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Toward a quantitative evaluation of Lewis acid strength. A ^{13}C NMR study of the interaction of boron trifluoride with diethyl ether [1]

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Abstract

The rate of exchange between boron trifluoride diethyl etherate and free diethyl ether can be conveniently measured by ^{13}C dynamic NMR spectroscopy (DNMR) between 25°C and -50°C in dichloromethane solution. The same rates and activation parameters are found by the line shape analysis of either the methyl or the methylene group. The rates do not vary with the ratio of free ether to complex between 0.61 and 2.4, indicating a rate-determining unimolecular decomposition of the latter. The literature claim of a bimolecular mechanism for the ether exchange is thus found to be incorrect. An enthalpy of activation ($\Delta H^{\ddagger}$) of 9.7 kcal/mol was calculated for this decomposition. This value is a good measure of the strength of interaction of BF_3 with diethyl ether, because the recombination to form the complex (**2**) should have a very low energy barrier, and it is close to the $\Delta H°$ value of 10.9 kcal/mol determined by Brown and Adams for the decomposition of **2** to gaseous diethyl ether and BF_3. The ^{13}C DNMR method can be applied in principle to the interaction of ether with other Lewis acids, thus providing a method for comparison of Lewis acid strengths. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Lewis acid strengths; ^{13}C dynamic NMR spectroscopy; Boron trifluoride; Diethyl ether

1. Introduction

There is a large body of literature on the evaluation of the strength of Brønsted acid–base interactions, but much fewer reports on the quantification of Lewis acid–base interactions. The most usual evaluation of Lewis sites on catalysts is based on the IR spectra of adsorbed molecules, like pyridine [1], ammonia [2], or carbon monoxide [3]. The main goal of such measurements is to distinguish between Brønsted and Lewis sites. Acetonitrile was also proposed as a probe base [4], but a case was reported for which it could not be ascertained whether the shift in the CN stretching band was due to reaction with Lewis centers or with Brønsted centers [5]. The comparison and ranking of Lewis sites by strength seems more problematic. A 2 cm^{-1} blue shift of the ν_{8a} band of adsorbed pyridine was considered an indication

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of stronger Lewis sites on sulfated zirconia (SZ, ν_{8a} 1610 cm^{-1}) than on zirconia itself (Z, ν_{8a} 1608 cm^{-1}) [6]. Such a marginal difference (equal to the reported spectral resolution, 2 cm^{-1}) cannot justify, however, the assessment of Lewis acidity as responsible for the great increase in catalytic activity of SZ over Z [7–9] or for a great increase in the strength of Brønsted sites alternatively proposed as an explanation for the high catalytic activity of SZ [10]. Moreover, rehydration of SZ led to a change in the intensities of bands assigned to Brønsted and Lewis sites, but did not appear to change the position of the 1450 cm^{-1} band assigned to Lewis sites [11], indicating either that the Brønsted and Lewis sites of the catalyst did not interact electronically, or that the position of the band does not reflect acid strength.

Likewise, it has been considered that stronger Lewis sites should produce a greater shift toward higher frequencies of the CO stretching band from the value for carbon monoxide (2143 cm^{-1}). Zirconia (ν 2185–2195 cm^{-1} [12]) thus has weaker Lewis sites than SZ, for which reported ν(CO) values range from 2200 [5] to 2212 cm^{-1} [13,14]. It is seen, however, that the spread of frequencies for each material is greater than the difference between the two. Moreover, the broad (25–30 cm^{-1}) stretching band of CO adsorbed on SZ was deconvoluted into at least two peaks, with maxima about 10 cm^{-1} apart, and addition of increasing amounts of water led to the decrease of the two peaks without a change in the ratio of their intensities [15]. If the differences in frequencies reflected differences in strength, the high frequency peak should disappear first. No satisfactory calibration of the relationship of the Lewis acid strength with the position of the stretching band of the adsorbed CO is available. As a matter of fact, the force constant for the vibration should be affected by the back donation of electrons from the solid, which we do not expect to have an importance for interactions with substrates of acid catalysis.

Based on the same postulated relationship between Lewis site strength and ν(CO), it was concluded that sulfation increases the strength of Lewis sites on zirconia, but poisons the strong Lewis sites existing on TiO_2 [16]. No molecular mechanism was offered for such a difference in behavior [16]. The effect of sulfation on catalytic activity is the same for the two metal oxides, that is a great enhancement [17,18]. Thus, the catalytic activity of sulfated titania should be inversely proportional with the strength of the Lewis acid sites.

Even the distinction of Lewis from Brønsted sites by IR spectroscopy of adsorbates is not always straightforward. Thus, deposition of Pt on SZ was reported by one group to increase the proportion of Brønsted sites and decrease that of Lewis sites upon exposure to hydrogen [19–21], but another group found that deposited Pt does not change the Brønsted/Lewis site ratio of SZ in the presence of H_2 [22]. Likewise, Lewis sites were identified on Pt-SZ by IR of pyridine adsorbate [19–22], but no band of adsorbed CO was obtained when the same catalyst was exposed to carbon monoxide by the standard procedure [23].

A difficulty in interpreting the literature data is brought about by incomplete characterization of the materials studied in different laboratories. In several cases it was not even tested whether the material had catalytic activity at all. We think that no characterization of catalysts should be published unless the catalytic activity of the material from the batch investigated is checked.

Determination of strength may be difficult even for molecular Lewis acids [24]. It was even indicated that the definition of strength has no real meaning for Lewis acids [25]. 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 [26–29] and the successful four-parameter correlation of Drago [29–31]. We hold the opinion that valid comparisons can be achieved for well determined series of related compounds and we report here an attempt at calibrating Lewis acidity from the strength of interaction with diethyl ether as a probe base, determined by ^{13}C dynamic NMR spectroscopy (DNMR).

2. Experimental

2.1. Materials

The diethyl ether used in the experiments was anhydrous reagent-grade material, which was opened and handled under nitrogen. As already noted [32], commercial boron trifluoride etherate (purified, redistilled grade) was found by ^{1}H NMR at −60°C to contain 5% uncomplexed ether and redistillation at atmospheric pressure under nitrogen gave a material of the same composition. The same results were obtained in a study of the basicity of ethers with the commercial material as with the one redistilled in the laboratory [32]. Therefore, the commercial material was used in the experiments described here. Dichloromethane was refluxed for 45 min over calcium hydride (3.05 g for 100 ml of CH_2Cl_2) under nitrogen and distilled from the same pot, after which it was stored and opened only under nitrogen. The purity of diethyl ether and dichloromethane was verified from the ^{1}H and ^{13}C NMR spectra.

2.2. NMR experiments

The NMR samples were prepared in 8 mm heavy-walled tubes (5.5 mm i.d.) pre-dried overnight in an oven at 120°C. The BF_3 etherate and free diethyl 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). Dry methylene chloride was added under nitrogen, to give the desired concentration of the reagents. The tube was then tightly capped again, re-weighed, and placed coaxially inside a 10 mm tube, containing $CDCl_3$ as lock solvent [33]. The spectra were run at 75.47 MHz for ^{13}C and 300.13 MHz for ^{1}H, as described in a previous report [32]. For the ^{13}C NMR a pulse length of 4 μs and a relaxation delay of 4 s were employed. Between 100 to 600 scans were acquired per spectrum. The largest number of scans were needed for the spectra run near the coalescence temperature, which gave the broadest peaks. The temperature controller of the NMR instrument was calibrated with a methanol sample and the actual probe temperature was rechecked after each experiment. The actual ratio of complexed and free ether was determined by integration of the ^{1}H NMR spectrum at low temperature (integration of the ^{13}C spectra gave the same ratios in all cases).

2.3. Data analysis

The calculation of rates by the NMR line shape analysis was conducted with the program DNMR-5 [34,35]. The region of methyl signals (8.02 to 19.77 ppm, 605.474 to 1492.203 Hz) and that of methylene signals (61.10 to 72.85 ppm, 4611.443 to 5498.172 Hz) were analyzed separately. The number of points for the analysis was 8080 in each case. The relaxation times were determined from the ^{13}C NMR spectra of the pure components by measuring the bandwidths at half intensity at several temperatures. The chemical shifts of the pure components were obtained by measuring the chemical shifts in mixtures of complex and ether at several temperatures in the range of slow exchange. A linear temperature dependence was observed for both parameters, which was used to calculate the chemical shifts of the components at higher temperatures. The following limits of uncertainty (variation) were allowed for the parameters used for the line shape analyses which gave the results listed in Table 1: chemical shifts of the components, ±3 Hz, ratio of the components, ±0.05, relaxation time, ±0.015 s for CH_3 and 0.02 s for CH_2, baseline increment, ±10, and tilting, ±1. The optimized parameter was the reaction rate constant (s^{-1}). The calcu-

Table 1
Rates of exchange in Eq. (2) and activation parameters for the exchange

n[a]	Peak analyzed	t (°C)	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (kcal/mol)
0.61 [**2**] = 0.621 M	CH_2	−32.2	39.99		
		−22.1	80.80		
		−14.8	142.4		
		−7.5	248.0		
		−0.3	471.1		
		12.8	1209.2		
		25.0	2468[b]		
		25.9	2701.6	10.09[c]	−9.18[c]
	CH_3	−32.2	39.50		
		−22.1	78.00		
		−14.8	144.1		
		−7.5	280.8		
		−0.3	529.9		
		12.8	1082	9.95[d]	−9.68[d]
		25.0	2413[b]		
0.61 [**2**] = 0.360 M	CH_2	−33.4	24.33		
		−21.4	53.50		
		−9.4	137.0		
		2.5	429.3		
		14.5	1128		
		25.0	2418[b]		
		26.5	3368	11.31[e]	−5.12[e]
	CH_3	−33.4	22.04		
		−21.4	51.72		
		−9.4	129.0		
		2.5	405.6		
		14.5	923.5		
		25.0	1805[b]		
		26.5	2123	10.57[f]	−8.19[f]
1.3 [**2**] = 0.435 M	CH_2	−35.1	29.28		
		−25.0	57.83		
		−14.8	123.2		
		−7.5	234.5		
		−0.3	416.2		
		12.8	1258.0		
		25.0	2711[b]		
		25.9	3441.1	10.66[g]	−7.08[g]
	CH_3	−35.1	25.47		
		−25.0	56.22		
		−14.8	111.0		
		−7.5	216.6		
		−0.3	406.7		
		12.8	951.0	9.82[h]	−10.57[h]
		25.0	1924[b]		
2.1 [**2**] = 0.323 M	CH_2	−46.7	14.24		
		−32.2	35.96		
		−22.1	71.16		
		−14.8	101.4		
		−7.5	176.3		
		−0.3	322.5		
		12.8	1076.0		
		25.0	1894[b]		
		25.9	3081.8	9.39[i]	−12.04[i]
	CH_3	−46.7	14.79		
		−32.2	36.45		

Table 1 (continued)

n[a]	Peak analyzed	t (°C)	k (s^{-1})	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (kcal/mol)
		−22.1	70.95		
		−14.8	108.5		
		−7.5	189.1		
		−0.3	399.7		
		12.8	507.3		
		25.0	1350[b]		
		25.9	2086.9	8.38[j]	−16.11[j]
2.4 [**2**] = 0.294 M	CH_2	−51.1	16.48		
		−40.9	38.53		
		−30.8	83.58		
		−20.6	174.0		
		−10.5	367.2		
		−0.3	694.0		
		12.8	1693.3	8.59[k]	−13.81[k]
		25.0	3007[b]		
	CH_3	−51.1	16.63		
		−40.9	38.43		
		−30.8	85.77		
		−20.6	218.5		
		−10.5	344.8		
		−0.3	689.0		
		12.8	1617.7	8.49[l]	−14.17[l]
		25.0	2975[b]		

[a] Molar ratio free ether/complex (**3**:**2**).
[b] Calculated from the rates at other temperatures.
[c] Correlation coefficient, $r = 0.9983$.
[d] $r = 0.9966$.
[e] $r = 0.9932$.
[f] $r = 0.9972$.
[g] $r = 0.9950$.
[h] $r = 0.9974$.
[i] $r = 0.9831$.
[j] $r = 0.9862$.
[k] $r = 0.9994$.
[l] $r = 0.9987$.

lated rates at different temperatures were used for the determination of the activation parameters with the program C2Plus [36,37].

3. Results and discussion

We decided to employ diethyl ether as the probe base for comparing the strength of Lewis acids from the stability of the corresponding complexes (**1**, Eq. (1)). The formation of complexes between ether and Lewis acids has been known for a long time [38]. The stability of the complex with boron trifluoride has been determined by Brown and Adams [39] from the dissociation constants (Eq. (1)) determined by vapor pressure measurements. Their findings were later confirmed by calorimetry [40,41].

$$\underset{\mathbf{1}}{R_2O{-}BF_3} \rightleftarrows R_2O + BF_3 \qquad K(R_2O) \qquad (1)$$

Vapor pressure measurements, however, are limited to volatile Lewis acids, whereas application of calorimetry for Lewis acidity measurements has the same drawbacks as its use for Brønsted acidity studies discussed earlier [33,42]. An alternative approach, interpolation of proton NMR chemical shifts [43–46] was also shown to be invalid [47].

The dissociation–recombination of complexes **1** is fast on NMR time scale at room temperature, a feature which we have exploited in the determination of relative basicities of ethers [32]. Variable temperature ^{19}F [48,49] and ^{13}C NMR [50] studies have shown, however, that the exchange of **1** with an excess of either BF_3 or ether can be slowed down sufficiently at low temperature to allow for integration of the separate signals of the two components. The line shape analysis of the ^{19}F spectrum has allowed determination of the rate of exchange [48,49]. Application of the same technique to the ^{13}C spectrum should allow a comparison of various Lewis acids, whether they contain fluorine or not. Because the energy barrier for the reverse reaction is small, the activation free energy and enthalpy for the exchange should be good measures of the corresponding parameters for the decomposition of the complex. We checked and calibrated the method on BF_3, because of the wealth of literature information on the complexes of this compound. The exchange of the diethyl ether complex **2** with excess ether (**3**) is described in Eq. (2).

$$\underset{\mathbf{2}}{Et_2O-BF_3} + n\,\underset{\mathbf{3}}{Et_2O} \rightleftarrows n\,\underset{\mathbf{3}}{Et_2O} + \underset{\mathbf{2}}{F_3B-OEt_2} \qquad (2)$$

It was found that the rates of exchange can be conveniently measured between −50°C and +25°C. As noted before, the methylene signal resonates at lower field in **2** than in **3**, whereas, the opposite is true for the methyl signal [32]. The change with temperature of the two signals is presented in Fig. 1. It can be seen that both the methylene and the methyl signals exhibit temperature dependence, but the coalescence temperatures are different, as expected from the different distances between the peaks for the respective carbons in **2** and **3**. The rates calculated from the analysis of methylene and methyl signals are both listed in Table 1. Because the actual temperature of the sample is sensitive to the exact location of the sample inside the cavity, the actual temperatures determined within one experiment carry a greater margin of error than the differences between the temperatures at which spectra were recorded in the same experiment.

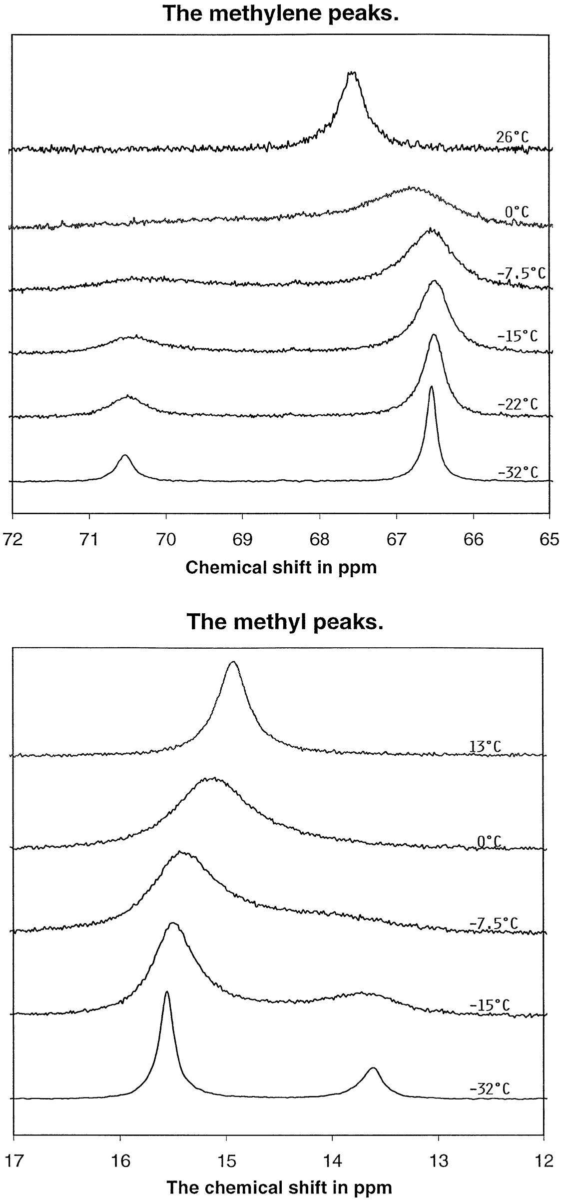

Fig. 1. Temperature dependence of the ^{13}C NMR spectrum of a mixture of **2** and **3** (1:2.4 mol/mol). Top: methylene signal. Bottom: methyl signal.

We conducted most of our experiments in dichloromethane solution. A few measurements with neat reactants gave rates in agreement with those measured in solution, but the scatter was greater. Likewise, the equilibrium constant for the exchange between a complex of an ether with BF_3 and another ether (Eq. (3)) was not sensitive to solvent [32], at variance with a literature claim to the contrary [45]. Another factor considered was the relative amount of free ether **3** present in the mixture (n in Eq. (2) and Table 1), which was varied between 0.61 and 2.4. The concentrations of complex **2** in individual experiments are also shown in Table 1. With the exception of the second experiment, the total concentration [**2** + **3**] was about 1 M in each case.

In a literature report of ^{19}F dynamic NMR studies, the exchange rates were analyzed in terms of a competition between two bimolecular steps, one involving a molecule of complex and a molecule of free ether (Eq. (3)), another involving the double exchange between two molecules of complex (Eq. (4), in which the asterisk was added to visualize better the fluorine exchange) [51]. It is rather difficult to represent mechanistically the latter process, which seems more likely a mere correction to improve the fit. The former is an S_N2 reaction with ether as the nucleophile.

$$R_2O\text{–}BF_3 + R'_2O \rightleftarrows R_2O + F_3B\text{–}OR'_2 \qquad (3)$$

$$R_2O\text{–}BF_3 + R'_2O\text{–}BF_3^* \rightleftarrows R_2O\text{–}BF_3^* + R'_2O\text{–}BF_3 \qquad (4)$$

The exchange rates determined in our experiments did not vary with the change in the ratio of free ether **3** to complex **2** (n). This feature is best evidenced by a comparison of rates at 25.0°C listed in Table 1. From the rates based on the analysis of the methylene peak, an average value $k = (2.50 \pm 0.41) \times 10^3\ s^{-1}$ is obtained, whereas, the average rate constant based on the analysis of the methyl is peak is $k = (2.09 \pm 0.69) \times 10^3\ s^{-1}$. The indicated uncertainties are standard deviations. There is more scatter in the results based on the analysis of the methyl peak, but the two averages differ by less than the uncertainty of each of them. A combined average $k = (2.3 \pm 0.5) \times 10^3\ s^{-1}$ is calculated. Our results thus show that the exchange of Eq. (2) comprises a unimolecular decomposition of the complex **2** as the rate-determining step. Indeed, a comparison of the rates at 25°C in the second and the fourth experiment in Table 1, in which the concentration of **2** is about the same and the concentration of **3** varies by a factor of 3.1 is quite conclusive. As a matter of fact, the proposed S_N2 mechanism [51] would not be expected for two reasons. Firstly, the nucleophilic attack at boron in **2** is similar to the nucleophilic attack to the central carbon of *tert*-butyl in $Me_3C\text{–}X$, which does not occur because of steric hindrance, as proven long ago by the lack of reactivity of HO^- toward *tert*-butyl chloride [52] and more recently by the absence of any effect of added nucleophiles on the rate of ethanolysis of methyl *tert*-butyl ether [53]. In addition, whereas in the *tert*-butyl case the nucleophile is electrostatically attracted by the positively charged hydrogens of the methyl groups, the ether nucleophile is electrostatically repelled by the negatively charged fluorine atoms of the complex with BF_3.

An important consequence of the unimolecular mechanism for the exchange reaction is that its energy barrier is a measure of the stability of the complex, because the barrier for the reverse process, recombination, should be very small. The activation parameters obtained from the exchange of methylene groups in all our experiments are $\Delta H^\ddagger = 10.0 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -9.5 \pm 3.5$ cal/mol deg; the analysis of the methyl peak gave the values $\Delta H^\ddagger = 9.4 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -11.8 \pm 3.3$ cal/mol deg, again in rather good agreement. It was found that the value calculated for the entropy of activation is somewhat sensitive to the stringency of limits set for the parameters of the DNMR5 (see Section 2.3), but the value of the enthalpy of activation changes little when those parameters are changed (in these tests the allowed range of variation in the optimization for chemical shifts was changed between 1 and 20 Hz, whereas the allowed range for the ratio of components was changed between 0.01 and 0.5). The combined average values for the analysis of methyl and methylene signals of the experiments in Table 1 are $\Delta H^{\ddagger} = 9.7 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -11 \pm 3$ cal/mol deg. We note that the value for the activation enthalpy is close to the value $\Delta H^{\circ} = 10.9$ kcal/mol determined for the decomposition equilibrium of complex **2** from vapor pressure measurements. An entropy change $\Delta S^{\circ} = 27.5$ cal/mol.deg was calculated for the latter process, which is reasonable for a decomposition to gaseous products [39]. Even though the actual value might be subject to some error, the entropy of activation for the decomposition in solution is negative, suggesting that the decomposition products, ether and BF_3 are stronger solvated than the complex and their formation produce a more organized solvent shell. Of the two products, it is BF_3 that could form some complex with dichloromethane. The complex should be very weak, but it could still produce reorganization of solvent. In addition to this, the diffusion of decomposition products from the solvent cage might become similar in rate with the decomposition and thus lower the measured entropy of activation. [3]

Our investigation has shown that $\Delta H^{\ddagger}$ for the exchange of ether with its complex with boron trifluoride determined by dynamic ^{13}C NMR spectroscopy can be used to evaluate the strength of interaction between the two. The applicability of the method to other molecular Lewis acids will be examined next and the results will be reported in due course.

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