Quantitative Aspects of Lewis Acidity. Part 17.† Equilibria between Covalent Metal Halides and Thiobenzamide in Diethyl Ether Solution

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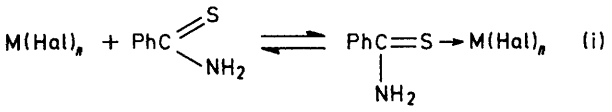
Covalent halides form 1 :1 adducts with thiobenzamide in diethyl ether solution. The site of co-ordination is probably the sulphur atom. The equilibrium constants (K) for adduct formation, determined spectroscopically at 25 °C, reveal the sequence of acidities $HgBr_2 \gtrsim HgCl_2 \simeq SnCl_4 > ZnCl_2 > GaCl_3 > AlCl_3 > BF_3 \gg AsCl_3$, $SbCl_3$. Comparison of the K values with those found under similar conditions for benzamides (structurally analogous O-bases) shows that whereas the group 3 and group 5 acids are relatively more acidic towards the O-bases than towards the S-base, the zinc and tin acids occupy an intermediate position (co-ordinating about equally well with either class), whilst the mercury acids display an exceptional affinity for the S-base.

RELATIVELY little quantitative information is available concerning interactions between Lewis acids and sulphur bases. We report now on the equilibria between several covalent metal halides and thiobenzamide in diethyl ether solution, and compare our results with those obtained under similar conditions with benzamide.[1] We find that thiobenzamide engages in equilibria such as (i) under most conditions.



EXPERIMENTAL

Materials.—Diethyl ether (May and Baker ' anhydrous ') was further dried by distillation from lithium aluminium hydride. The fraction of b.p. 34.5 °C was collected in a dessicated vessel. Thiobenzamide (Eastman Kodak) was purified by chromatography on neutral alumina. The product had m.p. 115 °C. Aluminium chloride (Fisons) was purified by repeated sublimation from aluminium metal and sodium chloride until the sublimate was white. The purest available commerical samples of arsenic, antimony, bismuth, and mercury halides were used without further purification. The other covalent halides were purified by methods previously described.[2-4]

Preparation of Solutions.—Solutions of the covalent halides in ether were prepared and handled in a dry box flushed with dry nitrogen. The concentrations of the various solutions were determined by titration for halide.

U.v. Spectra.—These were measured with a Unicam SP 800 recording spectrophotometer or, for measurements at fixed wavelength, a Unicam SP 500 instrument fitted with an SP 45 scale expander accessory. A few measurements were made with a Durrum–Gibson D 120 stopped-flow spectrophotometer. Solutions were normally thermostatted in Teflon-stoppered, silica cells of 10 mm path. For each covalent halide a series of solutions was made up containing a fixed quantity of thiobenzamide (*ca.* 10^{-4}M) and various (*ca.* ten) different concentrations of the Lewis acid (covering about a 20-fold range), and their spectra were taken. The acid was normally kept in at least a 10-fold excess over the thiobenzamide. Changes in the thiobenzamide absorption were noted (where necessary the blank cell contained the appropriate quantity of Lewis acid). Most of the solutions were stable during the short period needed for spectroscopic study but in cases where spectra showed a slow fall in absorption with time, sufficient measurements were taken to permit their extrapolation to the time of mixing. For each Lewis acid all the measurements were repeated with different batches of starting materials. Qualitative experiments carried out by a stopped-flow technique showed that the equilibria between thiobenzamide and the various acids were all established within the time necessary for mixing solutions. All experiments were performed at 25 °C.

N.m.r. Spectra.—Ethereal solutions containing thiobenzamide (0.1M) and sufficient zinc chloride for effectively complete conversion of the base into the adduct were prepared, and samples were added to capped n.m.r. tubes. (All these operations were conducted in the dry box.) Spectra were taken (at 37 °C) with a Perkin-Elmer R12B spectrometer.

RESULTS AND DISCUSSION

In diethyl ether, thiobenzamide has an absorption band centred at *ca.* 303 nm. As increasing amounts of Lewis acid are added to the solution this absorption is progressively reduced in intensity and a new band appears at shorter wavelength, the exact position and intensity of which depends upon the acid (Table). Good isosbestic points are obtained and the spectral changes are reversed on dilution. The results therefore suggest that addition of acid converts the base into a single new species, an acid–base adduct, in an equilibrium process. In each experiment the ratio [adduct]/[thiobenzamide] was

Equlibrium constants for reaction (i) in diethyl ether solution at 25 °C

For K (l mol^{-1}) see text; $\lambda_{max.}$ (nm) $\varepsilon_{max.}$ refer to the adduct absorption

Acid	$\lambda_{max.}$	$10^{-3}\varepsilon_{max.}$	$10^{-3}K$	pK
$HgBr_2$	293	10.4	7.60	−3.88
$HgCl_2$	288	16.2	4.25	−3.63
$SnCl_4$	282	17.5	4.00	−3.60
$ZnCl_2$	284	13.4	0.93	−2.97
$GaCl_3$	279	11.4	0.21	−2.32
$AlCl_3$	295	7.07	0.16	−2.20
BF_3	282	7.56	0.012	−1.08
$SbCl_3$			<0.001	>0
$AsCl_3$			$\ll 0.001$	$\gg 0$

† Part 16, K. Bukka and R. S. Satchell, *J.C.S. Perkin II*, 1976, 1058.

[1] R. S. Satchell, K. Bukka, and C. J. Payne, *J.C.S. Perkin II*, 1975, 541.

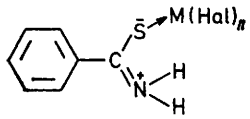
[2] A. Mohammad and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 403.

[3] R. M. Evans and R. S. Satchell, *J. Chem. Soc.* (*B*), 1970, 300.

[4] R. S. Satchell, *J. Chem. Soc.*, 1964, 5464.

varied over a substantial range. Since the various covalent halides are probably essentially monomeric in ether solution,[1,5,6] the simplest equilibrium to write is equation (i). Calculations on this basis, along the lines we have employed before,[7-9] with the absorption data referring to the thiobenzamide or adduct absorptions, led to values for the equilibrium constant K (= [adduct]/[thiobenzamide][acid]) which were reproducible to within ±20% for different batches of starting materials. Since in the present systems ε_{adduct} was normally available from measurements at high acid concentration, it was possible to calculate K directly at each intermediate acid concentration used, and to average these values. The average values so obtained were in close agreement with those obtained by our more usual graphical treatments.[7-9] Within any one experiment K was always satisfactorily constant (±8%) up to *ca.* 80% conversion of the base into the adduct; thereafter some acids ($SnCl_4$, $AlCl_3$) gave results suggesting that the predominant adduct stoicheiometry was changing from 1 : 1 to 1 : 2 (base : acid). However, in this region the changes in absorbance are small and difficult to measure accurately, and the reality of the 1 : 2 adducts is therefore uncertain. Of the acids studied, antimony and arsenic trichlorides proved feebly acidic in the present system and led to negligible spectral changes. Bismuth trichloride could not be studied owing to its strong absorption in the relevant spectral region. Our results are collected in the Table.

The sequence of acidity towards thiobenzamide is $HgBr_2 \gtrsim HgCl_2 \simeq SnCl_4 > ZnCl_2 > GaCl_3 > AlCl_3 > BF_3 \gg AsCl_3, SbCl_3$. In writing equation (i) it has been assumed that the important basic centre of thiobenzamide is the sulphur rather than the nitrogen atom. This is suggested by studies [10] of the protonation of thioamides in concentrated acids (where the stabilisation of the adducts by solvent is likely to be relatively weak, as in the present systems) and is strongly supported by two of our results. First, mercury(II) halides interact feebly with benzamides,[11] but strongly with thiobenzamide (Table). Were nitrogen the site of co-ordination this result would be difficult to understand, whereas the known great affinity of mercury for sulphur makes it easy to account for. Secondly, if $M(Hal)_n$ is co-ordinated to sulphur this should exaggerate any double-bond character of the C–N bond (1) and prevent its free rotation. This would lead to the N–H protons being non-equivalent, and two n.m.r. signals would be expected. If co-ordination is at nitrogen no such non-equivalence is likely. The argument is similar to that used to locate the site of co-ordination in *O*-amides.[1,10] In free thiobenzamide in ether the N–H protons give a broad band centred at δ *ca.* 8.0; in the zinc chloride adduct they give



(1)

two identical well-resolved bands at δ 10.3 and 10.8. If, as seems likely therefore, protons, mercury(II) halides and zinc chloride all co-ordinate at sulphur, rather than at nitrogen, in thiobenzamide in solvents which stabilise the adducts weakly, it seems likely too that the remaining covalent halides will share this preference.

Comparison of the present equilibrium constants with those found [1,11] for the same covalent halides, under similar conditions, with benzamide and various substituted benzamides, reveals (i) that the mercury halides are much (probably $>10^3$-fold) more strongly acidic towards the *S*- than towards the *O*-analogue, (ii) that the zinc halides and tin chloride co-ordinate about as readily at sulphur as they do at oxygen, and (iii) that the group 3 acids are *ca.* 30-fold, and the group 5 acids at least 30-fold, less acidic towards the *S*- than towards the *O*-analogue. As is well known the proton too normally co-ordinates less readily at sulphur than at oxygen in analogous compounds (*e.g.* carboxylic acids and esters).[12] The pK_a values for benzamide and thiobenzamide show that the latter compound is also somewhat (perhaps 5-fold [10,13,14]) the less basic towards the proton, but this particular comparison is not safe since in the dilute aqueous acid in which these pK_a values were determined the main site of protonation could be nitrogen.[10]

Our results are mostly compatible with the qualitative (hard–soft) predictions of Pearson.[15] Thus (i) the group 3 acids and arsenic chloride behave analogously to the proton, (ii) the zinc and tin acids occupy an intermediate (borderline) position, and (iii) the mercury acids display an exceptional affinity for sulphur relative to oxygen.

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