Kinetics of Reactions in Heterocycles. Part XIV.[1] Reactions of 2- and 4-Amino-, -Methylamino-, and -Dimethylamino-pyridine Methiodides and 2-Methylthiopyrimidine Methiodide with Hydroxide Ions in Water

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The kinetics of the reactions of 2- and 4-amino-, -methylamino-, and -dimethylamino-pyridine methiodides with hydroxide ions in water have been studied. At 20 °C, 2-dimethylaminopyridine methiodide was 8.5×10^3 times more reactive than its 4-isomer, owing mainly to a lower energy of activation (by 6.4 kcal mol^{-1}). The 2- and 4-dimethylaminopyridine methiodides were 2.3×10^{-4} and 3.1×10^{-6} times less reactive than their chloro-analogues. The reaction of 2-methylthiopyridine methiodide with hydroxide ions was found to proceed *via* a two-step process.

WE have previously reported kinetic results for the reactions of some substituted *N*-methyl-pyridinium, -quinolinium, and -isoquinolinium salts with hydroxide ions in water,[2,3] and also their reactions with piperidine in water and in ethanol.[1] We now report the kinetics of reactions of some 2- and 4-amino-*N*-methylpyridinium salts with hydroxide ions in water (and a study of the reactions of 2-methylthiopyrimidine methiodide). Previous kinetic studies of the displacement of amino-substituents from nitrogen heterocycles have been restricted to the alkaline hydrolysis of the neutral aminopyrimidines.[4,5]

The reactions of the amino-*N*-methylpyridinium iodides with hydroxide ions in water followed second-order kinetics, as shown by selected examples (Table 1), to give quantitative yields of the *N*-methylpyridones, which were identified by isolation and measurement of their u.v. spectra at various pH values. All kinetic results and the derived Arrhenius parameters are given in Tables 2 and 3, respectively. 4-Amino-, -methylamino-, and -dimethylamino-pyridinium salts showed similar reactivity towards hydroxide ions, the amino-compound being slightly the most reactive. Values for the ionization constants of these compounds are uncertain. Thus, Brown and

TABLE 1

Reactions with hydroxide ions

2-Aminopyridine methiodide at 57.3 °C
Hydroxide ion 4.973M; methiodide 0.00493M

Time (s)	5 700	10 680	15 300	20 760	31 200	37 800	74 280
Reaction (%)	16.5	29.3	38.3	47.9	63.5	69.4	90.8
10^5k/l mol^{-1} s^{-1}	0.641	0.657	0.640	0.637	0.654	0.634	0.650

Mean 10^5k 0.645 ± 0.009

2-Dimethylaminopyridine methiodide at 13.4 °C
Hydroxide ion 5.00M; methiodide 0.00454M

Time (s)	429	633	1 088	1 603	2 133	2 705	3250
Reaction (%)	15.9	22.0	34.1	46.2	56.8	64.7	71.2
10^5k/l mol^{-1} s^{-1}	8.09	7.84	7.66	7.73	7.87	7.69	7.68
Time (s)	4 231	5 572					
Reaction (%)	80.0	89.0					
10^5k/l mol^{-1} s^{-1}	7.62	7.93					

Mean 10^5k 7.79 ± 0.155

4-Methylaminopyridine methiodide at 76.2 °C
Hydroxide ion 4.971M; methiodide 0.00493M

Time (s)	2 220	2 520	3 540	6 480	8 400	10 140	15 420
Reaction (%)	13.2	15.0	20.3	34.3	41.9	48.0	63.0
10^5k/l mol^{-1} s^{-1}	1.304	1.316	1.310	1.325	1.325	1.322	1.320
Time (s)	18 060	20 400	31 560				
Reaction (%)	67.7	72.8	88.2				
10^5k/l mol^{-1} s^{-1}	1.282	1.308	1.386				

Mean 10^5k 1.320 ± 0.027

4-Dimethylaminopyridine methiodide at 64.2 °C
Hydroxide ion 4.918M; methiodide 0.005065M

Time (s)	7 010	9 940	17 070	25 310	38 010	57 600	95 600
Reaction (%)	11.5	16.0	36.2	36.2	49.9	63.4	80.7
10^5k/l mol^{-1} s^{-1}	0.354	0.357	0.360	0.362	0.370	0.355	0.361
Time (s)	111 465						
Reaction (%)	86.9						
10^5k/l mol^{-1} s^{-1}	0.371						

Mean 10^5k 0.361 ± 0.006

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Harper[6] reported a pK_a value of 13.25 ± 0.03 for 2-amino-1-methylpyridinium iodide as an acid which was 1 pK_a unit higher than an earlier reported value of

TABLE 2

Kinetic results for the reactions of aminopyridine methiodides with hydroxide ions

Temp.[a] (°C)	[OH⁻]/M	[10³N⁺Me]/ M	10^5k [b,c]	Analyt. λ/ nm [d]
	2-Aminopyridine methiodide			
57.3	4.937	4.93	0.645	299
64.2	4.916	4.95	1.242	299
72.8	4.89	4.96	2.729	299
	2-Methylaminopyridine methiodide			
65.3	4.91	4.61	1.44	315
	2-Dimethylaminopyridine methiodide			
3.6	5.01	4.18	2.585	329
13.4	5.00	4.54	7.79	329
18.4	5.00	5.09	13.50	329
	4-Aminopyridine methiodide			
54.3	4.943	4.99	0.289	269
57.3	4.94	4.99	0.393	269
64.2	4.916	5.016	0.822	269
73.9	4.892	4.92	2.356	269
	4-Methylaminopyridine methiodide			
52.8	4.947	5.56	0.1039	279
64.2	4.917	4.93	0.375	279
74.5	4.889	4.965	1.134	279
76.2	4.886	4.98	1.320	279
	4-Dimethylaminopyridine methiodide			
52.8	4.947	5.56	0.1048	288
64.2	4.918	5.065	0.361	288
76.2	4.886	5.08	1.288	288

[a] ±0.1 °C. [b] In 1 mol⁻¹ s⁻¹; the standard deviation was usually within ±3%. [c] Corrected for solvent expansion or contraction. [d] Analytical wavelength for the determination of percentage reaction at H_0 −2.4 and pH 0.0 for the 2- and 4-substituted compounds, respectively.

Angyal and Angyal,[7] who also gave a similar pK_a value for the 4-isomer (pK_a 12.5), and the pK_a values of 1,2-dihydro-2-imino-1-methylpyrimidine and 1,4-dihydro-4-imino-1-methylpyrimidine are 10.75 and 12.22, respectively.[8] This evidence together with the similarity of the u.v. spectra of 4-aminopyridine methiodide at pH 7.0 and in 5M-sodium hydroxide suggested to us that these amino-compounds reacted in a similar form and predominantly as their cations (the only form in which 4-dimethylaminopyridine methiodide can exist).

2-Amino- and 2-methylamino-pyridine methiodides showed similar reactivities in 5M-sodium hydroxide, but these differed significantly from that of 2-dimethylaminopyridine methiodide, which had a higher reactivity at 20 °C (*ca.* 1.5 × 10³ times) and must react as its cation. The reactivity of the 2-dimethylamino-compound was also higher than that of its 4-isomer. This difference was consistent with the higher reactivity of most 2-substituted pyridinium salts, but greater than observed previously.[2] The lower reactivity of 2-amino- and 2-methylamino-pyridine methiodides in comparison with the 2-dimethylamino-compound may be due either to a lower concentration of the cationic species in the reaction mixture or to the reactions involving the neutral species. Evidence for some contribution by an ionization process was obtained from comparison of the u.v. spectrum of 2-aminopyridine methiodide at pH 7.0 ($\lambda_{max.}$ 231 and 300 nm) with that in 5M-sodium hydroxide (250 and 332 nm).

2-Dimethylaminopyridine methiodide was 8.5 × 10³ times more reactive than its 4-isomer at 20 °C and its energy of activation was lower by 6.4 kcal mol⁻¹. The energies of activation for the reactions of the aminopyridine methiodides were much higher than literature values for other substituted pyridine methiodides,[2] and whereas the E values for the 4-aminopyridine methiodides were similar, the values for 2-amino- and 2-dimethylamino-pyridine methiodides differed by 3.2 units.

The calculated frequency factors of 2-amino- and 2-dimethylamino-pyridine methiodides were *ca.* 3 and 2 units less than for other 2-substituted pyridine methiodides,[2] and contrast with log A values (all of similar magnitude) shown by the 4-aminopyridine methiodides. The lower value of log A for 2-aminopyridine methiodide may be due to the reaction involving the neutral species but the possibility of multiple reacting species cannot be excluded.

The reactivities of 2- and 4-chloropyridine methiodides at 20 °C were 4.35 × 10³ and 3.20 × 10⁵ times greater than those of their dimethylamino-analogues, respectively. The energies of activation of the chloro-compounds were 3.0 and 7.2 kcal mol⁻¹ lower, and log A values were 1.4 and 0.2 units higher, respectively.

TABLE 3

Rate coefficients and Arrhenius parameters for reactions with hydroxide ions

Pyridine methiodide	$k_{20°}$ [a]	E [b]/ kJ mol⁻¹ (kcal mol⁻¹)	log A [c]	$\Delta H^{\ddagger}$/ kJ mol⁻¹ [b] (kcal mol⁻¹)	$-\Delta S^{\ddagger}$/ J mol⁻¹K⁻¹ (cal mol⁻¹ K[d]⁻¹)
2-NH_2	1.03 × 10⁻⁷	88.9 (21.2)	8.8	86.1 (20.6)	85.9 (20.5)
2-NMe_2	1.59 × 10⁻⁴	75.3 (18.0)	9.6	73.0 (17.4)	69.2 (16.5)
4-NH_2	3.63 × 10⁻⁸	101.6 (24.3)	10.6	98.7 (23.6)	51.3 (12.3)
4-NHMe	1.41 × 10⁻⁸	103.6 (24.8)	10.6	100.8 (24.1)	51.3 (12.3)
4-NMe_2	1.86 × 10⁻⁸	102.1 (24.4)	10.4	99.3 (23.7)	55.2 (13.2)

[a] Rate coefficients at 20 °C in 1 mol⁻¹ s⁻¹. Calculated from E and log A values or the rate coefficient at a nearby temperature. [b] Accurate to within ±5.0 kJ mol⁻¹; based on standard deviations. [c] Accurate to within ±0.8 units. [d] Accurate to within ±4.0 J mol⁻¹ K⁻¹.

Some preliminary investigations of the reactions of substituted diazine methiodides have also been carried out and investigations are continuing. 2-Methylthiopyrimidine methiodide with sodium hydroxide gave

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1-methylpyrimidin-2-one *via* a two-step process. This transformation was observed by use of both u.v. and n.m.r. spectroscopy; the n.m.r. spectrum appeared to show two distinct sets of signals for the intermediates, which could be isomeric Meisenheimer [9]-type compounds.

Preparation of Compounds.—2- and 4-amino-1-methylpyridinium iodides [10,11] were prepared by direct methylation. 1-Methyl-2-methylaminopyridinium iodide [12] was made from 2-amino-1-methylpyridinium iodide through 1,2-dihydro-2-imino-1-methylpyridine, 1-methyl-4-methylaminopyridinium iodide was produced by methylation of 4-methylaminopyridine, and 2-(and 4-)dimethylamino-1-methylpyridinium iodides were obtained from the halogenopyridine methiodides with dimethylamine. Tschitschibabin and Konowalowa [13] give an iodine analysis for 2-dimethylamino-1-methylpyridinium iodide but no m.p., and Magidson and Menschikoff [14] claim that this compound (prepared by another route) was extremely hygroscopic and not recrystallisable. Methylation of the substituted diazines gave only one isomer in each case as shown by the ^{1}H n.m.r. spectra, but the orientations have not been established.

EXPERIMENTAL

Solids for analysis were dried at 100 °C unless otherwise stated. M.p.s were taken for samples in Pyrex capillaries. All compounds were recrystallised to constant m.p., and were further examined for the presence of impurities by paper chromatography on Whatman no. 1 paper in (a) aqueous 3% ammonium chloride, and (b) butan-2-ol–5M-acetic acid (7:3), and by t.l.c.

Kinetic studies were carried out as described in Part X.[2] U.v. spectra were recorded with a Unicam SP 800 spectrophotometer and $\lambda_{max.}$ and ε values were checked with a Unicam SP 500 manual instrument. ^{1}H N.m.r. spectra were recorded for solutions in D_2O at 33.5 °C with a Perkin-Elmer R10 spectrometer, with sodium 3-trimethylsilylpropane-1-sulphonate as internal standard.

2-Amino-1-methylpyridinium iodide had m.p. 148—149° (from ethanol) (lit.,[10] 148—149°) (Found: C, 30.6; H, 4.1; N, 12.1. Calc. for $C_6H_9IN_2$: C, 30.5; H, 3.8; N, 11.9%), $\delta(D_2O)$ 3.9 (MeN^+); 1-methyl-2-methylaminopyridinium iodide had m.p. 162—163.5° (lit.,[12] 159—160°) (Found: C, 33.6; H, 4.4; N, 11.0. $C_7H_{11}IN_2$ requires C, 33.6; H, 4.4; N, 11.2%), $\delta(D_2O)$ 3.1 (MeNH) and 3.9 (MeN^+); and 4-amino-1-methylpyridinium iodide had m.p. 189—190° (from ethanol) (lit.,[11] 179—182°) (Found: C, 30.6; H, 4.0; N, 11.9%), $\delta(D_2O)$ 4.0 (MeN^+).

2-Dimethylamino-1-methylpyridinium Iodide.—2-Iodopyridine methiodide [15] (2.0 g) and aqueous dimethylamine (25—30%; 5.0 ml) were heated on a steam-bath for 1 h. Aqueous sodium hydroxide was added and the mixture evaporated, and the process was repeated until the aqueous solution remained at pH > 11. The product was recrystallised repeatedly from t-butyl alcohol to give *2-dimethylamino-1-methylpyridinium iodide* (1.003 g), m.p. 107—108° (Found, for compound dried at 80 °C for 6 h: C, 36.6; H, 5.2; N, 10.45. $C_8H_{13}IN_2$ requires C, 36.4; H, 5.0; N, 10.6%), $\delta(D_2O)$ 3.2 (6 H, Me_2N) and 4.1 (3 H, MeN^+).

1-Methyl-4-methylaminopyridinium Iodide.—4-Chloropyridine was heated with aqueous 40% methylamine at 140 °C for 20 h to give 4-methylaminopyridine,[16,17] m.p. 127—131° (from benzene) (lit.,[17] 124.5—125°). This compound (2.8 g), methyl iodide (15.0 ml), and ethanol (20 ml) were kept at 20 °C for 24 h. The crystalline solid was collected and recrystallised from ethanol to give *1-methyl-4-methylaminopyridinium iodide* (5.0 g), m.p. 223—225° (Found: C, 33.6; H, 4.65; N, 11.1%), $\delta(D_2O)$ 3.0 (MeNH) and 4.0 (MeN^+).

4-Dimethylamino-1-methylpyridinium Iodide.—4-Chloropyridine and aqueous dimethylamine at 140 °C for 20 h gave 4-dimethylaminopyridine which, after distillation under reduced pressure, had m.p. 114—115° (lit.,[17] 110—112°). 4-Dimethylaminopyridine with methyl iodide in ethanol at room temperature gave 4-dimethylamino-1-methylpyridinium iodide,[18] m.p. 245—246° (from propan-2-ol) (lit.,[18] 140°) (Found: C, 36.7; H, 5.0; N, 10.5%), $\delta(D_2O)$ 3.2 (6 H, Me_2N) and 3.9 (3 H, MeN^+).

2-Chloropyrazine Methiodide.—2-Chloropyrazine [19] (3.0 g), methyl iodide (7.0 ml), and benzene (7.0 ml) were refluxed on a water-bath at 52 °C for 8 days. After cooling, the crystalline solid (3.7 g) was collected and recrystallised from ethanol to give *2-chloropyrazine methiodide*, m.p. 182—183° (Found: C, 23.4; H, 2.5; N, 10.6. $C_5H_6ClIN_2$ requires C, 23.4; H, 2.4; N, 10.9%), $\delta[(CD_3)_2SO]$ 4.4 (MeN^+).

2-Methoxypyrazine Methiodide.—2-Methoxypyrazine [20] (1.9 g) and methyl iodide (3.0 ml) were kept at room temperature for 9 days. The product (3.6 g) was filtered off and recrystallised from a mixture of t-butyl alcohol and a little ethanol to give *2-methoxypyrazine methiodide*, m.p. 133—135° (Found, for material dried at 20 °C and 20 mmHg: C, 28.5; H, 3.6; N, 10.8. $C_6H_9IN_2O$ requires C, 28.6; H, 3.6; N, 11.1%), $\delta[(CD_3)_2SO]$ 4.15 (MeO), 4.4 (MeN^+), 8.75 (1H, m), and 9.15 (2 H).

2-Methylthiopyrazine Methiodide.—2-Methylthiopyrazine [21] (1.15 g), methyl iodide (5.0 ml), and benzene (17 ml) were refluxed under anhydrous conditions on a water-bath at *ca.* 52 °C for 2.5 days. The precipitate (1.4 g) was collected and recrystallised from t-butyl alcohol–methanol to give *2-methylthiopyrazine methiodide*, m.p. 162—163° (Found: C, 26.9; H, 3.2; N, 10.5. $C_6H_9IN_2S$ requires C, 26.9; H, 3.4; N, 10.4%), $\delta(D_2O)$ 2.75 (MeS), 4.4 (MeN^+), 8.55 (1 H, m), 8.95 (H-3), and 9.2 (1 H, m).

3-Methoxypyridazine Methiodide.—3-Methoxypyridazine [22] (1.0 g), methyl iodide (2.0 ml), and benzene (3.0 ml) were refluxed in a water-bath at 52 °C for 5 h. After cooling, the product (1.5 g) was collected and recrystallised from ethanol–t-butyl alcohol to give *3-methoxypyridazine methiodide*, m.p. 126—127° (Found, for product dried at 20 °C and

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20 mmHg: C, 28.6; H, 3.5; N, 11.3%), δ(D_2O) 4.2 (MeO), 4.6 (MeN^+), 8.1 (H-4), 8.5 (H-5), and 9.5 (H-6).

2-Methylthiopyrimidine Methiodide.—2-Methylthiopyrimidine [21] and methyl iodide were refluxed on a water-bath at 52 °C for 12 h to give 2-methylthiopyrimidine methiodide,[23] m.p. 155—156° (from ethanol) (lit.,[23] 152—153°) (Found: C, 26.7; H, 3.4; N, 10.3; S, 12.3%), δ(D_2O) 2.9 (MeS), 4.2 (MeN^+), 7.8 (H-5, q), 9.0 (1 H, q), and 9.2 (1 H, q). This compound (0.70 g) was shaken with freshly prepared silver chloride (2.0 g) in water; the solution was filtered and evaporated and the product recrystallised from t-butyl alcohol to give the hygroscopic *2-methylthiopyrimidine methochloride monohydrate* (0.31 g), m.p. *ca.* 120° with prior softening (Found, for material dried over sodium hydroxide at 20 °C and 20 mmHg: C, 37.2; H, 5.9; N, 14.3. $C_6H_9ClN_2S,H_2O$ requires C, 37.0; H, 5.7; N, 14.4%).

4-Methylthiopyrimidine Methiodide.—4-Methylthiopyrimidine [24] (2.0 g) and methyl iodide (10.0 ml) were refluxed under anhydrous conditions on a water-bath at 52 °C for 6 h. The solid (4.1 g) was collected and recrystallised from ethanol (charcoal) to give *4-methylthiopyrimidine methiodide*, m.p. 144—146° (with prior softening) (Found, for material dried at 20 °C and 20 mmHg over NaOH: C, 26.9; H, 3.3; N, 10.2; S, 12.0%), δ(D_2O) 2.75 (MeS), 4.2 (MeN^+), 7.95 (H-5, d), 8.6 (H-6, q), and 9.2 (H-2).

1-Methylpyrimidin-2-one.—(*a*) Dimethyl sulphate (1.25 ml) was added to a mixture of 2-hydroxypyrimidine (1.0 g) and potassium carbonate (2 g) in water (5.0 ml). The mixture was warmed at 70 °C for 15 min, then extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated and the product chromatographed in chloroform over alumina and recrystallised from benzene to give 1-methylpyrimidin-2-one (0.5 g), m.p. 130—132° (lit.,[8] 127—128°) (Found: C, 54.85; H, 5.8; N, 25.0. Calc. for $C_5H_6N_2O$: C, 54.5; H, 5.5; N, 25.4%), δ(D_2O) 3.6 (MeN), 6.75 (H-5, q), 8.25 (H-4, q), and 8.7 (H-6, q).

(*b*) A mixture of 2-methylthiopyrimidine methiodide (0.050 g) and 5N-sodium hydroxide (0.3 ml) in water (1.0 ml) was kept at room temperature for 20 min, then extracted with chloroform. The product had m.p. and mixed m.p.[8] 129—130°.

Reaction of 2-Methylthiopyrimidine Methiodide with Aqueous Sodium Hydroxide.—When an aqueous solution of 2-methylthiopyrimidine methiodide (which showed no u.v. spectral change at 20 °C over 16 h) was mixed with dilute sodium hydroxide solution and the u.v. spectrum scanned (reference cell compensated with iodide ion), a two-step process was observed to take place to give finally 1-methylpyrimidin-2-one [8] (see above). The first step involved a fast reaction ($t_{\frac{1}{2}} < 1$ s; [methiodide] 0.000075 mol l^{-1}; [OH^-] 0.05N; temp. 15 °C) and the product ($\lambda_{max.}$ *ca.* 325 nm) quickly underwent further change to the pyrimidinone.

The reaction of 2-methylthiopyrimidine methiodide (0.040 g) with 6.67N-sodium deuterioxide (0.5 ml) was also examined by ^1H n.m.r. spectroscopy. The data were consistent with a two-step mechanism proceeding through the same initial product (which appeared to be a mixture of two species) and this in turn gave 1-methylpyrimidin-2-one. The n.m.r. spectrum of the initial product showed δ(D_2O) 2.3 and 2.35 (3 H) and 2.95 and 3.15 (3 H).

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