Quantitative Aspects of Lewis Acidity. Part XV.[1] Basicity of Substituted Pyridines and Quinolines towards Metal Halides in Diethyl Ether

By **David Berry, Krishna Bukka, and Rosemary S. Satchell,*** Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH

BF_3, $GaCl_3$, $SnCl_4$, $ZnCl_2$, and $PhSnCl_3$ form 1 : 1 adducts with substituted pyridines in diethyl ether solution. 1 : 1 Adducts are also usually formed with quinolines, but 2-substituted quinolines sometimes lead to a 2acid : 1base species as the only observable adduct. Values of $K_{1,1}$ for 1 : 1 adduct formation with pyridines follow the sequence $BF_3 \geqslant SnCl_4 > GaCl_3 > ZnCl_2 > PhSnCl_3$, and with quinolines the sequence $BF_3 > GaCl_3 > ZnCl_2$. For $ZnCl_2$ and unhindered quinolines the correlation equation $pK_{1,1} = -0.68pK_a - 0.77$ obtains. Compared with pyridines of comparable pK_a values in water, quinolines are relatively weaker bases towards metal halides in diethyl ether. Both quinolines and pyridines are more basic towards metal halides in diethyl ether than are anilines of the same pK_a value. The pK_a values at 25° of 2-chloropyridine, 3,5-dichloropyridine, and 3-bromopyridine are 0.75, 0.70, and 2.85 respectively.

WE present quantitative measurements of the interactions between substituted pyridines and quinolines and various metal halides in diethyl ether solution. No previous measurements of this type exist.

EXPERIMENTAL

Materials.—'Anhydrous' diethyl ether was purified by methods previously used in this laboratory.[2] The majority of the bases were commercial samples, which were either recrystallised to constant m.p., or redistilled immediately prior to use. 4-Nitropyridine was prepared from 4-nitropyridine *N*-oxide.[3] All m.p.s and b.p.s agreed with literature values. Boron trifluoride–diethyl diether,[4] gallium chloride,[5] stannic chloride,[6] and zinc chloride [7] were purified by established methods. Trichlorophenyltin was prepared as previously.[8] All manipulations with the purified metal halides and their solutions were performed in a dry-box.

pK_a *Measurements.*—The pK_a values of 2-chloropyridine, 3,5-dichloropyridine, and 3-bromopyridine were determined spectrophotometrically in perchloric acid–water mixtures. The respective values are 0.75 ± 0.02, 0.70 ± 0.05, and 2.85 ± 0.02. A Unicam SP 800 was used for recording all spectra, and an SP 500 for accurately measuring absorbances.

Reaction Mixtures.—Stock solutions of the metal halides were prepared by methods we have used previously.[2,4,5,7] Most of the stock solutions were analysed for halide by conductimetric titration with silver nitrate.

Equilibrium Measurements.—The stoicheiometry of the adduct, and the equilibrium constant † $K = [\text{Adduct}]/[B][MX_nS_y]^x$ for reaction (1), were determined as before.[1]

$$B + xMX_nS_y \rightleftharpoons B(MX_nS_{y-1})_x + xS \qquad (1)$$

U.v.–Visible Spectra of the Adducts.—The spectra of solutions containing fixed amounts of base and varying amounts of metal halide were recorded as soon as possible after mixing. The spectra were stable, and showed excellent isosbestic points. Thus only one adduct is formed in significant amounts in these systems. The spectral changes accompanying adduct formation are very similar to those observed on protonation in aqueous systems. Generally the base's peak system in the region of 300 nm increases in intensity,

---

† The solvent concentration is omitted conventionally from the expression for *K*.

[1] Part XIV, K. Bukka and R. S. Satchell, *J.C.S. Perkin II*, 1975, 1110.

[2] R. M. Evans and R. S. Satchell, *J. Chem. Soc.* (*B*), 1970, 1667.

[3] E. Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

[4] R. S. Satchell and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 36.

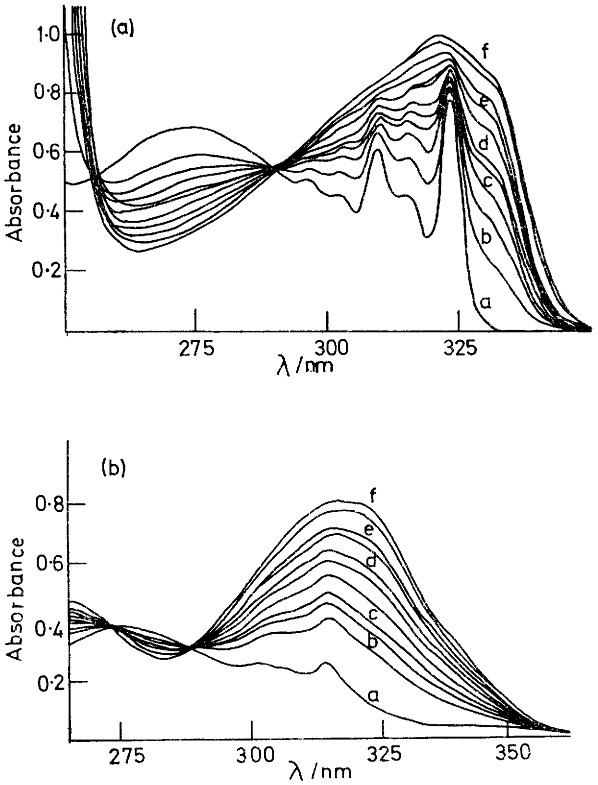
[5] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 403.

[6] R. M. Evans and R. S. Satchell, *J. Chem. Soc.* (*B*), 1970, 300.

[7] R. S. Satchell, *J. Chem. Soc.*, 1964, 5464.

[8] K. Bukka, C. J. Payne, and R. S. Satchell, *J.C.S. Perkin II*, 1975, 541.

and is replaced by a single broad peak [*e.g.* Figure (a) and (b)].



(a) Spectral changes of 3-bromoquinoline with $ZnCl_2$ in diethyl ether at 20°: a, 0.0000; b, 0.0009; c, 0.0026; d, 0.0043; e, 0.0087; f, 0.2167 mol dm^{-3}. (b) Spectral changes of 8-nitroquinoline with $GaCl_3$ in diethyl ether at 20°: a, 0.0000; b, 0.0013; c, 0.0020; d, 0.0039; e, 0.0066; f, 0.0262 mol dm^{-3}

RESULTS AND DISCUSSION

Adduct Stoicheiometry.—If D_o, D_e, and D_∞ represent the absorbances at some chosen wavelength in the absence of acid, at equilibrium for a given free acid concentration, and for complete conversion of base to adduct respectively, then the slope of the plot of $\log(D_o - D_e)/(D_e - D_\infty)$ against $\log [\text{Acid}]_{\text{free}}$ gives the stoicheiometry of the adduct.[1] For the majority of systems the slopes were close to unity, and thus the adducts formed had a stoicheiometry of 1 acid: 1 base (see Tables 1 and 2). This finding is in keeping with most earlier studies with nitrogen bases. However, in two systems (both involving 2-substituted quinolines) the slopes of the $\log(D_o - D_e)/(D_e - D_\infty) - \log [\text{Acid}]_{\text{free}}$ plots were close to 2. Thus in these cases the adduct stoicheiometry is 2 acid : 1 base (see Table 2). These unexpected stoicheiometries were reproducible and obtained under concentration conditions such that $[\text{Base}] \ll [\text{Acid}]_{\text{free}} \gg [H_2O]_{\text{solvent}}$; they are therefore unlikely to be the result of complications arising from the presence of water in the solvent, especially since all the other systems give clean 1 : 1 behaviour. Presumably the metal halide is dimeric in these 2 : 1 adducts, but why it should take up this form with 2-substituted quinolines and not with other bases is not easy to rationalise.

TABLE 1

$pK_{1,1}$ Values for 1 : 1 adduct formation between metal halides and substituted pyridines in diethyl ether

Units of $K_{1.1}$ are mol^{-1} dm^3

Pyridine derivative	pK_a	BF_3 at 25°	$SnCl_4$ at 25°	$GaCl_3$ at 20°	$ZnCl_2$ at 25°	$PhSnCl_3$ at 20°
3-Bromo	2.85				*ca.* -3.4 ± 0.1	
4-Nitro	1.23	*ca.* -3.5 ± 0.1		*ca.* -3.3 ± 0.1	-2.96 ± 0.10	
3,5-Dichloro	0.76	-2.77 ± 0.05	-2.72 ± 0.06	-2.62 ± 0.02	-2.21 ± 0.06	-0.92 ± 0.02
2-Chloro	0.75	-1.07 ± 0.02	-1.54 ± 0.02	-1.58 ± 0.01	-1.25 ± 0.02	

Equilibrium Constants.—Our $pK_{1,1}$ values for 1 : 1 adduct formation and $pK_{2,1}$ values for 2 : 1 adduct formation are summarised in Tables 1 and 2. As in earlier studies with anilines [1,4,9] and benzamides [8] we find, in the absence of steric complications, a rectilinear relationship between $pK_{1,1}$ and pK_a for the base in water. With quinolines and $ZnCl_2$ the relevant correlation equation is $pK_{1,1} = -0.68pK_a -0.77$. In Table 2 the $pK_{1,1}$ values calculated using this equation are compared with the observed values. Examination of the results for pyridines (Table 1) shows that a 2-chloro-group leads to a very large steric effect.

Comparison of the present results with those [9] for metal halide–substituted aniline equilibria reveals that anilines, quinolines, and pyridines of similar pK_a lead to very different pK values with a given metal halide. The quinolines are 2—20 fold, and the pyridines 30—500 fold more basic towards metal halides than expected, compared with an aniline of similar pK_a value. The largest differences are found with $ZnCl_2$ and the smallest with $SnCl_4$. Similar behaviour has been found in the interactions of pyridines and quinolines with the Lewis acid diacetyl (bisbenzoylhydrazone)nickel(II) in benzene solution.[10] The proper explanation of the behaviour is uncertain; it may be partly related to the fact that pyridines and quinolines are potentially capable of receiving back bonding *from* lone pair electrons in the acid where these are available.

Relative Acidities of Covalent Metal Halides.—Our values of $K_{1,1}$ for the unhindered pyridines with different acids follow the sequence $BF_3 \geqslant SnCl_4 > GaCl_3 > ZnCl_2 > PhSnCl_3$ (Table 1). For quinolines * the sequence is

---

* Studies of quinolines with the other acids were prevented by the low solubility of the adducts in diethyl ether.

[9] D. P. N. Satchell and R. S. Satchell, *Chem. Rev.*, 1969, **69**, 251.

[10] L. Sacconi, G. Lombardo, and P. Paoletti, *J. Chem. Soc.*, 1958, 848.

TABLE 2

pK Values for adduct formation between metal halides and substituted quinolines in diethyl ether at 20°

Units of $K_{1,1}$ and $K_{2,1}$ are mol^{-1} dm^3 and mol^{-2} dm^6 respectively; pK values in parentheses are $(\mathrm{p}K_{1,1})_{\mathrm{calc.}} = -0.68\ \mathrm{p}K_a - 0.77$ (see text)

Quinoline derivative	pK_a	BF_3	$GaCl_3$	$ZnCl_2$
2 acid : 1 base adducts				
2-Methyl	5.69			-3.21 ± 0.04
2-Chloro			-1.75 ± 0.03	
1 acid : 1 base adducts				
2-Methyl	5.69	*ca.* -4.5 ± 0.1		
Hydrogen	4.90			-4.08 ± 0.03 (-4.10)
6-Bromo	3.91			-3.45 ± 0.02 (-3.43)
4,7-Dichloro	2.80	-3.30 ± 0.05		-2.62 ± 0.02 (-2.67)
3-Bromo	2.69	-3.14 ± 0.04		-2.63 ± 0.01 (-2.60)
				-2.60 ± 0.01 *
8-Nitro	2.55		-2.74 ± 0.03	

* At 25°. $\Delta H^0 = -4.1 \pm 0.4$ kcal mol^{-1} (-17 ± 2 kJ mol^{-1}), $\Delta S^0 = -2.1 \pm 1.3$ cal mol^{-1} K^{-1} (9 ± 5 J K^{-1} mol^{-1}).

$BF_3 > GaCl_3 > ZnCl_2$ (Table 2). These sequences are the same as that found previously with aniline bases, but are different from that found with oxygen bases.[8]

ΔH^0 *and* ΔS^0 *Values*.—The ΔH^0 and ΔS^0 values for the 3-bromoquinoline–$ZnCl_2$ interaction are both small (Table 2). They are comparable with the corresponding values for the reaction of 3-methoxybenzamide with $ZnCl_2$ in tetrahydrofuran.[8]

In general the results now obtained with pyridines and quinolines fit into the pattern previously established for metal halide–organic base equilibria.[9]

[5/644 *Received, 7th April*, 1975]