Quantitative Aspects of Lewis Acidity Interaction of Arsenic (III) Chloride with Nitrogen Bases in o-Dichlorobenzene Solution

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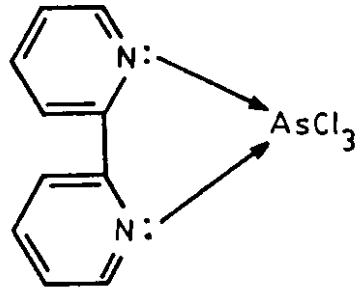
Summary: Equilibrium constants for the interaction of 2,2'-bipyridine, o-phenanthroline and 2,2'-biquinoline with arsenic (III) chloride have been determined spectrophotometrically. The bases show transitions in the UV region which shift towards longer wave length on adduct formation. The adducts formed, in o-dichlorobenzene solution, are very stable and 1:1 stoichiometry is ascertained. Arsenic trichloride behaves as a very strong Lewis acid towards the heteroaromatic bidentate nitrogen bases. Their basic strength is found to be in the following order, bipy > phen > biquinoline. The bases are found to follow the relationship, $p^{K} = - 0.81\ p^{Ka} - 1.475$.

Aresenic trihalides are covalent compounds and behave as acceptor molecules towards Lewis bases. Although these halides have been used as moderate catalysts in alkylation [1], haloalkylation [2] and the aromatic ring chlorination [3] but little is known about their comparative quantitative strengths as Lewis acids. The catalytic activity of a metal halide is presumably related to its Lewis acid strength which could be measured from its interaction with donor molecules.

Arsenic (III) chloride is known [4] to form 1:1 addition compounds with oxygen donors. In a recent study, arsenic (III) chloride has been shown [5] to behave as a very strong acid towards iron(III) acetyl acetonate in ether solution. Since there has been no quantitative measurements on the determination of its acidic strength, some nitrogen donor bases are chosen for their interactions with arsenic trichloride. The nitrogen bases studied are: 2,2'-bipyridine, o-phenanthroline and 2,2'-biquinoline. These compounds contain two donor nitrogen atoms adjacent to each other. Therefore, chelate formation is expected with arsenic trichloride interactions. For example, the 2,2'-bipyridine - arsenic trichloride adduct may be shown as follows:



where the arsenic atom readily becomes five coordinate. The presence of a lone pair of electrons on arsenic (III) compounds would confer the properties of an electron donor. Mulliken [6] has predicted a donor-acceptor properties for compounds of group Vb. The results of the previous [5] and the present work show that arsenic trichloride is a strong electron acceptor.

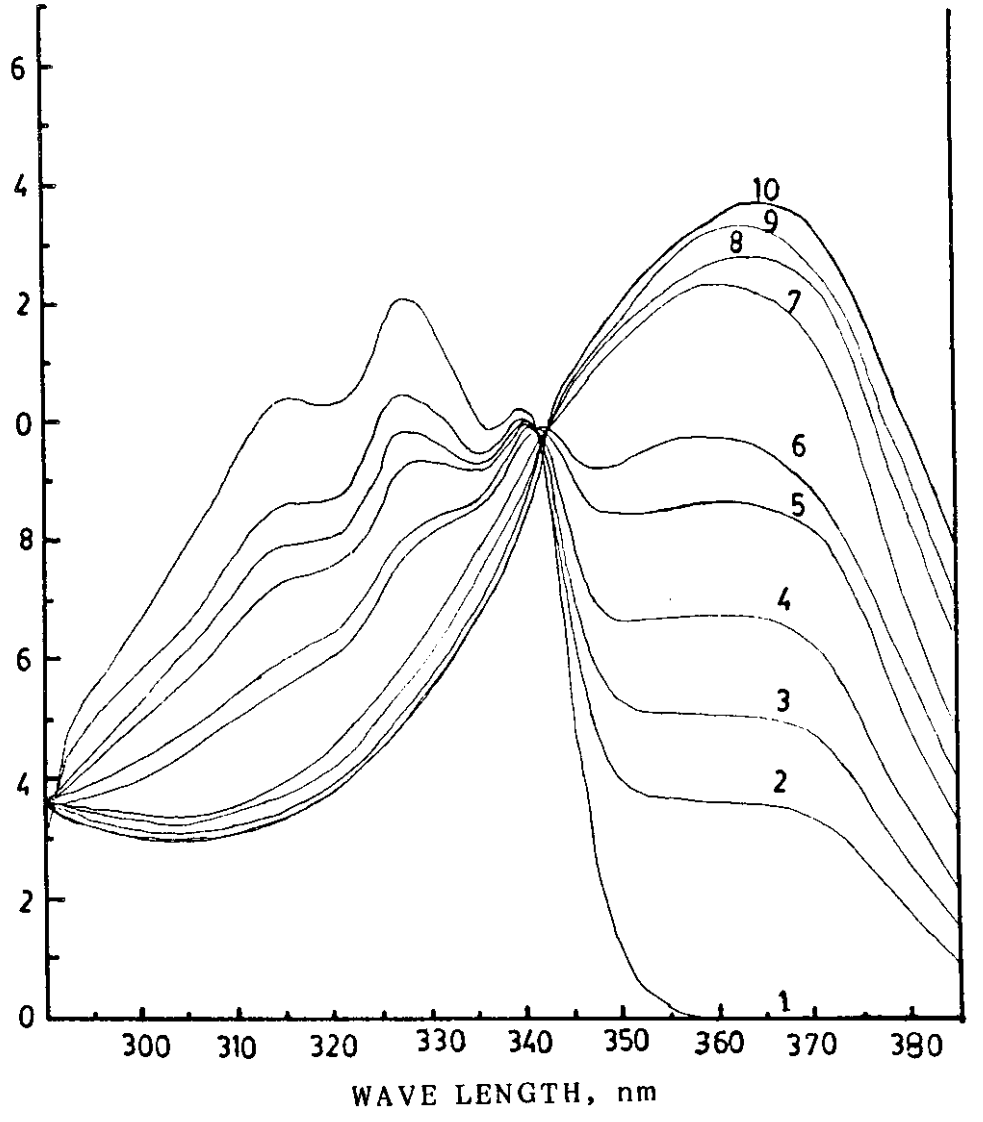


Fig.1: Electronic spectra of 2,2'-biquinoline (5.2475×10^{-5}M) containing different concentrations of arsenic trichloride in o-dichlorobenzene solution, M x 10^5. (1) 0.000 (2) 6.350 (3) 11.357 (4) 18.563 (5) 28.487 (6) 44.886 (7) 144.482 (8) 288.964 (9) 577.928 (10) α.

The behaviour of arsenic (III) chloride as a strong Lewis acid may be explained on the basis of the presence of chlorine atoms and the empty 4d orbitals. The chlorine atoms drain enough chrage from the central atom and the tendency of the lone pair of electrons for donation is greatly reduced. These affects lead to a significant increase in the effective nucelar charge which would contract the d-oribtals. Thus lowering of d-orbital energy takes place. The donor orbitals of nitrogen atoms, having same symmetry as the empty d-orbitals, would overlap to form 5-coordinate chelate structure. For an ortho bidentate donor, chelate formation has been established [7] for the interaction of aromatic o-diamines with aryltin trichloride. Similarly, antimony trichloride forms adducts with nitrogen donors. 2,2'-bipyridine forms a 1/1 adduct [8] with antimony trichloride which is presumably ioni-

Table-1: 2',2-Biquinoline-Arsenic (III) chloride interaction in o-dichlorobenzne solution at 25°C.

$[Base]_{stoich} = 5.25 \times 10^{-5}M$: $[AsCl_3]_{stoich} > 0.50 \times 10^{-5}M$.

λ_{max} for the adduct band = 365 nm; $\log\varepsilon_{365} = 4.413$

No.	$[AsCl_3]_{stoich.}$ M x 10^5	Absorbance at 365 nm	$[Base]_{eq}$ Mx10^5	$[AsCl_3]_{eq}$ Mx10^5	$[Adduct]_{eq}$ Mx20^5	p^K value
1.	000.000	0.000	-	-	-	-
2.	006.350	0.350	3.900	005.000	1.350	-3.84
3.	011.357	0.500	3.320	009.427	1.930	-3.79
4.	018.563	0.660	3.702	016.015	2.548	-3.77
5.	028.487	0.800	2.162	035.399	3.088	-3.75
6.	044.886	0.950	1.582	041.219	3.667	-3.75
7.	144.482	1.210	0.618	139.850	4.632	-3.73
8.	288.964	1.275	0.328	284.042	4.922	-3.72
9.	577.928	1.320	0.155	572.833	5.095	-3.76
10.	α	1.360	0.000	α	5.250	-

Average p^K = - 3.76±.08

sed, in nitrobenzene solution, giving $[bipy\ MX_2]^+$ ions. Graddon and Rana showed [9] that phenanthroline or bipyridine formed very stable 1:1 adducts with Lewis acids.

The heteroaromatic nitrogen compounds show absorption bands in the UV region. The longer wavelength absorption is assigned [10] as $\eta^*-\pi$ transition. In non-polar solvents, these bands show fine structures which become completely blurred in polar solvents. For 2,2'-biquinoline, vibrational structures are observed (Fig.1) in the electronic spectra which disappear on interaction with arsenic chloride indicating the formation of an un-ionised adduct in solution. The intramolecular charge transfer band is observed to shift towards the longer wavelength on complex formation. (cf. similar findings by Okawara et al [11] for carbonyl donors). This new absorption band, corresponding to the adduct formation, is usually attributed [12,13] to a charge transfer species.

For the interaction of arsenic trichloride with the bases, the equilibrium may be represented as follows:

$$Donor + AsCl_3 \overset{K}{\rightleftharpoons} AsCl_3 : Donor \quad ...(i)$$

The equilibrium constant values are computed at the new adduct band. All three bases were completely converted to adduct band. All three bases were completely converted to adduct formation by using an excess of arsenic chloride. Knowing the eqilibrium concentrations of all the species involved in eqilibrium, the p^K values are obtained by the following relationship:

$$p^K = - \log [Adduct] / [Base] [AsCl_3] \quad ..(ii)$$

Table 1 shows the p^K values for the 2,2'-biquinoline-Arsenic (III) chloride interaction. The p^K values are consistant, hence 1:1 stiochiometry is concluded. For dilute concentrations of the acid used, the p^K values were somewhat greater than the values obtained with higher concentrations of arsenic chloride. This strengthening of Lewis acidity is due to the possibility of formation of a conjugate Bronsted-Lewis acid i.e., $HAsCl_4$ (which may be formed due to traces of moisture at higher dilutions). It is known [14,15] that presence of a protonic acid increases the acidity of a Lewis acid. The dual acids have also been termed [16] as 'super' acids. The presence of moisture would give rise to $H - O \underset{H}{\text{---}} AsCl_3$ which shows a strong acidic behaviour (cf the stronger acidic properties [17] of $R - O \underset{H}{\text{---}} BF_3$).

The results of the acid - base interactions are shown in Table 2.

The p_k values indicate that the adducts formed in solution are very stable. Arsenic (III) chloride behaves as a strong Lewis acid. The basic strength of the heteroaromatic bidentate nitrogen donors is found to be in the following sequence; bipy> phen > biquinoline. Their basicity, towards arsenic trichloride, is established to be in the retios of 17.4: 13.3:1 in the aprotic medium.

It has previously been shown [18-20] that for similar Lewis acid-base interactions, a fair correlation exists between p^K and $p^K a$ values of bases. For two similar bases (1 and 3) studied in the present work, the data fits by the following relation: $p^K = -0.18\ p^K a - 1.475$. From this relationship, $p^K = -5.39$ for o-phenanthroline is predicted; a value greater than the experimentally determined value (-4.85±.1), o-phenanthroline, being a rigid structure, is expected to show steric effects which are manifested in lowering the stability of the adduct.

Experimental

Materials

The purification of the solvent was carried out as described by Satchell and Wardell [21]. The bases were obtained from BDH and purified by recrystallisation. 2,2-bipyridine and 2,2-biquinoline were crystallised from methanol and had m.p. 72 and 196°C respectively. O-phenanthroline was crystallised twice from ether (m.p. 117°C).

Arsenic trichloride was obtained from Fluka, which was distilled before use. First few drops were rejected and a few cm^3 distillate was collected at 130°C. The materials and solutions were handled in a dry box.

Equilibrium constant determination

This has been described by Satchell and Wadell [21]. Each p^K determination was repeated at least twice. For each

Table-2: p^K values for the interaction between bidentate heterocyclic bases and arsenic trichloride in o-dichlorobenzene solutionat 25°C.

No.	Base	λ_{max} nm (D)	λ_{max} nm (DA)	pK_a	p^K
1.	2,2'-bipyridine	293(log ε =3.95)	307 (log ε =4.15)	4.35*+	-5.00 ±.10
2.	O-phenanthroline	293(log ε = 3.66)	shoulder comes up	4.84*+	-4.85 ±.10
3.	2,2'-biquinoline	327(log ε = 4.36)	365(log ε =4.41)	2.82*	-3.76 ±.08

K_a = Dissociation constant of DH^+ in water at 25°C.

+ = Values for physical constants; * This work.

base, ten different concentrations of arsenic trichloride were used. The equilibrium positions were reached instantaneously. The spectra were recorded on SP8-400 UV/VIS Pye-Unicam spectrophotometer. The p^K value of 2,2-biquinoline was determined by the spectrophotometric method as described previously [4].

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