116. *Quantitative Aspects of Lewis Acidity. Part IV.*[1] *The Interaction of Antimony Halides with Nitroanilines in Ether and in Dichlorobenzene.*

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Antimony trichloride is a weaker acid towards amines than are stannic and zinc chlorides. Some equilibrium constants for the formation of 1 : 1 adducts with nitroanilines in ether solution are reported. At high concentrations of antimony chloride more than one molecule of this substance is involved in each adduct. The spectra of the adducts are probably similar to those of the corresponding anilinium ions. With very weakly basic nitroanilines, antimony halides associate (loosely) with the nitro-group rather than co-ordinating with the amino-group. This effect leads to a shift of the base's absorption towards long wavelengths and provides a visual colour change which can be mistaken for normal acid–base interaction.

Isolable (solvent-free) adducts have stoicheiometries which are not simply related to structure.

PREVIOUS studies [1] dealt with tin and zinc halides. We now report work with antimony.

EXPERIMENTAL

Materials.—The solvents and anilines, purified as previously described,[1] had the same physical constants. Commercial antimony trichloride and tribromide, recrystallised from carbon disulphide or carbon tetrachloride and dried *in vacuo*, had m. p. 73·5 and 96·5°, respectively.

Optical and Equilibrium Measurements.—These were conducted as before.[1]

Preparation of Solvent-free Adducts.—The mixing of concentrated solutions of a base and an antimony halide in carbon tetrachloride leads to the precipitation of the (usually solid) adduct. We have found, and the literature contains, no evidence for the elimination of hydrogen halide in such reactions; straightforward adduct formation seems to occur. The adducts were filtered (where appropriate), washed with solvent, and dried *in vacuo*. Analyses (commercial) are in Table 1.

TABLE 1.

Solvent-free adducts of $SbCl_3$.

Aniline (B)	Adduct form	Adduct analysis	Stoicheiometry
4-Methyl-3-nitro-	Yellow, crystalline powder	31·86% C 3·31% H 19·50% Cl	2·01B : $1SbCl_3$
6-Methyl-3-nitro-	Yellow, crystalline powder	27·66% C 3·04% H 23·55% Cl	1·50B : $1SbCl_3$ (3·00B : $2SbCl_3$)
2-Nitro-	Red, viscous oil	14·86% C 1·77% H 33·20% Cl	0·69B : $1SbCl_3$ (2·07B : $3SbCl_3$)

RESULTS AND DISCUSSION

(1) *Stoicheiometry of Solvent-free Adducts.*—Reproducible analyses were obtained which correspond closely to integral stoicheiometries (Table 1). However, the interpretation of these stoicheiometries is not obvious. In contrast to the tin and zinc systems,[1] factors other than acid–base interaction and the establishment of maximum co-ordination for the metal atom, appear to be involved. Similar results have been obtained with the antimony halides by other workers.[2] As shown below, the solvent-free stoicheiometries are different from those found in solution.

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[1] Parts I—III, Satchell and Wardell, *J.*, 1964, (*a*) 4134, (*b*) 4296, (*c*) 4300.

[2] Funk and Koehler, *J. Pract. Chem.*, 1961, **14**, 226; Menshutkin, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1128; Daasch, *Spectrochim. Acta*, 1959, **15**, 726; Prasad, Rao, Kumar, Reddy, and Kackar, *J. Ind. Chem. Soc.*, 1959, **36**, 129.

(2) *Spectral Effects and Equilibrium Constants.*—The addition of a stannic or zinc halide to an aniline in ether, or in an aromatic solvent, provides straightforward effects.[1] The base and halide interact (to an extent dependent in the relevant equilibrium constant) to give an adduct (usually of 1 : 1 stoicheiometry) in which the nitrogen atom's lone pair of electrons are engaged. As a result the base's original long-wavelength absorption is removed and the resulting spectrum either approximates to that of the corresponding anilinium ion or a new band appears. Study of these changes leads to an estimation of the equilibrium constant concerned. We expected to observe similar effects with the antimony halides but found new phenomena superimposed on them.

(a) *Weak bases.* We arbitrarily divide the bases (B) studied into two groups, strong and weak. The weakest base for which a pK value (K = [B,MXn]/[MXn][B]) can be accurately determined by our methods [1a] is one which displays (in the system concerned) a pK $\sim$0·6. Weaker bases will be rather little affected by molar concentrations of halide, and the use of very high concentrations is undesirable in these equilibrium studies and, in any case, often impossible because of solubility limitations.

In past work,[1] on taking such a weak base, and examining its spectrum in concentrated halide solutions, we have observed the (expected) small, or negligible, changes in absorption. In the present work with antimony halides a very pronounced red shift has been observed under similar circumstances. Fig. 1 shows examples. Little decrease in absorption *intensity* is found; most of that obseved for *p*-nitroaniline is probably due to its having a pK $\not>$0·6. Some broadening of the band occurs.

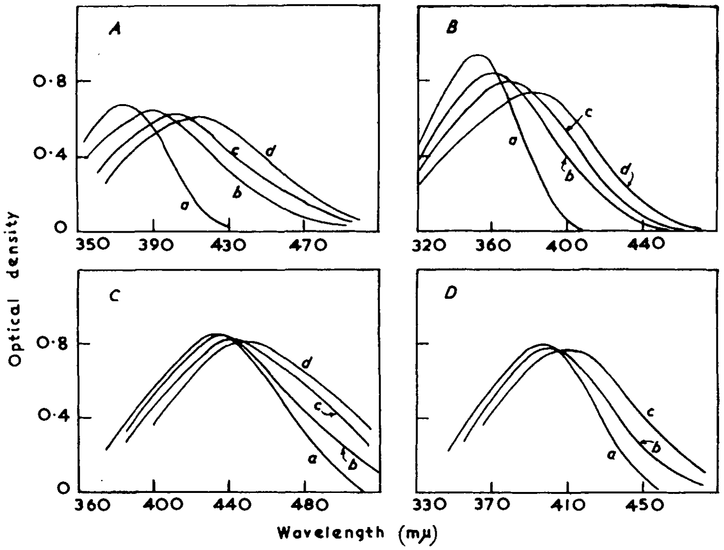

FIG. 1. Effect of antimony trichloride on weak bases.

A, 4-Nitrodiphenylamine in ether [$SbCl_3$] a, 0; b, 1·18; c, 2·38; d, 4·17. B, 4-Nitroaniline in *o*-dichlorobenzene [$SbCl_3$] a, 0; b, 0·24; c, 0·48; d, 1·08. C, 2-Nitrodiphenylamine in *o*-dichlorobenzene [$SbCl_3$] a, 0; b, 0·104; c, 0·311; d, 0·414. D, 2-Nitroaniline in *o*-dichlorobenzene [$SbCl_3$] a, 0; b, 0·104; c, 0·311. [Base] $\sim10^{-4}$, constant for each figure.

The effects are found in both ether and *o*-dichlorobenzene and with both antimony trichloride and tribromide. Visually the effects can be striking, the base solution turning from a pale yellow to an orange-red. At a qualitative level the visual change could be mistaken [3] for a conversion of the base (or indicator) into its " acid " form (*i.e.*, for engagement of its basic centre). Our previous data, and those below concerning stronger bases, show this not to be so. Moreover isobestic points are absent. We interpret the shifts

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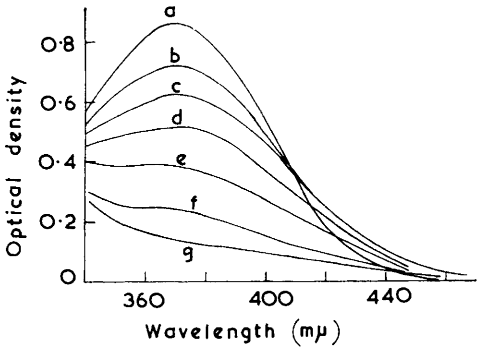
[3] Hawke and Steigman, *Anal. Chem.*, 1954, 1989.

as arising from solvation by the metal halide localised at the nitro-, rather than at the amino-, group of the base. We suggest that when the base's nitrogen atom falls below a certain basicity, the attentions of the halide molecules become focused instead on the polar nitro-group. If this is so, since the base's absorption is due to an intramolecular charge-transfer transition to the nitro-group,[4] the upper state of this transition will be stabilised, and a pronounced red shift would be expected, as found. Red shifts are expected with increases in dielectric constant generally,[4,1a] and such an increase must be involved as more and more metal halide is added, but the magnitude of the present effects at relatively small halide concentrations seem to indicate a rather specific solvation. We favour such an explanation. It appears from this, and from what follows, that antimony halides are particularly good solvating agents in the present systems. The occurrence of the effects with antimony, and not with zinc or tin,[1] halides is perhaps connected with the greater dipole moments of the former. The effects may prove characteristic for Lewis acids of the MX_3 type.

FIG. 2. 3-Nitroaniline with antimony trichloride in ether.

[Base] ~10^{-4}. [$SbCl_3$] a, 0·0; b, 0·354; c, 0·591; d, 0·708; e, 0·945; f, 1·18;g, 1·54.



(b) *Strong bases.* 6-Methyl-3-nitro-, 3-nitro-, and 4-methyl-3-nitro-aniline (some of the strongest bases we have studied previously) all behave more normally. Spectral data for 3-nitroaniline are in Fig. 2. Data for the other bases are similar. As antimony trichloride is added to the ether solution the base absorption falls, indicating adduct formation *via* the nitrogen lone pair.[1a] What is probably a small red shift of the residual base band may be discerned in Fig. 2. This shift is smaller than those discussed above. This is understandable in terms of our specific solvation hypothesis, for in associating with strong bases the antimony halide will pay most attention to the nitrogen atom.

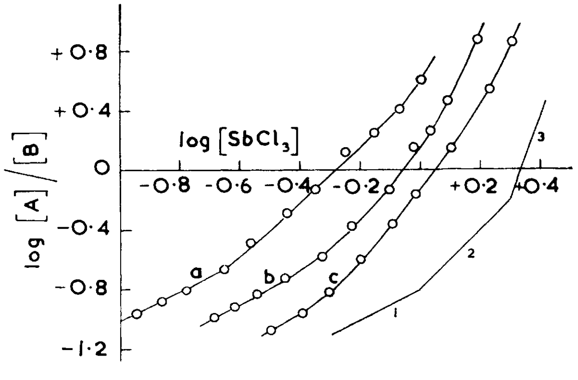


FIG. 3. Plots of log [A]/[B] against log [$SbCl_3$] for 3-nitroanilines.

a, 4-Methyl-3-nitroaniline.
b, 3,Nitroaniline.
c, 6-Methyl-3-nitroaniline.

Because of absorption by the metal halide, optical measurements below 3400 Å were impracticable. However, from Fig. 2 it appears that with antimony trichloride these bases

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[4] Murrell, *Quart. Rev.*, 1961, **15**, 2.

give adducts possessing no new charge-transfer absorption, and which probably have spectra similar to those of the corresponding anilinium ions.

Work in dichlorobenzene was not possible with these strong bases because of the insolubility of the adducts.

Fig. 3 shows plots of log [A]/[B] against log [$SbCl_3$] which may be used [1a] to estimate the stoicheiometries of the adducts (A) in solution, and also the p*K* values for their formation. A slope of unity indicates a 1B : 1$SbCl_3$ adduct, a slope of 2 a 1B : 2$SbCl_3$ adduct, etc. It is clear that at low halide concentrations 1 : 1 adducts occur, but that at higher concentrations progressively more molecules of halide are involved. (Lines of slopes 1, 2, and 3 have been drawn in Fig. 3). We have not previously observed this effect and attribute it also to the strong solvating proclivities of antimony trichloride.† Similar effects, in a different context, have been observed by Evans, James, and Owen.[5] p*K* values for the 1 : 1 adducts may be obtained from the low-concentration regions. In Table 2 these are compared with values for the weaker of the stannic and zinc halides in ether. It is seen that antimony trichloride is a notably weaker Lewis acid than any we have studied hitherto.

TABLE 2.

p*K* values for 1 : 1 adduct formation in ether solution at 20 ± 2°.

Aniline	$SbCl_3$	$ZnBr_2$ *	ZnI_2 *	$SnBr_4$ *
4-Methyl-3-nitro-	0·02	−1·55	−1·30	−2·27
3-Nitro-	0·18	−1·00	—	−1·53
6-Methyl-3-nitro-	0·52	—	—	−0·91

* Data from Parts II[1b] and III[1c].

We obtained broadly similar results with antimony tribromide in ether (it appearing, rather anomalously, a stronger acid than the chloride) but do not report them because they were not completely reproducible. We suspect that it is difficult to remove all traces of hydrogen bromide from these systems.

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† [*Added in Proof.*—Further work by one of us (J. L. W.) has shown that the data may be satisfactorily analysed in terms of 1 : 1 and 1 : 3 adducts only.]

[5] Evans, James, and Owen, *J.*, 1961, 3532.