The Kinetics and Mechanism of the Electrophilic Substitution of Heteroaromatic Compounds. Part XXXII.[1] Acid Catalysed Hydrogen Exchange of Azaindoles †

By **Ali El-Anani, Sergio Clementi,** and **Alan R. Katritzky,*** School of Chemical Sciences, University of East Anglia, Norwich NOR 88C
Leonid Yakhontov, Moscow, Zubovakaja 7, Unichfi, U.S.S.R.

4-Aza-, 5-aza-, and 4-methyl-7-aza-indole each exchange the 3-proton, and the last compound also reacts at the 2- and 5-positions. 3-Aminopyridine undergoes hydrogen exchange at the 2-position and 4-methyl- and 6-methyl-2-aminopyridine each react at the 3- and 5-positions although at different rates. Rate constants are extrapolated to 100° and pH 0 and compared with similar data for other heterocycles to obtain quantitative estimates of relative reactivities.

In connection with work on aminopyridines [2] and on azoles,[3] we have now studied the representative azaindoles † (1)—(3) which may be considered as related both to aminopyridines and to pyrroles. N.m.r. spectral data and pK_a values for the compounds studied are recorded in Tables 1 and 2. The literature pK_a values for 20° in protic media have been extrapolated to the reaction temperature using the standard technique.[1] N.m.r data have previously been reported for the azaindoles [4,5] and for 3-aminopyridine:[6] the chemical shifts are in good agreement with the present results.

4-Aza- and 5-aza-indole on heating in D_2SO_4 each underwent smooth exchange of the 3-proton (Figures 1 and 2). Further reaction at the other ring positions was observed only on protracted heating at high acidities and temperatures and was then accompanied by other reactions.

TABLE 1

N.m.r. chemical shifts (τ scale) and coupling constants (Hz) at 60 MHz and pK_a values for azaindoles

	τ Value at position [a]						Coupling constants					pK_a Values			
Azaindole	2	3	4	5	6	7	$J_{2,3}$	$J_{5,6}$	$J_{6,7}$	$J_{4,6}$	$J_{5,7}$	*b*	*c*	T/°C	*d*
4-Aza	2·33	3·62		1·90	2·75	1·95	3·0	6·0	8·0		1·0	6·94 [e]	6·24	65	$< -7·5$
5-Aza	2·59	3·45	1·50		2·12	2·62	4·2		7·0	1·0		8·26 [e]	7·41	65	$< -7·5$
4-Me-7-aza	2·80	3·75	7·79 [f]	3·10	2·20		4·5	7·0				5·23 [g]	4·71	65	$< -7·5$

[a] All n.m.r. data refer to *ca.* 10% (w/w) solutions in 10% D_3SO_4 with $(NMe_4)_2SO_4$ as internal standard at τ 6·81. [b] For first proton addition at 20°. [c] For first proton addition at temperature of the succeeding column. [d] For second proton addition. [e] T. K. Adler and A. Albert, *J. Chem. Soc.*, 1960, 1794. [f] τ For CH_3 group. [g] A. Albert and R. E. Willette, *J. Chem. Soc.*, 1964, 4063.

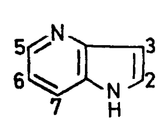
TABLE 2

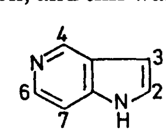
N.m.r. chemical shifts (τ scale) and coupling constants (Hz) at 60 MHz and pK_a values for aminopyridines

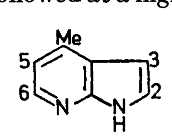
		τ Value at position					Coupling constants						pK_a Values					
Pyridine		2	3	4	5	6	$J_{2,6}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{5,6}$	$J_{4,6}$	*a, b*	*a, c*	*b, d*	*c, d*	T/°C	*m* [d,e]
3-NH_2	*f*	2·10		2·34	2·34	2·10	?			?	6	3	5·98 [l]	4·47	$-1·43$ [n]	$-1·59$	176	0·93 [n]
	g	1·95		3·00	3·00	2·20	4			?	6	2						
2-NH_2-4-Me	*h*	5·80 [j]	4·18	7·75 [k]	3·80	1·95					6		7·48 [m]	5·75	$-7·55$	$-6·16$	148	0·91
2-NH_2-6-Me	*h*	5·80 [j]	4·40	3·62	4·70	8·38 [k]		7		7			7·41 [m]	5·63	$-7·54$	$-6·03$	158	0·86
2-NHAc-6-Me	*i*	1·94 [j] 7·62 [k]	2·10	2·42	3·18	7·86 [k]		7		7								

[a] For first proton addition. [b] At 20°. [c] At temperature given in last column. [d] For second proton addition. [e] Gradient of log {[HB^+]/[B]} *vs.* H_0 defined as *m* value, see ref. 2. [f] N.m.r. data refer to *ca.* 10% (w/w) solutions in 10% D_2SO_4 with $(NMe_4)_2SO_4$ as internal standard at τ 6·81. [g] N.m.r. in Me_2SO. [h] N.m.r. of *ca.* 6% (w/w) solution in C_6D_6 with Me_4Si as internal standard. [i] N.m.r. in $CDCl_3$. [j] τ For NH_2 group. [k] τ For CH_3 group. [l] A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, 1948, 2240. [m] F. N. Fastier and M. A. McDowall, *Austral. J. Exptl. Biol.*, 1958, **36**, 491. [n] P. J. Brignell, C. D. Johnson, A. R. Katritzky, N. Shakir, H. O. Tarhan, and G. Walker, *J. Chem. Soc. (B)*, 1967, 1233.

4-Methyl-7-azaindole (3) on heating in D_2SO_4 initially exchanged the 3-proton, and this was followed at a higher


(1)


(2)


(3)

† IUPAC conventions require that these compounds be named as 1*H*-pyrrolopyridines or diazaindenes.

[1] Part XXXI, A. El-Anani, J. Banger, G. Bianchi, S. Clementi, C. D. Johnson, and A. R. Katritzky, preceding paper.
[2] A. El-Anani, P. E. Jones, and A. R. Katritzky, *J. Chem. Soc. (B)*, 1971, 2363.
[3] A. G. Burton, P. P. Forsythe, C. D. Johnson, and A. R. Katritzky, *J. Chem. Soc. (B)*, 1971, 2365.
[4] R. E. Willette, *Adv. Heterocyclic Chem.*, 1968, **9**, 100.
[5] P. G. Riley and B. Robinson, *Canad. J. Chem.*, 1969, **47**, 3257.
[6] R. F. C. Brown, L. Radom, S. Sternhell, and I. D. Rae, *Canad. J. Chem.*, 1968, **46**, 2584.

temperature by successive reaction at the 2- and 5-positions. Each of these exchanges could be followed by the changes in the n.m.r. spectrum (Figure 3): Figure

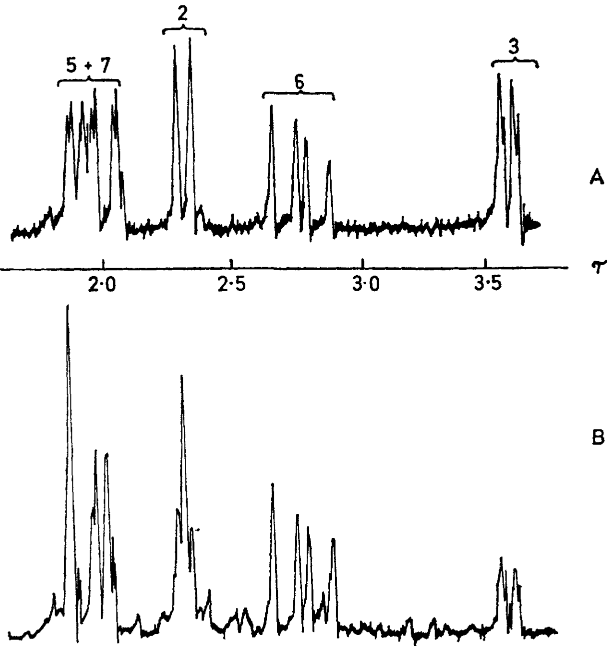


FIGURE 1 N.m.r. spectrum of 4-azaindole in 10% D_2SO_4: A, initially; B, after heating at 65° for 4 h

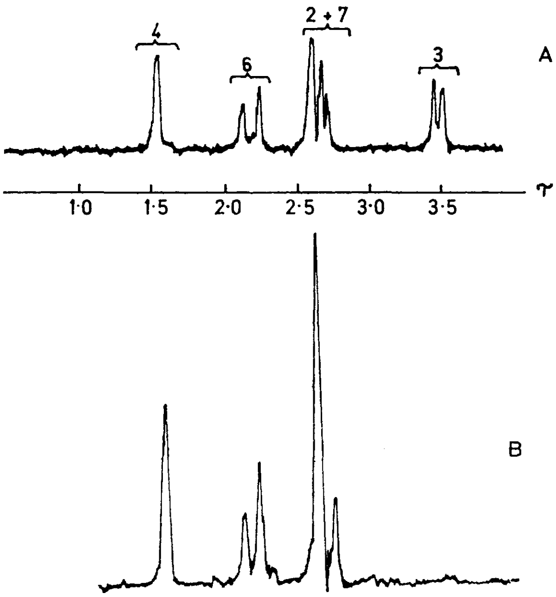


FIGURE 2 N.m.r. spectrum of 5-azaindole in 19·5% D_2SO_4: A, initially; B, after heating at 65° for 10 h

3A shows the initial spectrum and in Figure 3B, exchange is more than half completed at the 3-position. In Figure 3C, exchange at the 2-position is also almost complete, whereas in Figure 3D exchange has proceeded significantly at the 5-position.

The n.m.r. spectra of 3-aminopyridine showed two

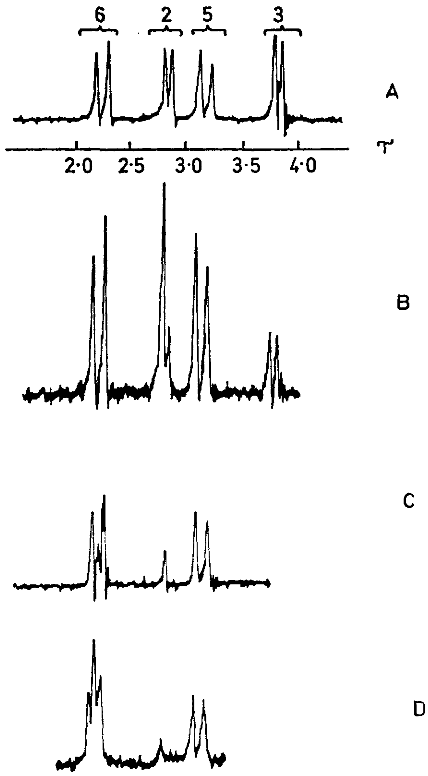


FIGURE 3 N.m.r. spectrum of 4-methyl-7-azaindole, aromatic proton region: A, in 10% D_2SO_4 initially; B, in 10% D_2SO_4 after heating for 6·3 h at 65°; C, in 27·5% D_2SO_4 after heating for 18·5 h at 150°; D, in 27·5% D_2SO_4 after heating for 62 h at 150°

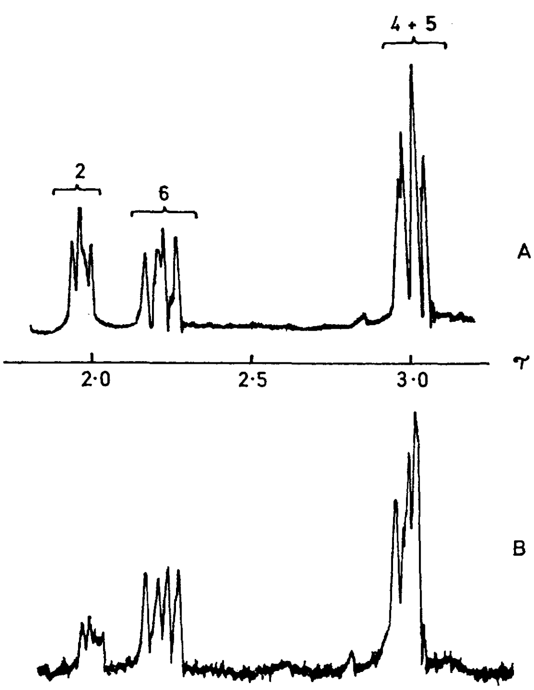


FIGURE 4 N.m.r. spectrum of 3-aminopyridine in $(CD_3)_2SO$: A, without treatment; B, of a specimen that had been previously heated for 34 h at 176° in 13·5% D_2SO_4 and reisolated

multiplets of equal area in 10% D_2SO_4, in D_2O, and in deuteriobenzene. However, in Me_2SO, the signals for the 2- and 6-position protons were resolved (Figure 4A); each was a multiplet as the *meta*-coupling constants are

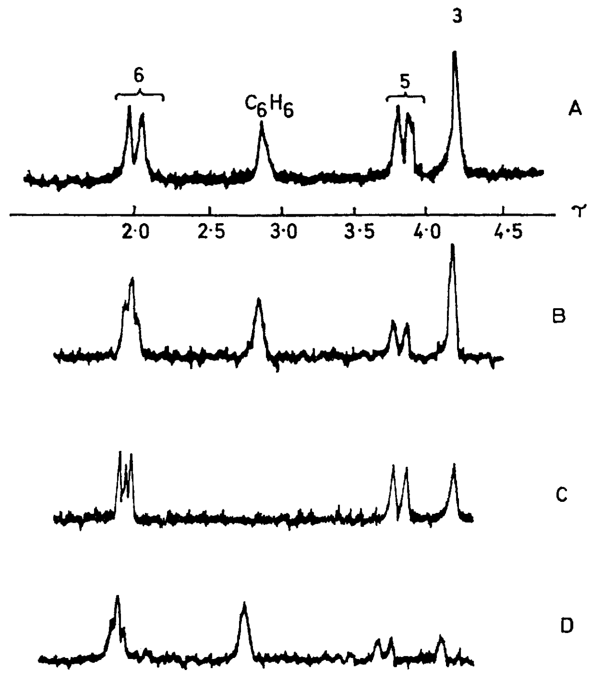


FIGURE 5 N.m.r. spectrum of 2-amino-4-methylpyridine in C_6D_6: A, without treatment; B, a specimen reisolated after heating in 10% D_2SO_4 for 14·75 h at 148° (to show preferential exchange at the 5-position); C, a specimen reisolated after heating for 1·3 h in 50% D_2SO_4 at 148° (to show preferential exchange at the 3-position); D, a specimen reisolated after heating for 13 h in 35·5% D_2SO_4 at 148°

appreciable (Table 2). The assignment was confirmed by measuring the spectrum in the presence of europium. On heating in D_2SO_4 at 176°, the integration ratio for the high : low field multiplet gradually changed from 2 : 2 to 2 : 1. The single proton which had exchanged was shown to be that at the 2-position by the n.m.r. spectrum in D_2SO_4 of the reacted compound which showed a low field signal for the 6-proton (dd, $J_{4,6}$ 3, $J_{5,6}$ 6 Hz). This was confirmed by isolation and measurement of the n.m.r. spectrum in Me_2SO (Figure 4B).

The n.m.r. spectrum of 2-amino-4-methylpyridine was well resolved only in deuteriobenzene and the exchange reaction was followed by the isolation technique. Exchange of the 3- and 5-protons could then be followed separately (Figure 5): at low acidities the 5-proton exchanged more rapidly (*cf.* Figure 5B) but at high acidities the 3-proton (*cf.* Figure 5C). In this case the assignment of the n.m.r. spectra is simple (Table 2).

The n.m.r. spectrum of 2-amino-6-methylpyridine showed in D_2SO_4 a multiplet for the 3- and 4-protons, but in C_6D_6 peaks for each of the ring protons were well resolved (Figure 6A). On heating in D_2SO_4, exchange occurred at both the 3- and 5-positions: however, measurement of the spectrum in C_6D_6 indicated that the reactions were proceeding at different rates (Figure 6B). A partially exchanged sample of 2-amino-6-methylpyridine was acetylated; the chemical shifts of ring proton peaks could be assigned (Table 2) using the known [6] influence of an acetamido-group in deshielding an *ortho*-proton compared to the *para*-proton. The spectrum (Figure 6C) clearly shows the faster exchange rate of the 5-proton compared to the 3-proton. The individual rates were now found by heating for known

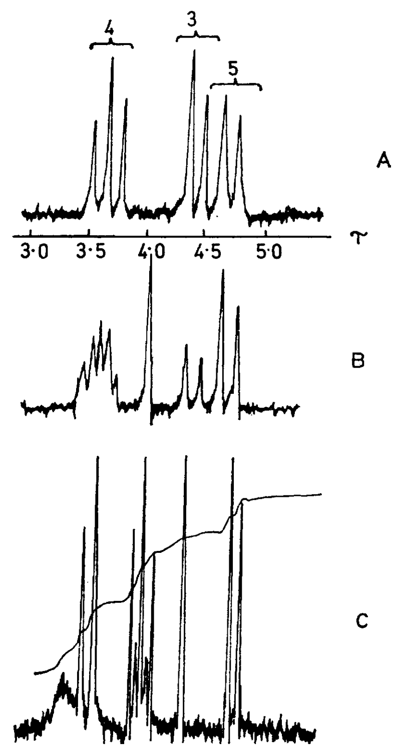


FIGURE 6 N.m.r. spectrum of 2-amino-6-methylpyridine in C_6D_6: A, without treatment; B, a specimen reisolated after heating for 9 h in 5% D_2SO_4 at 158°; C, N.m.r. spectrum in $CDCl_3$ of 2-acetamido-6-methylpyridine derived by acetylation of a specimen of 2-amino-6-methylpryidine heated for 1 h in 5% D_2SO_4 at 158°

times in D_2SO_4, reisolating, and integrating the spectrum C_6D_6, with the 4-proton as internal standard.

EXPERIMENTAL

Compounds.—The azaindoles were prepared by known methods and had m.p.s in agreement with literature data.[7] The aminopyridines were recrystallised commercial specimens: 3-amino-, m.p. 62° (lit.,[8] m.p. 64°); 2-amino-4-methyl-, m.p. 96—97° (lit.,[9] m.p. 98°); 2-amino-6-methyl-

[7] L. N. Yakhontov, M. Ya. Uritskaya, and M. V. Rubtsov, *Zhur. obshchei Khim.*, 1964, **34**, 1449; L. N. Yakhontov and E. I. Lapan, *Khim. geterotsikl. Soedinenii*, 1970, **5**, 27; L. N. Yakhontov and V. A. Azimov, *Doklady Akad. Nauk S.S.S.R.*, 1970, **192**, 583.

[8] F. Friedl, *Ber.*, 1912, **45**, 428.

[9] O. Seide, *Ber.*, 1924, **57***B*, 791.

pyridine, m.p. 40° (lit.,[10] 41°), 2-acetamido-6-methylpyridine, m.p. 88° (lit.,[10] m.p. 88°).

Spectroscopy and pK_a *Determinations.*—N.m.r. spectra were measured at 60 MHz on a Perkin-Elmer R12 instrument with sample spinning. pK_a Determinations were carried out using the spectrophotometric method as recommended by Albert and Serjeant.[11] Kinetic procedures were as described previously:[2] % D_2SO_4 quoted are corrected for salt formation, see ref. 1.

TABLE 3

Pseudo-first-order rate constants (s^{-1}) for hydrogen exchange in deuteriosulphuric acid

(i) 4-Azaindole, exchange of the 3-proton at 65°

% D_2SO_4	$-H_0$	$-\log k$
0·97	−0·81	4·29
6·65	0·01	3·88
9·57	0·26	3·44
14·0	0·63	3·32

(ii) 5-Azaindole, exchange of the 3-proton at 65°

% D_2SO_4	$-H_0$	$-\log k$
4·9	−0·20	4·64
8·1	0·23	4·43
12·8	0·55	4·24
20·6	1·07	3·87
42·1	2·63	2·89

(iii) 4-Methyl-7-azaindole, exchange of the 3-proton at 65°

% D_2SO_4	$-H_0$	$-\log k$
4·2	−0·28	4·31
8·2	0·24	4·05
15·7	0·74	3·79
19·8	1·01	3·63

(iv) 4-Methyl-7-azaindole, exchange of the 2- and 5-protons at 150°

% D_2SO_4	$-H_0$	2-H	5-H
15·7	0·59	5·13	5·57
27·0	1·24	4·87	5·59
48·2	2·65	3·72	4·81
57·8	3·33	3·25	4·32
65·1	3·88	2·81	4·00

(v) 3-Aminopyridine, exchange of the 2-proton at 176°

% D_2SO_4	$-H_0$	$-\log k$
0·5	−1·10	5·47
2·2	−0·80	5·40
4·2	−0·42	5·43
9·2	0·18	5·37
18·1	0·69	4·85
20·1	0·76	4·73
29·5	1·32	4·80
39·5	1·97	4·78

(vi) 2-Amino-4-methylpyridine, exchange of the 3- and 5-protons at 148°

% D_2SO_4	$-H_0$	3-H	5-H
2·0	−0·71	5·21	4·81
8·0	0·14	5·37	5·12
10·4	0·29	5·43	5·22
16·6	0·64	5·34	5·27
27·5	1·27	4·57	4·80
30·9	1·48	4·37	4·55
43·1	2·35	3·73	4·19

(vii) 2-Amino-6-methylpyridine, exchange of the 3- and 5-protons at 158°

% D_2SO_4	$-H_0$	3-H	5-H
2·5	−0·73	4·51	4·12
6·0	−0·20	4·58	4·36
8·3	0·14	4·63	4·44
19·4	0·79	4·40	4·01
29·0	1·33	4·05	3·63
32·6	1·57	3·77	3·51

RESULTS AND DISCUSSION

Pseudo-first-order rate constants are recorded in Table 3 and the rate profiles are plotted in Figures 7 and 8.

Reactive Species.—Exchange at the 3-position for 4-aza-, 5-aza-, and 4-methyl-7-aza-indole in each case occurs on the conjugate acid species, as shown by the rate profile slopes of 0·70, 0·63, and 0·52 respectively

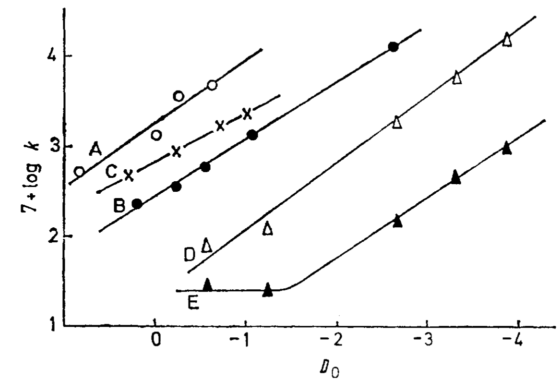


FIGURE 7 Rate profiles for azaindoles: A, 3-proton of 4-azaindole at 65°; B, 3-proton of 5-azaindole at 65°; C, 3-proton of 4-methyl-7-azaindole at 65°; D, 2-proton of 4-methyl-7-azaindole at 150°; E, 5-proton of 4-methyl-7-azaindole at 150°

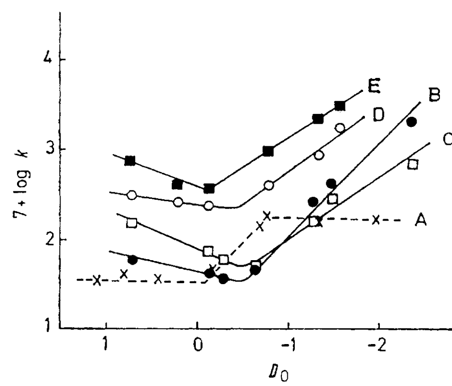


FIGURE 8 Rate profiles for aminopyridines: A, 2-proton of 3-aminopyridine at 176°; B, 3-proton and C, 5-proton of 2-amino-4-methylpyridine at 148°; D, 3-proton and E, 5-proton of 2-amino-6-methylpyridine at 158°

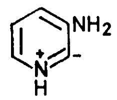
(Figure 7A—C). The exchange of the 2- and 5-protons of 4-methyl-7-azaindole, which takes place at higher temperature, is also a reaction of the conjugate acid (rate profile slopes of 0·73 and 0·66, respectively), except that at lower acidities the 5-proton exchanges as the free base form as shown by the rate becoming invariant with acidity (Figure 7E).

The zero slope rate profile (Figure 8A) for the exchange of the 2-proton in 3-aminopyridine for pH 1—0 may indicate either exchange as the free base or exchange by reaction of the conjugate acid with D_2O through the ylide intermediate (4). However, for acidities greater

[10] H. Meyer, *Rec. Trav. chim.*, 1925, **44**, 323.

[11] 'Ionisation Constants of Acids and Bases,' A. Albert and E. P. Serjeant, Methuen, London, 1962, p. 69.

than pH 0, exchange occurs on the conjugate acid, producing a rate profile slope of 1·06 from H_0 0 to —0·8 and then, above the second pK_a value of —1·18, again a zero slope.



(4)

At the higher acidities studied, the exchanges of the 3- and 5-protons of 2-amino-4- and 2-amino-6-methylpyridine are clearly reactions of the conjugate acids, with rate profile slopes in the range 0·63—0·93 (Figure 8B—E). At the lower acidities these slopes became negative, —0·13 to —0·39, probably indicating reaction on the free bases, although negative slopes are rather unusual. For 2-amino-4-methylpyridine (Figure 8B, C) the rate profiles cross, indicating preferential exchange of the 5-proton at low and the 3-proton at high acidities, confirming the qualitative results mentioned previously.

TABLE 4

Extrapolated rates at pH 0 and 100°

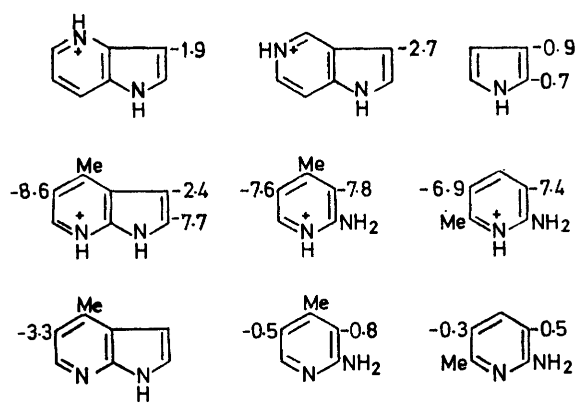
Compound	T/°C	Position	Species charge	Range % H_2SO_4	Range $-H_0$ (T)	Range −log k(stoich)	$\frac{d[\log k(\text{stoich})]}{d(-H_0)}$	−log k(stoich) at $H_0 = 0$	−log k(stoich) at $H_0 = 0$, T = 100°	pK_a [a] at 20 °C	pK_a [a] at 100 °C	m	−log k_s
4-Azaindole	65	3	+	1—14	−0·8—0·6	4·3—3·3	0·70	3·75	1·93				1·93
5-Azaindole	65	3	+	5—42	−0·2—2·6	4·6—2·9	0·63	4·55	2·73				2·73
4-Methyl-7-azaindole	65	3	+	4—20	−0·3—1·0	4·3—3·6	0·52	4·17	2·35				2·35
4-Methyl-7-azaindole	150	2	+	16—65	0·6—3·9	5·1—2·8	0·73	5·65	7·73				7·73
4-Methyl-7-azaindole	150	5	+	48—65	2·6—3·9	4·8—4·0	0·66	6·54	8·62				8·62
4-Methyl-7-azaindole	150	5	0	16—27	0·6—1·2	5·6—5·6	0·00	5·58	7·66	5·23	4·39	1	3·27
3-Aminopyridine	176	2	+ (min)	20—40	0·8—2·0	4·7—4·8	0·00	4·79	7·77	−1·03	−1·18	0·93	8·87
3-Aminopyridine	176	2	+ (maj)	9—20	0·2—0·8	5·4—4·7	1·06	5·56	8·54				8·54
3-Aminopyridine	176	2	0	1—4	−1·1 → −0·4	5·5—5·4	0·00	5·43	8·41	6·38	5·33	1	3·08 [b]
2-Amino-4-methylpyridine	148	3	+	17—43	0·6—2·4	5·3—3·7	0·93	5·83	7·84				7·84
2-Amino-4-methylpyridine	148	3	0	2—10	−0·7—2·3	5·2—5·4	−0·21	5·36	7·37	7·88	6·56	1	0·81
2-Amino-4-methylpyridine	148	5	+	17—43	0·6—2·4	5·3—4·2	0·63	5·61	7·62				7·62
2-Amino-4-methylpyridine	148	5	0	2—10	−0·7—2·3	4·8—5·2	−0·39	5·09	7·10	7·88	6·56	1	0·54
2-Amino-6-methylpyridine	158	3	+	19—36	0·8—1·6	4·4—3·8	0·78	5·03	7·40				7·40
2-Amino-6-methylpyridine	158	3	0	2—8	−0·7—0·1	4·5—4·6	−0·14	4·61	6·98	7·81	6·50	1	0·48
2-Amino-6-methylpyridine	158	5	+	8—36	0·1—1·6	4·4—3·5	0·66	4·53	6·90				6·90
2-Amino-6-methylpyridine	158	5	0	2—8	−0·7—0·1	4·1—4·4	−0·37	4·41	6·78	7·81	6·50	1	0·28

[a] pK_a Values in deuteriated media are reported; for a full discussion see ref. 1. [b] A different mechanism is possible; see text.

Rates at $H_0 = 0$ *and* 100°.—We have previously given [1] reasons for comparing rates at these conditions. The data were extrapolated as before [1] and are summarised in Table 4. For 3-aminopyridine conjugate acid, despite the poor accuracy involved in extrapolations of the rate profile, rates within the error involved in this procedure (±0·2) are obtained from both reactions as majority or minority species.

The standardised rates are compared in the Scheme with those for pyrrole. Two different studies on hydrogen exchange of this substrate were recently reported; Schwetlick *et al.* measured the dedeuteriation of a perdeuteriated sample at 20° in methanol–water containing 0·5% H_2SO_4,[12] and Bean determined the rate for deuteriation at 36° in dioxan–deuterium oxide containing 10% deuterioacetic acid.[13] The standardisation procedure applied to these sets leads to quite different values; we use the latter study, carried out close to $H_0 = 0$, without any acidity correction of the rates.

Fusion of a charged pyridinium ring with a pyrrole ring decreases the rate of exchange at the 3-position by a factor of 1—2 log units, and drastically decreases that at the 2-position from —0·7 to ⩽ —7·7. These results are in good agreement with the observed effect of benzo-fusion on the reactivity of furan and thiophen, despite the different orientation pattern in benzofuran and benzothiophen; on comparison with furan or thiophen respectively a large decrease in the reactivity at the α-position and a slight increase in the reactivity at the β-position were found in both systems.[14] Although hydrogen-exchange rates of indole have been studied only in basic media,[15] and the annelation effect in this system has not yet been reported, the reactivity towards electrophiles at the 3-position of indole is known to be close to that at the 2-position of pyrrole.[16] Accordingly, the effect of a fused pyridinium ring appears qualitatively very similar to a fused benzene ring,



SCHEME

[12] K. Schwetlick, K. Unverferth, and R. Mayer, *Z. Chem.*, 1967, 7, 58.
[13] G. P. Bean, *Chem. Comm.*, 1971, 421.
[14] S. Clementi, P. Linda, and G. Marino, *J. Chem. Soc.* (*B*), 1971, 79.
[15] B. C. Challis and E. M. Millar, *J.C.S. Perkin II*, 1972, 1111.
[16] S. Clementi, P. Linda, and G. Marino, *Chem. Comm.*, 1972, 427.

except that, since it is positively charged, it leads to a lower overall reactivity.†

The higher reactivity of the 4-aza- over the 5-aza-derivative is expected because of more effective electron withdrawal by the pyridine nitrogen atom in the 5-aza-compound: the reactivity of the 7-aza-derivative is expected to be, and is, intermediate, but a quantitative comparison is vitiated by the *C*-methyl group.

Exchange at the 5-position of 4-methyl-7-azaindole may be compared with that at the 5-position of 2-amino-4-methylpyridine. For both the cation and neutral species, the rate is slowed by incorporating the amino-group into a pyrrole ring.

† *Added in proof.* B. C. Challis and E. M. Millar (*J.C.S. Perkin II*, 1972, 1618) have recently reported kinetic data also for the acid-catalysed hydrogen exchange of indole in acetic acid buffer and in dilute hydrochloric acid at 25°. Their data in both systems indicate log k at pH 0 for the reaction at the 3-position at 25° as 0·0; which with $\Delta H^{\ddagger}$ 30 kcal mol^{-1} leads to log k_0 = 4·4. This value was expected to be close to that at the 2-position of pyrrole,[16] but it is far higher than those reported in the Scheme on the basis of ref. 13 (−0·7) and also higher than that obtained from ref. 12 (1·8). This work casts doubt on the comparison af the data for pyrrole (which refer to different solvents) with the present results

Comparison of the exchange rates of 2-amino-4-methyl- and 2-amino-6-methyl-pyridine (Scheme) shows (a) that log k_0 is always slightly greater for 5-exchange than for 3-exchange and (b) that for both positions the 6-methyl derivative possesses the larger log k_0 value. Detailed discussion of these and other aminopyridines is deferred, but we note that only near pH 0 are the rates similar for the 3- and 5-positions (see Figure 8). Evidently exchanges at these positions follow two distinct kinetic acidity functions, which recalls the changeover in relative rates of nitration of 2-pyridones at the 3- and 5-positions.[17] It is surprising that 3-aminopyridine showed exchange at the 2-position only; log (k_0/s^{-1}) for exchange at the other positions must be <-8.

We thank CNR (Italy) for a post-doctoral fellowship to S. Clementi.

[2/2483 *Received, 2nd November*, 1972]

[17] P. J. Brignell, A. R. Katritzky, and H. O. Tarhan, *J. Chem. Soc.* (*B*), 1968, 1477.