825. *Quantitative Aspects of Lewis Acidity. Part II. A Spectroscopic Study of the Equilibria in Ether Solution between the Zinc Halides and Aromatic Amines.**

By D. P. N. SATCHELL and (in part) J. L. WARDELL.

We report a spectroscopic study of the interactions, in ether solution, of the zinc halides with several substituted anilines (B). Adducts with a $1B : 1Zn(Hal)_2$ stoicheiometry are usually formed, though with zinc chloride some bases lead to other ratios. Equilibrium constants are quoted for the formation of the 1 : 1 adducts. The order of basicity towards a given zinc halide is very similar to that exhibited by the same bases towards the hydrogen ion in aqueous solution. Towards a given base the order of Lewis acidity is $ZnCl_2 \sim ZnBr_2 > ZnI_2$, the overall difference being small.

As with the stannic halides, the adducts fall into two classes. The stronger bases and acids tend to produce "anilinium" type species whose spectra closely resemble—though are not identical with—those of the corresponding anilinium ions. With sufficiently weak bases the adduct has a spectrum containing new long-wavelength absorption, and is better described as a charge-transfer species.

IN Part I we reported [1] a spectroscopic study of the equilibria, in dichlorobenzene solution, between aromatic amines and stannic halides. In this Paper we deal with zinc. Zinc halides are poorly soluble in benzenoid solvents, and we have used instead ether, for which fairly concentrated solutions may be obtained. There are few, or no, previous quantitative data concerning acid–base equilibria involving the zinc halides, save some measurements for the chloride acting as a chloride-ion acceptor.[2] The only information about the relative acidities of the halides stems from scattered kinetic data, some of them qualitative, the rest complex.[3] Numerous adducts between zinc halides and different classes of base have been obtained in preparative studies. Adducts involving aromatic amines appear normally to have a $2B : 1Zn(Hal)_2$ stoicheiometry.[4]

The objects of the present work were mainly three-fold: (i) to investigate the stoicheiometry for interaction with nitrogen bases in solution, (ii) to obtain a quantitative comparison of acceptor properties, and (iii) to discover if zinc halides, as well as those of tin, lead to both charge transfer and "anilinium" type interaction with bases.

EXPERIMENTAL

Materials.—Ether was refluxed over sodium and fractionally distilled. A cut, b. p. 34·5°, was collected. Nitromethane was fractionally distilled from phosphorous pentoxide and collected at 101°. Nine anilines were used in all. They were recrystallised commercial samples and in all cases their melting points agreed closely with the literature value. Zinc chloride (B.D.H., anhydrous sticks) was used as such. Commercial zinc bromide was purified by vacuum sublimation and the iodide by heating it for 2 hr. at 150—200°. Stock solutions of the halides were prepared by dissolving the solid in ether and finally centrifuging the liquid free from the small residue of insoluble oxide. The iodide solutions were protected from the light and under these conditions remained colourless to the eye for long periods. The concentrations of the stock solutions were estimated by solvolysis of a sample in an excess of water, followed by titration for halogen. All reagents and stock solutions were stored in a dry atmosphere.

Measurement of Equilibrium Constants.—The methods were essentially those previously

* Part I, *J.*, 1964, 4134. See *Chem. and Ind.*, 1963, 2011, for a preliminary report of this work.
[1] Part I, Satchell and Wardell, *J.*, 1964, 4134.
[2] Baaz, Gutmann, and Masaguer, *Monatsh.*, 1961, **92**, 582; Gutmann and Hampel, *ibid.*, p. 1048.
[3] R. S. Satchell, *J.*, 1963, 5963; Olah, " Friedel–Crafts and Related Reactions," Interscience, 1963, Vol. 1, p. 861.
[4] Ablov and Bornasheva, *Z. neorg. Khim.*, 1960, **5**, 604.

described.[1] All the base spectra obeyed Beer's law. Experiments showed that contamination by small amounts of water has relatively little effect on the spectra, and it therefore proved possible to work, for the most part, on the open bench, rather than in a dry box.

RESULTS AND DISCUSSION

Adduct Stoicheiometry in Solution.—As noted, in the solid state anilines prefer a $2B : 1Zn(Hal)_2$ stoicheiometry.[4] The same is generally true for the corresponding tin halide adducts studied previously.[1] In solution, however, the tin adducts proved invariably $1B : 1Sn(Hal)_4$. With the zinc halides in solution intermediate behaviour is found. The bromide and the iodide give largely 1 : 1 proportions, but for the chloride a stoicheiometry of roughly $1B : 2Zn(Hal)_2$ and other intermediate values are also found. (See Table.) The origin of this effect is uncertain. Perhaps some participation by dimeric zinc chloride may be involved in adduct formation, *i.e.*, more than one equilibrium may be operative in the examples showing an apparent stoicheiometry of between 1 : 1 and 1 : 2. Equilibrium constants have not therefore been calculated for these cases. The lower incidence of non-integral stoicheiometry for the bromide and the iodide seems to support the notion that the phenomenon is related to a property of the chloride, rather than to a general solvent effect.

It seems likely that the zinc atom is 4-co-ordinate in all the adducts, the strongly co-ordinating solvent taking up the last site.

Relative Acidities of the Zinc Halides.—Comparison of the equilibrium constants involving a common base shows that the acidity order is $ZnCl_2 \sim ZnBr_2 > ZnI_2$,* the overall difference being rather small. It is significant that (a) this order is *not* that observed[3] in situations when the acid accepts a halide ion, and (b) that relative acidity is to some extent a function of the base used for comparison (see Table).

Relative Basicities of the Bases.—The order observed in aqueous solution (as defined by pK_a) is retained in ether, and the relative basicities (ΔpK) are often surprisingly similar, though not exactly the same. Analogous phenomena were found for the stannic halides in dichlorobenzene.

Spectral Effects on Adduct Formation.—An advantage of the zinc halide–ether systems over those of tin halide–dichlorobenzene is that optical measurements can be made further into the ultraviolet region. Zinc chloride indeed absorbs strongly only at 2250 Å and zinc bromide at 2350 Å. The situation is less favourable for the iodide but satisfactory measurements could be made above 2700 Å.

The stannic halides led to two sorts of adduct, which we characterised as " anilinium " and charge-transfer in type. Strong acids and bases tend to give the former, while weak acids with weak bases provide the latter.[1] Formation of the less stable, charge-transfer adducts removed observable (>3100 Å) free-base absorption, but gave new absorption, on the long-wavelength side of the base band, in the visible region. Formation of the " anilinium " adducts also removed the base absorption and presumably provided new absorption in the ultraviolet region, on the short-wavelength side of the base band, as happens typically on anilinium-ion formation.[5] Hence our terminology. In dichlorobenzene this latter point could not be checked because of the strong solvent absorption below 3100 Å. It has been possible to check it for the present systems.

The zinc halides proved to behave generally as do those of tin: (i) adducts exhibiting new, long-wavelength absorption are formed as well as adducts not showing such absorption, and (ii) the former class are apparently formed most readily the weaker the acid and the base concerned. Thus, in the present work, only 4-nitroaniline and 6-methyl-4-nitroaniline gave such absorption, and for 4-nitroaniline it was more prominent for the bromide and the iodide than for the chloride (see $\varepsilon_A/\varepsilon_B$ in the Table). As previously discussed, we attribute the new, visible absorption to the fact that the ground-state adduct species

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* Owing to an error these signs were interchanged in *Chem. and Ind.*, 1963, 2011.

[5] Jaffé and Orchin, " Theory and Applications of Ultra-violet Spectroscopy," Wiley, 1962.

in these cases are more closely approximated by the non-bonded structure B, $Zn(Hal)_2$ than by $B^+-Zn^-(Hal)_2$. This provides the possibility of " intermolecular " charge-transfer transitions.[6] The weaker the Lewis acid the more pronounced this effect should be, as found.

For all the bases (4-nitroaniline and 6-methyl-4-nitroaniline included) adduct formation

Equilibrium constants and spectral details for zinc halide–aniline base adduct formation in ether at $20 \pm 2°$.

A = Adduct; $pK = -\log [A]/[B][Zn(Hal)_2]$; ε = extinction coefficient at band maximum; $\lambda^{max.}$ = wavelength of maximum absorption in Å; λ_p refers to spectra of protonated aniline (P); for each species A, B, and P all bands observed (>2200 Å) are quoted; for 3-nitroanilines one maximum was not located because of very strong absorption at the concentrations used; H implies that bands are hidden by zinc halide absorption; $\varepsilon_A/\varepsilon_B$ compares the adduct absorption with that of the base band of longest wavelength; sh = shoulder.

Aniline derivative	pK	pK_a ‡	$\lambda_B^{max.}$	$\lambda_A^{max.}$	$\varepsilon_A/\varepsilon_B$	$\lambda_P^{max.}$	Apparent stoicheiometry † 1B : xZn(Hal)$_2$
(i) ZnCl$_2$							
4-Bromo-	$-2\cdot20$	$3\cdot91$	2500 / 3050	2230	$\sim1\cdot1$ / $\sim11\cdot0$	2200	1 : 1·05
4-Methyl-3-nitro-	—	$2\cdot90$	<2700 / 3700	<2700 / 3100	$1\cdot1$	<2700 / 3000sh	1 : 1·90
3-Nitro-	—	$2\cdot50$	<2700 / 3700	<2700 / 3100sh	$\sim0\cdot75$	<2700	1 : 1·50
2,4-Dichloro-	$-0\cdot71$	$2\cdot00$	2480 / 3080	2700	$\sim0\cdot35$		1 : 1·00
2,3-Dichloro-	$-0\cdot47$	$1\cdot83$	2400 / 3000	2700	$\sim0\cdot50$		1 : 1·01
2,5-Dichloro-	$-0\cdot28$	$1\cdot50$	2400 / 3020	2750	$\sim0\cdot50$		1 : 0·98
4-Nitro-	—	$0\cdot99$	2300 / 3530	2700 / 4600	$1\cdot1$ / $0\cdot06$	2610	1 : 1·65
2-Methyl-4-nitro-	$0\cdot75$	$0\cdot94$	2370 / 3600	H / 2900 / 4500	$0\cdot65$ / $0\cdot30$	2370 / 2640	1 : 1·01
4-Methyl-2-nitro- *	—	$0\cdot45$	2400 / 2900 / 4050	2700 / 3150	— / —	2270 / 2670 / 3100sh	—
(ii) ZnBr$_2$							
4-Bromo-	$-2\cdot10$	$3\cdot91$	2500 / 3050	H	—	2200	1 : 1·08
4-Methyl-3-nitro-	$-1\cdot55$	$2\cdot90$	<2700 / 3700	<2700 / 3150	$\sim1\cdot0$	<2700 / 3000sh	1 : 1·10
3-Nitro-	$-1\cdot00$	$2\cdot50$	<2700 / 3700	<2700 / 3100sh	$\sim1\cdot0$	<2700	1 : 1·07
2,5-Dichloro-	$-0\cdot48$	$1\cdot50$	2400 / 3020	H / 2800	$0\cdot4$		1 : 1·00
4-Nitro-	$-0\cdot08$	$0\cdot99$	2300 / 3530	2900 / 4250	$\sim0\cdot50$ / $0\cdot12$	2610	1 : 0·95
(iii) ZnI$_2$							
4-Bromo-	—	$3\cdot91$	2500 / 3050	H	—	2200	1 : 1·30
4-Methyl-3-nitro-	$-1\cdot30$	$2\cdot90$	<2700 / 3700	H / 3100	$\sim2\cdot0$	<2700 / 3000sh	1 : 1·93
4-Nitro-	$0\cdot20$	$0\cdot99$	2300 / 3530	H / 4350	$0\cdot35$	2610	1 : 1·00

* Solutions unstable, pK not quoted. † Calculated from slope of plot of log $[Zn(Hal)_2]$ against log $[A]/[B]$ (see Ref. 1). ‡ See Ref. 1.

provides other changes in absorption very similar to (though not exactly the same as) those produced by protonation * of the bases (see Table). These substituted anilines normally have two main absorption bands in the region accessible to us (>2200 Å), the

* The anilinium ions were obtained either by adding acetic acid to a solution of the base and the zinc halide in ether, or by dissolving the base in a solution of hydrogen chloride in nitromethane. The positions of the bands differed little in the two cases.

6 See, *e.g.*, Murrell, *Quart. Rev.*, 1961, **15**, 191.

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longer-wavelength band (L) * often extending into the visible region, and usually having the smaller extinction coefficient of the two. It is this band which was observed in the stannic halide experiments and it is the band used when these bases are employed as Hammett indicators.[7] On protonation, or metal halide adduct formation, this band is removed and its fall may be used to calculate the equilibrium constant involved.[1]

The other base band (S),* at shorter wavelengths, is normally also affected in position (blue shift) and intensity on protonation or adduct formation, but is only totally lost for the halogenoanilines. Anilinium ion, or adduct formation, also provides a new band (or a shoulder) in the ultraviolet region, on the long wavelength side of band S (see Table). The considerable similarity (see Figure and Table) of the effects observed on protonation and adduct formation justify our labelling those adducts, which do not also show charge-transfer absorption, " anilinium " in type. It is clear that the proton and the Lewis acid are having much the same effect on the electronic energy levels and transitions, and that the Lewis acid is located on the amino-nitrogen atom.

It is often considered that band L may itself be approximately regarded as an intra-molecular charge-transfer band (between the nitrogen lone pair and the nitro or halogen

Ultraviolet spectra of 4-methyl-3-nitroaniline.

A, Free base. B, Zinc chloride adduct. C, Anilinium ion. Concentrations $2 \cdot 0 \times 10^{-4}$M.
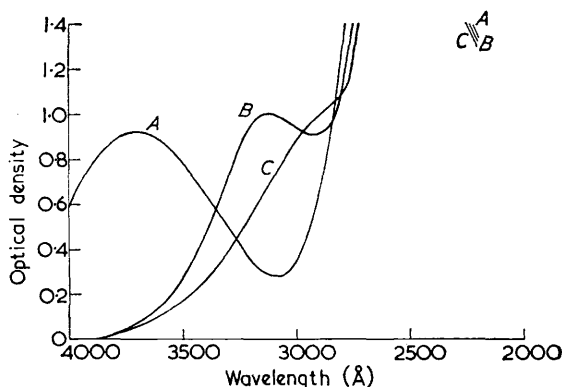
substituent).[5,6] Such a band will obviously be inhibited on protonation, or adduct formation, and if still extant at least suffer a blue shift. The characteristic new, short wave-length adduct bands for all bases *might* represent this band shifted, but it seems very unlikely that protonation at least will permit any such charge-transfer to be retained. Some other explanation of the adduct bands seems more likely. The extent to which band S (probably best classified as arising from a $\pi \longrightarrow \pi^*$ transition)[5] is affected, is presumably a measure of the extent to which the nitrogen lone-pair orbital is involved in this transition also.

The simplest imaginable spectral result on protonation, or adduct formation, is that the resulting spectrum should closely resemble that of the corresponding benzene derivative without the NH_2 substituent.[5] For instance, the parent anilinium ion, $Ph\overset{+}{N}H_3$, has a spectrum very similar to that of benzene.[5] In the present examples the situation is clearly not so simple. Thus the nitroaniline spectra do not always reduce to an absorption similar to that of nitrobenzene (which previous work[8] shows to have a band maximum at *ca.* 2600 Å, and no band or shoulder in the 2900—3100 Å region). It seems that the presence of a positive pole does significantly affect the π-electron system of a nitro- and probably therefore also of a halogeno-benzene residue.[5] The observed adduct spectra

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* Our terminology.

[7] Long and Paul, *Chem. Revs.*, 1957, **57**, 1.

[8] Brown and Regan, *J. Amer. Chem. Soc.*, 1947, **69**, 1032; Burroway and Chamberlain, *J.*, 1952, 3736.

therefore most probably arise from possible $\pi \longrightarrow \pi^*$ transitions in the nitro- and halogeno-benzene residues as perturbed by the substituents NH_3^+ and co-ordinated nitrogen. The fact that the truly anilinium-ion spectra and those of the corresponding adducts are similar, but not identical, is understandable: the perturbations will be different in the two cases.

DEPARTMENT OF CHEMISTRY,
KING'S COLLEGE, STRAND, LONDON W.C.2.