Quantitative Aspects of Lewis Acidity. Part XIV.[1] Comparison of the Acidity of Tin Tetrachloride, Tellurium Tetrachloride, and Zirconium Tetrabromide towards Substituted Anilines in Dioxan

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Whereas $TeCl_4$ and $SnCl_4$ form 1 : 1 adducts with nitroanilines in dioxan solution, $ZrBr_4$ forms 2acid : 1base adducts in which both the amino- and the nitro-group of the base are probably involved. The strengths of the acids, judged by the values of $K_{1,1}$ for 1 : 1 adduct formation and by the concentration of acid required to convert the base into the adduct, follow the sequence $ZrBr_4 > TeCl_4 > SnCl_4$, and it can also be concluded that the sequence $ZrCl_4 \gg TeICl_4 > SnCl_4$ obtains. This sequence supports our earlier predictions concerning the effects of the electronic structure of the metal atom on the acidity of covalent halides. Adduct formation between $SnCl_4$ and a series of unhindered anilines in dioxan solution is related to the protonation of the bases by the equation $pK_{1,1} = -0.96pK_a - 0.21$, although p-nitro-substitution provides anomalous high $K_{1,1}$ values. This result is discussed. Towards anilines $SnCl_4$ provides slightly more acidic solutions in dioxan than in diethyl ether.

No equilibrium constants have been determined for adduct formation between $TeCl_4$ and any class of base, and few data exist for $ZrBr_4$. In one study the reaction of $Zr(Hal)_4$ with ethyl acetate in benzene solution was investigated;[2] 1acid : 2base complexes were found to be the dominant adduct species. Comparison of the results with those of an analogous study of $SnCl_4$, which forms both 1 : 1- and 1 : 2-adducts,[3] shows that the equilibrium constants, K, for reaction (1), are in the sequence $ZrCl_4 \gg ZrBr_4 > SnCl_4$. We report here upon the reaction of $TeCl_4$, $ZrBr_4$, and $SnCl_4$ with substituted

$$(MeCO_2Et)MX_4 + MeCO_2Et \rightleftharpoons (MeCO_2Et)_2MX_4 \quad (1)$$

anilines in dioxan solution. Since tellurium, tin, and zirconium are members of the same period in the Periodic Table, the present study permits instructive comparisons to be made of the effects on acidity of (i) the use by the central metal atom of inner d-orbitals and of outer d-orbitals, and (ii) the completion of a shell of 12 electrons, and the expansion of an octet of electrons, around the central metal atom. In previous articles[4,5] we have made predictions about the relative importance of such effects.

EXPERIMENTAL

Materials.—Anhydrous dioxan was fractionally distilled twice from sodium, and then once from lithium aluminium hydride. It had b.p. 102° at 760 mmHg. Karl Fischer titration showed the water level in the purified solvent to be *ca*. 3×10^{-3} mol dm^{-3}. Stannic chloride was purified as previously.[6] Tellurium tetrachloride and zirconium tetrabromide were purified by vacuum sublimation. The majority of the bases were commercial samples recrystallised to constant m.p.s in good agreement with literature values. 3-Methyl-4-nitroaniline was a previous sample.[7]

Reaction Mixtures.—Reaction mixtures were prepared in a dry box frequently flushed with pre-dried nitrogen. Stock solutions of base and of $TeCl_4$ were made up by weight. Stock solutions of $SnCl_4$ and $ZrBr_4$ were analysed for halide by conductimetric titration with silver nitrate.

Equilibrium Constants.—With the overall base concentration constant, the variation, with increasing acid concentration, of the free base concentration at equilibrium was followed spectrophotometrically. The u.v.–visible spectra of the various solutions, contained in stoppered (0.2 or 1 cm pathlength) cells, were recorded with a Unicam SP 800 spectrophotometer. Measurements at fixed wavelengths were also made with an SP 500 instrument. The reference cell contained the same concentration of acid as the sample. The cell compartment was thermostatted at 25.0 ± 0.1°. As in the earlier studies with metal halides and anilines in ether,[8] it was observed that on adduct formation the bases' longest wavelength absorption band was removed, and a new band appeared at a shorter wavelength.

For a given acid–base interaction the sets of spectra usually showed excellent isosbestic points. Thus only one adduct is formed in significant amounts. In a few cases (*e.g.* $ZrBr_4$ with 3,5-dinitroaniline) the absorption by the metal halide was too strong to permit detection of the isosbestic point. Such absorption limited the study of $TeCl_4$ and $ZrBr_4$ to bases which absorb at wavelengths >400 nm.

RESULTS AND DISCUSSION

Adduct Stoicheiometry and the Equilibrium Constants.—In our previous studies at least a 10-fold excess of acid over the base has been used. In the present work, since this type of concentration ratio was not always practicable owing (i) to the acid strength of $TeCl_4$ and $ZrBr_4$, and (ii) to the use of a higher base concentration with the shorter pathlength cell in order to minimise interference by the acid's absorption, our method of obtaining the adduct's stoicheiometry, and the equilibrium constant, has had to be modified, as described below.

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[5] D. P. N. Satchell and R. S. Satchell, *Quart. Rev.*, 1971, **25**, 171.

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

[7] D. P. N. Satchell and R. S. Satchell, *Trans. Faraday Soc.*, 1965, **61**, 1118.

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

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 equilibrium constant ($K_{1.1}$) for 1 : 1 adduct formation [reaction (2)] is given by equation (3), where B represents the base. Provided D_∞ is known, $K_{1.1}$ can be found

$$\mathrm{B} + \mathrm{MX_4} \overset{K_{1,1}}{\rightleftharpoons} \mathrm{BMX_4} \tag{2}$$

$$K_{1.1} = \frac{[\mathrm{BMX_4}]_e}{[\mathrm{B}]_e[\mathrm{MX_4}]_e} = \frac{(D_o - D_e)}{(D_e - D_\infty)} \frac{1}{[\mathrm{MX_4}]_e} \tag{3}$$

$$\begin{aligned}[\mathrm{MX_4}]_e &= [\mathrm{MX_4}]_{\mathrm{Total}} - [\mathrm{BMX_4}]_e \\ &= [\mathrm{MX_4}]_{\mathrm{Total}} - \frac{(D_o - D_e)}{(D_o - D_\infty)} [\mathrm{B}]_{\mathrm{Total}} \end{aligned} \tag{4}$$

using equations (3) and (4). For most systems involving $SnCl_4$ and $TeCl_4$, plots of $\log (D_o - D_e)/(D_e - D_\infty)$ against $\log [\mathrm{MX_4}]_e$ are good straight lines with slopes close to unity (Figure 1). This result shows that the stoicheiometry of the adducts in these cases is 1 : 1.

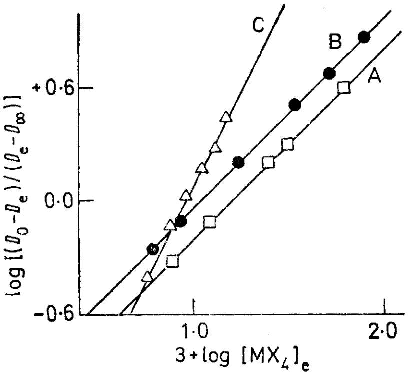


FIGURE 1 Plots of $\log[(D_o - D_e)/(D_e - D_\infty)]$ against $\log [\mathrm{MX_4}]_e$: A, $TeCl_4$ with 4-methyl-2-nitroaniline; B, $SnCl_4$ with 3-methyl-4-nitroaniline; C, $ZrBr_4$ with 3,5-dinitroaniline

In some systems D_∞ could not be measured directly. It was then obtained by the following procedure. (i) A plot of $(D_o - D_e)/[\mathrm{MX_4}]_{\mathrm{Total}}$ against D_e was extrapolated to give an approximate value of D_e ($= D_\infty$) when $(D_o - D_e)/[\mathrm{MX_4}]_{\mathrm{Total}} = 0$ {see equation (3) with $[\mathrm{MX_4}]_e$ replaced by $[\mathrm{MX_4}]_{\mathrm{Total}}$}. (ii) This value for D_∞ was substituted into equation (4) to obtain $[\mathrm{MX_4}]_e$. (iii) $(D_o - D_e)/[\mathrm{MX_4}]_e$ was now plotted against D_e to give a revised value for D_∞. For $TeCl_4$ and $SnCl_4$ systems this latter plot was always a good straight line and no further refinement of D_∞ was necessary. All the systems involving either $TeCl_4$ or $SnCl_4$ were thus shown to obey equations (3) and (4).

Systems involving $ZrBr_4$, on the other hand, do not obey equations (3) and (4) but can be analysed in terms of equilibrium (5) and the relevant equations (6) and (7). D_∞ was here obtained by a method analogous to that used for the systems involving 1 : 1 adducts. Plots of

$$2\mathrm{MX_4} + \mathrm{B} \overset{K_{2,1}}{\rightleftharpoons} \mathrm{B(MX_4)_2} \tag{5}$$

$$K_{2.1} = \frac{[\mathrm{B(MX_4)_2}]_e}{[\mathrm{B}]_e[\mathrm{MX_4}]_e{}^2} = \frac{(D_o - D_e)}{(D_e - D_\infty)} \times \frac{1}{[\mathrm{MX_4}]_e{}^2} \tag{6}$$

$$\begin{aligned}[\mathrm{MX_4}]_e &= [\mathrm{MX_4}]_{\mathrm{Total}} - 2[\mathrm{B(MX_4)_2}]_e \\ &= [\mathrm{MX_4}]_{\mathrm{Total}} - \frac{2(D_o - D_e)}{(D_o - D_\infty)} [\mathrm{B}]_{\mathrm{Total}} \end{aligned} \tag{7}$$

$\log (D_o - D_e)/(D_e - D_\infty)$ against $\log [\mathrm{MX_4}]_e$ are rectilinear with slopes close to 2 (Figure 1).

Our values of $K_{1.1}$ and $K_{2.1}$ are in the Table.

pK Values for adduct formation between metal halides and substituted anilines in dioxan at 25°

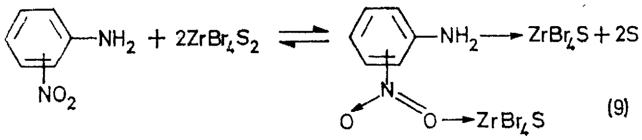
The units of $K_{1.1}$ and $K_{2.1}$ are $\mathrm{mol^{-1}\,dm^3}$ and $\mathrm{mol^{-2}\,dm^6}$ respectively. The standard error on pK = ±0.02. The values in parentheses are calculated values using the equation $\mathrm{p}K_{1.1} = -0.97\mathrm{p}K_a - 0.21$

Aniline derivative	pK_a	$SnCl_4$ p$K_{1.1}$	$TeCl_4$ p$K_{1.1}$	ZrB_4 p$K_{2.1}$
(1) 3,4-Dichloro	2.93 *	−2.94 (−3.05)		
(2) 4-Methyl-3-nitro	2.90	−3.06 (−3.02)		
(3) 3-Nitro	2.50	−2.62 (−2.64)		
(4) 3,5-Dichloro	2.37 *	−2.19 (−2.51)		
(5) 6-Methyl-3-nitro	2.32	−2.13		
(6) 2,4-Dichloro	2.00	−1.76		
(7) 4-Chloro-3-nitro	1.93	−2.09 (−2.08)		
(8) 2,3-Dichloro	1.83	−1.25		
(9) 3-Methyl-4-nitro	1.45	−1.96 (−1.62)		
(10) 4-Nitro	0.99	−1.69 (−1.17)		
(11) 2-Methyl-4-nitro	0.94	−1.18		
(12) 4-Methyl-2-nitro	0.45		−1.80	−5.58
(13) 3,5-Dinitro	0.22			−4.15
(14) 2-Nitro	−0.29		−1.22	−4.78

* These values were determined by us. They are in good agreement with reported values [P. A. Robinson, *J. Res. Nat. Bur. Standards*, 1964, **68A**, 159; P. D. Bolton and F. M. Hall, *J. Chem. Soc.* (*B*), 1970, 1247].

The NH_2 group is the most basic site in substituted anilines and the 1 : 1-adducts will doubtless have a structure in which this group is co-ordinated to the metal. If we assume that the halide is solvated by two dioxan molecules (S) then the $SnCl_4$ and $TeCl_4$ equilibria will approximate to (8). For the 2 : 1-adducts formed between nitroanilines and $ZrBr_4$ another basic site is required. This seems likely to be the NO_2 group [equation (9)]. Nitro-compounds are known to form complexes with very powerful Lewis acids.[9]

$$\mathrm{RC_6H_4NH_2} + \mathrm{MX_4S_2} \rightleftharpoons \mathrm{RC_6H_4NH_2} \rightarrow \mathrm{MX_4S} + \mathrm{S} \tag{8}$$



(9)

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[9] H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, 1956, **78**, 2173.

Relative Basicities.—The pK values for 1 : 1-adduct formation between $SnCl_4$ and unhindered, substituted anilines in diethyl ether[4] are related to the base's pK_a values by the equation $pK = -0.65pK_a - 0.80$. A plot (Figure 2) of the pK values for $SnCl_4$ in dioxan against the pK_a values, shows that the points for bases **1**, **2**, **3**, and **7** fall on a good straight line, whose equation is $pK = -0.97pK_a - 0.21$. The majority of the remaining bases contain 2-methyl and 2-chloro-substituents, which will be expected[4,7,8,10] to lead to steric effects and the points for these bases do fall below the line. However, three bases that fall off the line (3,5-dichloro-, 3-methyl-4-nitro-, and 4-nitro-aniline) do not contain 2-substituents. A 4-nitro-substituent has often been found in the past[4,8,10] to lead to K values greater than those predicted by the relevant K_a values. It appears therefore that substituents with strongly electron-withdrawing mesomeric effects do not reduce the basicity of anilines towards covalent metal halides as much as they do towards the proton. The exact implications of this for the bonding between the nitrogen and metal atoms is, however, uncertain. Why too 3,5-dichloroaniline often deviates[11] from plots like that in Figure 2 is also mysterious.

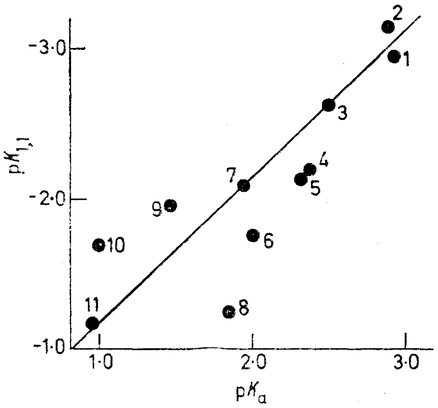

FIGURE 2 Plot of $pK_{1,1}$ against pK_a for $SnCl_4$

The results for $ZrBr_4$, reflecting as they do 2 : 1-adduct formation, would not necessarily be expected to have any simple regularity. However, $\Delta pK_{2,1}$ for the two *ortho*-nitro-bases is comparable with ΔpK_a, although for 3,5-dinitroaniline $K_{2,1}$ is appreciably smaller than the value for the normally much weaker base 2-nitroaniline (Table).

Solvent Effects.—For a given aniline and $SnCl_4$ $pK_{1,1}$ in dioxan is 0.2—0.4 units more positive than in diethyl ether;[12] *i.e.* the acidity of $SnCl_4$ is slightly greater in dioxan than in diethyl ether. Since dioxan (ε 2.2) has a lower dielectric constant than has diethyl ether (ε 4.3), it will therefore be expected to support the formation of a polar adduct less well. It is possible that it is also a weaker base than diethyl ether, so being more readily displaced by the anilines. Little is indeed known about the relative basicities of these two ethers.

Relative Acidity.—Although the adduct stoicheiometries are different, since the $ZrBr_4$ concentrations required for adduct formation are much smaller than for $TeCl_4$ and $SnCl_4$, we can safely conclude that, towards substituted anilines in dioxan, the acid strengths follow the sequence $ZrBr_4 > TeCl_4 > SnCl_4$ (Table). However, it is also known[2] qualitatively that $ZrCl_4$ is a much more powerful acid than is $ZrBr_4$. Hence we may conclude that the sequence $ZrCl_4 \gg TeCl_4 > SnCl_4$ obtains. The greater acidity of $TeCl_4$ compared with that of $SnCl_4$ suggests, in agreement with our predictions,[4] that the acidity of compounds in which the central metal atom has already expanded its outer electron shell beyond the octet is likely to be slightly greater than that of comparable compounds in which the central metal atom has still to expand this shell beyond the octet. The much greater acidity of $ZrCl_4$ compared with $SnCl_4$ also nicely supports our views about the behaviour of compounds which use inner and outer *d*-orbitals respectively in adduct formation.

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[11] K. Bukka and R. S. Satchell, unpublished data.

[12] A.Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1966, 527.