Reactions of *N*-Heteroaromatic Bases with Nitrous Acid. Part 4.[1] Kinetics of the Diazotisation of 2- and 4-Aminopyridine 1-Oxide

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The kinetics of the diazotisation of 2- and 4-aminopyridine 1-oxide have been studied in 0.0025—5.0M-perchloric acid. The reaction is of the first order in both the amine and nitrous acid. The rate coefficient of the reaction increases with an increase in the concentration of perchloric acid and of sodium perchlorate. In perchloric acid solutions whose ionic strength is maintained constant by the addition of sodium perchlorate the rate constant for the reaction does not show a linear dependence on the h_0 parameter for the medium, in contrast to the reported linear relationship between the rate coefficient for the diazotisation of 2- and of 4-aminopyridine and the h_0 function. The results suggest that diazotisation of 2- and 4-aminopyridine 1-oxide proceeds by two simultaneous reaction paths both of which contribute significantly to the overall reaction rate. The first involves attack of the nitrous acidium ion on the free amine whilst the second involves attack of the same nitrosating agent on the protonated amine. The amines react faster in the free than in the protonated form. The free and protonated forms of 4-aminopyridine 1 oxide are diazotised at a greater rate than the corresponding forms of 2-aminopyridine 1-oxide.

DIAZOTISATION of 2- and 4-aminopyridine with nitrous acid in dilute perchloric acid solutions proceeds mainly by an acid catalysed reaction whose kinetic form is of the first order with respect both to the amine and to nitrous acid and which involves only one mechanism.[1,2] The reaction takes place by the interaction between the protonated amine and the nitrous acidium ion.[1,2b] The formation of the nitrosamine was considered to be the rate-determining step because of the similarity of the kinetics of the diazotisation of 2- and 4-aminopyridine [1,2b] to the kinetics of the nitrosation and the diazotisation of aromatic amines.[3]

This paper presents a study of the kinetics of the diazotisation of 2- and 4-aminopyridine 1-oxide in 0.0025—5.0M-perchloric acid. The results indicate that this diazotisation proceeds by the simultaneous reaction between the protonated and the free amine and the nitrous acidium ion, which acts as the nitrosating agent.

TABLE 1

Diazotisation of 2- and 4-aminopyridine 1-oxide at 2.0°; constancy of $\bar{k}_2$ [equation (1)] at a given acidity

2-Aminopyridine 1-oxide

$[HClO_4]$/M	0.05			2.00			4.00			
$10^3[Amine]_i$/M	1.0	2.0	2.0	1.0	1.0	2.0	1.0	1.0	2.0	2.0
$10^3[Nitrous\ acid]_i$/M	4.0	4.0	8.0	4.0	8.0	4.0	2.0	4.0	4.0	8.0
$10^2\bar{k}_2$/l mol^{-1} s^{-1}	1.60	1.53	1.70	4.30	4.34	4.58	14.4	15.0	15.5	14.6
Mean $10^2\bar{k}_2$/l mol^{-1} s^{-1}	1.61 ± 0.08			4.40 ± 0.15			14.8 ± 0.5			

4-Aminopyridine 1-oxide

$[HClO_4]$/M	0.002 5				2.50			5.00		
$10^3[Amine]_i$/M	1.0	1.0	2.0	2.0	0.50	0.50	2.0	0.01	0.01	0.02
$10^3[Nitrous\ acid]_i$/M	1.0	2.0	1.0	2.0	4.0	2.0	1.0	0.01	0.02	0.01
$10\bar{k}_2$/l mol^{-1} s^{-1}	0.157	0.161	0.152	0.157	21.5	21.2	20.4	626	576	600
Mean $10\bar{k}_2$/l mol^{-1} s^{-1}	0.157 ± 0.004				21.0 ± 0.6			600 ± 25		

RESULTS AND DISCUSSION

In 0.0025—5.0M-perchloric acid solutions the stoicheiometric second-order rate coefficients ($\bar{k}_2$) for the diazotisation of 2- and 4-aminopyridine 1-oxide obtained by

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[1] Part 3, E. Kalatzis and Ch. Mastrokalos, *J.C.S. Perkin II*, 1974, 498.

[2] E. Kalatzis, *J. Chem. Soc.* (*B*), 1967, (*a*) 273; (*b*) 277.

[3] (*a*) E. Kalatzis and J. H. Ridd, *J. Chem. Soc.* (*B*), 1966, 529; (*b*) E. C. R. de Fabrizio, E. Kalatzis, and J. H. Ridd, *ibid.*, p. 533.

using rate expression (1) were satisfactorily constant

$$\text{Rate} = \bar{k}_2[\text{Amine}][\text{Nitrous acid}] \qquad (1)$$

(Table 1) for more than 75% reaction (Table 2).

TABLE 2

Diazotisation of 2-aminopyridine 1-oxide at 2.0°; constancy of $\bar{k}_2$ [equation (1)] during the reaction and in great excess of sodium perchlorate and nitrous acid $[\text{Amine}]_i$ 4.0 × 10^{-3}M, $[\text{Nitrous acid}]_i$ 16.0 × 10^{-3}M

	$[HClO_4]$ 0.25M		$[HClO_4]$ 0.05M + $[NaClO_4]$ 2.95M	
t/min	10^3[Product]/ M *	$10^2\bar{k}_2$/ l mol^{-1} s^{-1}	10^3[Product]/ M *	$10^2\bar{k}_2$/ l mol^{-1} s^{-1}
5			1.14	7.27
10			1.85	6.90
15	0.98	2.02	2.42	7.07
20			2.85	7.26
25			3.08	7.02
30	1.69	2.02	3.33	7.19
40	2.08	2.06	3.64	7.40
50	2.35	2.01		
60	2.66	2.11		
75			3.94	7.22
92	3.15	2.00		
135	3.56	2.02		

* Taken as equivalent to the concentration of the amine reacted.

That expression (1) describes the kinetics of the above reaction is 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 (Figure 1).

TABLE 3

Diazotisation of 2- and 4-aminopyridine 1-oxide at 2.0°; dependence of $\bar{k}_2$ [equation (1)] on the concentration of an excess of perchloric acid

	2-Aminopyridine 1-oxide		4-Aminopyridine 1-oxide	
$[HClO_4]$/M	H_0	$10\bar{k}_2$/l mol^{-1} s^{-1}	H_0	$10\bar{k}_2$/l mol^{-1} s^{-1}
0.002 5	+1.80 *	0.185 ± 0.007	+2.45 *	0.157 ± 0.004
0.010	+1.62 *	0.202 ± 0.001	+2.00 *	0.199 ± 0.007
0.050	+1.40 *	0.161 ± 0.008	+1.50 *	0.302 ± 0.006
0.10	+1.05 *	0.207 ± 0.007	+1.00 *	0.405 ± 0.003
0.25	+0.60	0.192 ± 0.010	+0.60	0.670 ± 0.028
0.50	+0.20	0.167 ± 0.011	+0.20	1.07 ± 0.010
1.00	−0.22	0.241 ± 0.008	−0.22	2.55 ± 0.11
1.50	−0.53	0.345 ± 0.012	−0.53	5.25 ± 0.32
2.00	−0.78	0.440 ± 0.015	−0.78	10.7 ± 0.8
2.50	−1.01	0.592 ± 0.024	−1.01	21.0 ± 0.6
3.00	−1.23	0.901 ± 0.041	−1.23	38.8 ± 1.4
3.50	−1.47	1.03 ± 0.07	−1.47	75.2 ± 2.3
4.00	−1.72	1.48 ± 0.05	−1.72	148 ± 5.4
5.00	−2.21	2.18 ± 0.12	−2.21	600 ± 25

* Values determined with pH meter. The other values of H_0 taken from ref. 6*a*.

Although $\bar{k}_2$ remains constant at a given acidity with change in the initial concentration of the reactants (Table 1), the results obtained show that $\bar{k}_2$ increases with an increase in the acidity of the medium (Table 3). The plots of the values of log $\bar{k}_2$, however, against the values of H_0 for the acid solutions are curves with a rising slope in contrast to the similar plots for the diazotisation of 2- and 4-aminopyridine [1,2b] which are straight lines (Figure 2) with slopes 1.07 and 1.33 respectively.

Curves were also obtained when the values of log $\bar{k}_2$ for the diazotisation of 2- and 4-aminopyridine 1-oxide in solutions of perchloric acid kept at constant ionic strength of 3.0 by the addition of sodium perchlorate (Table 4) were plotted against the corresponding values of H_0. These results show that the dependence of the rate coefficient for the reaction on the acidity of the medium kept at constant ionic strength is not linear. A rectilinear dependence on the acidity of the medium was, however, observed for the rate coefficient for the diazotisation of 2- and 4-aminopyridine under similar conditions [1,2b] (Figure 3).

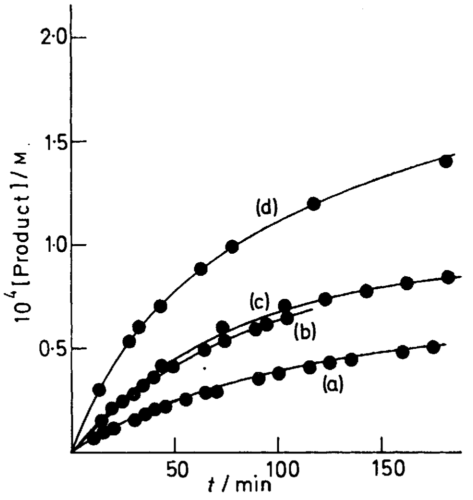

FIGURE 1 Diazotisation of 4-aminopyridine 1-oxide in 2.00M-perchloric acid and at 2.0°; variation of reaction rate with initial concentration of amine and nitrous acid: (a) 1.0 × 10^{-4} and 1.0 × 10^{-4}M; (b) 1.0 × 10^{-4} and 2.0 × 10^{-4}M; (c) 2.0 × 10^{-4} and 1.0 × 10^{-4}M; (d) 2.0 × 10^{-4} and 2.0 × 10^{-4}M. Initial rates (a) 0.65 × 10^{-6}; (b) 1.19 × 10^{-6}; (c) 1.2 × 10^{-6}; (d) 2.62 × 10^{-6} mol l^{-1} min^{-1}

A contribution from the nitrous anhydride mechanism [3,4] to the diazotisation of 2- and 4-aminopyridine

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[4] (*a*) J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418; (*b*) E. D. Hughes, C. K. Ingold, and J. H. Ridd, *J. Chem. Soc.*, 1958, 58 and subsequent papers.

1-oxide can be excluded even for low acidities, *i.e.* <0.5M-perchloric acid, because the second-order rate expression (1) was obeyed throughout the acid range studied and there were no signs of it changing to a third-order rate expression (second order with respect to nitrous acid [3,4]) in spite of the variations in the initial concentration of the reactants and the use of a large excess of nitrous acid (Table 1). The above is confirmed by the fact that rate expression (1) is also obeyed when a large excess of sodium perchlorate is added in dilute perchloric acid solutions (<0.5M) to keep the ionic strength of the medium constant (Tables 2 and 5), because sodium perchlorate greatly catalyses the formation of nitrous anhydride in very dilute acid solutions.[5a]

TABLE 4

Diazotisation of 2- and 4-aminopyridine 1-oxide at 2.0°; dependence of $\bar{k}_2$ [equation (1)] on the concentration of perchloric acid and sodium perchlorate

		Perchloric acid and sodium perchlorate to ionic strength of 3.0		Perchloric acid (1.0M) and sodium perchlorate	
		2-Aminopyridine 1-oxide	4-Aminopyridine 1-oxide	2-Aminopyridine 1-oxide	4-Aminopyridine 1-oxide
$[NaClO_4]$/M	H_0 *	$10\bar{k}_2$/l mol^{-1} s^{-1}	$10\bar{k}_2$/l mol^{-1} s^{-1}	$10\bar{k}_2$/l mol^{-1} s^{-1}	$10\bar{k}_2$/l mol^{-1} s^{-1}
3.50				1.88 ± 0.10	45.1 ± 1.0
3.00				1.67 ± 0.09	28.3 ± 0.7
2.95	+0.66 †	0.727 ± 0.015	2.21 ± 0.03		
2.90	+0.34 †	0.755 ± 0.007	3.05 ± 0.02		
2.75	−0.09 †	0.819 ± 0.010	4.52 ± 0.25		
2.50	−0.40	0.789 ± 0.013	7.40 ± 0.22	1.17 ± 0.07	18.3 ± 0.6
2.00	−0.71	0.933 ± 0.018	12.8 ± 0.4	0.933 ± 0.018	12.7 ± 0.4
1.50	−0.90	0.943 ± 0.018	18.5 ± 0.7	0.620 ± 0.028	8.08 ± 0.20
1.00	−1.04	1.05 ± 0.07	23.8 ± 0.6	0.471 ± 0.019	5.65 ± 0.04
0.50	−1.17	1.10 ± 0.01	31.0 ± 0.8	0.326 ± 0.019	4.04 ± 0.21
0.00	−1.23	0.901 ± 0.042	38.8 ± 1.4	0.241 ± 0.008	2.55 ± 0.1

* These values were taken from ref. 5*b*. † Values obtained by extrapolation of those from ref. 5*b*.

TABLE 5

Diazotisation of 4-aminopyridine 1-oxide at 2.0°; constancy of $\bar{k}_2$ [equation (1)] in a large excess of sodium perchlorate and nitrous acid

	0.05M-$HClO_4$ +2.95M-$NaClO_4$			0.10M-$HClO_4$ +2.90M-$NaClO_4$				0.25M-$HClO_4$ +2.75M-$NaClO_4$				0.50M-$HClO_4$ +2.50M-$NaClO_4$				
10^4[Amine]$_i$/M	1.0	1.0	2.0	0.50	0.50	1.0	2.0	1.0	1.0	1.0	2.0	0.50	0.50	1.0	1.0	1.0
10^4[Nitrous acid]$_i$/M	1.0	2.0	2.0	4.0	2.0	2.0	1.0	1.0	2.0	4.0	1.0	4.0	2.0	1.0	2.0	4.0
$10\bar{k}_2$/l mol^{-1} s^{-1}	2.17	2.23	2.22	3.07	3.07	3.02	3.04	4.26	4.85	4.54	4.44	7.60	7.34	7.00	7.61	7.47
Mean $10\bar{k}_2$/l mol^{-1} s^{-1}	2.21 ± 0.03			3.05 ± 0.02				4.52 ± 0.25				7.40 ± 0.25				

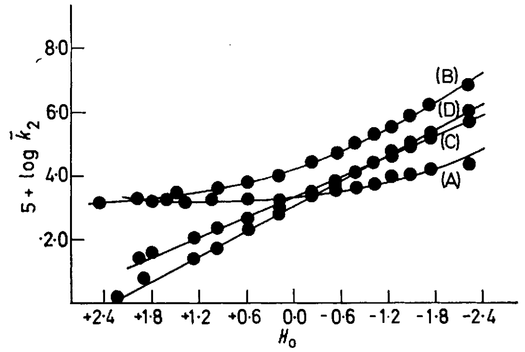

FIGURE 2 Plot of log $\bar{k}_2$ [equation (1)] against $-H_0$ for the diazotisation of 2-aminopyridine 1-oxide (A), 4-aminopyridine 1-oxide (B), 2-aminopyridine [1] (C), and 4-aminopyridine [2b] (D) in perchloric acid solutions (see Table 4)

Similar results were found for the diazotisation of 2- and 4-aminopyridine.[1,2b]

The rate coefficient for the diazotisation of 2- and 4-aminopyridine 1-oxide in 1.0M-perchloric acid solutions containing various concentrations of sodium perchlorate (which was used to simulate the catalytic medium effect of perchloric acid apart from its acid catalysis) shows an exponential dependence on the ionic strength of the medium (μ), because a plot of log $\bar{k}_2$ (Table 4) against μ gave straight lines with slopes of 0.282 and 0.355 respectively. The $\bar{k}_2$ values, however, cannot be easily corrected to refer to a common value of h_0 corresponding to 1.0M-perchloric acid,[5b] because $\bar{k}_2$ does not vary rectilinearly with h_0 (Figure 3). This correction is

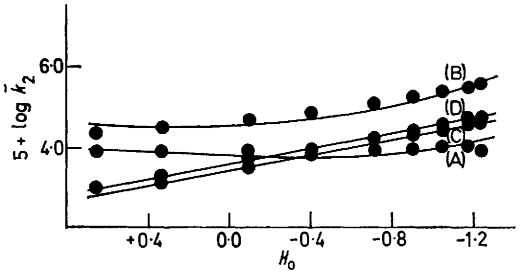

FIGURE 3 Plot of log $\bar{k}_2$ [equation (1)] against $-H_0$ for perchloric acid solutions containing sufficient sodium perchlorate to bring the ionic strength to 3.0: (A) 2-aminopyridine 1-oxide; (B) 4-aminopyridine 1-oxide; (C) 2-aminopyridine;[1] (D) 4-aminopyridine.[2b] The slopes rise for (A) and for (B), and are 0.96 for (C) and for (D)

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[5] B. C. Challis and J. H. Ridd, *J. Chem. Soc.*, 1962, (*a*) 5197; (*b*) 5208.

necessitated by the fact that the addition of sodium perchlorate increases the h_0 values of the perchloric acid solutions.[6] The above results, however, resemble those for the diazotisation of 2- and 4-aminopyridine [1,2b] under the same conditions, because similar plots of log $\bar{k}_2$ (values of $\bar{k}_2$ not corrected) against μ are also straight lines with slopes of 0.360 and 0.454.

The diazotisation of 2- and 4-aminopyridine has been shown to proceed mainly by one mechanism only, which is acid catalysed and has the kinetic form (2).[1,2b] This

$$\text{Rate} = k_3[\text{Protonated amine}][\text{HNO}_2]h_0 \qquad (2)$$

has been interpreted as direct attack of the nitrous acidium ion on the protonated 2- and 4-aminopyridine.[1,2b] However, this acid catalysed mechanism alone cannot explain the results of the present work on the diazotisation of 2- and 4-aminopyridine 1-oxide because the dependence of the rate coefficient for this reaction on the acidity of the medium at constant ionic strength is not rectilinear (Table 4 and Figure 3).

A comparison of the pK_a values of the 2- and 4-aminopyridine (6.82 [7] and 9.11 [7] respectively) with those of 2- and 4-aminopyridine 1-oxide (2.67 [8] and 3.69 [8] respectively) indicates that the free form of the latter amines, especially at low acidities, is present in sufficient amounts under the present experimental conditions for diazotisation by the interaction of these amines in the free form with the nitrosating agent to be quite significant. Such a mechanism of diazotisation involving the interaction of the non-protonated amine molecules with the nitrous acidium ion has been observed earlier in the aromatic series in the case of the less basic amines, as for example in the diazotisation of *p*-nitroaniline which reacts only in the non-protonated form [9] (pK_a 0.99 [10]). It has also been observed recently in the heteroaromatic series for the diazotisation of 2-amino-5-chloropyridine 1-oxide [11] (pK_a 1.73 [11]). The kinetic form for this mechanism is given in equation (3).

$$\text{Rate} = k_3'[\text{Free amine}][\text{HNO}_2]h_0 \qquad (3)$$

The results of the present work on the diazotisation of 2- and 4-aminopyridine 1-oxide can, therefore, be explained by accepting that each of the two mechanisms described by kinetic forms (2) and (3) makes a measurable contribution to the overall reaction because of the relatively low pK_a values of the amines concerned. Under these conditions rate expression (1) should still be obeyed at a given acidity because the order of the reaction with respect to the amine and the nitrous acid is the same in the kinetic forms (2) and (3).

It is therefore important to evaluate the contribution of the two reaction paths separately, as has also been carried out for nitrosation and diazotisation of the aromatic amines.[3b,5b] Since [Free amine]h_0 = [Protonated amine]K_a where K_a is the thermodynamic dissociation constant of the conjugate acid of the amine, equation (4) is the result of a combination of equations

$$\text{Rate} = (k_3'K_a + k_3h_0)[\text{Protonated amine}][\text{HNO}_2] \qquad (4)$$

(2) and (3). Thus equation (4) applies. From equations (1) and (4), equation (5) follows for constant ionic strength because 2- and 4-aminopyridine 1-oxide are

$$\bar{k}_2 = k_3'K_a + k_3h_0 \qquad (5)$$

present almost entirely as the conjugate acids under the present experimental conditions.

According to equation (5) a plot of $\bar{k}_2$ against h_0 should give a straight line with a slope of k_3 and an intercept of $k_3'K_a$. Such plots for the diazotisation of 2- and 4-aminopyridine 1-oxide are indeed straight lines (Figure 4) from which the values of k_3 and k_3' can be calculated (Table 6).

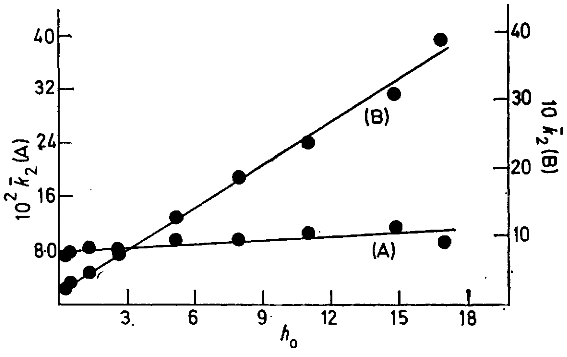

FIGURE 4 Plot of $\bar{k}_2$ [equation (1)] against h_0 for the diazotisation of 2-aminopyridine 1-oxide (A) and 4-aminopyridine 1-oxide (B) in perchloric acid solutions containing sufficient sodium perchlorate to bring the ionic strength to 3.0

TABLE 6

Diazotisation at 2.0°; values of k_3' and k_3 obtained from equation (5), *i.e.* $\bar{k}_2 = k_3'K_a + k_3h_0$, and Figure 4

	pK_a	$\bar{k}_2$/ l mol^{-1} s^{-1}	$k_3'K$	k_3'/ l^2 mol^{-2} s^{-1}	k_3/ l^2 mol^{-2} s^{-1}
2-Aminopyridine 1-oxide	2.67	0.110	0.076	35.5	0.002 3
4-Aminopyridine 1-oxide	3.69	3.88	0.21	1 028	0.204

The incursion of another mechanism for the diazotisation of 2- and 4-aminopyridine 1-oxide whose kinetic form should show an acid catalysis intermediate between those of equations (2) and (3) is not considered likely, because the plots of $\bar{k}_2$ against h_0 should be non-rectilinear due to a non-integral order with respect to h_0. Furthermore, as for the diazotisation of 2- and 4-aminopyridine,[1,2b] it is unlikely that the diazotisation of 2- and 4-aminopyridine 1-oxide proceeds by a path which involves the interaction between the nitrosonium ion and the imine-tautomers (II) and (V) instead of the protonated amines (III) and (VI), because the concentration of the imine tautomers [10^8 and 10^7 less than

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[6] (*a*) M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1; (*b*) G. Harbottle, *J. Amer. Chem. Soc.*, 1951, **73**, 4024.

[7] A. Albert, R. Goldacre, and J. N. Phillips, *J. Chem. Soc.*, 1948, 2240.

[8] J. N. Gardner and A. R. Katritzky, *J. Chem. Soc.*, 1957, 4375.

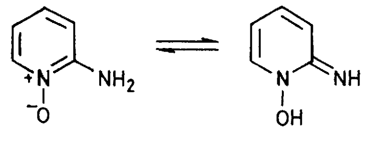
[9] L. F. Larkworthy, *J. Chem. Soc.*, 1959, 3304; B. C. Challis, L. F. Larkworthy, and J. H. Ridd, *ibid.*, 1962, 5203.

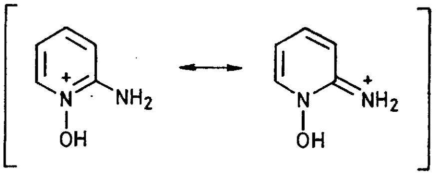
[10] M. Kilpatrick and C. A. Arenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 3812.

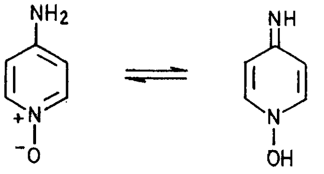
[11] E. Kalatzis and Ch. Mastrokalos, following paper.

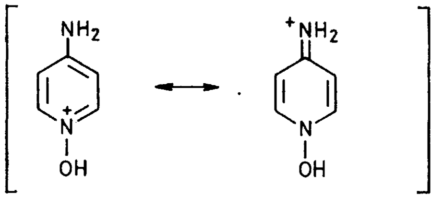
those of the amine tautomers (I) and (IV) respectively[8]] is far too low to account for the observed rates of the reaction.

The results in Table 6 show that the free form of the amines is more reactive towards the nitrous acidium ion than the protonated form and that 4-aminopyridine 1-oxide in the free or in the protonated form is diazotised at a much greater rate than 2-aminopyridine 1-oxide in the free or in the protonated form respectively.


(I) (II)


(III)


(IV) (V)


(VI)

EXPERIMENTAL

Materials.—2-Aminopyridine 1-oxide was prepared by the oxidation of the *N*-acetyl derivative of 2-aminopyridine (Fluka; puriss) dissolved in acetic acid with 50% hydrogen peroxide.[12] The product was sublimed three times at 110 °C and 0.5 mmHg. 4-Aminopyridine 1-oxide was prepared by the reduction of 4-nitropyridine 1-oxide (Fluka; purum) with hydrogen and 2% palladium on strontium carbonate (Pfaltz and Bauer) as catalyst, and recrystallised from ethanol–ethyl acetate.[8] 2-(2-Hydroxy-1-naphthylazo)pyridine 1-oxide was prepared by coupling diazotised 2-aminopyridine 1-oxide with 2-naphthol (Fluka; purum) in alkaline solution and recrystallising the product obtained from alcohol.[13] All purified products had satisfactory elemental analyses. Sodium perchlorate (Fluka; puriss), which gave a negative chloride test, was dried at 140 °C for 4 h. Sodium nitrite (AnalaR) was used without further purification after being dried under vacuum over phosphorus pentaoxide. Perchloric acid (Fluka; puriss) was diluted and molarities of stock 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 calculated concentrations of amine, perchloric acid (concentration adjusted to allow for the conversion of the amine into the perchlorate salt and sodium nitrite into nitrous acid), and, when required, sodium perchlorate were mixed to such a volume (55—59 ml) that after the addition of temperature adjusted aqueous sodium nitrite (5—1 ml) the total volume was 60.0 ml. The reaction mixture was then vigorously shaken.

For the diazotisation of 2-aminopyridine 1-oxide samples (2.0 or 5.0 ml) taken at intervals were diluted 10—50 times with hydrochloric acid solution to a final strength of 3.0M. Under these conditions, the reaction is very slow and the u.v. spectra show no further changes for *ca.* 5 min (experimental error 5%). The u.v. spectra of the diluted solutions were recorded immediately after dilution on a Unicam SP 8000 or 1800 recording spectrophotometer and the absorption due to 2-aminopyridine 1-oxide was read at 301 nm (ε 5.61×10^{3}). At the same wavelength 1-oxidopyridine-2-diazonium ion has a smaller absorption (ε 1.50×10^{3}) under the same conditions.

For the diazotisation of 4-aminopyridine 1-oxide in 0.0025—0.05M-perchloric acid the procedure was similar to that used for the diazotisation of 2-aminopyridine 1-oxide. The absorption due to 4-aminopyridine 1-oxide was read at 270 nm (ε 1.66×10^{4}) from the recorded u.v. spectra of the diluted solutions. At the same wavelength the 1-oxidopyridine-4-diazonium ion has a small absorption (ε 800) under the same conditions. For acidities $>$0.05M-perchloric acid a portion of the reaction mixture was placed in a pre-cooled Unicam cell (1.0 cm) maintained at 2.0 °C and the decrease in the absorption at 270 nm was measured automatically. Temperature equilibrium could be reached in $<$3 min under these conditions.

1-Oxidopyridine-2- and -4-diazonium ion were stable in perchloric acid solutions (1.0—4.0M) for at least 4 h, as indicated by the recorded u.v. spectra of diazotised 2-aminopyridine 1-oxide solutions (4.0×10^{-3}—5.0×10^{-3}M) containing an excess of nitrous acid (4.0×10^{-2}—5.0×10^{-2}M). This was confirmed by taking samples (2.0 ml) from these solutions and diluting (100 times) with a solution of 2-naphthol in sodium hydroxide (final pH 12) and then recording the spectra of the diluted solutions containing the 2-(2-hydroxy-1-naphthylazo)pyridine 1-oxide formed. These spectra were then compared with those of the appropriate solutions (at pH 12) of the authentic azo-oxide prepared as indicated above. Absorbances were read at 510 nm (ε 1.60×10^{4}).

Determination of pH.—Because the reactants were present as 2- and 4-aminopyridinium 1-oxide perchlorate and as free nitrous acid in high concentrations in the kinetic solutions containing $<$0.10M-perchloric acid, it was necessary to determine, by pH meter, the pH of the final solutions. The values were 1.80, 1.62, 1.40, and 1.05 for 2-aminopyridine 1-oxide and 2.45, 2.00, 1.50, and 1.00 for

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[12] J. Delarge and L. Thunus, *Il Farmaco*, 1966, 846.

[13] A. R. Katritzky, *J. Chem. Soc.*, 1957, 191.

4-aminopyridine 1-oxide, for 0.0025, 0.01, 0.05, and 0.10M excess of perchloric acid, respectively.

Calculation of Rate Coefficients.—The concentration of the 2- and 4-aminopyridine 1-oxide in the reaction mixtures was calculated from the expression [Amine] = $(D - A\varepsilon_2)/(\varepsilon_1 - \varepsilon_3)$ where D is the observed optical density measured at a particular wavelength, A is the initial concentration of the amine, and ε_1 and ε_2 are the extinction coefficients of the amine and the corresponding diazonium ion respectively. The absorption of nitrous acid under the conditions used is negligible. The rate coefficients were calculated from the usual second-order rate expression [14] by using the individual values of absorbances. For the diazotisation of 2-aminopyridine 1-oxide it was necessary, as for the diazotisation of 2- and 4-aminopyridine,[1,2b] to use an excess of nitrous acid in the initial reactants. The results were satisfactory and in agreement with second-order kinetics.

Typical data are in Table 2.

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[14] *Cf.* S. W. Benson, ' The Foundations of Chemical Kinetics,' McGraw-Hill, New York, 1960, p. 17.