Strength of Lewis acid–Lewis base interactions. A ^{13}C NMR study of the ether interchange in boron trifluoride complexes

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The intramolecular chemical shift difference previously used for calibration of Brønsted acid strengths (the $\Delta\delta$ method) has been extended to the study of Lewis acid–base interactions. The exchange between an ether complexed with boron trifluoride and another ester is fast on the ^{13}C NMR timescale (75.4 MHz, 22 °C) and allows the determination of the equilibrium constant by interpolation of chemical shifts. Using boron trifluoride diethyl etherate as the standard, equilibrium constants for the reaction ($Et_2O{\cdot}BF_3 + ROR' \rightleftharpoons Et_2O + RR'O{\cdot}BF_3$) have been measured both in dichloromethane and without solvent for R, R′: Bu, Bu; Me$_2$CH, Me$_2$CH; Me, CH$_2$CH$_2$Cl; CH$_2$CH$_2$Cl, CH$_2$CH$_2$Cl; Me, C$_6$H$_5$; Et, C$_6$H$_5$. The values agree in some cases with literature values obtained by other methods and do not agree in other cases. The electronic and steric effects of substituents upon the stability of complexes are evidenced in the results.

Introduction

There is a large body of literature on the evaluation of the strength of Brønsted acid–base interactions, but many fewer reports on the quantification of Lewis acid–base interactions, which has been considered a rather difficult undertaking.[1] It was even indicated that the definition of strength has no real meaning for Lewis acids.[2] Nonetheless, some attempts at generating scales of Lewis acid and Lewis base strength were made, for example the donor and acceptor numbers of solvents, introduced by Gutmann[3] and the four-parameter correlation of Drago.[4,3d] We hold the opinion that valid comparisons can be made for well determined series of related compounds.

The complexes of boron trifluoride with various oxygen bases, including ethers, have long been known.[5] The stability of a few of these complexes was first compared by Brown and Adams from the dissociation constants [eqn. (1)] determined

$$R_2O\text{–}BF_3 \rightleftharpoons R_2O + BF_3 \quad K_{R_2O} \qquad (1)$$

by vapor pressure measurements. Steric effects were found to control the relative stability: $K_{Me_2O} < K_{Et_2O} < K_{Pr^i_2O}$.[6] These findings were later confirmed by similar experiments[7] and by calorimetry.[8]

Subsequent investigations by IR spectroscopy,[9] by ^1H NMR spectroscopy,[10] and by ^{19}F NMR spectroscopy[11] have again indicated Me$_2$O to be more strongly bound than Et$_2$O, but by a narrower margin than the vapor pressure studies had given. Examination of the same group of ethers as in the work of Brown and Adams by ^1H NMR spectroscopy in dichloromethane solution gave, however, a completely different order of stability in eqn. (1): $K_{Et_2O} < K_{Pr^i_2O} \ll K_{Me_2O}$. The discrepancy was rationalized as a solvent effect.[12]

A comparison of Et$_2$O and anisole through the determination of the rate of exchange between boron trifluoride diethyl etherate (**1**) and varying amounts of anisole [**2**, eqn. (2), R = Ph,

$$\underset{\mathbf{1}}{Et_2O\text{–}BF_3} + \underset{\mathbf{2}}{ROR'} \rightleftharpoons \underset{\mathbf{3}}{RR'O\text{–}BF_3} + \underset{\mathbf{4}}{Et_2O} \qquad (2)$$

A: R = R′ = Bu; **B**: R = R′ = Me$_2$CH; **C**: R = Me, R′ = CH$_2$CH$_2$Cl;
D: R = R′ = CH$_2$CH$_2$; **E**: R = Me, R′ = C$_6$H$_5$; **F**: R = Et, R′ = C$_6$H$_5$

R′ = Me] established that the equilibrium constant must be less than 0.005. An activation energy of 10.6 ± 0.6 kcal mol^{-1} (ref. 13) was determined for the forward reaction.[14] The same group reported, however, a heat of formation of −12.3 kcal mol^{-1} for the complex of anisole (**3**, R = Ph, R′ = Me) from its components [reverse of eqn. (1)],[15] which is about 1 kcal mol^{-1} less exothermic than for the complex of dimethyl ether[6,7,16] and is somewhat more exothermic than for the complex of diethyl ether.[6,7] Unless there is a very large difference in the entropy terms for the formation of the two complexes, which is rather difficult to rationalize, the ether exchange equilibrium of eqn. (2) for Et$_2$O and PhOMe should, therefore, have an equilibrium constant not far from one.

The complexes of anisole, phenetole and bis(β-chloroethyl) ether were studied with Brown's vapor pressure method[6] by Katal'nikov *et al.* and found to be of similar stability.[17] A linear dependence of the logarithm of the dissociation constant [eqn. (1)], $\log K_{R_2O} = A - B/T$ held in all three cases. For anisole, $A = 2.791$, $B = 977$, this led to a dissociation constant of 0.301 atm at 295 K. From the corresponding equation for the diethyl ether complex, **1**, ($A = 6.013$, $B = 2384$)[6] one obtains a value of 0.008 54 atm for the dissociation constant of **1** at the same temperature, whence an equilibrium constant for the exchange in eqn. (2) (R = Ph, R′ = Me) of 2.83×10^{-2} is calculated, different from both values given above. (It has to be mentioned that the values calculated[17] for the enthalpies, entropies and free energies of dissociation are in error; they do not agree with the reported data.[17])

As part of our studies of acid–base interactions by ^{13}C NMR spectroscopy,[1] we undertook a comparison of the Lewis basicities of ethers. We present the full report here.

Experimental

Materials

The ethers used in the experiments were reagent-grade chemicals and were used as purchased. Commercial boron trifluoride etherate (purified, redistilled grade) was found by ^1H NMR spectroscopy at −60 °C to contain 5% uncomplexed ether. Interestingly, redistillation at atmospheric pressure under nitrogen gave a material of the same composition. The same results in the equilibrium constant measurements were obtained with

Table 1 Calculation of equilibrium constants for the reaction of **1** with phenetole (**2F**)

No.	n_1/mmol	n_4[a]/mmol	n_{2F}[b]/mmol	δ_{CH_2}	δ_{CH_3}	$\Delta\delta$(mix)[c]	n_4(eq)/n_1(eq)[d]	x[e]	10^3K[f]
1	4.417	0.2325	2.186	69.899	12.526	57.373	0.098 27	0.1836	9.01
2	4.306	0.2266	3.231	69.851	12.542	57.309	0.107 9	0.2147	7.68
3	4.132	0.2174	4.079	69.737	12.575	57.162	0.132 6	0.2919	10.2
4	3.545	0.1866	4.335	69.737	12.574	57.163	0.132 1	0.2489	7.04
5	2.705	0.1423	4.266	69.656	12.591	57.065	0.148 9	0.2266	8.35
6	2.909	0.1531	4.995	69.640	12.591	57.049	0.151 7	0.2502	8.00
7	2.973	0.1565	6.253	69.592	12.591	57.001	0.160 1	0.2755	7.38

[a] $19n_4 = n_1$. [b] Ratios n_{2F}/n_1 in experiments 1–7 are 0.4949, 0.7502, 0.9873, 1.223, 1.577, 1.717 and 2.103, respectively. [c] From eqn. (6). [d] From eqn. (3). [e] From eqn. (4). [f] From eqn. (5).

the commercial material as with the one redistilled in the laboratory. The equilibrium constants reported were, therefore, corrected for the free ether contained in the etherate. Dichloromethane was refluxed for 1 h from calcium hydride (3.05 g for 100 ml) under nitrogen and distilled from the same pot, after which it was stored and opened only under nitrogen. The complex of phenetole with BF_3 was obtained by bubbling BF_3 through the dry ether in a Teflon bottle cooled at 0 °C. The end of the reaction was indicated by the appearance of white fumes at the end of the apparatus.[18] The composition of the complex was determined by a two-step titration of boron trifluoride, as described earlier,[18] allowing several seconds for the indicator to change color, because the indicator partitions between the aqueous solution and the phenetole.

NMR experiments

The NMR samples were prepared in 5 mm tubes pre-dried overnight in an oven at 120 °C. The BF_3 complex of an ether (usually $Et_2O{-}BF_3$) and another Lewis base (usually another ether) were introduced into the tube under nitrogen and the tube was tightly capped after each addition. The weight of each material was determined with an analytical balance (0.1 mg accuracy). The tube was then tightly capped again and analyzed by NMR spectroscopy at room temperature (*i.e.* the normal probe temperature, 22 °C). For studies in CH_2Cl_2 solution, a 1 M batch solution of complex was made, appropriate volumes of it were placed into the NMR tubes and checked by weighing, after which the Lewis base was added into each tube, which was then weighed again. For analysis, the 5 mm tube was placed coaxially inside a 10 mm tube, containing $CDCl_3$ as lock solvent. The spectra were run at 75.468 MHz, with a spectral width of 15 kHz, a number of 16 K points in the time domain and 16 K points for the Fourier transform. An excitation pulse of 5.0 μs (90 deg pulse: 9.0 μs), a receiver blanking delay of 30 ms and a relaxation delay of 3 s were used. Proton decoupling was achieved by a Waltz sequence,[19] the 90 deg pulse for decoupling being 100 μs. The chemical shifts were measured from the center line of $CDCl_3$ in the outer tube, taken as 77.0 ppm.

Calculation of equilibrium constants

The reaction of **1** with phenetole (**2F**) will be presented for illustration. The internal chemical shift difference for diethyl ether, $\Delta\delta_4$ in a 1 : 1 (mol : mol) mixture with anisole was 50.450 (65.600–15.150). For the neat complex (95%) a $\Delta\delta$ value of 57.670 (70.140–12.470) was measured. It can be seen that upon complexation the methylene signal moves downfield and the methyl signal moves upfield. From these values an internal chemical shift difference in the pure complex, $\Delta\delta_1$, of 58.050 was calculated.

Seven mixtures of the diethyl ether complex and phenetole were prepared. The numbers of mmoles of **1** (n_1), free diethyl ether introduced with **1** (n_4), and phenetole (n_{2F}) are shown in Table 1, together with the chemical shifts for the methylene signal, methyl signal and the value $\Delta\delta$(mix) for the fast exchanging (**1** + **4**) mixture. The molar ratio **4** : **1** at equilibrium, n_4(eq)/n_1(eq) was calculated from eqn. (3) and the number of mmoles

$$n_4(\mathrm{eq})/n_1(\mathrm{eq}) = [58.050 - \Delta\delta(\mathrm{mix})]/[\Delta\delta(\mathrm{mix}) - 50.450] \quad (3)$$

of **1** converted to **4** by reaction with phenetole [equal to the number of mmoles of $Ph(Et)O{-}BF_3$ formed at equilibrium], x, by eqn. (4). Both these quantities are also shown in Table 1. The

$$x = \{n_1[n_4(\mathrm{eq})/n_1(\mathrm{eq})] - n_4\}/[1 + n_4(\mathrm{eq})/n_1(\mathrm{eq})] \quad (4)$$

equilibrium constant K for eqn. (2) was calculated using eqn. (5) and is given in the last column of Table 1.

$$K = x(n_4 + x)/(n_1 - x)(n_{2A} - x) \quad (5)$$

As the value of K obtained in experiment no. 3 differed by more than 2.5 standard deviations from the average of all other determinations, $K_{av} = (7.9 \pm 0.7) \times 10^{-3}$, it was discarded. Its inclusion would give $K_{av} = (8.2 \pm 1.1) \times 10^{-3}$, which is not significantly different from the previous value.

For the complex of phenetole in CH_2Cl_2, the ^{13}C NMR spectrum gave the values of 75.45, 12.78 and 62.67 for δ_{CH_2}, δ_{CH_3} and $\Delta\delta$ respectively, whereas for the free phenetole the corresponding values were 63.02, 14.56 and 48.46.

Results and discussion

We have established that ^{13}C NMR spectroscopy can be successfully used for the characterization of the strength of the Brønsted acid–base interaction, either through the determination of acidity functions,[20] or, for non-Hammett acids,[1] through an empirical relative hydronating ability parameter (RHA).[1,21] In both cases, the technique consisted of a comparison of the difference between the chemical shifts of two carbon atoms in the molecule of probe base or indicator, in media of different acidity ($\Delta\delta$ method).[1] The same technique was adapted for the comparison of the strength of ethers (**2**) relative to diethyl ether (**4**) as standard. Interpolation of the $\Delta\delta$ parameter [eqn. (6)] for diethyl ether between the values for

$$\Delta\delta = \delta_{CH_2} - \delta_{CH_3} \quad (6)$$

complex **1** and the free ether **4** was used to calculate the equilibrium constant of the exchange in eqn. (2), as shown in the Experimental section. The ^{13}C spectrum of **1** had been published previously.[22]

The ethers investigated were dibutyl ether (**2A**), diisopropyl ether (**2B**), methyl 2-chloroethyl ether (**2C**), bis(2-chloroethyl) ether (**2D**), anisole (**2E**) and phenetole (**2F**). In order to check the literature claim of a pronounced solvent effect upon the reaction,[12] we examined the reactions of pure, neat reactants, as well as the reactions in dichloromethane solutions. The results are presented in Table 2.

The first observation is that the relative stability of complexes of dialkyl ethers exemplified by **1** > **2A** > **2B** is, indeed, con-

Table 2 Equilibrium constants for the reaction of oxygen bases with boron trifluoride etherate at 22 °C

No.	Lewis base	Medium	K^a	n^b	**2**:**1**^{c} (mol:mol)
1	Bu_2O (**2A**)	Neat reactants	0.59 ± 0.03	5	0.5–1.5
			0.52 ± 0.08^d	6	0.8–2.3
2	—	CH_2Cl_2	0.63 ± 0.10	4	0.4–1.75
			0.58 ± 0.06^d	6	0.7–2.3
3	2-Pr_2O (**2B**)	Neat reactants	$(7.8 \pm 0.80) \times 10^{-2}$	6	0.5–2.5
4	—	CH_2Cl_2	$(7.8 \pm 1.9) \times 10^{-2}$	6	0.55–2.4
5	$MeOCH_2CH_2Cl$ (**2C**)	Neat reactants	$(5.6 \pm 0.4) \times 10^{-2}$	6	0.3–2.3
6	—	CH_2Cl_2	$(3.7 \pm 0.5) \times 10^{-2}$	6	0.5–2.2
7	$O(CH_2CH_2Cl)_2$ (**2D**)	Neat reactants	$(7.6 \pm 0.7) \times 10^{-3}$	8	0.4–2.3
			$(8.6 \pm 0.7) \times 10^{-3d}$	6	0.8–2.3
8	—	CH_2Cl_2	$(6.3 \pm 1.9) \times 10^{-3}$	5	0.7–2.15
9	PhOMe (**2E**)	Neat reactants	$(4.7 \pm 0.6) \times 10^{-3}$	8	0.5–6.7
10	PhOEt (**2F**)	Neat reactants	$(7.9 \pm 0.7) \times 10^{-3e}$	6	0.5–2.1
			$(8.6 \pm 0.6) \times 10^{-3d}$	6	0.8–2.3
11	—	CH_2Cl_2	$(3 \pm 1.5) \times 10^{-3}$	4	0.35–1.8

[a] Uncertainty given as standard deviation. [b] Number of measurements. [c] Range of ratios of reactants in the experiments. [d] The second series of experiments was conducted on a different date. [e] The experimental data used to calculate this value are presented in Table 1.

trolled by steric effects.[6] The steric control does not hold, however, for the pair anisole (**2E**)–phenetole (**2F**). Note that from vapor pressure measurements it was concluded that the complexes of **2E** and **2F** have similar stabilities.[17] The aromatic ring can adopt an orientation bisecting the B–O–CH_2R angle, in which the steric interaction with the radical R (H or Me) is minimized. This explanation does not hold, however, for the pair **2C** and **2D**. The electronic effect of the remote chlorine substituent in **2C** should contribute to K by a factor of 0.09 (the square root of the equilibrium constant for **2D**). Next, comparisons of **4** with ethyl methyl ether[10] and with dimethyl ether[6,8] indicate that the replacement of the ethyl group by the smaller methyl group should increase the equilibrium constant by a factor of two or more. A value of $K \approx 0.18$ is thus predicted for **2C**, instead of the experimental value of 0.056 (Table 2). It is conceivable that very weak complexes, like **2D**, **2E** and **2F**, have longer boron–oxygen bonds and are, therefore, less sensitive to steric effects. Of the three estimates for the equilibrium constant of the reaction of **1** with anisole (**2E**),[14] the one based on the examination of the rate of ether exchange agrees best with our results.

As mentioned in the Introduction, the dissociation of **2D** was also studied by the vapor pressure method.[17] A dissociation constant of 0.294 atm at 295 K is obtained from the published data. From it and from the dissociation equilibrium constant for **1** (see above)[6] an equilibrium constant for the exchange in eqn. (2) of 2.90×10^{-2} is obtained for **2D**,[17] significantly larger than the one obtained by us (Table 2).

It can be also observed that the values for the equilibrium constants in dichloromethane solution are not significantly different from the values obtained in the absence of solvent, with the possible exception of phenetole (**2F**), for which the properties of the aromatic ether as solvent might have an effect. From the equilibrium constants reported for the reaction of BF_3 with **4** and with **2B** in dichloromethane,[12] a value $K = 0.623$ is calculated for the reaction of **2B** with **1**, one order of magnitude too large. The method employed in that work, measurement of chemical shifts as a function of the ratio of BF_3 to ether[10,12,23] cannot be considered to be reliable.

The molar enthalpies of complex formation between BF_3 and a few ethers, including **2B** and **4** in dichloromethane solution have been reported,[8b,12] thus allowing us to calculate a value of $\Delta H° = 0.516$ kcal mol^{-1} for the enthalpy of reaction of **1** with **2B** according to eqn. (2). From this quantity and the equilibrium constant of Table 2 ($K = 0.078$, $\Delta G° = 1.5$ kcal mol^{-1}) we can calculate an entropy of reaction $\Delta S° = 3.3$ e.u.,† which indicates a greater degree of organization in the complex of **2B** (or in the solvent surrounding it) than in **1**.

We also attempted to determine the relative basicities of some Lewis bases (LB) other than ethers by examining their exchange with the complex of phenetole [**3F**, eqn. (7)] in

$$\underset{\mathbf{3F}}{F_3B\text{–}O(Ph)CH_2CH_3} + n(LB) \rightleftharpoons F_3B(LB)_n + \underset{\mathbf{2F}}{Ph\text{–}O\text{–}CH_2\text{–}CH_3} \quad (7)$$

dichloromethane solution, interpolating the parameter $\Delta\delta$ for phenetole between the values for **2F** and **3F**. The example of phenyl acetate (LB = PhOAc) is used here to illustrate the method.

The calculated equilibrium constants were found to vary with the ratio of Lewis base to **3F**. Thus, PhOAc was studied at molar ratios PhOAc: **3F** of 1.02, 1.24, 1.56, 1.96 and 2.84. The values of K, calculated for eqn. (7) with $n = 1$,[24] were 46.9, 28.7, 23.1, 18.8 and 17.0, respectively. Some possible reasons for these results might be contamination of the solution of the complex by a small amount of a more strongly basic material or loss of BF_3 by evaporation from the solution of very weakly basic materials. (The Teflon–FEP bottle containing the complex **3F** was stored in a can with drying agent, in a freezer, but the NMR spectra were run at 22 °C.) If either hypothesis was correct, extrapolation to infinite excess of Lewis base would correct the errors. The extrapolated equilibrium constant for PhOAc is 15, but we cannot attach too much value to this number. An attempt at studying the reaction between the neat reactants led to a complex spectrum, indicating that the ester had partially reacted by a Fries rearrangement.

A similar behavior was shown by phenol (LB = PhOH) and 2-chloro-*p*-cresol (LB = 2-Cl-4-Me-C_6H_3), for which formation of a 2:1 complex was considered [$n = 2$ in eqn. (7)].[25] The former is a stronger, while the latter is a weaker Lewis base, than **2F**.

Acknowledgements

This work was supported by a grant (CTS-9528412) from the US National Science Foundation and by a grant, also from the NSF (CTS-9413698), for the purchase of a DMX300 NMR instrument.

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Paper 7/09073K
Received 18*th December* 1997
Accepted 24*th February* 1998