

792. Quantitative Aspects of Lewis Acidity. Part I. A Spectroscopic Study of the Equilibria in Solution between Stannic Halides and Aromatic Amines.*

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Stannic chloride, bromide, and iodide, and substituted anilines (B) interact reversibly, in dilute solution in *o*-dichlorobenzene, to form 1B : 1 SnHal₄ adducts. From concentrated solutions solids are precipitated. These are normally brightly coloured, and for the primary anilines studied have a 2B : 1 SnHal₄ stoichiometry. For secondary and tertiary anilines the stoichiometry found was 1 : 1. Steric factors probably prevent octahedral structures involving two bulkily substituted nitrogen atoms. Equilibrium constants have been measured for the interactions in solution and, in all, twenty-three bases have been studied, mostly with stannic chloride. The general order of increasing basicity towards a given stannic halide is very similar to that exhibited towards Brønsted acids, though relative basicities are by no means exactly the same. The order of acid strength is SnCl₄ > SnBr₄ > SnI₄ and towards a given base the respective equilibrium constants are roughly in the ratios 20,000 : 20 : 1.

From a spectroscopic and structural viewpoint the adducts fall into two types: "anilinium" type species involving spectral behaviour similar to that attendant on anilinium-ion formation, and charge-transfer species which possess new, long wavelength absorption. The former adducts result from strong acid-strong base pairs, while progressive weakening of either partner favours charge-transfer interaction. Solvent effects on the charge-transfer absorption and the related equilibrium constants have been studied.

A number of new pK_a values for aqueous solution are also reported.

EQUILIBRIUM constants for reactions between bases and Lewis acids of the metal halide type have rarely been measured. Most existing data concern Lewis acids derived from boron.¹ Other data² refer to a variety of metal chlorides and fluorides, acting as chloride and fluoride ion acceptors, and to a few other scattered systems.³ Most of the studies have been calorimetric.

For stannic chloride constants have been obtained for its reaction with benzaldehyde,^{3a} benzonitrile,^{3b} tetrahydrofuran (THF),^{3c} tetrahydropyran,^{3c} and a few substituted derivatives of these compounds, though it has not always been clear that a homogeneous solution equilibrium was involved. The benzonitrile and THF equilibria seem unambiguous. For the former compound in benzene a 1 : 1 stoichiometry predominates, whereas for the latter it is 2THF : 1SnCl₄. No constants for stannic bromide and iodide appear to exist.

The vast majority of the many adducts between stannic halides and bases (B) which have been isolated have a 2B : 1SnHal₄ stoichiometry.⁴ A few are 1 : 1 and in at least one of these cases, and possibly in more, the tin atom is 5-co-ordinate.⁵ For a 1 : 1 adduct

* Preliminary reports of this work were given in *Proc. Chem. Soc.*, 1963, 86, and in *Chem. and Ind.*, 1963, 2011.

¹ (a) Brown, *J. Chem. Educ.*, 1959, **36**, 424; (b) McLaughlin, Tamres, Searles, and Nutkina, *J. Inorg. Nuclear Chem.*, 1961, **17**, 112; (c) Moodie, *Chem. and Ind.*, 1961, 1269.

² Clifford and Kongpricha, *J. Nuclear Inorg. Chem.*, 1961, **20**, 147; Baaz, Gutmann, and Masaguer, *Monatsh.*, 1961, **92**, 582; Gutmann and Hampel, *ibid.*, p. 1048; Cotter and Evans, *J.*, 1959, 2988.

³ (a) Dilke and Eley, *J.*, 1949, 2601; (b) Brown and Kubota, *J. Amer. Chem. Soc.*, 1961, **83**, 331, 4175; (c) Zenchelsky and Segatto, *J. Amer. Chem. Soc.*, 1958, **80**, 4796; Cioff and Zenchelsky, *J. Phys. Chem.*, 1963, **67**, 357; (d) Ulrich, Hertel, and Nespital, *Z. phys. Chem.*, 1932, **B17**, 21.

⁴ Beattie, *Quart. Rev.*, 1963, **17**, 382; Lindqvist, "Inorganic Adduct Molecules of Oxo-compounds," Springer-Verlag, Berlin, 1963.

⁵ (a) Beattie, McQuillan, and Hulme, *Chem. and Ind.*, 1962, 1429; (b) Brune and Zeil, *Z. phys. Chem.* (Frankfurt), 1962, **32**, 384.

in solution there is always the chance that the solvent completes the octahedron. A number of the adducts are coloured.⁶

In this paper we describe a spectrophotometric study of the equilibria, in *o*-dichlorobenzene, between the stannic halides and a series of substituted anilines.

EXPERIMENTAL

Materials.—All solvents (*o*- and *m*-dichlorobenzene, chlorobenzene, and toluene) were the purest available commercial samples and were dried by prolonged refluxing over calcium hydride, followed by distillation in a dry atmosphere. Stannic chloride and bromide were purified by distillation *in vacuo* and stannic iodide by recrystallisation from dry carbon tetrachloride; the last had m. p. 144°.

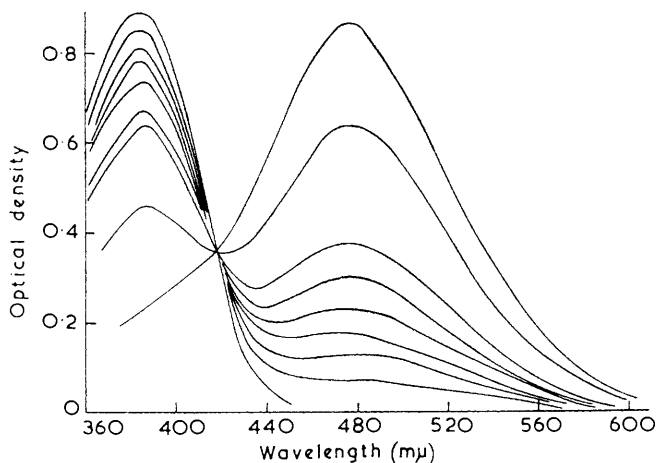


FIG. 1. Adduct formation between stannic chloride and 4-nitrodiphenylamine at various acid concentrations.

Twenty-three aromatic amines were used in all. The majority were commercial samples, recrystallised to constant melting point. 2,6-Dimethyl-4-nitroaniline, 5-chloro-2-nitroaniline, 3-chloro-4-nitroaniline, and 6-chloro-2-nitroaniline were prepared and purified by methods

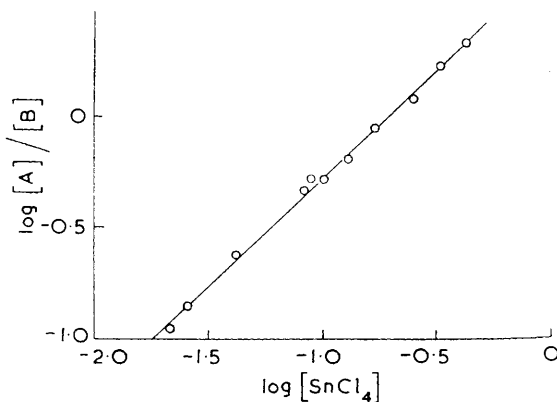


FIG. 2. Plot of $\log [A]/[B]$ against $[\text{SnCl}_4]$ for 4-chloro-2-nitroaniline.

described in the literature.⁷ In all cases the observed melting points agreed closely with previously reported values.

Handling.—Whenever possible materials were handled in a dry-box. Solutions were always made up, and cells filled, under such conditions. Stannic iodide is so little hygroscopic

⁶ E.g., Hiebner and Wagner, *Annalen*, 1925, **444**, 256.

⁷ Hodgson and Kershaw, *J.*, 1929, 2917; Jørgenson and Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878; Wepster, *Rec. Trav. chim.*, 1954, **73**, 809.

that work with it may equally well be done on the bench. As will be seen, the nature of the reported spectra provide strong reasons for thinking that adventitious moisture (which would lead to the formation of strong dual-acids, like H_2OSnCl_4 , and hence to anilinium ion spectra throughout) has been adequately excluded.

Measurement of Equilibrium Constants in Organic Solvents.—Two main spectral effects were observed (and used in equilibrium measurements) when progressively larger amounts of stannic halides were added to solutions of the bases (*ca.* 10^{-3} – 10^{-4}M). Either the base absorption was simply progressively reduced, or it was reduced while a new band, characteristic of the adduct, appeared on its long wavelength side. Sometimes these new and old bands overlapped, but this complication could usually be allowed for. When no new absorption was observed it is probable (p. 4140) that the adduct absorption lies on the short wavelength side of the original base band and was hidden under the strong stannic halide and solvent absorption. In the solvents used stannic chloride begins to absorb strongly at *ca.* 3100 Å, stannic bromide at 3900 Å, and stannic iodide at 4100 Å. Consequently, it was usually desirable to work with bases which had absorption maxima at longer wavelengths than these. Stannic halide was often included in the reference sample to minimise this problem, but it seriously limited the number of bases studiable with the bromide and iodide (see p. 4139). Being weak acceptors these compounds need strong bases to interact with, and the more basic anilines tend to absorb

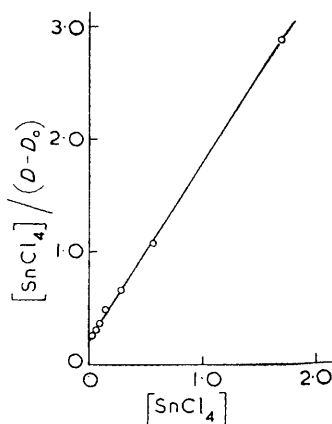


FIG. 3. Plot of $[\text{SnCl}_4]$ against $[\text{SnCl}_4]/[D - D_0]$ for 6-methyl-2-nitroaniline.

in the ultraviolet rather than in the visible region. When a base gave an adduct with a new long wavelength band it was sometimes not essential for the base absorption to be detectable, for measurements could equally well be made on the adduct band.

Solutions for optical measurements were made up, in volumetric flasks, from solvent and stock solutions of halide and base. Usually the stoichiometric base concentration was kept constant, and the halide concentration varied. Whenever possible the spectrum corresponding to complete adduct formation (D_∞) was recorded. Measurements were made, using ground-glass stoppered cells of 1 cm. (or 2 mm.) path, with either (or both) a Unicam S.P. 500 or a Perkin-Elmer U. 137 spectrophotometer. The temperature was $20 \pm 2^\circ$. Typical spectra are shown in Fig. 1. For a 1:1 adduct (A) the equilibrium constant is given by $\text{p}K = -\log [A]/[B][\text{SnHal}_4]$. When D_∞ is available $[A]/[B]$ can be calculated directly from the spectra. A plot of $\log [A]/[B]$ against $\log [\text{SnHal}_4]$ should be a straight line of unit slope. A typical plot of this sort is shown in Fig. 2. The observed slopes were always close to unity. Alternatively, $[A]/[B]$ may be plotted against $[\text{SnHal}_4]$ when the slope gives K directly. When D_∞ was not available the following procedure was adopted. For any given base

$$[A]/[B] = (D - D_0)(D_\infty - D)$$

where D_0 , D , and D_∞ are respectively the optical densities of the adduct band (at some chosen wavelength) in the absence of tin halide, at a given concentration of halide, and for complete adduct formation. Thus

$$K = \frac{1}{[\text{SnHal}_4]} \cdot \frac{D - D_0}{D_\infty - D}$$

It follows that a plot of $[\text{SnHal}_4]$ against $[\text{SnHal}_4]/(D - D_0)$ should be rectilinear giving D_∞ from the slope and KD_∞ from the intercept. Such a plot is in Fig. 3. In this way the extinction coefficient of the adduct band can be found even if in practice the base can only be partially converted owing to its low basicity, or to the solubility limits of the tin halide. When both base and adduct bands were detectable good isobeistic points were normally obtained (Fig. 1) and similar values of K obtained from either band. Since the free base spectra always obeyed Beer's law, the adduct spectra may be assumed therefore to do so also. D was usually measured at the band maximum, but it was checked that measurements at other wavelengths led to essentially the same value for K . Solvent effects on band positions appeared quite small, even at high (*ca.* 1.0M) concentrations of tin halide. Tin halides are, of course, non-polar. In no case did assumed stoicheiometries other than 1:1 (*e.g.*, 2:1, 2:2, etc.) provide constant values for K .

Some systems (especially those involving stannic bromide) gave very stable spectra, but most showed some small change in optical density with time, owing to precipitation of the adduct. In a few cases (notably for anilines with 2- and 4- or 6-alkyl substituents) this effect prevented accurate measurements, but generally any necessary extrapolation to time of mixing involved a negligible error and the measured solutions were essentially homogeneous. The recorded pK values were reproducible to ± 0.05 units unless otherwise stated.

Measurement of pK_a in Aqueous Solution.—Certain of the bases have not previously been studied in aqueous solution. Their pK_a values were determined by the standard methods, using the H_0 data compiled by Long and Paul.⁸ The results are in Table 2.

Preparation of Solid Adducts.—A few typical bases were chosen for study of the adduct stoicheiometry in the solid state. When large concentrations of base and tin halide are used coloured solid adducts are readily precipitated. Carbon tetrachloride is a satisfactory solvent and the filtered solid can easily be pumped free of it. In the absence of moisture the solids are stable. A few (*e.g.*, stannic bromide-diphenylamine) are relatively stable in moist air. The solids were analysed for halogen (as were samples of the stock solutions used for the spectral measurements) by solvolysis in dilute nitric acid, followed by potentiometric titration. The stoicheiometry is usually 2B:1 SnHal₄, though the secondary and tertiary anilines appear 1:1. Table 1 gives the colours and compositions of the solids. They normally decompose before melting.

RESULTS AND DISCUSSION

Adduct Stoicheiometries.—No matter what the spectral effects observed, all the adduct formations in solution involved 1:1 stoicheiometry. For the most basic amines the stannic halide concentrations used were comparable with the base concentration (Table 2), yet no indication of 2B:1SnHal₄ interaction was noticed. However, could the

TABLE 1.

Solid adducts.

(a) Stannic chloride.

Aniline (B)	Adduct colour	Ratio B : SnCl ₄
2-Nitro-	dull red	1.96 : 1
2,5-Dichloro-	white	2.00 : 1
4-Nitro-	orange	1.98 : 1
4-Chloro-2-nitro-	red-brown	2.01 : 1
NN-Diethyl-2,4-dinitro-	red	1.12 : 1
NN-Dimethyl-2,4-dinitro-	red	1.10 : 1
4-Nitro-N-phenyl	violet	
2-Nitro-N-phenyl	violet	

(b) Stannic bromide.

Aniline (B)	Adduct colour	Ratio B : SnBr ₄
N-Phenyl-	pale yellow	1.04 : 1
4-Methyl-3-nitro-	buff	1.90 : 1
4-Methyl-2-nitro-	orange	1.95 : 1
NN-Diethyl-2,4-dinitro-	red	

⁸ Long and Paul, *Chem. Rev.*, 1957, 57, 1.

systems have been studied with a sufficient excess of base (rather than excess of stannic halide, as was usual) it is possible that some 2:1 adduct would have been formed. Previous evidence implies that 2:1 adducts can exist in benzene-like solvents and they certainly exist when the pure liquid base is used as solvent.⁹ As noted on p. 4134 the stereochemistry of the 1:1 adducts is uncertain: they may involve 5-co-ordinate tin, but on the other hand, the solvent may complete the octahedron, its very weakly basic character (compared with the amine) being compensated for by its much greater concentration.

The solid adducts were all 2B:1SnHal₄ (Table 1) except for those involving secondary and tertiary amines. Most solvent-free adducts of stannic halides have proved 2:1. The 1:1 compounds could either involve 5-co-ordinate tin or be halogen-bridged 6-co-ordinate structures. It would seem, however, that octahedral arrangements involving two bulkily substituted nitrogen atoms are sterically hindered. Some further evidence supporting this generalisation may be found in the literature.^{5b,10}

TABLE 2.

Adducts with stannic chloride in *o*-dichlorobenzene at 20 ± 2°.[B] ~ 10⁻⁴M; [SnCl₄] ~ 10⁻⁴—1M; ε = extinction coefficient at band maximum (λ_{max.}) in all Tables.

No.	Aniline derivative	10 ⁻³ ε _B	10 ⁻³ ε _A	λ _A max. (Å)	λ _B max. (Å)	pK	pK _a (at 25°)
1	4-Methyl-3-nitro- †	1.81	—	—	3690	-3.60	2.90 ^a
2	3-Nitro- †	1.81	—	—	3660	-3.60	2.50 ^b
3	6-Methyl-3-nitro- †	2.12	—	—	3670	-3.35	2.32 ^a
4	4-Nitro- †	15.7	—	—	3470	-3.18	0.99 ^b
5	2,6-Dimethyl-4-nitro- *	14.7	13.2	4650	3630	—	0.95 ± 0.10 ^c
6	2-Methyl-4-nitro-	13.7	v. small	(4550)	3580	-2.38	0.94 ^a
7	4-Methyl-2-nitro- †	7.93	—	—	4120	-2.50	0.45 ^a
8	2,4-Dimethyl-2-nitro- *	4.57	1.37	{ 3520 5180	4180	—	-0.02 ^a
9	2-Nitro- †	5.02	—	—	3980	-2.30	-0.29 ^b
10	6-Methyl-2-nitro-	4.74	3.32	4800	4040	-0.80	-0.71 ^a
11	2-Chloro-4-nitro-	12.6	7.81	4250	3520	-0.70	-0.94 ^a
12	4-Chloro-2-nitro-	4.77	1.67	4180	4100	-0.70	-1.03 ^b
13	5-Chloro-2-nitro-	5.51	3.20	4440	3930	-0.34	-1.54 ^a
14	2,5-Dichloro-4-nitro-	9.26	10.1	4100	3470	+0.15	-1.78 ^b
15	6-Chloro-2-nitro-	4.71	3.77	4300	4000	-0.06	-2.43 ^d
16	4-Nitro- <i>N</i> -phenyl-	21.6	22.6	4760	3840	-0.96	-2.48 ^b
17	2-Nitro- <i>N</i> -phenyl-	6.96	7.00	5100	4320	+0.26	-2.96 ^b
18	2,6-Dichloro-4-nitro-	11.5	16.9	4150	3500	+0.53	-3.20 ^a
19	2,4-Dinitro-			No detectable reaction			

* Solutions particularly unstable; pK not calculated. † No detectable new, long-wavelength absorption at >3100 Å.

^a This work. ^b Long and Paul, ref. 8. ^c Gillois and Rumpf, *Bull. Soc. chim. France*, 1954, **21**, 112. ^d Jorgenson and Hartter, ref. 7.

Equilibrium Constants in o-Dichlorobenzene.—(a) *Stannic chloride.* Our pK values are collected in Table 2, together with the corresponding values of pK_a (K_a = [B][H₃O⁺]/[BH⁺]) for the bases in aqueous solution. It is clear that there is a general parallelism between the basicity towards protons and towards stannic chloride. In aqueous solution the proton is considered to add to the amino, rather than to the chloro, or nitro, substituents of these bases. The parallelism seems sufficient to justify the assumption that stannic chloride also engages the amino-group in preference to any other structural feature. In spite of the general parallelism, some of the relative basicities (ΔpK_a) in water are notably changed for the dichlorobenzene-stannic chloride system (ΔpK). All are changed to some extent and the overall basicity range is compressed. The changes do not appear systematically related to structure; it is, for instance, not possible to identify

⁹ E.g., Beattie, McQuillan, Rule, and Webster, *J.*, 1963, 1514.

¹⁰ (a) Shuba and Zenchelsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4136; (b) Fergusson, Grant, Hickford, and Wilkins, *J.*, 1959, 99; (c) Madelung, Reiss, and Herr, *Annalen*, 1927, **454**, 7.

TABLE 3.
Adducts with stannic bromide in *o*-dichlorobenzene at $20 \pm 2^\circ$.

No.	Aniline derivative	$10^{-3}\epsilon_B$	$10^{-3}\epsilon_A$	λ_A max. (Å)	λ_B max. (Å)	p <i>K</i> *	p <i>K</i> _a (at 25°)
20	3-Chloro-4-nitro †	9.50	—	—	3460	—	0.27 ^a
4	4-Nitro-	15.7	3.1	4000	3470	+0.10	0.99
6	2-Methyl-4-nitro-	13.7	3.9	4150	3580	-0.05	0.94
7	4-Methyl-2-nitro-	7.93	2.1	4200	4120	+0.60	0.45

^a This work.

* Accurate to ± 0.10 units. † New, long-wavelength absorption apparent, but obscured by base band.

a steric effect arising from the fact that stannic chloride is bulkier than a proton. Indeed, many of the comparisons in Table 2 are probably free from steric complications. One seemingly consistent feature is that bases 6 and 10, which are the first two to give stable long-wavelength absorption on adduct formation, are both unexpectedly weak towards stannic chloride compared with their nearest neighbours which do not give such absorption.

(b) *Stannic bromide*. The absorption and relative weakness of this acid permitted study of only a limited basicity range (p. 4136). Thus diphenylamine and 3-chloro-4-nitroaniline provide new long-wavelength absorption but only a tail extends beyond the stannic bromide absorption, and this is insufficient for accurate measurements. The base absorption of 3-nitroanilines is obscured, and these compounds give no detectable new long wavelength bands beyond 3900 Å. Most 2-nitroanilines, for which the base band extends beyond the tin bromide absorption, are unfortunately too little basic to give significant adduct formation at accessible concentrations of acid. In spite of these unfavourable circumstances, three p*K* values were obtained (Table 3).

TABLE 4.
Solvent effects on charge-transfer interaction.
(a) SnCl₄ and 4-nitrodiphenylamine (base 16).

Solvent	ϵ_A/ϵ_B	λ_A max. (Å)	λ_B max. (Å)	p <i>K</i>	D.C.*
<i>m</i> -Dichlorobenzene	1.10	4530	3780	-0.46	5.04
Chlorobenzene	1.10	4680	3780	-0.72	5.62
<i>o</i> -Dichlorobenzene (DCB)	1.06	4770	3840	-0.96	9.93
DCB + 25% v/v toluene	1.24	4750	3815	-0.95	8.04
DCB + 50% v/v toluene	1.10	4680	3810	-0.91	6.16
DCB + 75% v/v toluene	1.21	4640	3770	-0.72	4.27
DCB + 90% v/v toluene	1.20	4560	3760	-0.61	3.13
Toluene	1.08	4520	3735	-0.54	2.38

(b) SnCl₄ and 6-methyl-2-nitroaniline (base 10).

Toluene	0.57	4600	3970	-0.62	2.38
<i>o</i> -Dichlorobenzene	0.69	4800	4040	-0.80	9.93

* Dielectric constant for mixtures based on assumed linear relationship.

Comparison of the stannic chloride and bromide data shows (i) that adducts with new long-wavelength bands are formed with stronger bases for stannic bromide, and (ii) that stannic chloride is notably the more acidic. For a given base the ratio of the equilibrium constants is *ca.* 1000, though exact comparison is difficult because the hiatus (see above) in the stannic chloride basicity series occurs in the region of the bases available for stannic bromide. Comparison of bases 4, 6, and 7 for stannic chloride, and bromide, emphasises how significantly relative basicity can be influenced by the acceptor molecule.

(c) *Stannic iodide*. The limitations on measurements proved even more severe for the iodide. 4-Chloroaniline (p*K*_a = 3.83),¹¹ 4-bromoaniline (p*K*_a = 3.91),¹² and 2-chloroaniline (p*K*_a = 2.64)¹² provide increased long-wavelength absorption but only as a tail

¹¹ Hall, *J. Phys. Chem.*, 1956, **60**, 63.

¹² Kilpatrick and Arenberg, *J. Amer. Chem. Soc.*, 1953, **75**, 3813.

on the iodide band. The interaction is also far from complete, even for the most concentrated tin iodide solutions obtainable. An equilibrium constant ($pK = 0.3 \pm 0.1$) may be roughly calculated for the most favourable case, 2-chloroaniline. 3-Nitroanilines and weaker bases are not detectably affected; bases stronger than 4-bromoaniline were not studied.

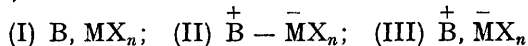
It proved possible to corroborate the datum for 2-chloroaniline by reversing our usual technique. The base absorbs at shorter wavelengths than does the tin iodide. If the latter is used (at *ca.* $10^{-4}M$) and increasing amounts of base added (up to *ca.* $3.0M$ with proper compensation in the reference beam) the fall in iodide absorption can be followed. The adduct absorption is revealed as a very feeble flat band. The pK determined this way is 0.10 ± 0.10 . We hope to extend this technique to other stronger bases with suitable spectra.

The above facts, though meagre, show (i) that new long-wavelength adduct absorption probably sets in with stronger bases for stannic iodide than for the bromide, and (ii) that the iodide is notably less acidic than the bromide. Assuming, as a rough measure, that $\Delta pK_a = \frac{2}{3}\Delta pK$ for a given pair of bases, the equilibrium constants for stannic bromide and iodide for a given base are found to be in the rough ratio 20 : 1. This result, and the corresponding comparison between chloride and bromide are in agreement with previous qualitative conclusions about the tin halides.⁴

Spectral Effects.—As noted in the Experimental section, these were of two kinds. The first kind, where the adduct absorption presumably lies hidden under the stannic halide absorption on the short wavelength side of the original base band, we term "anilinium" type behaviour, because when anilines are protonated in aqueous acids the anilinium ions formed absorb at considerably shorter wavelengths than do the parent bases.¹³ The second kind, in which a new long wavelength band is observed, has no parallel in aqueous systems. As noted, the onset of this type of behaviour is a function both of the acid and the base strength (p. 4139 and Tables 2 and 3).

Previous work^{14,1c} on interactions in solution of Lewis acids of the metal halide type (MX_n) with different classes of "indicator" base (B), *e.g.*, aromatic hydrocarbons, ketones, and amines, has usually led to one or other of two distinct spectral effects. Either the adduct's spectrum is similar to that of the protonated base, or it is that characteristic of the free radical ions ($B^+ \cdot MX_n^-$). In the latter case paramagnetic effects are also observed. Our "anilinium" adducts probably fall into the first category but our adducts with new long-wavelength absorption do not fall into the second, for the solutions exhibit negligible paramagnetism.* We consider that the new bands constitute charge-transfer spectra and that the corresponding adducts are what are usually known as charge-transfer species.¹⁵ The $AlHal_3$ -benzene interactions and spectra have also been interpreted in this way.¹⁶ Mixtures of stannic chloride with toluene,¹⁷ dichlorobenzene,¹⁸ and other aromatic compounds probably involve similar effects. For nitrogen bases a previous hint of the phenomenon may be found in Shuba and Zenchelsky's data^{10a} for the $FeCl_3$ -aniline system.

Progressive stages in the interaction of a metal halide with a base may be represented as in (I), (II), and (III) below.



* We thank Mr. G. A. Allen and Dr. G. R. Wilkinson for assistance with the electron spin resonance measurements which established this result.

¹³ Jaffé and Orchin, "Theory and Applications of Ultra-violet Spectroscopy," Wiley, New York, 1962.

¹⁴ (a) Aalbersberg, Hoijsink, Mackor, and Weijland, *J.*, 1959, 3055; (b) Kainer and Hausser, *Chem. Ber.*, 1953, 86, 1563.

¹⁵ (a) Mulliken, *J. Amer. Chem. Soc.*, 1952, 74, 811; (b) Murrell, *Quart. Rev.*, 1961, 15, 2.

¹⁶ Eley and King, *J.*, 1952, 4972.

¹⁷ Satchell, *J.*, 1960, 4388.

¹⁸ Hunt and Satchell, unpublished observations.

(II) corresponds to electron-pair donation and sharing, the usual dative bond, which in electronic effect is analogous to protonation of the base and therefore might be expected to produce analogous spectral effects. (III) corresponds to free-radical ion formation, and represents a stronger type of interaction than (II), and is usually only found for the most powerful Lewis acids and/or in media of high dielectric constant. (I) represents charge-transfer interaction,¹⁵ the ground state comprising, in fact, mostly the non-bonded structure (I), together with a small admixture of (II). The charge-transfer transition is between this species and an excited state in which the relative contributions of (I) and (II) to the total wave function are roughly reversed. (I) represents a weaker kind of interaction than (II) or (III); very little electron transfer has occurred. With an appropriate series of bases one would expect to be able to obtain adducts ranging from close to (I), through (II), to close to (III) in electron distribution. Our study covers the range (I) to (II). It is obvious to look for a smooth change in spectral behaviour. Our data show the change to be there, but to be not particularly smooth. Thus, for stannic chloride, the only base showing intermediate behaviour is 6, which gives a very weak charge-transfer band. Normally either there is new, high intensity absorption on the long wavelength side of 4100 Å, or there is no adduct band at >3100 Å. The narrow range of frequencies covered by the charge-transfer bands is interesting. There appears to be no obvious change in the band's position with base strength. This is unusual. Charge-transfer absorption, for a given acceptor, is often dominated by the donor's ionisation potential.^{15,19} In the present case the variation in ionisation potential is rather small, and other more important factors are involved.¹⁹

The nitroanilines are thought to owe their own long-wavelength absorption around 3500—4000 Å (that visible in the present systems) to a charge-transfer transition between the lone pair of electrons on the amino-nitrogen atom to the oxygen atoms of the nitro group.^{15b} In the anilinium ion the lone pair is engaged, and this absorption is therefore removed, the remaining bands (in the ultraviolet region) being more characteristic of the substituted nitrobenzene residue.¹³ Hence the use of these anilines as acid-base indicators.⁸ When a metal halide engages the nitrogen lone pair then, as we have suggested, either similar effects ensue [when the adduct resembles (II)] though we cannot observe the ultraviolet bands because of the stannic halide absorption, or [when the adduct resembles (I)] the intramolecular charge transfer band is removed but replaced by an intermolecular effect as described. The new charge-transfer bands are not to be thought of as the base's original charge transfer absorption shifted to longer wavelengths. The metal doubtless engages the amino lone pair (rather than the nitro-group, see p. 4138) and this process, even if it does not destroy the intramolecular charge transfer, could only shift it to *shorter* wavelengths. Other facts which argue against the adduct bands being stabilised base transitions are (i) the effects are more prominent the *weaker* the acid, and (ii) not only nitro, but also the colourless chloroanilines and diphenylamine exhibit similar effects. The intensities of the adduct spectra ($\epsilon_A \sim \epsilon_B$) takes them out of the realm of crystal-field effects, and of ligand field explanations we consider that given the most satisfactory.²⁰ The colours of the solid adducts may, of course, involve crystal field effects also. Bases not giving charge transfer effects in solution do form coloured solids (*e.g.*, 4).

The intensities of the charge-transfer bands calls for comment. No regularities are necessarily to be expected.²¹ Murrell^{15b} has shown how the charge-transfer absorption may "borrow" some intensity from a suitable donor transition. Our data seem best interpreted this way. There is a significant resemblance between the trends in ϵ_A and ϵ_B (Table 2).

Solvent Effects.—Charge-transfer transitions are made energetically easier by increases

¹⁹ Briegleb and Czekalla, *Z. Elektrochem.*, 1955, **59**, 184.

²⁰ Dunn, in "Modern Co-ordination Chemistry," ed. Lewis and Wilkins, Interscience, New York, 1960.

²¹ Foster and Thomson, *Trans. Faraday Soc.*, 1963, **59**, 2287.

in both the solvating power and the dielectric constant of the medium, because such increases favour and stabilise ionic species.^{15b} The expected red shifts were found and are illustrated in Table 4. They occur, of course, for both the base and the adduct bands. It is interesting that in the sequence of increasing polarity toluene, *m*-dichlorobenzene, chlorobenzene, and *o*-dichlorobenzene the second member provides anomalous data. This is very marked when the pK values are compared. Apart from the data for *m*-dichlorobenzene, these show a steady decrease with increasing polarity, as expected.

Table 4 also shows how the relative basicities of 6-methyl-2-nitroaniline (base 10) and 4-nitrodiphenylamine (base 16) are a function of the solvent.²¹

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