Lewis Acid Strength and Nuclear Magnetic Resonance Measurements

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IN recent years much attention[1] has been given to the possible existence of correlations between different measures of the Lewis acidity of covalent metal halides and related compounds towards bases, and various n.m.r. measurements. Some authors have claimed that rectilinear relationships exist between the chemical shifts and the i.r. frequency and enthalpy changes which occur on adduct formation, while others have stressed the absence or the very limited applicability of such relationships. In all this work (i) no correlations have been tested which are not restricted to acids derived from Group (III) (indeed, most of the measurements are confined to boron acids), and (ii) no correlations have been attempted between n.m.r. data and equilibrium constants for adduct formation obtained under similar conditions. Such constants are regarded by many as the most satisfactory measure of acidity, but are more difficult to obtain than n.m.r. or i.r. shifts, or ΔH values; a reliable and convenient semiquantitative approach to such constants *via* n.m.r. data would therefore be of considerable value. We report here on equilibrium and n.m.r. measurements for 1 : 1 adduct formation, in ether solution, between two benzamides and a number of covalent metal halides of widely varying acidity (Equation 1). Our data (Table) are free from steric effects arising from either *N*- or *ortho*-substituents. The n.m.r. measurements employed a sufficient excess of metal halide to ensure complete

$$RC_6H_4{\cdot}CO{\cdot}NH_2 + M(Hal)_n \rightleftharpoons RC_6H_4{\cdot}C(NH_2){=}O : M(Hal)_n \qquad (1)$$

conversion of the amide to the adduct. The resonance positions were independent of the concentrations of the metal halide and adduct. The adduct spectra contained two broad NH signals of equal size. In some cases one NH peak was hidden under the aromatic CH resonance (as shown by integration of the peak areas). The existence of two NH signals shows[2] that in each adduct the acid co-ordinates to the amide oxygen atom (Equation 1). The chemical shifts (δ) from the internal reference Me_4Si for both NH signals of *m*-methoxybenzamide, and for the low-field NH signal for *p*-nitrobenzamide, are in the Table. Examination of the results reveals (i) that the chemical shift is generally more negative (*i.e.*, the signals move closer towards that characteristic of a highly acidic free proton) the stronger the Lewis acid; (ii) that plots of δ *versus* K are straight lines; and (iii) that the data for boron fluoride fall well off such plots. The general trend in δ reflects the increasing drain upon the electrons associated with the *N*-bound protons as the stability of the adduct rises. The rectilinear relationship between K and δ found with the present systems indicates that n.m.r. data *can* provide a convenient guide to K values, although care must be exercised in view of possible anomalous behaviour. In our opinion the anomalous boron fluoride results arise from intramolecular hydrogen bonding between fluorine and the NH proton *cis* to the carbonyl group (a six-membered ring is possible).

Chemical shifts and equilibrium constants for reaction (1)

	m-Methoxybenzamide				*p*-Nitrobenzamide		
$M(Hal)_n$	pK	K	$-\delta_{cis}$	$-\delta_{trans}$	pK	K	$-\delta_{cis}$
$AsCl_3$	*ca.* −0·80	*ca.* 6·3	*ca.* 8·0				
$SbCl_3$	−1·76	58	8·01	*ca.* 7·4			
BF_3	−2·93	850	9·30	8·15	−1·86	72	*ca.* 9·6
$ZnBr_2$	−2·94	870	8·60	8·00	−2·17	148	8·90
$ZnCl_2$	−2·94	870	8·58	8·02	−2·17	148	8·92
$GaBr_3$	−3·40	2510	9·60	8·64	−2·49	310	10·10
$GaCl_3$					−2·53	340	10·12

For δ (p.p.m. at 37°) see text; δ_{cis} and δ_{trans} represent respectively the shifts for the NH protons *cis* and *trans* to the carbonyl group.[2] (Sometimes the *trans* NH signal was obscured by the aromatic proton signals); $K(25°) = [\text{adduct}]/[\text{amide}][M(Hal)_n]$; p$K = -\log K$; p$K$ values reproducible to $\pm 0{\cdot}05$ and δ to $\pm 0{\cdot}04$, except where indicated.

The rectilinear relationship between K and δ implies that, over the wide range of acidity used here (K changes 400-fold), there exists no similar relationship between δ and $\Delta G^0 (= -RT\ln K)$, although such a relationship can be obeyed approximately over narrow parts of the range. The same is probably true for ΔH, for this quantity often parallels $\Delta G°$. The simple dependence of δ on K, rather than on pK, is unexpected.

Our pK data are the first available for amides with a variety of metal halides; their pattern is similar to that established for unambiguous keto-bases[3] and thus supports co-ordination *via* oxygen rather than nitrogen.

Experimental details will be given in our fuller report of this work.

N.m.r. measurements were made using the Perkin–Elmer R. 10 instrument operated by the University of London Intercollegiate Research Service.

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