1} s^{-1}	$[NaClO_4]$/M	h_0^*	$\bar{k}_2$/l mol^{-1} s^{-1}
0.05	0.66	0.146 ± 0.002	0.00	1.78	0.295 ± 0.008
0.10	0.34	0.296 ± 0.016	0.50	2.42	0.579 ± 0.023
0.25	−0.09	0.836 ± 0.018	1.00	3.15	1.04 ± 0.04
0.50	−0.40	1.60 ± 0.04	1.50	4.01	2.02 ± 0.18
1.00	−0.71	3.19 ± 0.08	2.00	5.12	3.31 ± 0.27
1.50	−0.90	4.88 ± 0.13	2.50	7.02	5.16 ± 0.14
2.00	−1.04	6.47 ± 0.21	3.00	9.00	8.23 ± 0.37
2.50	−1.17	8.42 ± 0.29			
3.00	−1.23	10.1 ± 0.3			

* *Cf.* ref. 3.



Scheme 2.

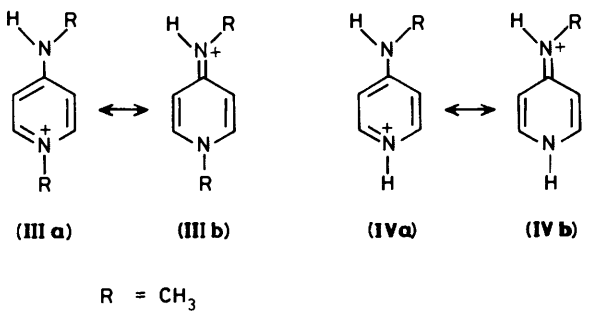
expanded to (5) since 1-methyl-4-methylaminopyridinium ion,

$$\text{Rate} = k_3[\text{1-Me-4-MeNH-pyridinium ion}][HNO_2]h_0 \quad (5)$$

like 4-methylaminopyridinium ion,[2a] is expected to be present entirely as the monocation under the present experimental conditions. This expression is similar to that of the nitrosation of 2- and 4-methylaminopyridinium ion[2a] and provides direct evidence that these reactions proceed by an interaction of the protonated amines with the nitrosating species, and that the presence of an easily removable proton on the ring nitrogen is not a prerequisite for reaction to occur. Moreover the presence of a methyl in the 1-position does not alter the mechanism of the reaction.

The above results confirm that the rate-determining step of the diazotisation of 1-methoxy- and 1-methyl-4-aminopyridinium ion[1] and of the diazotisation of the protonated 2- and 4-aminopyridine,[3] is the nitrosation of these amines and that these reactions proceed by an initial association of the nitrosating species with the *N*-heteroaromatic nucleus of the substituted aminopyridinium ions[2a] (Scheme 2).

The value of k_3 for the nitrosation of 1-methyl-4-methylaminopyridinium perchlorate (**III**) was found to be 0.592 l^2 mol^{-2} s^{-1}. This is higher than the value of k_3 (0.378 l^2 mol^{-2} s^{-1}) determined[2a] for the nitrosation of 4-methylaminopyridinium ion (**IV**). This increase in the rate is most probably due to the electronic contribution of the methyl group (+*I* effect) to the *N*-heteroaromatic nucleus thus enhancing its initial association with the nitrosating species (Scheme 2). The introduction of a

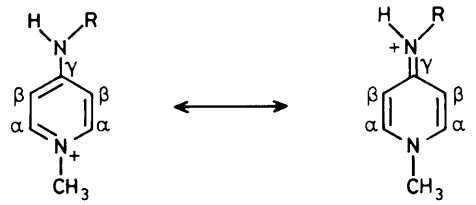


methyl group on the ring nitrogen most probably disrupts its solvation[5] by the water molecules thus making it more positively charged. This alone should retard the association of the π-electron system of the nucleus with the nitrosating species. However, it seems that this effect is more than counterbalanced by the +*I* effect of the methyl group resulting in a small increase (1.6 times) in the reaction rate. It is also likely that the small change in the rate could be due to the acidity dependence of the activity coefficients for the pyridinium ion substrates.

Additional support for the conclusions which were drawn on the mechanisms of the reactions involving the protonated 2- and 4-aminopyridines[1,2a,3] comes from a study of the ^{13}C n.m.r. spectra of 1-methyl-4-methylamino-, 1-methyl-4-ethylamino-, and 1-methyl-4-dimethylamino-pyridinium perchlorate and, in the case of the first two amines, the determination of the

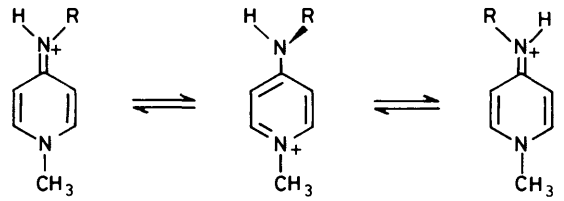
energy barrier of rotation around the exocyclic carbon–nitrogen bond.

As in the case of the protonated 4-aminopyridine,[3a,6] the aminopyridinium salts under discussion would exist in a resonance hydrid represented by structures (**Va**) and (**Vb**).



(**Va**) (**Vb**)

The ^{13}C n.m.r. spectra (Table 5) in the case of the 1-methyl-4-methylaminopyridinium ion show that the two α-carbons resonate at δ 143.66 and 146.04 p.p.m. and the two β-carbons resonate at δ 106.60 and 111.85 p.p.m., respectively, whilst in the case of the 1-methyl-4-ethylaminopyridinium ion they show that the two α-carbons resonate at δ 146.07 and 143.89 p.p.m. and the two β-carbons resonate at δ 112.00 and 106.76 p.p.m., respectively. Therefore at ordinary temperatures the above amines exist as structure (**VIa** or **c**) and the bond between the γ-carbon and the exocyclic amino nitrogen has substantial double-bond character. Thus the two α- and the two β-carbons are non-equivalent and isomerisation between structures (**VIa** and **b**) is restricted.



(**VIa**) (**VIb**) (**VIc**)

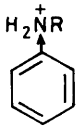
It should also be noted that the ^{13}C n.m.r. spectrum of 1-methyl-4-dimethylaminopyridinium perchlorate shows single absorptions for the two α- and the two β-carbons at δ 144.32 and 109.04 p.p.m., respectively.

The temperature dependence of the n.m.r. spectra of 1-methyl-4-methylamino- and 1-methyl-4-ethylamino-pyridinium perchlorate was studied between 33 and 140 °C and the coalescence temperatures of the two signals of the α- and two signals of the β-carbons were determined and the energy barrier of rotation (ΔG^*) around the exocyclic carbon–nitrogen bonds were calculated using standard methods[7] (Table 5).

The values of ΔG^* of 17.6 and 17.3 kcal mol^{-1} for 1-methyl-4-methylamino- and 1-methyl-4-ethylamino-pyridinium perchlorate, respectively, are somewhat lower than the predicted value of *ca.* 21 kcal mol^{-1} for the energy barrier of rotation around an amide bond, which corresponds[7a,8] to a double-bond character of *ca.* 40%. Furthermore, no steric hindrance was observed since the introduction of an ethyl instead of a methyl in the amino group does not alter the energy barrier of rotation significantly (Table 5).

Planar structures, such as (**Vb**), are therefore very significant at ordinary temperatures thus supporting the mechanisms already suggested for the nitrosation and the diazotisation of the protonated 2- and 4-aminopyridines[1,2a,3] (Scheme 2).

It is noteworthy that the nitrosation of the *N*-methylanilinium ion (**VII**) is much slower (k_3 0.044 l^2 mol^{-2} s^{-1} at 0 °C)[9] than the nitrosation of 4-methylamino- (**IV**) and 1-methyl-4-methylamino-pyridinium ion (**III**) although it is expected that the availability of the π-electrons of the *N*-heteroaromatic nucleus, which is positively charged [resonance structures (**IIIa**) and (**IVa**)], would be less than that of the aromatic ring, which is affected only by the $-I$ effect of the ammonium group (**VII**). This may mean that the methyl of the amino group in the case of the γ-methylaminopyridinium ion has a greater effect (enhancement) on the π-electron system of the *N*-heteroaromatic nucleus, whilst in the case of the anilinium ion it has a greater effect (decreasing) on the acidity of the amino hydrogen.



(**VII**)

Experimental

Materials.—1-Methyl-3-methylaminopyridinium perchlorate was prepared by heating 3-methylaminopyridine[2a,10] (0.54 g) with methyl toluene-*p*-sulphonate (0.93 g; Fluka; pract.) until a yellowish glassy material was formed and then left overnight. The solid obtained was triturated in 70% perchloric acid (0.8 g; Fluka; puriss) until complete dissolution. The mixture was washed several times with diethyl ether until a yellowish crystalline precipitate was obtained which was further washed with dry diethyl ether. It was then recrystallised (charcoal) three times from absolute ethanol, dried at 85 °C and 0.01 mmHg over phosphorus pentaoxide to give *1-methyl-3-methylaminopyridinium perchlorate* (1.0 g, 90%), m.p. 110 °C (Found: C, 38.1; H, 4.7; N, 12.3. $C_7H_{11}ClN_2O_4$ requires C, 37.8; H, 4.9; N, 12.6%).

1-Methyl-4-methylaminopyridinium perchlorate was prepared by the dropwise addition of methyl iodide (8 g; Fluka; purum) in a solution of 4-methylaminopyridine[11] (2.2 g) in acetone while stirring. After 3 h the crystalline precipitate was filtered (5 g, 98%) and dried at 80 °C and 0.10 mmHg over phosphorus pentaoxide to give the iodide salt, m.p. 222—224 °C, which was then mixed with silver perchlorate (4.15 g; Fluka; purum), previously dried at 140 °C and 0.1 mmHg for 5 h, and water (5 ml) and triturated. The filtrate which was tested for the absence of silver and iodide ions was evaporated to dryness and the solid obtained was recrystallised twice from absolute ethanol (charcoal) to give needles which were dried at 80 °C and 0.01 mmHg over phosphorus pentaoxide to give *1-methyl-4-methylaminopyridinium perchlorate* (2.1 g, 95%), m.p. 142—143 °C (Found: C, 38.0; H, 4.95; N, 12.0, $C_7H_{11}ClN_2O_4$ requires C, 37.8; H, 4.9; N, 12.6%).

1-Methyl-4-ethylaminopyridinium perchlorate was prepared by heating 4-ethylaminopyridine[11] (0.5 g) with methyl toluene-*p*-sulphonate (0.75 g; Fluka; pract.) and using the above procedure. The crystals obtained were dried at 50 °C and 0.01 mmHg over phosphorus pentaoxide to give *1-methyl-4-ethylaminopyridinium perchlorate* (0.83 g, 87%), m.p. 75—77 °C (Found: C, 40.8; H, 5.4; N, 11.7. $C_8H_{13}ClN_2O_4$ requires C, 40.6; H, 5.5; N, 11.8%).

1-Methyl-4-dimethylaminopyridinium perchlorate was prepared by heating 4-dimethylaminopyridine[11] (1.22 g) with methyl toluene-*p*-sulphonate (2 g; Fluka; pract.) and using the above procedure. The crystals obtained were dried at 100 °C and 0.01 mmHg over phosphorus pentaoxide to give *1-methyl-4-dimethylaminopyridinium perchlorate* (2.1 g, 89%), m.p. 189—

Table 5. ^{13}C N.m.r. chemical shifts and energy barrier for the rotation of C=NHR bonds in [$^2H_6$]DMSO

	1-Me-4-MeNH-pyridinium			1-Me-4-EtNH-pyridinium			1-Me-4-Me_2N-pyridinium
	δ(p.p.m.)	T_c°/K	ΔG^*/kcal mol^{-1}	δ(p.p.m.)	T_c°/K	ΔG^*/kcal mol^{-1}	δ(p.p.m.)
α-Carbons (A and B)	A 143.66 B 146.04	355	17.6	A 143.89 B 146.07	347	17.2	144.32
β-Carbons (A and B)	A 106.60 B 111.85	366	17.6	A 106.76 B 112.00	360	17.3	109.04
γ-Carbon	158.84			158.01			157.27
CH_3 (ring N)	45.89			45.94			45.65
CH_3 (amino N)	30.71						
CH_3 | CH_2– (amino N)				15.09 38.31			
$(CH_3)_2$= (amino N)							41.21

Table 6. Nitrosation of 1-methyl-3- and 1-methyl-4-methylaminopyridinium perchlorate (amine salt) at 2.0 °C; constancy of k_2 [equations (1) and (3)] during the reaction

[$HClO_4$] 0.01M; [$NaClO_4$] 0.05M; [Amine Salt]$_i$ 1.0×10^{-3}M; [Nitrous acid]$_i$ 1.0×10^{-3}M			[$HClO_4$] 0.1M; [$NaClO_4$] 2.9M; [Amine Salt]$_i$ 1.0×10^{-4}M; [Nitrous acid]$_i$ 1.0×10^{-3}M		
t/mim	10^4[Product]/M	$10k_2$/l mol^{-1} s^{-1}	t/min	10^5[Product]/M	$10k_2$/l mol^{-1} s^{-1}
6	2.58	5.67	2.45	0.420	2.95
8	2.95	5.77	4.45	0.740	2.93
10	3.28	5.75	6.45	1.06	2.96
12	3.56	5.67	8.45	1.37	2.99
22	4.75	5.77	12.45	1.92	2.96
32	5.58	5.86	16.45	2.41	2.94
42	6.20	5.92	24.45	3.30	2.95
62	7.01	5.93	46.45	4.98	2.86
82	7.54	5.94	66.45	5.95	2.83
112	8.02	5.83	96.45	6.83	2.78

191 °C (Found: C, 40.7; H, 5.3; N, 11.5. $C_8H_{13}ClO_4N_2$ requires C, 40.6; H, 5.5; N, 11.8%).

Sodium perchlorate (Merck; puriss P.A.) was dried at 140 °C for 4 h. Sodium nitrite (AnalaR) was dried under vacuum over phosphorus pentaoxide. Perchloric acid (Fluka; puriss) solutions were determined by titration against standard alkali solutions. Microanalyses were carried out by Dr. Ch. Mantzos.

Kinetics.—Runs were carried out at 2.0 °C. Temperature-adjusted aqueous solutions of 1-methyl-3- and 1-methyl-4-methylaminopyridinium perchlorate (amine salt), perchloric acid and, when required, sodium perchlorate were mixed with temperature-adjusted aqueous sodium nitrite. The mixture was then vigorously shaken. U.v. spectra of reaction mixtures were recorded on an SP 1800 Unicam spectrophotometer at regular intervals after placing a portion of these mixtures in a pre-cooled silica cell and maintaining the temperature at 2.0 °C.

For the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate absorbances were read at 346 nm at which extinction coefficient ε of the amine salt is 3.35×10^3, ε of the respective nitrosamine is 0.19×10^3, and ε for nitrous acid is 0.036×10^3 at all acidities examined. For the nitrosation of 1-methyl-4-methylaminopyridinium perchlorate absorbances were read at 295 nm at which ε of the amine salt is 8.20×10^3, ε of the respective nitrosamine is 17.20×10^3, and ε for nitrous acid is 0.002×10^3 at all acidities examined.

Calculation of Rate Coefficients.—The concentration of the amine salt in the reaction mixtures was calculated from expression (6), where D is the observed absorbance measured at

$$[\text{Amine salt}] = \frac{D + (A - B).\varepsilon_2 - A\varepsilon_3}{\varepsilon_1 + \varepsilon_2 - \varepsilon_3} \qquad (6)$$

the preselected wavelength, A and B are the initial concentrations of the amine salt and of nitrous acid, whilst ε_1, ε_2, and ε_3 are the extinction coefficients of the amine salt, nitrous acid, and the corresponding nitrosamine, respectively. Rate coefficients of the nitrosation of 1-methyl-3-methylaminopyridinium perchlorate were calculated from the usual second-order expression.[4b] Rate coefficients of the nitrosation of 1-methyl-4-methylaminopyridinium perchlorate were calculated by using a previous method.[2a] Typical data are in Table 6.

N.m.r. Spectra.—These were recorded on a Varian FT-80A spectrometer (20 MHz) and using a variable-temperature controller.

Determination of pH.—This was carried out with a Philips 9414 pH meter.

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