

826. *Quantitative Aspects of Lewis Acidity. Part III.¹ A Spectroscopic Study of the Equilibria in Ether Solution between Stannic Bromide and Some Aromatic Amines.*

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Stannic bromide and nitroanilines form 1:1 adducts in reversible equilibria in ether solution. Equilibrium constants for seven bases are recorded. The spectra of the adducts (which differ from those of the corresponding anilinium ions) possess new long-wavelength absorption arising from charge-transfer transitions. In ether, stannic and zinc bromides exhibit similar acid strengths and, surprisingly, that of stannic bromide is also similar to its strength in *o*-dichlorobenzene. The behaviours in ether and in dichlorobenzene are compared generally. Some anomalous solvent effects are noted.

OUR previous studies dealt with stannic halides in aromatic solvents² and with zinc halides in ether.¹ The present work connects these previous studies. It has not been possible to use stannic chloride or iodide in ether solution. The former because of the insolubility of its adduct with this solvent; the latter because of absorption difficulties similar to those noted for the aromatic systems.

EXPERIMENTAL

The materials and techniques employed were similar to those previously described.^{1,2} A limitation on our study of stannic bromide in *o*-dichlorobenzene was the powerful absorption of the halide in this solvent at wavelengths <3900 Å. This effect, due to charge-transfer interaction between halide and solvent,* restricted study to those bases, of appropriate strength, whose adducts possessed new long-wavelength absorption at >3900 Å. In ether circumstances are somewhat better, but measurements below 3400 Å were not generally practicable even in the most favourable cases. We were able to obtain useful data with 7 anilines in all. Values of *K* (the equilibrium constant for adduct formation) were calculated as before.² They were reproducible to within ±0.05 units.

RESULTS AND DISCUSSION

Stoichiometry.—For all the bases (B) the adduct stoichiometry in solution was shown¹ to be 1 B : 1 SnBr₄. Solid adducts, isolated from concentrated solutions, proved (as with the aromatic systems²) to be of 2 : 1 stoichiometry for primary amines.

Spectra.—We have demonstrated previously that, on forming adducts with Lewis acids, nitroanilines display one of two distinct spectral effects.^{1,2} The base's long-wavelength absorption is removed and the resulting spectrum either closely approximates to that of the corresponding anilinium ion, or it contains a new absorption band. In our previous examples this new absorption has appeared on the long-wavelength side of the

* Possibly of the contact variety.³

¹ Part II, Satchell and Wardell, preceding Paper.

² Part I, Satchell and Wardell, *J.*, 1964, 4134.

³ Orgel and Mulliken, *J. Amer. Chem. Soc.*, 1957, 79, 4839.

original base band. We have shown that it probably arises from intermolecular charge-transfer between the components of the adduct. We recall also that the base's long-wavelength absorption band is generally considered to arise from an intramolecular charge-transfer transition.⁴

Relevant spectral data are in Table I. Bases 4, 5, and 6 provide the most straightforward results. For these bases the observed effects with stannic bromide in ether and in *o*-dichlorobenzene are very similar. New charge-transfer absorption is found on the long-wavelength side of the original base band in roughly the same position in both

TABLE I.
Spectral details.

λ = Absorption maximum in Å; A = adduct; B = base; DCB = *o*-dichlorobenzene.

| No. | Aniline | $\lambda_B(\text{DCB})^2$ | $\lambda_B(\text{Et}_2\text{O})$ | $\lambda_A(\text{DCB})^2$ | $\lambda_A(\text{Et}_2\text{O})$ | $\lambda_A(\text{Et}_2\text{O}-\text{ZnBr}_2)^1$ |
|-----|-------------------|---------------------------|----------------------------------|---------------------------|----------------------------------|--|
| 1 | 4-Methyl-3-nitro- | 3690 | 3700 | * | ~3500 | 3150 † |
| 2 | 3-Nitro- | 3660 | 3700 | * | 3400 < λ_A < 3700 | 3100 † |
| 3 | 6-Methyl-3-nitro- | 3670 | 3680 | * | 3400 < λ_A < 3700 | — |
| 4 | 4-Nitro- | 3470 | 3530 | 4000 | 4100 | 4250 |
| 5 | 2-Methyl-4-nitro- | 3580 | 3600 | 4150 | 4250 | — |
| 6 | 4-Methyl-2-nitro- | 4120 | 4050 | 4200 | 4150 ± 100 | — |
| 7 | 3-Chloro-4-nitro- | 3460 | 3520 | — | λ_A < 4000 | — |

* No detectable new absorption > 3800–3900 Å. A maximum at 3500 Å or above leads to easily detectable absorption at 3900 Å. † Spectra similar to corresponding anilinium ions.

solvents. There is a slight red shift ($\sim 100 \text{ m}\mu$) in ether compared to dichlorobenzene and it is interesting that a similar, though smaller, shift is generally* found for the base absorption (λ_B) itself. The direction of this shift is at first sight surprising because charge-transfer absorption normally shifts to shorter wavelengths on reduction of the dielectric constant, the upper (polar) state being destabilised.² However, in this case ether probably provides a compensating solvation effect,* not available in aromatic solvents, and so leads to a net shift in the opposite direction. The existence of this phenomenon renders suspect calculations of transition moments from equations relating frequency shifts to bulk dielectric constant.⁵

Base 7 also behaves similarly with stannic bromide in ether and dichlorobenzene, but the positions of the adduct maxima were not obtainable because of experimental difficulties.

Bases 1, 2, and 3 behave differently in the two solvents. In dichlorobenzene no evidence of charge-transfer absorption was found, and the spectra were presumed similar to those of the corresponding anilinium ions. This was proved to be the case for interaction with zinc halides in ether (where the ultraviolet region is more accessible).¹

With stannic bromide in ether, however, we now find new absorption, not attributable to anilinium ion type spectra, which lies partly under, and is obscured by, the original base absorption. These new adduct maxima probably all occur around 3500 Å. In our view these bands are again properly described as intermolecular charge-transfer absorptions and derive from a stronger acid–base interaction than do those occurring around 4000 Å and above, but nevertheless not from so strong an interaction that the possible electronic excitation is reduced to that found in the anilinium ion. We have discussed the possibility of such intermediate examples previously.² If our interpretation is correct, stannic bromide must be supposed to attract the nitrogen lone pair more strongly in dichlorobenzene than in ether. This seems quite possible.

Acidity Comparisons.—Relevant equilibrium constants are collected in Table 2.

* That base 6 proves an exception is probably due to the possibility of intramolecular hydrogen bonding in this case. This would make solvation stabilisation by ether less important and so lead to the normal blue shift.

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

⁵ Chakrabarti and Basu, *Trans. Faraday Soc.*, 1964, **60**, 465.

TABLE 2.

Equilibrium constants in ether and in dichlorobenzene at $20 \pm 2^\circ$.
 $K = [A]/[B] [M(Hal)_x]$; K_a = acidity constant of BH^+ in water at 25° .*

| No. | pK_a | SnBr ₄ | | ZnBr ₂ |
|-----|--------|--------------------|---------------------------|-----------------------------|
| | | $pK(\text{DCB})^2$ | $pK(\text{Et}_2\text{O})$ | $pK(\text{Et}_2\text{O})^1$ |
| 1 | 2.90 | — | -2.27 | -1.55 |
| 2 | 2.50 | — | -1.53 | -1.00 |
| 3 | 2.32 | — | -0.91 | — |
| 4 | 0.99 | +0.10 | 0.08 | -0.08 |
| 5 | 0.94 | -0.05 | 0.38 | — |
| 6 | 0.45 | +0.60 | 0.50 | — |
| 7 | 0.27 | — | 0.62 | — |

* See references 2 for sources.

(i) *Stannic bromide in ether and dichlorobenzene.* Surprisingly there is no great difference between the extent of adduct formation, with a given base, in these two solvents. Because of its much greater basicity and lower dielectric constant ether as a medium might have been expected to greatly reduce the acidity displayed in dichlorobenzene. It seems, however, that its correspondingly greater solvating power provides compensating stabilisation of the polar adduct. An alternative explanation is that in *o*-dichlorobenzene stannic bromide is essentially 4-co-ordinate and that on 1:1 adduct formation a change in hybridisation is involved, the resulting adduct being 5-co-ordinate. In ether stannic bromide is probably 6-co-ordinate, the solvent occupying two co-ordination sites. On adduct formation one solvent molecule is displaced by a molecule of base. No rehybridisation is necessary. These two rather different equilibrium processes could involve similar free energy changes.

(ii) *Stannic and zinc bromides in ether.* Again somewhat surprisingly these acids appear here of similar strength. In two of the three comparisons available, the tin compound appears the stronger. It is interesting that, for bases 1 and 2, while more adduct is formed with stannic bromide than with zinc, the spectra indicate that the zinc compound forms the stronger bonds in the adducts. We conclude that zinc bromide also forms proportionately stronger bonds with the solvent. This appears possible. Zinc halides may have steric advantages over those of tin in these contexts.

(iii) *Comparison to pK_a .* The order of basicity found in water is again maintained, but as in the previous data ΔpK does not display any systematic relationship to ΔpK_a .

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